

**UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY**

DOCTORAL THESIS SUMMARY

**TRANSITION METAL COMPLEXES WITH
HYDRAZONES DERIVED FROM ISONICOTINIC ACID
HYDRAZIDE**

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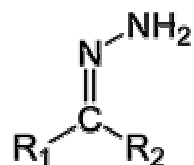
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CHAPTER I

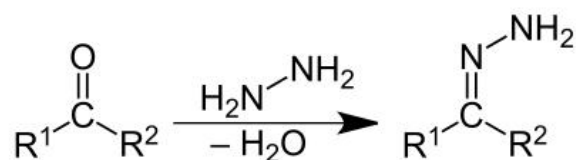
OVERVIEW

COMPLEXES WITH HYDRAZONES DERIVED FROM ISONICOTINIC ACID
HYDRAZIDE

Hydrazones are a class of organic compounds with the structure $R_2C=NNR_2$.



They are formed usually by condensation of hydrazine with aldehydes or ketones, as shown in figure:

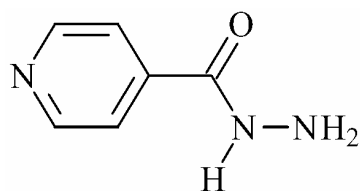


Isonicotinyldiazine (INH) also known as isoniazid (Laniazid, Nydrazid), is an organic compound that is the first-line medication in prevention and treatment of tuberculosis. The compound was first synthesized in 1912, but its activity against tuberculosis was first reported in the early 1950s. It has a very high *in vivo* inhibitory activity towards *Mycobacterium tuberculosis* H37Rv.

Tuberculosis is still a serious health problem that causes the death of about three million world people every year.

Isoniazid is never used on its own to treat active tuberculosis because it develops resistance quickly. Increasing resistance of *Mycobacterium tuberculosis* strains against anti-mycobacterial drugs such as rifampicin and isoniazid has further complicated the problem. This indicates the need for new effective anti-tuberculosis drugs.

Later, it was proved that isoniazid has also has an antidepressive effect, being one of the first antidepressive drugs discovered. It is also used in a wide range of bacterial diseases. [1-5]



Isoniazid

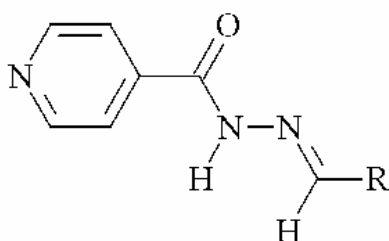
Hydrazones derived from condensation of isoniazid with pyridine-aldehydes and ketones have been found to show better anti-tubercular activity rather than INH [6]. This was proved by its ability to form stable complexes with *d* and *f* block metal ions [7-10].

It was demonstrated that the hydrazones have antibacterial, antimycobacterial, anticonvulsant, analgesic, anti-inflammatory and antitumor activities.

There has been growing interest in the study of hydrazones because of their physiological activity, coordinative capability, and applications in analytical chemistry [11-13]. Compared to the simple hydrazone Schiff bases, aroyl or heteroaroyl Schiff bases have additional donor sites. This introduces a wider range of properties for these substances. The study of ligands involving such hydrazones is interesting as they demonstrate versatility in coordination, a tendency to yield stereochemistry [3] of higher coordination number, an ability to behave as neutral or deprotonated ligands, and flexibility in assuming different conformations.

Recently, several metal complexes of Schiff bases containing N,S and N,O donors have been synthesized and studied [14 – 18].

As mentioned before, the hydrazone derived from isonicotinic acid hydrazide was initially synthesized in 1954. Sah and co-worker [19] synthesized INH hydrazide-hydrazones 1 by reacting isoniazid with various of aldehydes and ketones.



hydrazone - Type 1

These compounds were reported to have inhibitory activity in mice infected with various strains of *M. tuberculosis*. The authors also showed less toxicity than isoniazid [19, 20].

It was synthesized some hydrazide-hydrazones that were reported to have lower toxicity than hydrazides because of the blockage of -NH_2 group [21].

Paul V. Bernhard and co-workers [28] studied chelators such as 2-pyridinecarbaldehyde-isonicotinoyl hydrazone (HPCIH) (fig I.1), that showed highly efficacy in mobilizing Fe, both in *vitro* [29] and in *vivo*, in mice by oral administration [30]. The investigation shows that di-2-

pyridylketone-isonicotinoyl hydrazone (HPKIH) (fig. I.1) has potential applications in the treatment of cancer [31].

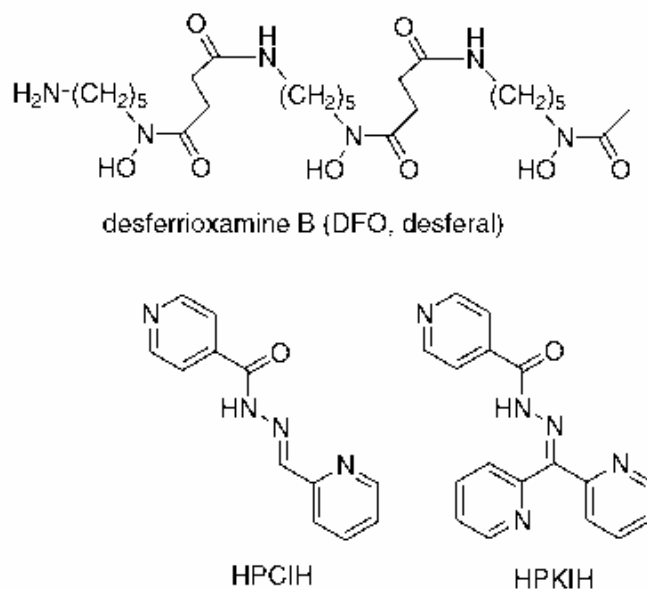


Fig. I.1. Structure of desferal, 2-pyridinecarbaldehyde-isonicotinoyl hydrazone (HPCIH) and di- 2-pyridylketone-isonicotinoyl hydrazone (HPKIH)

The same researchers have used as precursor the isonicotinic acid hydrazide which leads to hydrazones with moderate iron chelation activity. They also synthesized the hydrazone starting from benzophenone-isonicotinoyl hydrazone, HBIH, fig. I.2.

Crystal structure of HBPIH ligand was determined and is shown in figure I.3

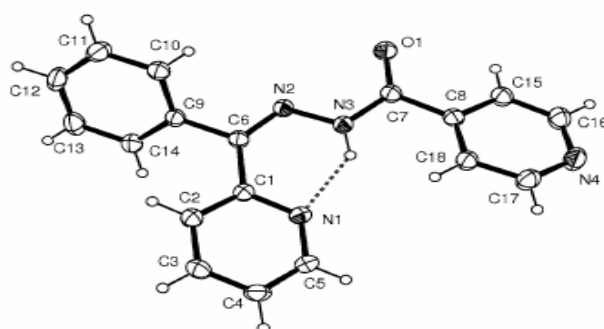


Fig. I.3 Crystal structure of HBPIH

The ligands from this series are potential NNO chelators. The 2-pyridyl ring and the amide group are on the same side of the C=N double bond (*Z* isomer). This conformation enables an intramolecular H bond between the 2-pyridyl group and the *syn* amide proton. Which is apparent in both structures. Thus, an inversion at N2 (to the *E* isomer) must occur before complexation.

Crystal structure of Fe(BPIH)₂ complex is shown in figure I.4.

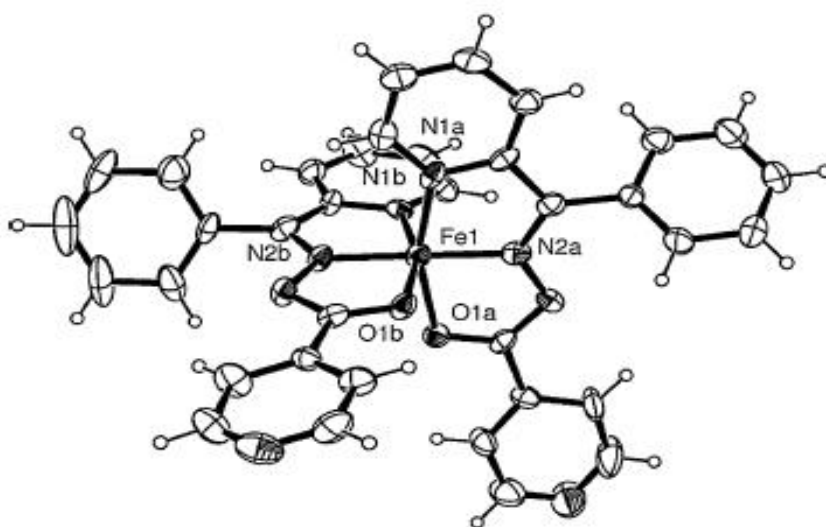


Fig. I.4. Crystal structure of Fe(BPIH)₂ complex

Tridentate NNO coordination of each monoanionic ligand is apparent to afford a charge-neutral six-coordinate Fe^{II} complex. The planar nature of the ligands enforces a meridional coordination geometry. The phenyl rings adjacent to the 2-pyridyl ring are twisted out of this plane so as to avoid H---H repulsion with the proton in the 3-position of the pyridyl ring. By contrast the aromatic rings attached to the carbonyl group are close to parallel with the plane of the coordinated ligand.

The coordinate bond lengths are characteristic of low-spin Fe^{II} and are essentially the same as those reported for complexes of the HPKIH analogs [32]. The central (imine) N donor forms the shortest coordinate bond owing to the fact that it is involved in two five-membered chelate rings on either side. The crystal structure of bivalent transition metal complexes of Cu, Co, Zn, Mn with 2-pyridinecarbaldehyde-isonicotinoyl hydrazone (HPCIH) were also studied.

The Fe complex formation constants are determined by potentiometric titrations. The obtained values are in agreement with those of similar tridentate ligands [32].

Molecular structure of [Cu(PCIH)₂] complex is shown in figure I.5.

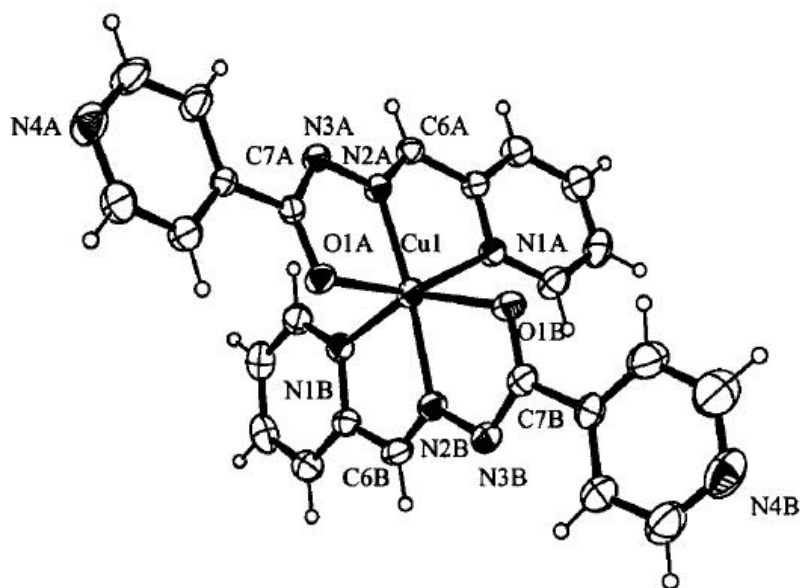


Fig. I.5 The molecular structure of $[\text{Cu}(\text{PCIH})_2]$

The metal ion has in the coordination sphere a *cis*- N_4O_2 . The two ligands were coordinated to the metal ion through pyridinic and amine nitrogen and carbonylic oxygen. The ligand coordinates to the metal ion in the enol form.

Another complex of $\text{Co}(\text{II})$, $[\text{Co}(\text{HPCIH})(\text{PCIH})](\text{NO}_3)_2$, showed a similar structure with $\text{Cu}(\text{II})$ complex. In the $\text{Co}(\text{II})$ complex the isonicotinic nitrogen of one ligand is protonated (figure I.6).

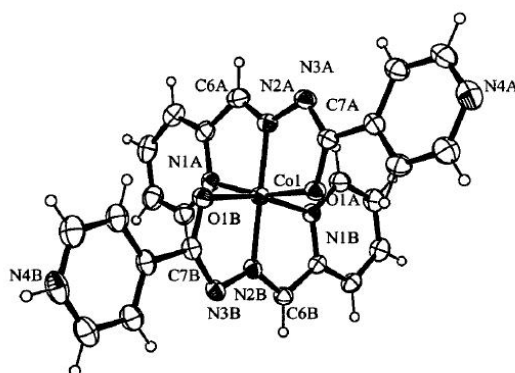


Fig. I.6. The structure of $[\text{Co}(\text{HPCIH})(\text{PCIH})](\text{NO}_3)_2$

Other Co(III) complex with HPCIH (1:2 molar ratio) have a structure with two Co(II) ions. One of Co(II) ion have an octahedral environmental, and the second one a tetrahedral environment (figure I.7).

