



Research Article

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## Physicochemical and antimicrobial investigation on some selected arylhydrazone complexes

Ayman H. Ahmed<sup>1\*</sup> and Emad A. Ewais<sup>2</sup>

<sup>1</sup> Department of Chemistry, Faculty of science, Al-Azhar University. Nasr city, Cairo, Egypt

<sup>2</sup> Botany and Microbiology Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt

### ABSTRACT

Some selected transition ( $\text{Cu}^{\text{II}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$ ) and non-transition ( $\text{Zn}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ ) metal complexes of arylhydrazones, namely *o*-hydroxyacetophenone benzoylhydrazone (HBH) and *o*-methoxybenzaldehyde benzoylhydrazone (MBH) have been isolated and characterized by a combination of elemental analysis, spectral (UV-Vis., IR,  $^1\text{H}$  NMR) and magnetic measurements. Only two divalent metals ( $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$ ) yield stable complexes with MBH. The mode of bonding as well as the geometry of the solid complexes was identified. The results and discussion pointed out that HBH and MBH coordinate to the central metal ion in a bi and/or tridentate manner with forming a dimeric structures in case of  $\text{Cu}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ -HBH while a classic mononuclear structures in case of ( $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ -MBH) and ( $\text{Cr}^{\text{III}}$ ,  $\text{Mn}^{\text{II}}$ -HBH) complexes. The amount of solvent inside and outside the coordination sphere of solid samples was determined by the aide of thermal measurements. The prepared ligands and their metal complexes have been evaluated for their antimicrobial activity against Gram-positive and Gram-negative bacteria as well as for antifungal activity. The metal complexes were much more active than the original compound. In addition, the complex  $\text{Ni}^{\text{II}}$ -HBH showed the highest both antifungal and antibacterial activities against all microbial tested whilst the compound MBH revealed the lowest.

**Key words:** benzoylhydrazone complexes; synthesis; stereochemistry; biological activity

### INTRODUCTION

Hydrazones are versatile ligands occupied a central role in the development of coordination chemistry. This feature comes from the fact, the hydrazones derived from condensation of *o*-hydroxy, methoxy-aldehydes and ketones with hydrazides are potential polynucleating ligands passing azomethine, amide and phenol or methoxy functions which offer varying bonding possibilities in metal complexes. Studies of metal chelates of hydrazone derivatives have been recognized in literature [1]. Moreover, the biological activity of complexes derived from hydrazones has been widely studied and contrasted, acting in processes such as antibacterial, antitumoral, antiviral, antimalarial and antituberculosis effects [2]. The most studied among benzoylhydrazones are the benzoylhydrazones of salicylaldehyde (or its substituted), which hesitate in their coordination with the metal ions within a bi- or tridentate via (C=O), (C=N) and (OH) groups forming a five or six chelate ring around the central metal. Indeed, several metal complexes [M = VO(IV), Mn(II), Fe(III), Fe(II), Co(II), Ni(II) and Cu(II), Cr(III), Zn(II) and Pt(II)] of benzoylhydrazones of salicylaldehyde, substituted-salicylaldehyde and 2-hydroxynaph-1-aldehyde have been extensively studied [3]. Otherwise, Ln(III) complexes of orthohydroxy-aldehydes and ketone with benzoyl and 2-picoloyl hydrazide [M = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Y] have been investigated and showed a non-electrolytic nature in DMF [4]. Literature survey showed also that benzoylhydrazone of benzaldehyde, *o*-methoxybenzaldehyde (anisaldehyde) and acetophenone can be oxidized by nickel peroxide [5] in addition, quantitative determination of the Schiff bases of *o*-hydroxyaldehyde benzoylhydrazone can be carried out using bromometric titration [6].