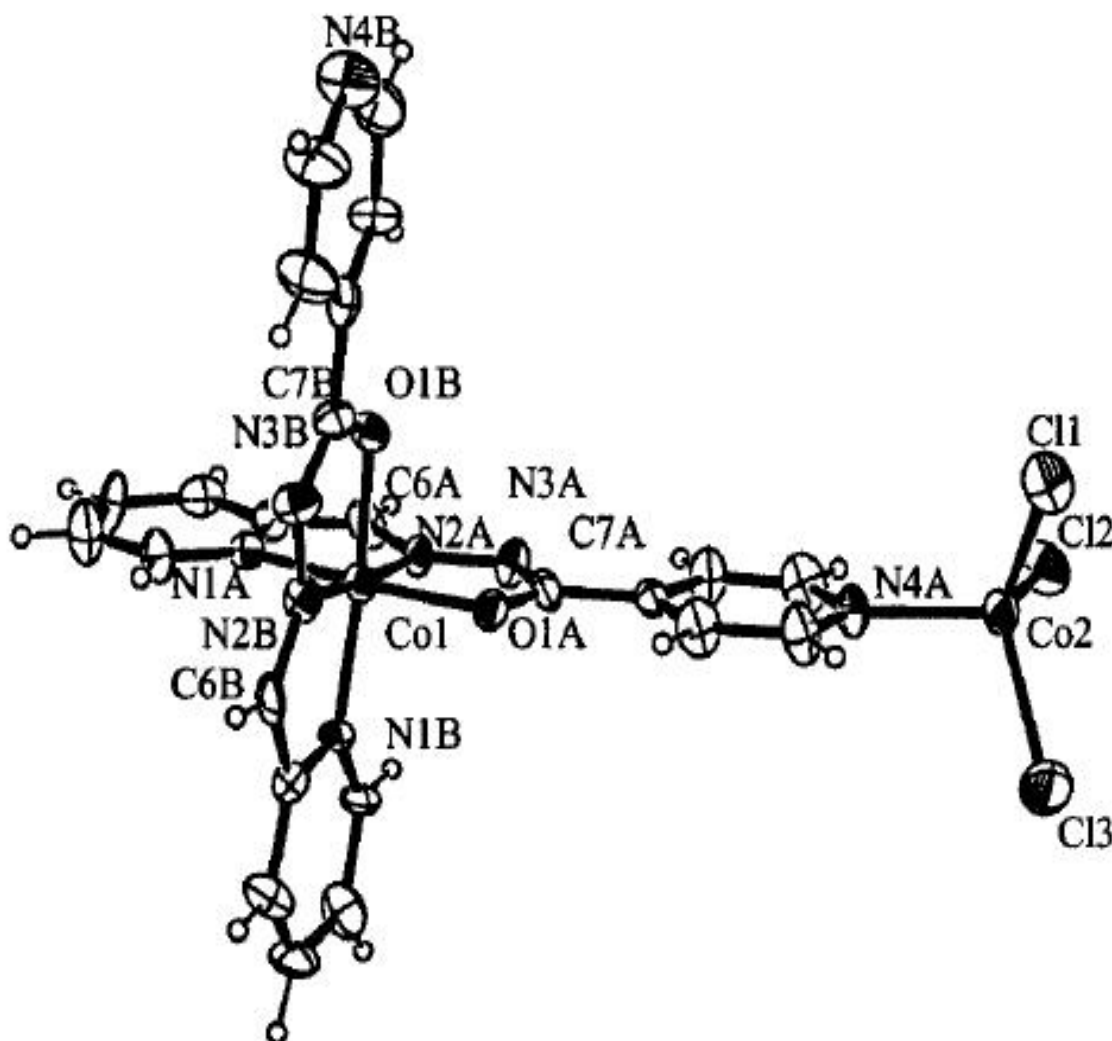


Fig. I.7. The structure of complex $[\text{Co}(\text{HPCIH})_2\text{Co}(\text{INH})_2]\text{Cl}_2$

A new complex of Mn(II) with DMSO as liigand having formula of type M_3L_2 $[\{\text{MnCl}_2(\text{DMSO})(\text{HPCIH})\}_2\text{Mn}(\text{DMSO})_2\text{Cl}_2]$, (figure I.8) was synthesized and characterized.

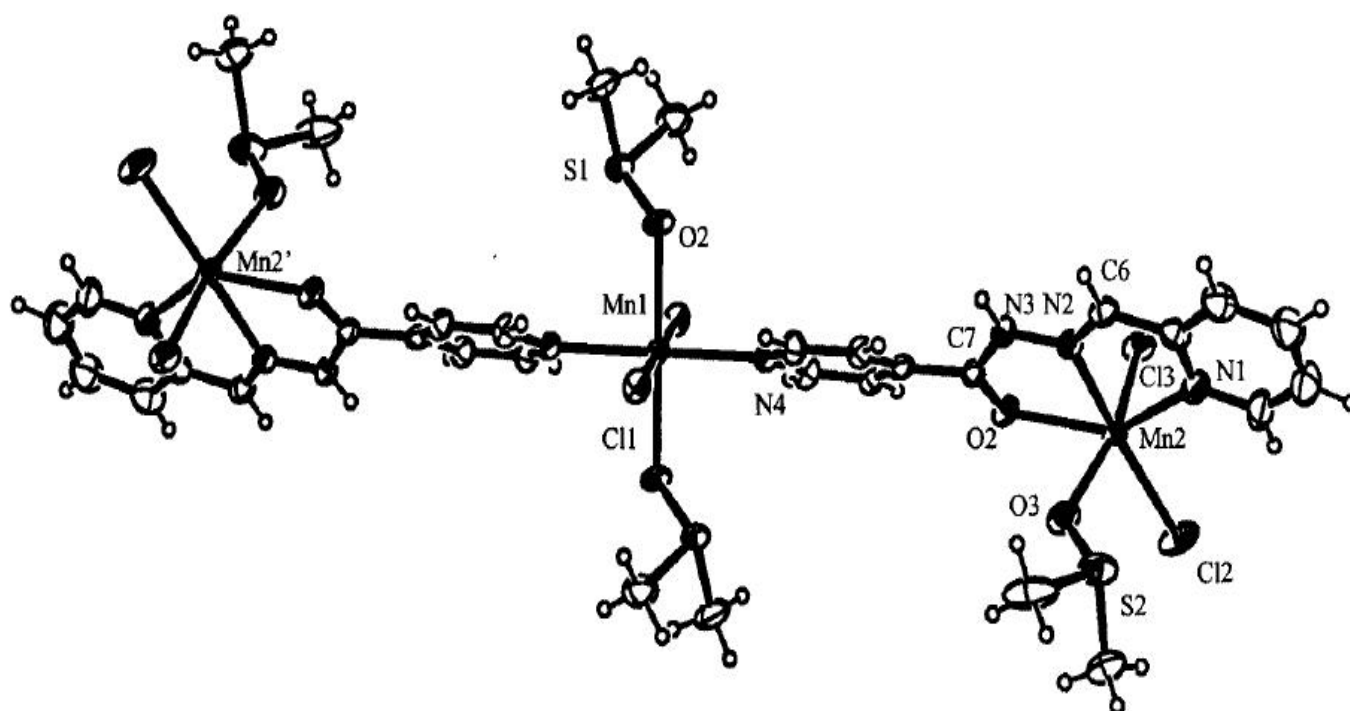


Fig. I.8 The structure of $[\{MnCl_2(DMSO)(HPCIH)\}_2Mn(DMSO)_2Cl_2]$

Two DMSO ligands, two Cl^- ions and two isonicotinoyl fragments are in the coordination sphere of metal ion. The DMSO acts as a tridentate ligand.

The Zn(II) complex of HPCIH, with formula of type $[Zn(HPCIH)SO_4]$, has a tridimensional polymeric structure (figure I.9). HPCIH acts as a tridentate ligand.

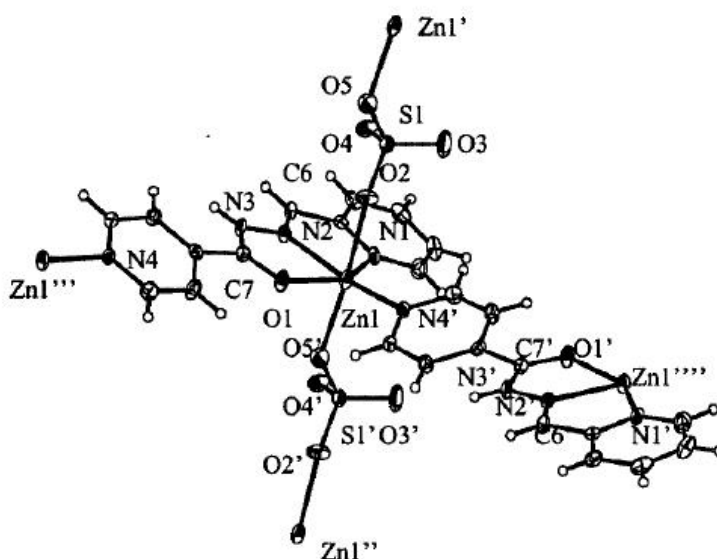


Fig. I.9 The structure of $[Zn(HPCIH)SO_4]$

Chapter II

ORIGINAL CONTRIBUTION

II.1 Transition metal complexes with isoniazid

The remarkable biological activity of isoniazid derivatives and the dependence of their activity on the mode of chelating with transition metal ions have been studied. According to previous investigations first we had as a task the synthesis of new complexes with isoniazid [66a-b, 67a-b].

The structural ligand formula is shown in figure II.1.

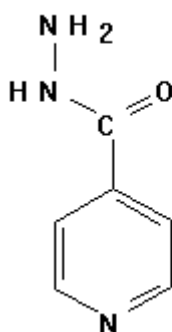


Fig. II.1. Ligand formula

II.1.1. Complexes of some mononuclear transition metals with isoniazid

Complexes were prepared using perchlorate, nitrate, acetate and sulphate compounds of following transition metals: Cu(II), Co(II), Ni(II), Mn(II) and Zn(II). The synthesis of complexes is given in Annex I.

The following 13 complexes were obtained:

- $[M(INH)_2(H_2O)_2]X_2$ where $X=NO_3^-$, and $M= Cu^{II}, Co^{II}, Ni^{II}$,
 $X= ClO_4^-$ and $M= Cu^{II}, Co^{II}, Ni^{II}, Mn^{II}$ and Zn^{II}
- $[M(INH)(ac)_2]$, $M= Co^{II}, Ni^{II}, Mn^{II}$
- $[M(INH)(SO_4)(H_2O)_2]$, $M= Cu^{II}$ and Zn^{II}

The mononuclear complexes are powders. The complexes obtained from perchlorate and nitrate are soluble in methanol, ethanol, acetone and DMF. The molar conductivity values show that the complexes are 1:2 electrolytes. Acetate and sulphate complexes are insoluble or partially soluble in common organic solvents (methanol, ethanol, acetone, DMF and acetonitrile).

IR spectra

The coordination of ligand to the metal ion is shown by the presence of some characteristic IR spectra. The assignments of the important characteristic IR bands are presented in Table II.2. IR spectra are given in Annex 2.

In the IR spectrum of isoniazid, the average intensity bands appears at 3304 cm^{-1} and 3110 cm^{-1} , which were assigned to the $\nu(\text{NH}_{\text{as}})$ and $\nu(\text{NH}_{\text{sym}})$ vibrations, and very intense bands at 1669 cm^{-1} and 1558 cm^{-1} , which were assigned to amide-I and amide-II groups. The average intensity band at 887 cm^{-1} was assigned to the N-N vibration frequency [68].

In the IR spectra of complexes **1-5** of type $[\text{M}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, complexes **6-8** of type $[\text{M}(\text{INH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$, complexes **9-11** of type $[\text{M}(\text{INH})(\text{ac})_2]$ and complexes **12-13** of type $[\text{M}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]$, the corresponding band of amide-I group appears displaced with $\Delta\nu = 6\text{-}74\text{ cm}^{-1}$ towards lower values, which indicates the involvement of carbonyl group in coordination [69].

The vibration frequencies $\nu\text{N-H}$ are strongly displaced in all complexes. The displacements towards lower values of band which appears 3304 cm^{-1} 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 $\nu\text{N-N}$ is displaced towards lower values in IR spectra of complexes.

The bands in the $3362\text{-}3470\text{ cm}^{-1}$ and $901 - 924\text{ cm}^{-1}$ domain, from IR spectra of the complexes, suggest the existence of coordination water [70].

In the IR spectra of complexes **1-5** a very intense band appears in $1085 - 1122\text{ cm}^{-1}$ (ν_3) range and a band of medium intensity appears at 627 cm^{-1} (ν_4). This proves the existence of the ClO_4^- ion, and indicates that T_d symmetry is not distorted. The ClO_4^- ion is presented outside of the coordination sphere [61].

In the IR spectra of complexes **6-8**, a very intense band appears in $1383 - 1389\text{ cm}^{-1}$ range, which is assigned to NO_3^- anion.[71]

From literature, the acetate ion is characterized by bands at 1578 and 1411 cm^{-1} , which are commonly assigned to the asymmetric $\nu_{\text{as}}(\text{COO})$ and the symmetric $\nu_{\text{sym}}(\text{COO})$ stretching vibrations of the carboxylate group.

In complexes **9-11** of type $[\text{M}(\text{INH})(\text{ac})_2]$, the frequency of $\nu_{\text{as}}(\text{COO})$ appears in $1416 - 1453\text{ cm}^{-1}$ range, while those characteristic of $\nu_{\text{sym}}(\text{COO})$, ranged from 1320 to 1384 cm^{-1} .

Other vibrations of $-\text{COO}^-$ group are identified: i) deformation vibration at δ_{COO^-} (708 , 776 and 701 cm^{-1}) and ii) wagging vibration, ω_{COO^-} (690 , 693 and 670 cm^{-1}) [73]

The presence of SO_4^{2-} anionic in the coordination sphere of the complexes **12-13** of type $[\text{M}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]$, is supported by the appearance of three bands in the range of $969 - 983\text{ cm}^{-1}$, $1042 - 1065\text{ cm}^{-1}$ and $1209 - 1215\text{ cm}^{-1}$, respectively [70].

	Compound	$\nu(\text{OH})$	$\nu\text{N-H}$	$\nu\text{C=O}$ amide I	ν amide II	$\delta\text{H}_2\text{O}$ coord	$\nu\text{N-N}$	νClO_4^-	νNO_3^-	$\nu_{\text{as}}\text{COO}^-$	$\nu_{\text{sym}}\text{COO}^-$	$\Delta\nu$	δ_{COO^-}	ω_{COO^-}	νSO_4^{2-} dicoord
	INH	-	3304 3110	1669	1558	-	888	-	-	-	-	-	-	-	-
1.	$[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	3444	3227 3087	1612	1500	924	828	1118 626	-	-	-	-	-	-	-
2.	$[\text{Co}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	3418	3156	1654	1547	901	849	1085 628	-	-	-	-	-	-	-
3.	$[\text{Ni}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	3390	3163	1653	1550	906	849	1099 628	-	-	-	-	-	-	-
4.	$[\text{Mn}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	3435		1623	1544	918	851	1116 626	-	-	-	-	-	-	-
5.	$[\text{Zn}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	3429	3248	1655	1546	919	848	1122 627	-	-	-	-	-	-	-
6.	$[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	3426	3054	1654	1539	902	851	-	1383	-	-	-	-	-	-
7.	$[\text{Co}(\text{INH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	3425	3156 3060	1654	1548	902	850	-	1383	-	-	-	-	-	-
8.	$[\text{Ni}(\text{INH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	3401	3152	1653	1550	907	849	-	1389	-	-	-	-	-	-
9.	$[\text{Co}(\text{INH})(\text{ac})_2] \cdot 3\text{H}_2\text{O}$	3363	3245	1595	1548	-	832	-	-	1417	1384	33	708	690	-
10.	$[\text{Ni}(\text{INH})(\text{ac})_2] \cdot 2\text{H}_2\text{O}$	3384	3257	1660	1550	-	857	-	-	1416	1320	96	776	693	-
11.	$[\text{Zn}(\text{INH})(\text{ac})_2] \cdot 2\text{H}_2\text{O}$	3421	3057	1626	1550	-	850	-	-	1453	1340	113	701	670	-
12.	$[\text{Cu}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	3413	3249 3116	1655	1540	910	866	-	-	-	-	-	-	-	1215 1149 1042 969
13.	$[\text{Zn}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]$	3470	3264 3103	1663	1548	903	855	-	-	-	-	-	-	-	1209 1065 983

Electronic and EPR spectra

From electronic spectra and magnetic moment values, information concerning the stereochemistry of the studied compounds were obtained (table II.3).

Isoniazid presents in UV two bands at 220 and 260 nm, assigned to transitions $n, \pi \rightarrow \pi^*$. The electronic spectra of complexes show the same bands, displaced at higher wavenumber. This suggests the coordination of ligand to the metallic ions.

The electronic spectra of Cu(II) complexes **1** and **6** $\{[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}$, present a large band at 600 nm and 762 nm, respectively, which can be attributed to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$, transition, proper for an octahedral geometry. The electronic spectrum of complex **12**, $[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2$ presents two bands at 400 and 570 nm, which can be attributed to the $xy \rightarrow x^2-y^2$ and $z^2 \rightarrow x^2-y^2$ transitions, proper for the same octahedral geometry [74] (Figs. II.2, II.3 and II.4)

The magnetic moments determined for the studied complexes are 2.1 BM, 1.8 BM and 2.2 BM, respectively. The determined magnetic moments reasonably corresponds in the range 1.7 – 2.2 BM, characteristic to Cu(II) complexes with octahedral geometry [61].

The analysis of EPR spectra of **1**, $[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ and **12**, $[\text{Cu}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ complexes, give the values of g_{\parallel} and g_{\perp} and the corresponding magnetic moments (Table II.4). Complex **6**, $[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2$ presents an isotropic signal. From its EPR spectrum cannot propose the exact geometry of the metal ion ($g_{\text{isotropic}} = 2.0937$).

Table II.4 EPR values of Cu(II) complexes

No.	Compound	g		H (mT)	
		g_{\parallel}	g_{\perp}	H_{\parallel}	H_{\perp}
1	$[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	2,4184	2,0678	278,909	326,195
12	$[\text{Cu}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	2,3107	2,0988	291,718	321,169

The EPR spectra (figures II.5, II.6 and II.7) and the values of the magnetic field parameters plead for an elongated octahedral symmetry.

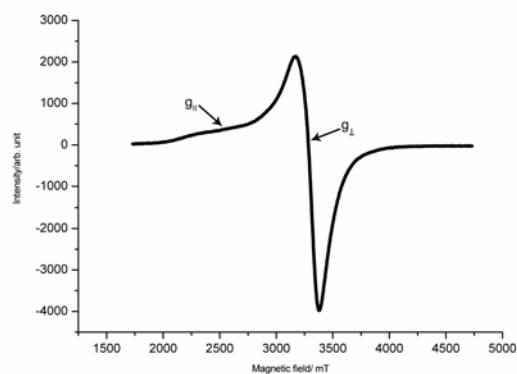
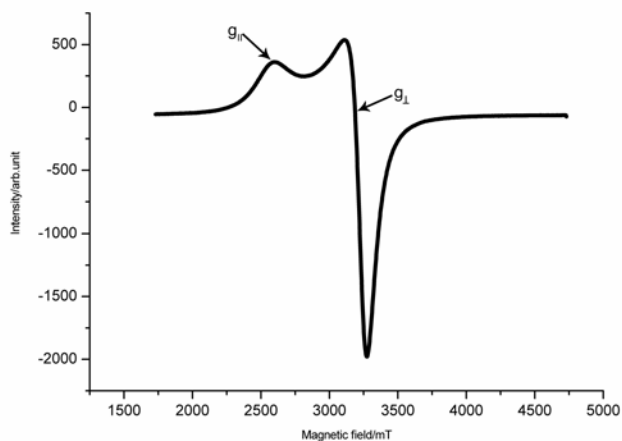
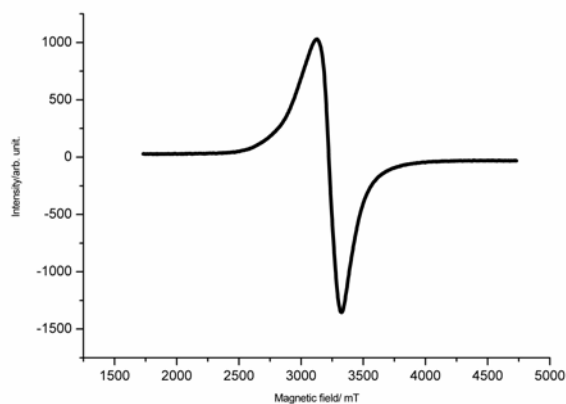
**Fig. II.5** EPR spectrum of $[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ **Fig. II.6** EPR spectrum of $[\text{Cu}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ **Fig. II.7** EPR spectrum of $[\text{Cu}(\text{INH})_2(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2$

Table II.3. Electronic spectral data, magnetic moments and magnetic field parameters of **INH** and complexes **1-13**

No.	Compound	Bands cm ⁻¹ /nm	Assignments	μ_{eff} BM	Geometry	10Δq	B	β
	INH	45454/ 220 38461/ 260	n, π→π*	-	-	-	-	-
1	[Cu(INH) ₂ (H ₂ O) ₂](ClO ₄) ₂	26595/ 376 16666/ 600	n→π* ² E _g → ² T _{2g}	2,11	Octahedral	-	-	-
2	[Co(INH) ₂ (H ₂ O) ₂](ClO ₄) ₂	19047/ 520 13793/ 725 7400/ 1351	⁴ T _{1g} → ⁴ T _{1g} (P) ⁴ T _{1g} (F)→ ⁴ A _{2g} ⁴ T _{1g} → ⁴ T _{2g}	4,69	Octahedral	6393	709,33	0,730
3	[Ni(INH) ₂ (H ₂ O) ₂](ClO ₄) ₂	25000/ 400 17543/ 570 10204/980	³ A _{2g} → ³ T _{1g} (P) ³ A _{2g} → ³ T _{1g} ³ A _{2g} → ³ T _{2g}	3,01	Octahedral	7339	795,4	0,772
4	[Mn(INH) ₂ (H ₂ O) ₂](ClO ₄) ₂	31250/ 320	TS	5,91	Octahedral	-	-	-
5	[Zn(INH) ₂ (H ₂ O) ₂](ClO ₄) ₂	45045/ 222 37313/ 268	n, π→π*	Dia	Octahedral	-	-	-
6	[Cu(INH) ₂ (H ₂ O) ₂](NO ₃) ₂	47619/ 210 38759/ 258 25000/ 400 17543/ 570	n, π→π* d _{xy} →d _{x²-y²} d _{z²} →d _{x²-y²}	2.20	Octahedral	-	-	-
7	[Co(INH) ₂ (H ₂ O) ₂](NO ₃) ₂	46296/ 216 39062/ 256 20000/ 500 18181/ 550 9523/ 1050	n, π→π* ⁴ T _{1g} → ⁴ T _{1g} (P) ⁴ T _{1g} (F)→ ⁴ A _{2g} ⁴ T _{1g} → ⁴ T _{2g}	5.44	Octahedral	8658	640.8	0.660
8	[Ni(INH) ₂ (H ₂ O) ₂](NO ₃) ₂	46511/ 215 38759/ 258 25000/ 400 17482/ 572 10438/ 958	n, π→π* ³ A _{2g} → ³ T _{1g} (P) ³ A _{2g} → ³ T _{1g} ³ A _{2g} → ³ T _{2g}	3,12	Octahedral	10438	744.5	0,722
9	[Co(INH)(ac) ₂] ₃ H ₂ O	40983/ 244 36764/ 272 24390/ 410	n, π→π* ⁴ T _{1g} → ⁴ T _{1g} (P)	4.02	Octahedral	2188	592	0.609

		11037/ 906 8849/ 1130	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ ${}^4T_{1g} \rightarrow {}^4T_{2g}$					
10	$[Ni(INH)(ac)_2]2H_2O$	40000/ 250 33745/ 296 25641/ 390 15432/ 648 9225/ 1084	$n, \pi \rightarrow \pi^*$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}$ ${}^3A_{2g} \rightarrow {}^3T_{2g}$	3.38	Octahedral	9225	893.2	0.867
11	$[Zn(INH)(ac)_2]2H_2O$	39062/ 256 34246/ 292	$n, \pi \rightarrow \pi^*$	Dia	Octahedral	-	-	-
12	$[Cu(INH)(SO_4)(H_2O)_2].H_2O$	13123/ 762	${}^2E_g \rightarrow {}^2T_{2g}$	1,88	Octahedral	-	-	-
13	$[Zn(INH)(SO_4)(H_2O)_2]$	30120/ 332	$n \rightarrow \pi^*$	Dia	Octahedral	-	-	-

The Cu(II) complexes **2**, **6** and **9** present three bands in the electronic spectra, attributed to the d-d transitions, ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$, and ${}^4T_{1g} \rightarrow {}^4T_{2g}$. These transitions and the values of the ligand field parameters correspond to those characteristic for an octahedral geometry [74].

For these complexes, the experimentally determined magnetic moments were 4.69, 4.02 and 5.44 BM, indicating a high-spin character and excluding oxidation to Co(III). These values are within the range of 4.3 – 5.7 BM, corresponding to an octahedral geometry for Co(II) ion [61].

The electronic spectra of studied Ni(II) complexes, **3** - $[Ni(INH)_2(H_2O)_2](ClO_4)_2$, **8** - $[Ni(INH)_2(H_2O)_2](NO_3)_2$ and **10** - $[Ni(INH)(ac)_2]2H_2O$ present a shoulder and two bands, assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, which correspond to an octahedral geometry for Ni(II) ion [74].

The experimentally determined magnetic moments were 3.01, 3.12 and 3.38 BM. These values are within the range of 2.8 – 3.5 BM, which corresponds to those characteristic for an octahedral geometry of Ni(II) complexes [61].

The ligand field splitting energy $10\Delta_q$, the interelectronic repulsion parameter Racah B and the nephelauxetic β - for Co (II) and Ni(II) complexes were calculated using the secular equations given by E. Konig [75] and the values are presented in Table II.3.

- for $Co^{2+} (d^7)$

$$10\Delta_q = \nu_2 - \nu_1$$

$$B = (\nu_3 + \nu_2 - 3\nu_1) / 15$$

- for $Ni^{2+} (d^8)$

$$10\Delta_q = \nu_1$$

$$B = (\nu_3 + \nu_2 - 3\nu_1) / 15$$

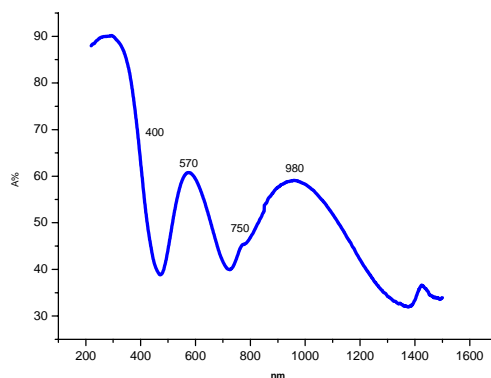


Fig. II.8 EPR spectrum of $[Ni(INH)_2(H_2O)_2](ClO_4)_2$ complex

In the electronic spectra of Zn(II) complexes **5**, **11**, and **13** (Figure II.12), the bands of the ligand $n, \pi \rightarrow \pi^*$ appear displaced to higher values. For d^{10} ions, the electronic spectrum provides no information about the environment. However, according to elemental analysis, IR spectra and thermal analysis, an octahedral environment of the metallic ion is proposed.

Thermal analysis

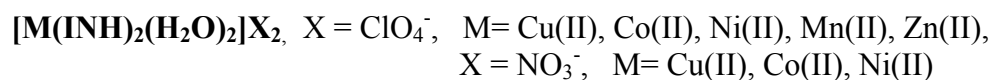
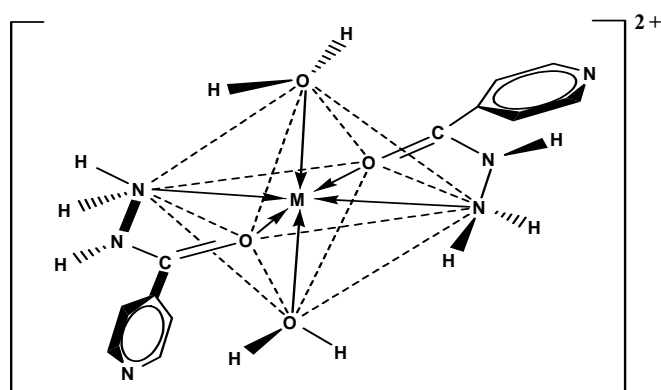
Due to the explosive nature of perchlorate and nitrate complexes, the thermal properties of only the acetate and sulphate complexes were investigated. The DTA and TG curves, the determined temperature ranges and the corresponding percent mass losses of the complexes are given in Figure II.13 and Table II.5.

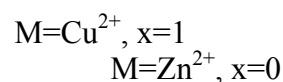
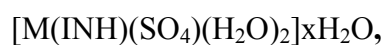
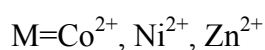
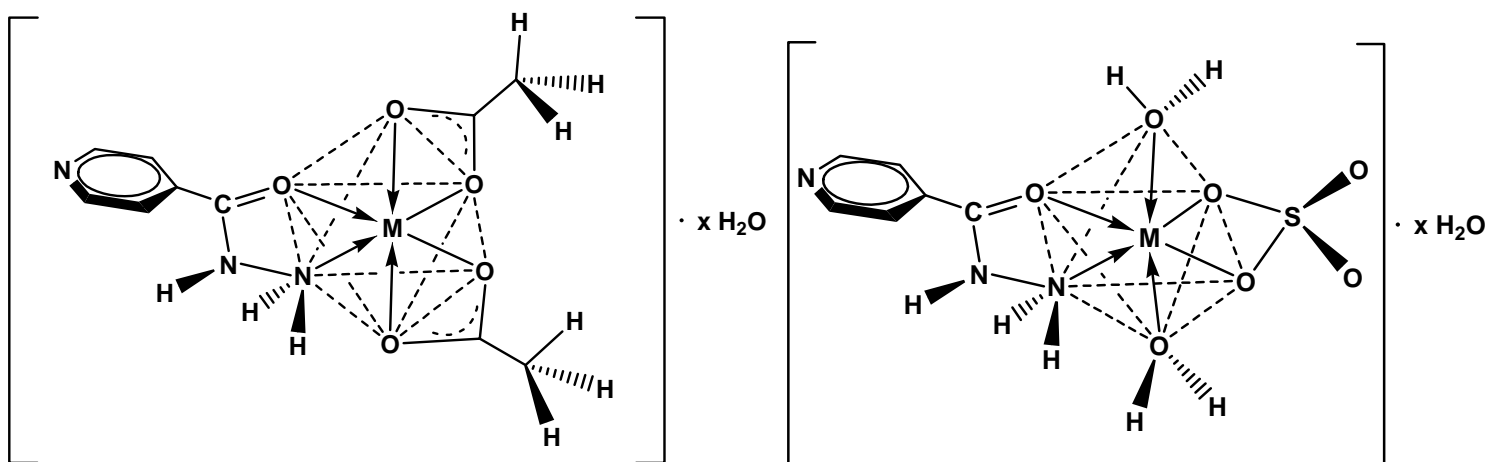
The final residues are metal oxides.

The analysis of TG curve of the acetate complexes shows the presence of water molecules outside the coordination sphere, and the final residue is estimated as stable metal oxide.

Based on the above spectral and thermal studies, together with magnetic susceptibility analysis an octahedral environment of metallic ion was proposed. The ligand acts as a neutral bidentate coordinated through the carbonyl oxygen and aminic nitrogen. The proposed structural formula were given in Figure II.14

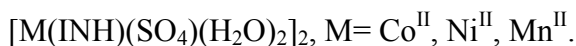
Fig. II.14 Proposed structural formula of complexes with isoniazid





II.1.2. Complexes of some binuclear transition metals with isoniazid

The synthesized binuclear complexes have the general formulae:



The obtained complexes were thermally stable and they are insoluble in common organic solvents (methanol, ethanol, acetone, DMF and acetonitrile). Elemental analysis and some physical properties of the complexes are given in Table II.6.

Table II.6 The elemental analysis and physical and chemical properties of binuclear complexes

No.	Compound	colour	Melting point, (°C)	Elemental analysis			
				Found (calcd)			
				M%	C%	H%	N%
14	$[Co(INH)(SO_4)(H_2O)_2]_2$	pink	>325	16.84 (17.18)	21.85 (22.15)	3.12 (3.41)	12.74 (12.92)
15	$[Ni(INH)(SO_4)(H_2O)_2]_2$	Blue crystals	314*	18.38 (17.90)	22.28 (21.96)	2.87 (3.38)	13.06 (12.81)
16	$[Mn(INH)(SO_4)(H_2O)_2]_2$	yellow	>325	17.30 (16.95)	21.80 (22.22)	3.12 (3.42)	12.79 (12.96)

* with carbonization

IR spectra

The position and intensity of the absorption bands from IR spectra of complexes compared with the ligand ones provide details about the type of chemical bond involved in the complex formation.

The IR spectra ($4000 - 400\text{ cm}^{-1}$) for the ligand and its complexes **14 -16** are presented in Table II.7.

In the IR spectrum of isoniazid the medium intensity bands appear at 3304 cm^{-1} and 3110 cm^{-1} , which are assigned to the vibration frequency $\nu(\text{NH}_{\text{as}})$, $\nu(\text{NH}_{\text{sym}})$. The very intense bands from 1669 cm^{-1} and 1558 cm^{-1} , are due to amide-I and amide-II groups. The band of medium intensity from 887 cm^{-1} is due to the vibration frequency N-N [77].

The vibration frequencies $\nu\text{N-H}$ are strongly displaced towards lower values in all complexes, suggesting the involvement of the amino nitrogen in coordination with metallic ions. For the same thing pleads the movement to lower values of the vibration frequency $\nu\text{N-N}$ as compared with the ligand spectrum.

In the complexes, the corresponding band of amide-I group appears displaced towards lower values, which indicates the involvement of carbonyl group in coordination [78].

The bands in the domains $3381 - 3444\text{ cm}^{-1}$ and $894 - 905\text{ cm}^{-1}$, respectively from the IR spectrum of $[\text{M}(\text{INH})(\text{SO}_4)(\text{H}_2\text{O})_2]_2$ complex, suggest the existence of coordination water [79].

The characteristic bands of pyridine nitrogen appeared in the spectra of the ligand and the complexes at the same position, confirming that the nitrogen of pyridine group does not participate in the coordination.

All of these IR data confirm a bidentate ligand (isoniazid) coordination, through the carbonyl oxygen and imine nitrogen to the metallic ions.

According to literature data, a low symmetry of SO_4^{2-} group from the complexes are probably due to the reducing of Td arrangement towards C_{2v} and the ν_3 and ν_4 frequencies are each split into three bands. The bands from the domains $967 - 984\text{ cm}^{-1}$, $1060 - 1070\text{ cm}^{-1}$ and $1107 - 1118\text{ cm}^{-1}$ are attributed to the ν_3 vibration mode [80]. The bands from the domains $480-529\text{ cm}^{-1}$, $538 - 616\text{ cm}^{-1}$ and $601 - 705\text{ cm}^{-1}$ from the IR spectra of complexes **15 – 17** are attributed to the ν_4 vibration mode. It can be concluded that the anion is being coordinated in a bridge binding mode.

Thermogravimetric analysis

The TG and DTA curves and thermal data of investigated compounds are given in Table II.8 and Figures II.15 a-c; The final residue of Co(II), Ni(II) and Mn(II) complexes obtained from sulphate compounds are estimated as metal sulphate.

Magnetic moments

It is known that in the approximation “spin only” can be calculated magnetic moment of a compound based on the hypothesis non-matched numbers of electrons, so the value of the spin associated with the paramagnetic ions components. The validity of the hypothesis results from comparing the magnetic moment calculated with that determined from measurements. Nothing is changed if it is considered only one or more molecules, as long as the assumption of no interaction between the paramagnetic centers within a molecule, intermolecular dipolar interaction or orbital contributions will be used.

Based on this hypothesis and the determined susceptibilities values at room temperature, the magnetic moments for dimmer complexes were calculated. Thus:

- for the Cu(II) complex, the experimentally determined magnetic moments is 2.1 BM, which corresponds to an octahedral geometry [85]

- for the complex Co (II), the experimentally determined magnetic moment is 5.7 BM, indicating a high spin and excluding the oxidation to Co(III). The value determined is perfectly in the 4.3 - 5.7 BM range, which corresponds to an octahedral geometry for the Co(II) ion [86]

- for the complex of Ni (II) the value determined for the magnetic moment is 3.2 BM. This value is in the range of (2.8 - 3.5) BM for Ni (II) complexes with an octahedral geometry [61].

- the magnetic moment determined for Mn(II) complex is 5.65 BM. This value falls in the range (5.65 – 6.10) BM, which corresponds to the Mn(II) ion with an octahedral environment [76].

The spectral, thermal and magnetic susceptibility data show that in all complexes, the metallic ions are in an octahedral environment and the ligand acts as neutral bidentate being coordinated through the imine nitrogen and carboxylic oxygen. All four studied complexes are dimmer ones. The thermal analysis indicates the presence of molecules of crystallization water.

Structural formula proposed for complexes are given in Figure II.20

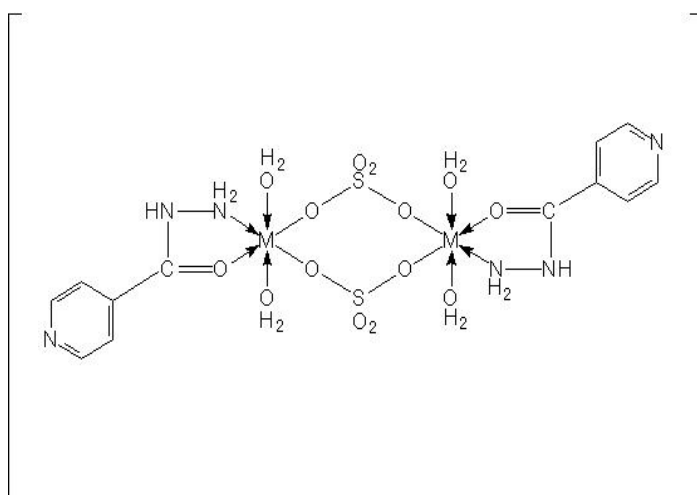
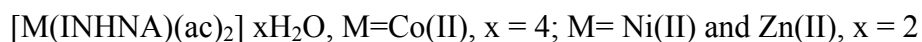


Fig. II.20 Proposed structural formula of binuclear complexes of isoniazid
 $[ML(SO_4)(H_2O)_2]_2$, $M = Co^{II}, Ni^{II}, Mn^{II}$.

II.2 Some transition metals complexes with isonicotinamido- naphthalaldimine

A new hydrazone was obtained by condensation of isoniazid with naphthaldehyde. The elemental analysis and IR spectrum confirmed the obtained isonicotinamido-naphthalaldimine – INHNA. Slow diffusion process was used to obtain single crystals of INHNA suitable for X-ray diffraction studies (Figure II.21). Details of crystal structure determination are summarized in Table II.10, and bond lengths and the angles are collected in Table II.11. The molecular formula is $C_{17}H_{13}N_3O_1$ and structure refinement parameters are: $a = 9.1732(9)$, $b = 11.3415(13)$, $c = 13.1611(13)$, $\beta = 99.400(7)$. The ligand crystallized in a monoclinic system and it belongs to space group $P2_1/n$.

Cu(II), Co(II), Ni(II) and Zn(II) complexes were obtained by template synthesis [87], which may be formulated as:



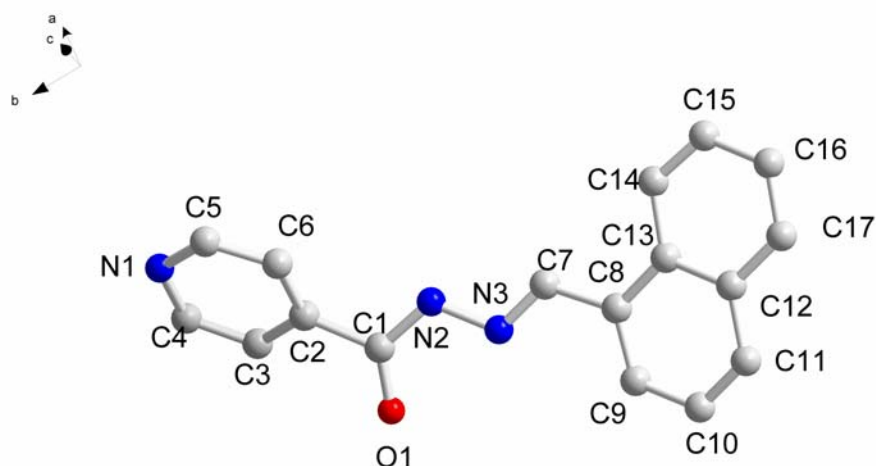


Fig. II.21 The crystal structure of INHNA

The selected values of bond angles ($C1N2N3 = 118.5^\circ$, $C7N3N2 = 115.72^\circ$, $N2C1C2 = 115.6^\circ$ and $N3C7C8 = 121.1^\circ$) are deviated from the ideal value of 120° , characteristic to a sp^2 hybridization of C7 and N3 atoms from azomethine group. Also, the nitrogen atoms from naphthaldehydic part are approximately coplanar with atoms from isonicotinic ring, and that is a consequence of steric effect.

Table II.10 Crystallographic data of **INHNA**

Chemical formula	C ₁₇ H ₁₃ N ₃ O ₁
<i>M</i> (g mol ⁻¹)	275.30
Temperature, (K)	293(2)
Wavelength, (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/n
<i>a</i> (Å)	9.1732(9)
<i>b</i> (Å)	11.342(1)
<i>c</i> (Å)	13.161(1)
α (°)	90.00
β (°)	99.400(7)
γ (°)	90.00
<i>V</i> (Å ³)	1350.9(2)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.354
<i>F</i> (000)	576
<i>R</i> _{int}	0.0421
Reflections collected	5171
Unique reflections	3440
Goodness-of-fit on <i>F</i> ²	1.073

x, *y*, *z*; -*x*+1/2, *y*+1/2, -*z*+1/2; -*x*, -*y*, -*z*; *x*-1/2, -*y*-1/2, *z*-1/2

Electronic spectra

The electronic spectra and the magnetic moments of complexes are presented in Table II.14.

The Schiff base INHNA presents in the electronic spectrum two bands at 39682 cm⁻¹ and 30864 cm⁻¹, assigned to *n*, $\pi \rightarrow \pi^*$ transitions.

The electronic spectrum of Cu(II) complex (**20**) (Figure II.21), presents a bands at 13020 cm⁻¹ (768 nm), attributed to *xy*→*x*²-*y*² transitions. This transition and the value of magnetic moment of 2.13 BM plead for an octahedral geometry of Cu(II) ion.

The electronic spectrum of complex **17**, [Co(INHNA)(ac)₂].4H₂O (Figure II.22) presents two bands at 560 nm and 1000 nm, assigned to d-d transitions, ⁴T_{1g}→⁴T_{1g}(P),

${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$. The electronic spectrum of complex **21** (Figure II.23), $[\text{Co}(\text{INHNA})(\text{H}_2\text{O})_2(\text{SO}_4)]$ presents three bands at 560, 630 and 1260 nm, assigned to d-d transitions, ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$, and ${}^4T_{1g} \rightarrow {}^4T_{2g}$. These transitions correspond to those characteristic for an octahedral geometry. The values of magnetic moments experimentally determined are 5.02 BM for complex **17** and 4.33 BM for complex **21**, indicating a high-spin character and excluding the oxidation to Co(III). These values are within the range (4.3 – 5.7 BM), corresponding to an octahedral geometry for Co(II) ion.

The electronic spectra of Ni(II) complexes (**18** and **22**) (Fig. II.24 and Fig. II.25), present three bands at 345 nm, 580 nm and 970 nm for the first complex, and 350 nm, 580 nm and 950 nm for the second one, assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}$, transitions, proper to an octahedral geometry. The values of the magnetic moments are 2.80 BM and 3.19 BM, respectively. These values are within the range (2.8 – 3.5) found for Ni(II) complexes with an octahedral geometry.

EPR spectra

The EPR spectrum of complex **20**, $[\text{Cu}(\text{INHNA})(\text{H}_2\text{O})_2(\text{SO}_4)]$ (Figure II.26) and the values of $g_{\parallel} = 2.29$ and $g_{\perp} = 2.1$ plead for an octahedral symmetry for the Cu(II) complex. The trend $g_{\parallel} > g_{\perp}$ indicates that the unpaired electron is located in the $d_{x^2-y^2}$ orbital of the Cu^{2+} ion, characteristic of a axial symmetry [90].

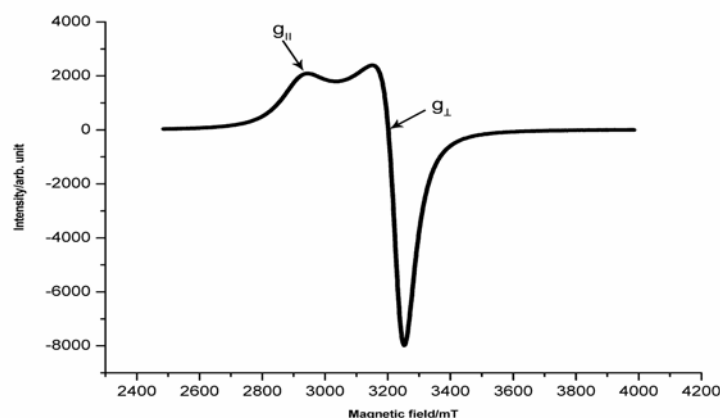


Fig. II.26 EPR spectrum of complex **20**, $[\text{Cu}(\text{INHNA})(\text{H}_2\text{O})_2(\text{SO}_4)]$

Thermogravimetric analysis

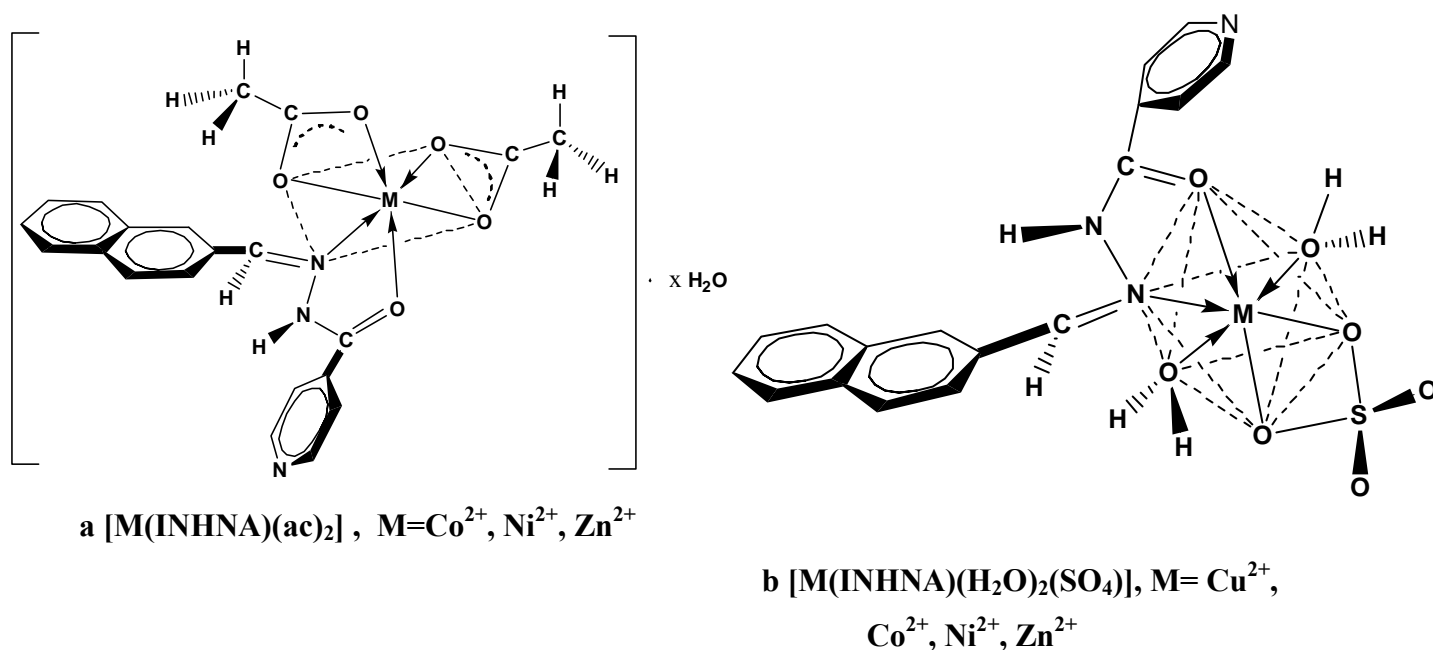
The TG and DTA thermodynamic parameters of complexes **17 – 19**, formulated as $[M(\text{INHNA})(\text{ac})_2] \cdot x\text{H}_2\text{O}$, $M=\text{Co}(\text{II})$, $y=4$, $M=\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, $x=2$, are given in Table II.15. The TG/DTA curves are shown in Figure II.27.

Analyses of TG curves show the presence of water molecules outside of coordination sphere. The final residue is estimated as stable metal oxides.

The exothermal effects which accompanied the mass losses and the experimental values are according with calculated ones.

Based on the above experimental data an octahedral stoichiometry was proposed. The anionic groups act in a chelating binding mode. Based on all data, the structural formula for complexes **17 - 23** was proposed (Figure II.28).

Fig. II.28 Structural formula proposed for complexes with INHNA

**II.3 Complexes of some transition metals with isonicotinamido-4-chlorobenzalaldimine**

A new Schiff base was obtained by condensation of p-chloro-benzaldehyde (CBA) with isoniazid (INH), named isonicotinamido-4-chlorobenzalaldimină (INHCBA). The structural formula of the ligand is shown in Figure II.30. The synthesis and characterization of 15 new complexes of $\text{Cu}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$, (ten complexes with neutral bidentate ligand [91] and five with monobasic bidentate ligand) are reported herein.

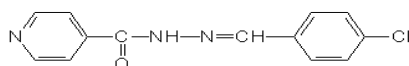
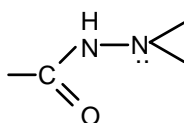
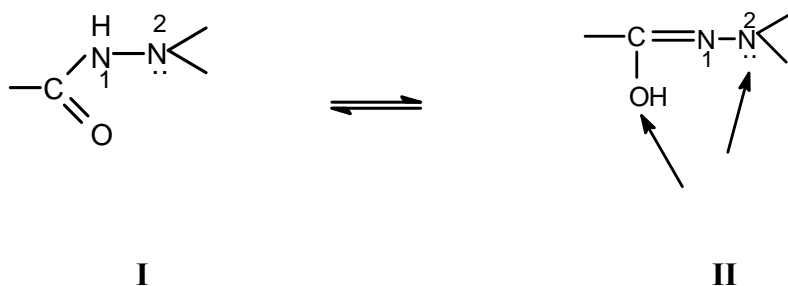


Fig. II.30 The structural formula of isonicotinamido-4-chloro-benzalaldimine (INHCBA)

The ligand presents as a principal part the group:



which can exhibit keto-enol tautomeric form.



In solid state, the ligand remains predominantly keto tautomer. However, in solution it was found to convert to the keto tautomeric form in an aqueous acidic solution or to the enol tautomeric form in an aqueous basic solution.

The ligand acts as:

- neutral bidentate, coordinated through the carbonylic oxygen and azomethyne nitrogen to the metal ion;
- mononegative bidentate ligand, coordinated through the carbonylic oxygen from deprotonated enol form and hydrazinic N(2) nitrogen, depending upon the pH medium.

II.3.1 Complexes of transition metals with neutral bidentate ligand - INHCBA

Ten new complexes having formula of type:

$[M(\text{INHCBA})(\text{ac})_2] \cdot x\text{H}_2\text{O}$ **24 - 26**, where $M=\text{Cu}^{2+}$, and $x=1$; $M=\text{Co}^{2+}$, and $x=2$; $M=\text{Cd}^{2+}$, and $x=0$

$[M(\text{INHCBA})_2(\text{H}_2\text{O})_2]\text{SO}_4 \cdot x\text{H}_2\text{O}$ **27 - 29**, where $M=\text{Cu}^{2+}$, Mn^{2+} , and $x=2$; $M=\text{Zn}^{2+}$ and $x=2.5$

$[M(\text{INHCBA})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ **30 - 33** where $M=\text{Cu(II)}$, Co(II) , Cd(II) and Zn(II) were synthesized and characterized.

The solid products of complexes, as powder, are stable in air. Complexes **30 - 33** were soluble in DMF and methanol, and the others in DMF only.

IR spectra.

The coordination mode of ligand to the metallic ions is proved by the presence of characteristic bands in the IR region. The main bands from the IR spectra are presented in Table II.18 and the IR spectra in Annex 2. INHCBA is expected to act as a bidentate ligand through the azomethine nitrogen and carbonyl oxygen of the amide group. INHCBA acts also as a tridentate ligand, the possible coordination sites being the pyridinic nitrogen, the azomethyne nitrogen and the carbonyl oxygen of the amide group. INHCBA acts also as monodentate, the possible coordination sites being the pyridinic nitrogen.

Generally, in the IR spectra of amide two absorption bands appeared.

1) the absorption band of carbonyl group at $\sim 1640\text{ cm}^{-1}$ corresponding to amide-I band.

2) an intense band in the domain of $1500 - 1600\text{ cm}^{-1}$, corresponding to amide-II band.

In the IR spectra of hydrazones the vibration frequencies of the band corresponding to amide-I group are displaced towards lower intensity rather than in amide compounds [92]. The $\nu\text{C=O}$ band appeared in the spectrum of the ligand at 1668 cm^{-1} . In the IR spectra of complexes **24 - 33** this band is shifted towards lower values by $\Delta\nu$ between 6 and 69 cm^{-1} , which indicates the involvement of the carbonyl group in the coordination.

The νNH stretching band of the free ligand occurs at 3192 and 3091 cm^{-1} [93], respectively, and remains unaffected after complexation. This excludes the possibility of coordination through the imine nitrogen atom.

Another important band occurs at 1592 cm^{-1} , attributed to the $\nu(\text{C}=\text{N})$ azomethine mode, which appears in the IR spectrum of ligand [94]. In the IR spectra of complexes **24** - **33**, the $\nu(\text{C}=\text{N})$ azomethine band appear shifted in the $1586 - 1543\text{ cm}^{-1}$ region. This suggests the involvement of the azomethine nitrogen in the coordination of ligand with the metal ions.

The overall IR spectra suggest that INHCBA acts as a bidentate ligand and it is coordinated to the metal ions by the azomethyne nitrogen and the carbonyl oxygen, whereby a five-member chelate ring is formed.

The IR spectra of complexes **30** – **33** show a very intense band in the $1383\text{-}1384\text{ cm}^{-1}$ domain, assigned to the NO_3^- ion.

The IR spectra of complexes **24** – **26** show two absorption bands at 1490 cm^{-1} and 1358 cm^{-1} , assigned to antisymmetric and symmetric acetate group frequencies. The difference $\Delta\nu (\nu_{\text{as}} - \nu_{\text{sym}})$ suggests an asymmetric bidentate ligand. This leads to the conclusion that the acetate group isn't in chelating binding mode [95].

Electronic spectra

The electronic spectral data and the magnetic moments of the complexes are shown in Table II.19.

The electronic spectrum of INHCBA presents two bands at 270 nm and 354 nm, assigned to $n, \pi \rightarrow \pi^*$ transitions.

The electronic spectra of the Cu(II) complexes (**24**, **27** and **30**) (Figures II.31- II.33), exhibit bands at 645 nm, 725 nm and 690 nm, which can be attributed to $xy \rightarrow x^2 - y^2$ transitions. These values together with the magnetic moments (1.90 BM, 2.07 BM and 2.25 BM) suggest an octahedral geometry for the Cu(II) complex [74].

The electronic spectra of Co(II) complexes (**25** and **31**) (Figures II.34 and II.35), exhibit bands attributes to d-d transitions, ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$, and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$. These transitions correspond to those characteristic for an octahedral geometry. The values of magnetic moments experimentally determined of Co(II) complexes are 5.51 BM and 4.30 BM. These values are within the range of 4.3 – 5.7 BM corresponding to an octahedral geometry of Co(II) complex.

The ligand field splitting energy $10\Delta_q$, the interelectronic repulsion parameter B and the nephelauxetic ratio β , for the Co(II) complexes were calculated using the secular equations given by E. Konig and the values are presented in Table II.19.

In the IR spectra of Zn(II) and Cd(II) complexes, the bands of the ligand appear shifted to lower values, which prove the coordination of ligand to the metal ion. Also, these complexes are diamagnetic ones, which is a characteristic for d^{10} ions [96].

The Mn(II) complex **28** (Figure II.36) presents a signal in UV domain at 328 nm assigned to a transfer of electric load, according with the theory data for a d^5 ion. [76]. It is well known that the d-d transitions occur in the d^5 systems but those transitions are of very low intensities and hence any d-d bands for such transitions weren't observed. The magnetic moment determined for Mn(II) complex is 5.78 BM. The value falls in the range (5.65 – 6.10) BM, corresponding to the manganese ion with an octahedral environment.

Based on the above electronic, spectral and magnetic moments values experimentally determined an octahedral geometry was proposed.

EPR spectra

The EPR spectrum of complex **24**, [Cu(INHCBA)(ac)₂] shows the value of “g” parameter of $g_{\text{isotropic}} = 2.1096$ and $H_{\text{isotropic}} = 319.971$ mT. The values of the magnetic field parameter and the allure of EPR spectra (Figure II.37) require a regular quasi-isotropic octahedral geometry.

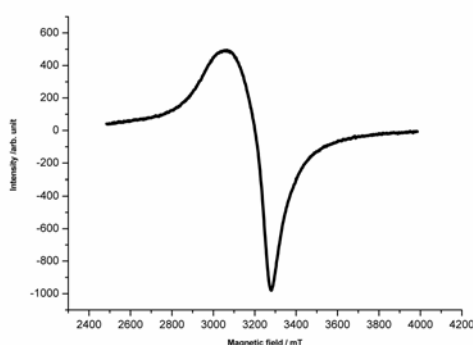
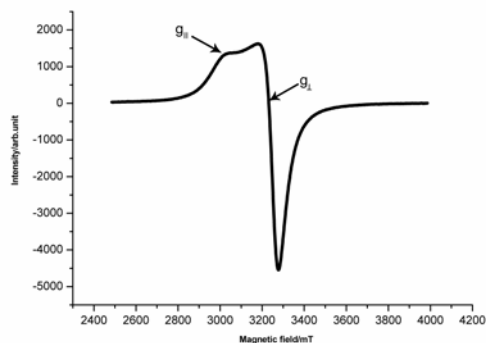
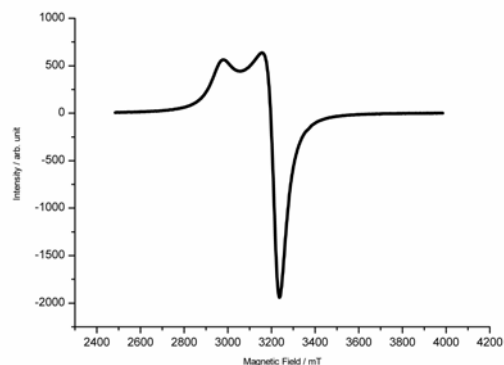


Fig. II.37 EPR spectrum of complex **26**, [Cu(INHCBA)(ac)₂]

The EPR spectra of complexes **30**, [Cu(INHCBA)₂(H₂O)₂](NO₃)₂ and **27**, [Cu(INHCBA)₂(H₂O)₂](SO₄) (Figures II.38 and II.39) plead for an octahedral geometry. The values of the magnetic field parameters are: $g_{\parallel} = 2.2648$, $g_{\perp} = 2.1129$ and $g_{\parallel} = 2.2237$, $g_{\perp} =$

2.0878. The trend $g_{\parallel} > g_{\perp}$ indicates that the unpaired electron is located in the $d_{x^2-y^2}$ orbital of the Cu^{2+} ion, characteristic of an axial symmetry [90].

**a****Fig. II.38** EPR spectrum of complex **30****b****Fig. II.39** EPR spectrum of complex **27**

Thermal behavior of complexes

From the TG, DTA and DTG curves of ligand and its complexes some information and physical parameters are obtained, such as: thermal stability of ligand and its complexes, the presence or absence of coordinated water molecules, thermal decomposition.

The decomposition stages, determined temperature ranges and the corresponding percent mass losses (experimental and calculated ones) are given in Table II.20.

The TG/DTA and DSC curves of the ligand are represented in Fig.II.40. The TG/DTA curves of ligand show an exothermal decomposition with maximum at $T_{\text{max}} = 603$ K on DTG curve. The evaluation of peak area on DSC curve gives the value of decomposition heat of $\Delta H = -122.5 \text{ Jg}^{-1}$.

Table II.20 The thermal results for complexes **26 -31**

No.	Compound	TG range / K	Mass loss exp (calc.) / %	Assignments
24	[Cu(INHCBA)(ac) ₂]·H ₂ O	323-373	4.04 (4.08)	Loss of crystallization water molecule
		373-483	10.15 (10.45)	Loss of CO ₂
		483-1260	50.00 (58.84)	Removal of the ligand
		>1260	35.81	Residue CuO + C
25	[Co(INHCBA)(ac) ₂]·2H ₂ O	323-450	8.03 (8.26)	Loss of crystallization water molecule
		450-650	35.39 (35.67)	Removal of one part of the the ligand
		650-760	10.00 (10.98)	Loss of CO ₂
		760-1260	24.61 (23.78)	Removal of the remaining part of the ligand
		>1260	22.97 (17.16)	Residue Co ₂ O ₃
26	[Cd(INHCBA)(ac) ₂]	500-670	72.73 (70.97)	Loss of CO ₂ and decomposition of the ligand
		>670	24.27 (26.12)	Residue CdO
27	[Cu(INHCBA) ₂ (H ₂ O) ₂](SO ₄)·2H ₂ O	323-383	7.31 (7.34)	Loss of crystallization water molecules
		383-470	6.86 (7.34)	Loss of two coordinated water molecules
		470-773	56.79 (56.9)	Expulsion of one molecule of SO ₃ and one part of the ligand
		773-1240	10.63 (13.76)	Removal of the remaining part of the ligand
		>1240	18.12 (17.48)	Residue CuO
28	[Mn(INHCBA) ₂ (H ₂ O) ₂](SO ₄)·2H ₂ O	323-388	8.00 (7.46)	Loss of crystallization water molecules
		388-523	7.83 (7.46)	Loss of two coordinated water molecules
		523-653	16.31 (17.92)	Expulsion of one molecule of SO ₃
		653-1270	37.0 (43.89)	Removal of one part of the the ligand
		>1270	29.38 (29.00)	Residue MnO
29	[Zn(INHCBA) ₂ (H ₂ O) ₂](SO ₄)·2.5H ₂ O	323-383	9.11 (9.05)	Loss of crystallization water molecules
		383-473	6.28 (6.72)	Loss of two coordinated water molecules
		473-673	16.32 (17.51)	Expulsion of one molecule of SO ₃
		673-1270	26.87 (38.43)	Removal of one part of the the ligand
		>1270	28.51 (32.33)	Residue ZnSO ₄

On the above elemental analysis, spectral (IR, UV-Vis-NIR and EPR) data, electrical conductivity, magnetic susceptibility and thermal analysis the possible structural formula were proposed (Figure II.47 and Figure.II.48).

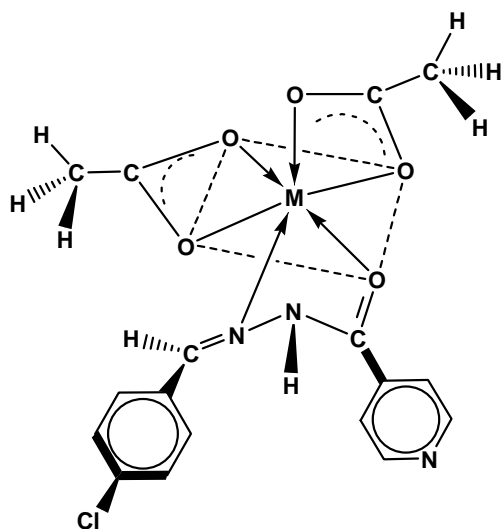


Fig. II.47 Proposed structural formula for complexes **24 – 26**
[M(INHCBA)(ac)₂]. xH₂O where M=Cu²⁺, and x=1; M=Co²⁺, and x=2; M=Cd²⁺, and x=0

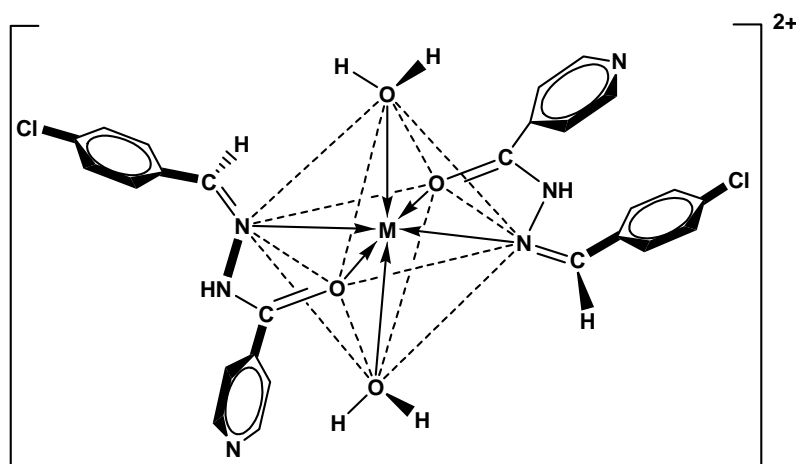
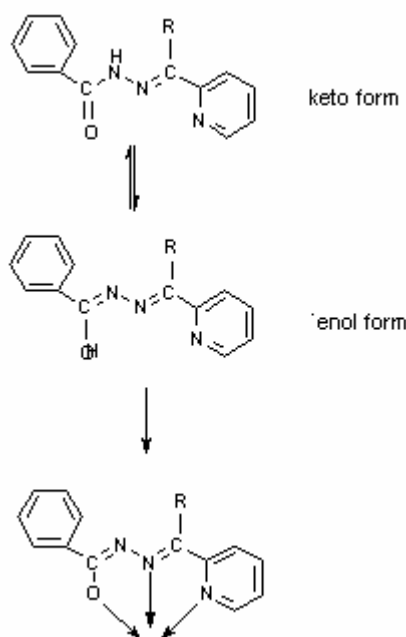


Fig. II.48 Proposed structural formula for complexes **27 - 33**

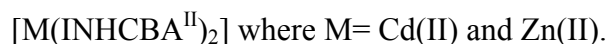
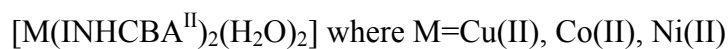
II.3.2. Complexes with monobasic bidentate INHCBA ligand

Based on the hydrazones keto-enol tautomerism in aqueous solution, new complexes of divalent transition metals with hydrazones obtained from condensation of INH and p-CBA (INHCBA^{II}) (enol form) were synthesized and characterized [99].



The experimental parameters (pH value) of synthesis reactions were determined by several experiments, in order to obtain the enol II form of ligand. The complexes were obtained using the Cu, Co, Ni, Cd and Zn nitrates.

New five complexes of type:



were studied by spectral and thermal analyses.

Template synthesis favors the obtaining of complexes with the enol form of ligand. It was obtained compounds with higher purity (annex 1). All the complexes are colored powders. Some complexes were purified by recrystallization. The complexes were insoluble in common organic solvents and soluble in DMF. By elemental analysis the chemical formula was established.

IR spectra

The characteristic IR bands were used in order to establish the coordination of $\text{INHCBA}^{\text{II}}$ ligand to the metallic ions. The main absorption IR bands are summarized in Table II.23, and the IR spectra are given in Annex 2.

Comparing the IR spectra of complexes **24 – 33** (keto form) with INHCBA , with IR spectra of complexes **34 -38** with $\text{INHCBA}^{\text{II}}$ obtained by template synthesis with pH adjustment, it was observed intense bands, assigned to NO_3^- anion, only for the first ones.

This suggests that the complexes were non-electrolytes. The molar conductivity measurements in DMF (Table II.22) showed that the complexes were non-electrolytes.

In the IR spectra of complexes **34** – **38**, appears a new band in 1599 -1601 cm^{-1} domain, assigned to valence vibrations of C=N due to the enol form of INHCBA. The valence vibration of C=O group is disappeared from the IR spectra of these complexes [100]. According to literature data [56], in the IR spectra of complexes **34** – **38**, the new bands which appeared at 1599 – 1601 cm^{-1} , indicate that the INHCBA^{II} acts in enol form and was coordinated as monoanionic bidentate ligand. A new band appears at 1365 cm^{-1} , assigned to enol form of deprotonated hydrazone ($\nu_{\text{C-O}}$) [32].

In the IR spectra of the complexes **34** – **38** the frequencies of azomethyne group, which in IR spectrum of ligand appeared at 1592 cm^{-1} , are shifted towards lower values, in 1569 – 1572 cm^{-1} domain. This proves that the ligand acts as monoanionic bidentate through oxygen atom of deprotonated enol form and azomethyne nitrogen [101].

In IR spectra of complexes **34** - **36**, the bands which appear in domains 3390 – 3422 cm^{-1} and 890- 928 cm^{-1} , suggest the presence of coordinated water molecules [102].

Based on the above data, it can be concluded that in complexes **34** – **38** the ligand acts as monobasic bidentate, coordinated through the azometinic nitrogen and oxygen tom of deprotonated enol form, which form five chelate rings with metal ion.

Electronic spectra

The electronic spectra and the magnetic moments values are given in table II.24.

The electronic spectrum of the INHCBA Schiff base shows two bands at 37037 cm^{-1} and 28248 cm^{-1} , which are assigned to $n, \pi \rightarrow \pi^*$ transitions.

In the electronic spectrum of complexes, very intense bands from UV domain appears, assigned to ligand transitions, and atwo or three medium intensity bands, due to the interelectronic transitions of metal ions. The intraligand transitions which appears in free ligand are slightly shifted in the electronic spectra of complexes, proving the coordination of ligand to the metal ions

The values of magnetic moments (Table II.24) correspond to an octahedral geometry. For the complex **34**, the value of the magnetic moment is 2.2 BM. The value is within the range 1.7 – 2.2 BM found for an octahedral environment of Cu(II) ion. For the complex **35**, the value of the magnetic moment experimentally determined is 4.97 BM, which is within the range 4.3 – 5.7 BM found for an octahedral geometry of Co(II) complex. The magnetic

moment value of complex **36** is 3.23 BM, which is within the range 2.8 – 3.5 BM, found for an octahedral environment of Ni(II) ion

Thermal analysis

The decomposition stages, the temperature ranges, and the corresponding percent mass losses (experimental and calculated ones) are given in Table II.25

Table II.25 Thermal results of complexes 36 - 40

No.	Compounds	TG range/ K	Mass loss found (calc.) / %	Assignments
34	$[\text{Cu}(\text{INHCBA}^{\text{II}})_2(\text{H}_2\text{O})_2]$	303 – 508	5.10 (5.80)	Loss of two coordinated water molecules
		508 – 1473	76.50 (83.90)	Removal of the ligand
		>1473	23.28 (23.13)	CuO + Cu
35	$[\text{Co}(\text{INHCBA}^{\text{II}})_2(\text{H}_2\text{O})_2]$	303 – 533	4.80 (5.80)	Loss of two coordinated water molecules
		533 – 1473	68.00 (84.40)	Removal of the ligand
		>1473	27.20 (27.00)	Co ₂ O ₃
36	$[\text{Ni}(\text{INHCBA}^{\text{II}})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]$	303-373	5.88 (5.86)	Dehydration process (loss of two water molecules)
		373 – 1473	66.82 (84.00)	Decomposition of ligand
		>1473	27.30 (25.15)	NiO + Ni + C (organic residue)
37	$[\text{Cd}(\text{INHCBA}^{\text{II}})_2]$	303 – 394	83.20 (82.20)	Removal of the ligand
		>900	16.80 (20.33)	CdO
38	$[\text{Zn}(\text{INHCBA}^{\text{II}})_2]$	303 – 1473	85.40 (88.80)	Removal of the ligand
		>1473	14.60 (13.92)	ZnO

Based on the above spectral data (IR, electronic and UV-Vis-NIR) and magnetic moments, together with molar conductivity and thermal studies the new obtained complexes have the following proposed structural formula presented in Figs. II.58 and II.59.

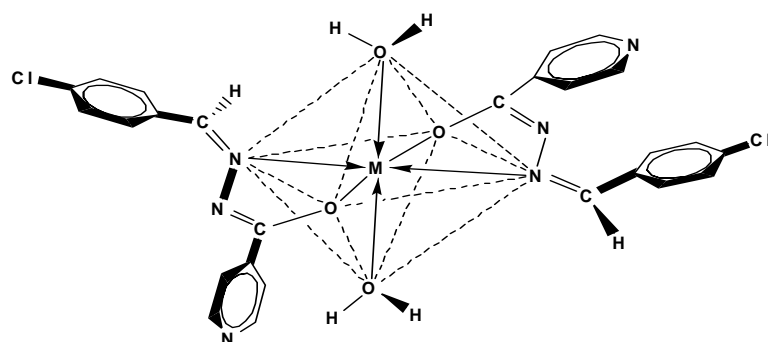


Fig. II.58 Proposed structural formula of complexes **34 - 36** $[\text{M}(\text{INHCBA}^{\text{II}})_2(\text{H}_2\text{O})_2] \cdot x\text{H}_2\text{O}$

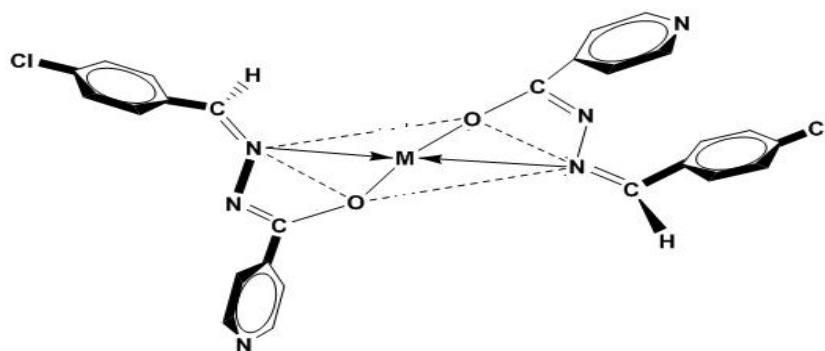


Fig. II.59 Proposed structural formula of complexes **37 - 38** $[M(INHCBA^{II})_2]$, $M=Cd^{2+}$, Zn^{2+}

II.4. Complexes of some transition metals with 2-benzoyl-pyridyl-isonicotinoyl-hydrazone

By condensation of 2-benzoylpyridine with isonicotinoic acid hydrazide a new compound was obtained. The ligand was characterized on the basis of elemental analysis, IR spectroscopy and UV-Vis-NIR. Slow diffusion process was used to obtain single crystals of ligand, suitable for X-ray diffraction studies.

Details of crystal structure determination are summarized in Table II.26, and bond lengths and the angles are collected Table II.27. The molecular formula is $C_{18}H_{14}N_4O_1$ and structure refinement parameters: $a = 8.3167(11)$, $b = 8.6834(11)$, $c = 11.0790(14)$, $\beta = 93.941(10)$. The ligand crystallized in triclinic system and belongs to space group P-1.

The crystal structure of INHFPC is given in Figure II.60.

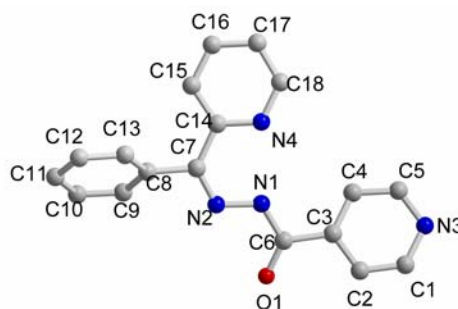


Fig. II.60 The crystal structure of INHFPC

The ligands acts as NNO tridentate. The 2-pyridyl ring and the amide group are on the same side of the C=N double band (Z isomer). This conformation enables an intermolecular H bond between the 2-pyridyl group and the *syn* amide proton. Thus, an inversion at N2 (to the *E* isomer) must occur before complexation.

The selected bond angles ($C6N1N2 = 120.3^\circ$, $C7N2N1 = 117.8^\circ$, $C3C6N1 = 113.3^\circ$ and $N2C7C8 = 114.5^\circ$) are deviated from the ideal value of 120° , characteristic to a sp^2 hybridization of C7 and N2 atoms from azomethine group. Also, the nitrogen atoms from 2-benzoyl-pyridine part are approximately coplanar with atoms from isonicotinic ring, and that is a consequence of steric effect.

Table II.26 Crystallographic data of **INHFPC**

Chemical formula	$C_{18}H_{14}N_4O_1$
M / g mol ⁻¹	302.33
Temperature / K	293(2)
Wavelength / Å	0.71073
Crystal system	Triclinic
Space group	P-1
a / Å	8.317(1)
b / Å	8.683(1)
c / Å	11.079(1)
$\alpha / ^\circ$	91.599(1)
$\beta / ^\circ$	93.941(1)
$\gamma / ^\circ$	109.486(1)
V/Å ³	751.38(2)
Z	2
F(000)	316
Reflections collected	5693
Unique reflections	4212
Goodness-of-fit on F ²	1.050

x, y, z; -x, -y, -z

Complexes with 2-benzoyl-pyridil-isonicotinoylhydrazone (INHFPC) ligand are obtained by template synthesis. Thirteen new complexes of bivalent transition metals were characterized by spectral (IR, UV-Vis-NIR, EPR) and thermal analysis, magnetic moment measurements and electrical conductivities [103].

Complexes are of type:

$[M(INHFPC)_2](X)_m$, were M= Cu(II), Co(II) and Ni(II), and m=2, X= ClO_4^- , NO_3^- and CH_3COO^- ,

M= Cu(II), Co(II), Ni(II) and Mn(II)), for m=1, and X= SO_4^{2-}

The complexes **39** - **51** are soluble in DMF and methanol and insoluble in other common organic solvents (ethanol, acetone, diethyl ether, chloroform). Molar conductivity measurements in DMF show that the perchlorate, nitrate and acetate complexes are 1:2 type electrolytes and sulphate complexes are 1:1 type electrolytes. [88].

IR Spectra

In the IR spectra of 2-benzoyl- pyridyl-isonicotinoyl hydrazone (INHFPC), a very intense band appears at 1691 cm^{-1} and a strong band appears at 1668 cm^{-1} , which are assigned to the vibration frequency $\nu(\text{C=O})$ [104] and $\nu\text{C=N}$ azomethine [68].

For complexes **39** -**51**, the vibration frequencies of carbonyl and azomethine groups appear shifted to lower values, which indicate the involvement of carbonyl oxygen and azomethine nitrogen in coordination [105].

In the IR spectrum of the ligand, three middle intensity bands appear at 1548 cm^{-1} , 1000 cm^{-1} and 743 cm^{-1} , which are assigned to vibration frequency $\nu(\text{Py ring})$, Py ring bending and γ (Py ring outside the plan), respectively.

According with literature data [106, 107] when a ligand is coordinated by the nitrogen of the Py ring, all three frequencies appears shifted to another values in IR spectra of complexes. In the IR spectra of complexes the band corresponding to $\nu(\text{Py ring})$ is displaced to lower frequency (Py ring bending) and the band corresponding to $\gamma(\text{Py ring outside the plan})$ is displaced lo higher values.

In studied complexes, the vibration frequency due to the Py ring is displaced to lower values. On the other hand, the band corresponding to the Py ring bending, which in ligand is at 1000 cm^{-1} , is shifted to higher values, with $\Delta\nu = 16 - 57\text{ cm}^{-1}$. Displacement to higher values with $\Delta\gamma = 12 - 14\text{ cm}^{-1}$, also appear for the band of γ (Py ring outside the plan).

These information lead to the idea that pyridine nitrogen of 2-benzoyl-pyridine is involved in the coordination with metal ions.

All the data support the idea that the INHFPC ligand works as neutral tridentate NNO, being coordinated through the azomethine nitrogen, the pyridine nitrogen and carbonylic oxygen.

Based on the spectral data (IR, electronic and UV-Vis-NIR) and magnetic moments, together with molar conductivity and thermal studies the new obtained complexes have the following proposed structural formula presented in Fig. II.80.

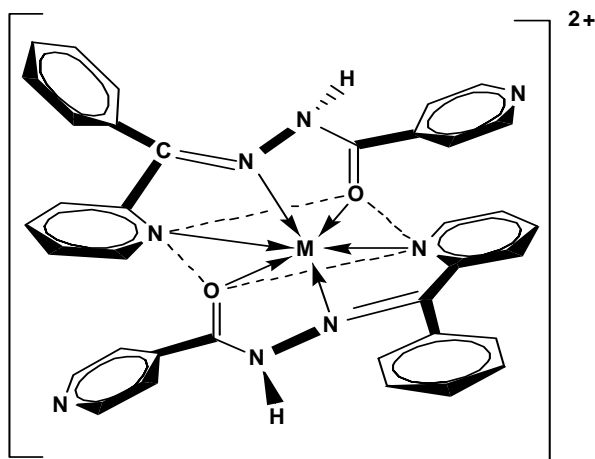


Fig. II.80 Proposed structural formula of complexes of type $[M(INHFPC)_2](X)_m$,

$m=2$, $X=NO_3^-$, ClO_4^- , CH_3COO^- , $M=Cu^{2+}$, Co^{2+} , Ni^{2+}

$m=1$, $X=SO_4^{2-}$, $M=Cu^{2+}$, Co^{2+} , Ni^{2+} , Mn^{2+}

II.5 Complexes of some transition metals with 2-acetyl-pyridyl-isonicotinoylhydrazone

By condensation of 2-acetylpyridine with isonicotinic acid hydrazide a new compound, named as 2-acetyl-pyridyl-isonicotinoylhydrazone (INHMPC), was obtained. The structure of ligand is presented in Figure II.82.

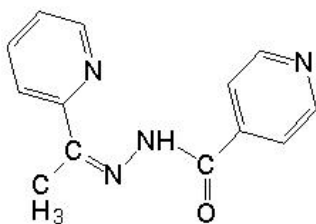


Fig. II.82 The structure of 2-acetyl-pyridyl-isonicotinoylhydrazone (INHMPC)

By template synthesis, thirteen new complexes of bivalent transition metals [116] of type:

- $[M(INHMPC)_2](X)_m$, where $M= Cu(II)$, $Co(II)$, $Ni(II)$, $Mn(II)$ and $Zn(II)$, for $m=2$, $X= ClO_4^-$, $M= Cu(II)$, $Co(II)$, $Ni(II)$, for $X= NO_3^-$, $M= Co(II)$ and $Ni(II)$ for $m=1$, $X= SO_4^{2-}$
- $[M(INHMPC)_2(H_2O)_2](SO_4)$, $M= Cu(II)$, $Mn(II)$ and $Zn(II)$.

were synthesized.

A new Mn(II) complex of type $[\text{Mn}(\text{INHMPc})_2](\text{ClO}_4)$, with a deprotonated Schiff base was also obtained. Single-crystal X-ray diffraction was used for crystal structure determination of the Mn(II) complex.

The complexes are crystalline (nitrate and perchlorate complexes) or powder (sulphate complexes) compounds. The nitrate and perchlorate complexes are soluble in methanol, ethanol, DMF and acetone. The sulphate complexes are insoluble in most common organic solvents. The molar conductivity measurements in methanol show that the nitrate and perchlorate complexes are 1:2 electrolyte types.

IR Spectra

The main IR spectra recorded in $4000 - 400 \text{ cm}^{-1}$ of ligand and its metal complexes are presented in table II.35.

In the IR spectra of 2-acetyl-pyridyl-isonicotinoylhydrazone (INHMPc) a very intense band appears at 1671 cm^{-1} and a medium band appears at 1623 cm^{-1} , which are assigned to vibration frequencies $\nu(\text{C}=\text{O})$ [117] amide and $\nu(\text{C}=\text{N})$ azomethine [118].

For the complexes **54 - 67**, the bands corresponding to carbonyl group appear shifted toward lower frequencies by $\Delta\nu = 5 - 45 \text{ cm}^{-1}$, and the frequency characteristic to azomethine group by $\Delta\nu = 9 - 82 \text{ cm}^{-1}$, respectively, which indicates the involvement of these groups in coordination with metallic ions.

In the IR spectra of Schiff base, three bands of middle intensity appear at 1581 cm^{-1} , 991 cm^{-1} and 753 cm^{-1} , which are assigned to vibration frequency $\nu(\text{Py ring})$, Pt ring bending and γ (Py ring outside the plan), respectively.

In complexes **52 - 60, 62 and 63** vibration frequency due to the Py ring is shifted to lower values by $\Delta\nu = 28 - 87 \text{ cm}^{-1}$. On the other hand, in the IR spectra of the complexes the band corresponding the Py ring bending, which in ligand is at 991 cm^{-1} , is shifted to higher values. Displacements to higher values with $\Delta\gamma = 3 - 24 \text{ cm}^{-1}$ also appear for the typical band of γ (Py ring outside the plan).

All these information lead to the idea that in complexes **52 - 60, 62 and 63** the pyridine nitrogen of 2-acetylpyridine is involved in the coordination with metal ions [106, 107].

All data support the idea that in the studied complexes, the ligand works as tridentate NNO, being coordinated through the azomethine nitrogen, the pyridine nitrogen and carbonylic oxygen.

A different behavior is observed for complexes **61**, **64** and **65**, which are obtained started from Cu(II), Mn(II) and Zn(II) sulphates. In the IR spectra of these complexes the displacement of Py ring bands proved that the pyridine nitrogen is not involved in coordination with metallic ions, as literature shown [106, 107]. In these complexes the ligand acts as a neutral bidentate being coordinated through the azomethine nitrogen and carbonyl oxygen.

The existence of ClO_4^- ions in complexes **52** - **57** is sustained by the presence of a very intense band in the domain $1096 - 1117 \text{ cm}^{-1}$ (ν_3) and a medium band at about 620 cm^{-1} (ν_4). This indicates that Td symmetry is not distorted and the ClO_4^- ion is outside the coordination sphere.

In the IR spectra of complexes **58** – **60**, very intense bands appear at 1384 cm^{-1} , which are assigned to vibration ν_3 of uncoordinated nitrate ion.

The IR spectra of complexes **61** - **65** show intense bands which appear in the region $1104 - 1124 \text{ cm}^{-1}$ and bands of medium intensity at $603 - 628 \text{ cm}^{-1}$, which are assigned to the SO_4^{2-} anion.

The IR spectrum of Mn(II) complex, **56** is different as compared with the ligand and the above studied complexes. Two new bands appear: the vibration frequency $\nu_{\text{C-O}}$ at 1333 cm^{-1} assigned to deprotonated hydrazones (enol form Mn-O-C=N^-) and another at 1580 cm^{-1} , which is assigned to C=N group from enol form [119-122]. The $\nu_{\text{C=O}}$ frequency is not observed in the IR spectra of Mn(II) complex, **56**.

In complex **56**, the ligand acts as monobasic tridentate one. This is confirmed by the X-ray diffraction study.

Crystalline structure description

Single-crystal X-ray diffraction was used for crystal structure determination of **53** $[\text{Co}(\text{INHMPc})_2](\text{ClO}_4)_2$ and **56**, $[\text{Mn}(\text{INHMPc})_2](\text{ClO}_4)_2$ $[\text{CoL2}](\text{ClO}_4)_2$ complexes, using a STOE IPDS II diffractometer, at room temperature. The important crystallographic data are summarized in Table II.36. Selected bond lengths and angles are given in Table II.37.

The structures were solved by direct methods and refined with anisotropic displacement parameters, using Stoe X-Area [123], SHELXS 97 [124] and SHELXL 97 crystallographic software packages.

Table II.36 Crystal data for complexes $[Co(INHMPC)_2](ClO_4)_2$ and $[Mn(INHMPC)_2](ClO_4)_2$

Chemical formula	$C_{27}H_{24}Cl_2CoN_8O_{11}$	$C_{26}H_{22}ClMnN_8O_6$
M / g mol ⁻¹	766.37	632.91
Temperature / K	293(2)	293(2)
Wavelength / Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P21/n	P21/n
a / Å	11.2526(6)	11.741(2)
b / Å	13.3767(9)	9.5288(16)
c / Å	20.7681(11)	26.100(5)
α / °	90.00	90.00
β / °	95.751(4)	98.261(16)
γ / °	90.00	90.00
V/Å ³	3110.3(3)	2889.7(10)
Z	4	4
F(000)	1564	1296
Reflections collected	5606	5693
Unique reflections	4107	4212
R-Factor	0.0697	0.1889
Goodness-of-fit on F ²	1.024	1.059

x, y, z; -x+1/2, y+1/2, -z+1/2; -x, -y, -z; x-1/2, -y-1/2, z-1/2

Table II.37 Selected bond angles and bond lengths for complexes $[Co(INHMPC)_2](ClO_4)_2$ and $[Mn(INHMPC)_2](ClO_4)_2$

$C_{27}H_{24}Cl_2CoN_8O_{11}$	$C_{26}H_{22}ClMnN_8O_6$
N3 Co1 N4 82.9(2)	N1 -Mn1- N2 71.1(3)
N3 Co1 N7 177.8(2)	N1- Mn1- N5 94.2(3)
N3 Co1 N8 97.2(2)	N1- Mn1- N6 90.1(3)
N3 Co1 O1 82.3(2)	N1- Mn1- O1 144.6(3)
N3 Co1 O2 97.8(2)	N1- Mn1- O2 90.2(3)
N4 Co1 N7 99.3(2)	N2- Mn1- N5 95.1(3)
N4 Co1 N8 92.0(2)	N2- Mn1- N6 155.8(3)
N4 Co1 O1 165.1(2)	N2- Mn1- O1 73.6(3)
N4 Co1 O2 90.8(2)	N2- Mn1- O2 122.1(3)
N7 Co1 N8 83.1(2)	N5- Mn1- N6 70.6(3)
N7 Co1 O1 95.5(2)	N5- Mn1- O1 90.7(3)
N7 Co1 O2 81.9(2)	N5- Mn1- O2 141.8(3)
N8 Co1 O1 91.2(2)	N6- Mn1- O1 124.4(3)
N8 Co1 O2 165.0(2)	N6- Mn1- O2 71.4(3)
O1 Co1 O2 89.8(1)	O1- Mn1- O2 107.1(3)
N3 Co1 1.845(4)	Mn1- N1 2.351(8)
N4 Co1 1.925(4)	Mn1- N2 2.20(1)
N7 Co1 1.848(5)	Mn1- N5 2.319(8)
N8 Co1 1.921(4)	Mn1- N6 2.205(8)
O1 Co1 1.904(3)	Mn1- O1 2.131(8) 1
O2 Co1 1.913(3)	Mn1- O2 2.138(8) 1
O3 Cl1 1.549(11)	
O4 Cl1 1.429(6)	
O5 Cl1 1.398(5)	
O6 Cl1 1.349(8)	
O7 Cl2 1.397(6)	
O8 Cl2 1.437(1)	
O9 Cl2 1.352(1)	
O10 Cl2 1.383(1)	
O8A Cl2 1.32(3)	
O9A Cl2 1.32(2)	
O10A Cl2 1.475(2)	

Crystallographic analysis reveals that the complex $[Co(INHMPC)_2](ClO_4)_2$ belongs to space group $P21/n$. Each molecular unit is composed by complex divalent cations $[Co(INHMPC)_2]^{+2}$, with two perchlorate groups as counteranions. From fig. II.85 Co(II) ion is in a distorted octahedral geometry having six coordinating environment by two azomethine nitrogen (Co-N7 = 1.848(5), Co-N3 = 1.845(4) Å), two pyridinenitrogen (Co-N8 = 1.921(4), Co-N4 = 1.925(4) Å) and two carbonylic oxygen (Co-O1 = 1.904(3), Co-O2 = 1.913(3) Å) from the two 2-acetyl-pyridyl-isonicotinoylhydrazones ligands.

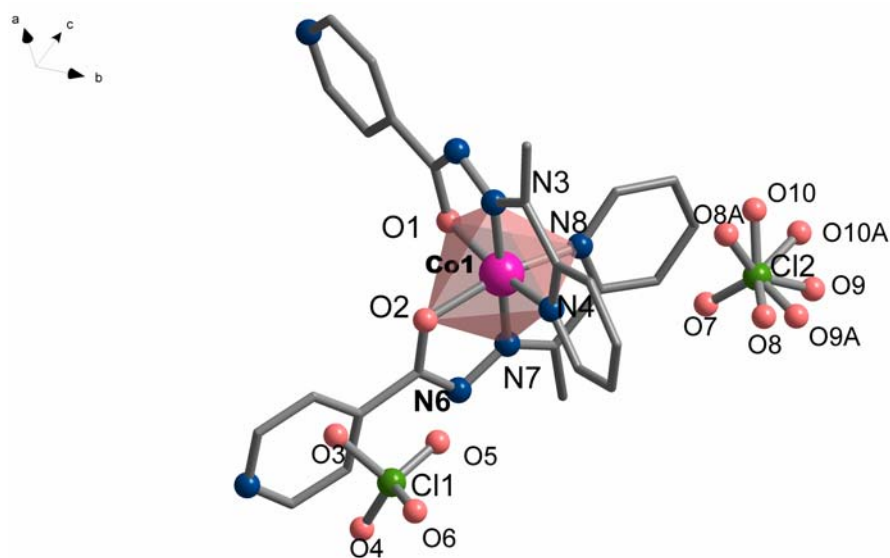


Fig. II.83 Crystal structure of complex $[Co(INHMPc)_2](ClO_4)_2$

Formally, the complex units define the zigzag rows which are arranged in parallel according to the sequence ABAB..., where the discrimination factor is the opposite direction of the chelated tridentate ligands (Fig. II.86). Thus, layers with profiles of “zipper” are generated. The layers are placed parallel and they are separated by wave planes containing ClO_4^- anions and solvent molecules.

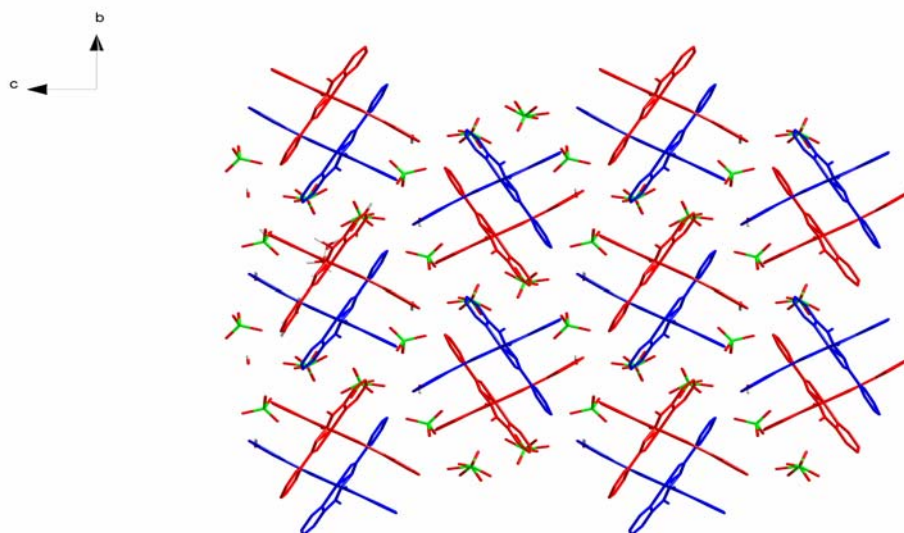


Fig. II.84 Molecular packing of $[Co(INHMPc)_2](ClO_4)_2$

Mononuclear complexes form supramolecular chains parallel to each other via π - π type interactions stacking. Within such a supramolecular chain, two adjacent complex units have opposite orientations.

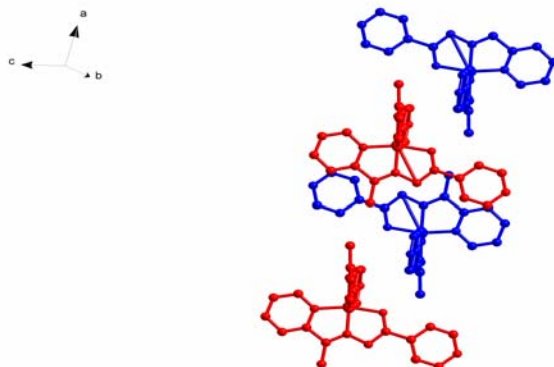


Fig. II.85a. π - π type interactions stacking of $[Co(INHMPC)_2](ClO_4)_2$

It is noted that methanol molecule participates in hydrogen bonding. In the formation of hydrogen bonds are involved either O10A atom ($O11...O10A=2.461(2)$ Å) or O9 ($O11...O9=3.058(2)$ Å), both belonging to the type of anion ClO_4^- .

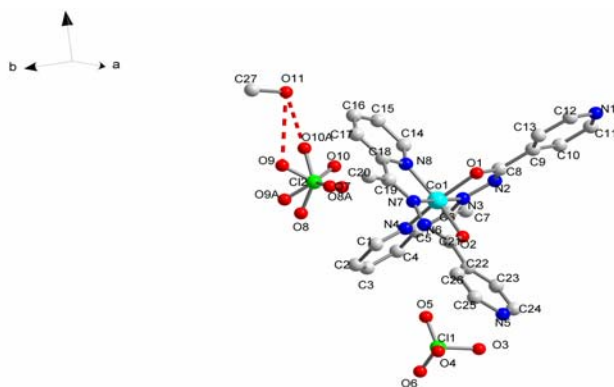


Fig. II.85 Hydrogen bonds in $[Co(INHMPC)_2](ClO_4)_2$

Crystallographic analysis reveals that the complex $[Mn(INHMPC)_2](ClO_4)$ belongs to space group $P21/n$. Each molecular unit is composed by complex monovalent cations $[Mn(INHMPC)_2]^+$, with one perchlorate groups as counteranions. From fig. II.86 Mn(III) ion is in a distorted octahedral geometry having six coordinating environment by azomethine nitrogen, pyridine nitrogen and enol form of oxygen which form five chelate rings with metal ion, from the two deprotonated tridentate 2-acetyl-pyridyl-isonicotinoylhydrazone ligand.

Monomer units have a centrosymmetrical structure, in a distorted octahedral manner (Figure II.86).

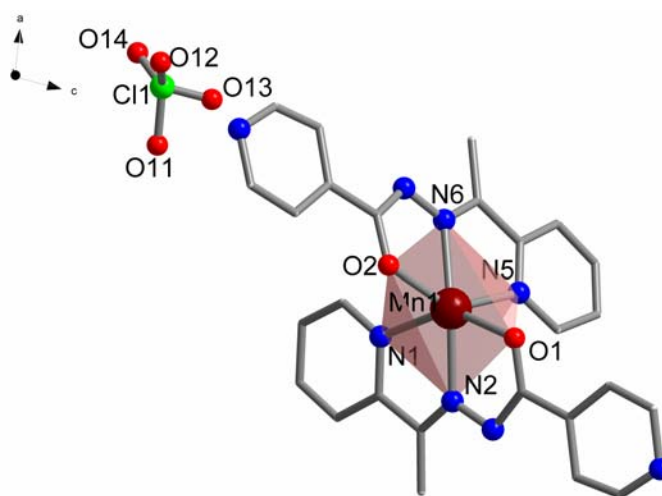


Fig. II.86 Crystal structure of $[Mn(INHMPC)_2](ClO_4)$

Formally, the complex units are arranged according to the sequence ABAB..., (Fig. II.87). Thus, layers with profiles of “zipper” are generated. In the case of $[Mn(INHMPC)_2](ClO_4)$ the layers are separated by rows containing ClO_4^- anions.

Based on the above elemental analysis, spectral data and magnetic moments, together with thermal decomposition studies the structural formula and stoichiometry for complexes indicated in figure II.106 were proposed.

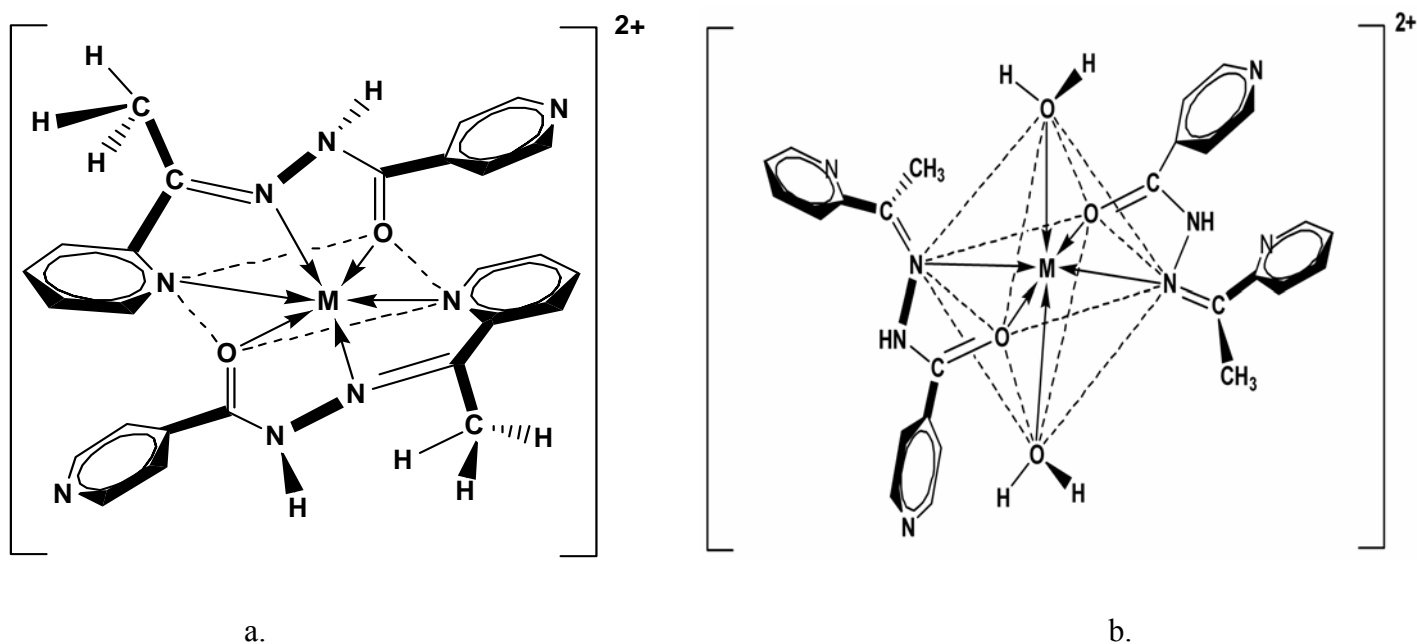


Fig. II.106 Proposed structural formula for complexes with **INHMPC**

a. $[M(\text{INHMPC})_2](\text{X})_m$, (for $m=2$, $\text{X} = \text{ClO}_4^-$ $\text{M} = \text{Cu}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Mn}(\text{II})$ and $\text{Zn}(\text{II})$, for $\text{X} = \text{NO}_3^-$, $\text{M} = \text{Cu}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, for $m=1$, $\text{X} = \text{SO}_4^{2-}$, $\text{M} = \text{Co}(\text{II})$ and $\text{Ni}(\text{II})$)

b. $[M(\text{INHMPC})_2(\text{H}_2\text{O})_2](\text{SO}_4)$, ($\text{M} = \text{Cu}(\text{II})$, $\text{Mn}(\text{II})$ and $\text{Zn}(\text{II})$).

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