Actually, investigation on new antimicrobial agents is important due to the resistance acquired by several pathogenic microorganisms. The synthesized chemical compounds, which are used for the treatment of infectious diseases, are known as chemotherapeutic agents. Every year thousands of compounds are synthesized to find out potential chemotherapeutic agent to combat pathogenic microorganisms. In this regard, heterocyclic bases have great importance in biological and industrial fields. Most of them are used as corrosion inhibitors [7] and their complexes with platinum and copper tested as antitumor [8] and antibacterial [9]. Further, mixed ligand metal complexes of ampicillin and chloramphenicol prepared by using Ni(II), Co(II) and Fe(III) chlorides hexahydrate disclosed that the activity of the metal complexes was more potent antibacterial than the parent drugs against the three bacteria species [10].

In view of the importance of hydrazones and their chelates, we have undertaken the synthesis and structural characterization studies on bivalent (Mn, Co, Ni, Cu, Zn, Pb) and trivalent (Cr, Fe) metal complexes with *o*-hydroxyacetophenone and *o*-methoxybenzaldehyde benzoylhydrazone (HBH and MBH, respectively). The effect of methyl group (that represents the only difference between the two synthesized hydrazones) on their coordinating nature has been illustrated. Also, the objective of this investigation is to establish whether some metals have a role in enhancing the antimicrobial activity of the two synthesized hydrazones depicted in Fig. 1.

## EXPERIMENTAL SECTION

### *Materials and physical measurements*

All chemicals and solvents utilized were of Merck, BDH or AR quality and used as received without further purification. Benzoylhydrazide (BH) was prepared following the method described in literature [11]. The physical measurements were carried out using the methods and appliances models reported earlier [12,13] as follows. The elemental analysis for carbon, hydrogen and nitrogen was performed on Perkin Elmer 2400 at Microanalytical Unit of Cairo University, Egypt. Metal contents (%wt) were estimated complexometrically by EDTA using xylenol orange as indicator and solid hexamine as buffer (pH = 6). FT-IR spectra of the ligand as well as the complexes were recorded as KBr pellet on a Bruker (Vector 22) single beam spectrometer at a spectral resolution of 2.0 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer at 25 °C using DMSO solvent and TMS as an internal standard. Mass spectra of the HBH and MBH were recorded on Shimadzu-GCMS-Q5050 instrument using the direct inlet system. UV-Vis. spectra of the samples were recorded in Nujol mull using λ35 Perkin-Elmer UV/Vis. Spectrophotometer. Thermal measurements (TG) were done on a Shimadzu 50 H thermal analyzer. Mass susceptibility of the solid samples ( $\chi_g$ ) was measured at room temperature with a magnetic susceptibility balance of models Johnson Metthey and Sherwood. The effective magnetic moments  $\mu_{\text{eff}}$  were calculated according to the subsequent relation. Antimicrobial assay was done at the Regional Center for Mycology and Biotechnology (RCMB), Cairo, Egypt.

$$\mu_{\text{eff}} = 2.84 [\chi_M \cdot T]^{1/2}$$

### *Preparation of hydrazones (HBH and MBH)*

The two ligands were prepared using the recipe described elsewhere [14] as follows. Benzoylhydrazide (3.0 g, 0.022 mole) was dissolved in absolute ethanol (50 cm<sup>3</sup>) and the resulting solution was then added to an ethanolic solution (50 cm<sup>3</sup>) of *o*-hydroxyacetophenone or *o*-methoxybenzaldehyde (2.99 g, 0.022 mole). The reaction mixture was prolonged under reflux for 2 h in the presence of 2 ~ 3 drops glacial acetic acid. The separated product was filtered, washed with ethanol, recrystallized using ethanol and finally dried in oven at 80 °C for 24 h. The resulting ligands having the similar chemical formula C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> are shown accompanied with their <sup>1</sup>H NMR spectra in Fig. 1. The authenticity of the ligands was proved by elemental analyses, (IR, mass and <sup>1</sup>H NMR) spectroscopy (Table 1).

The synthesized hydrazones are insoluble in petroleum ether and soluble in most common organic solvents e.g. alcohol, acetone, benzene, chloroform, DMF and DMSO.

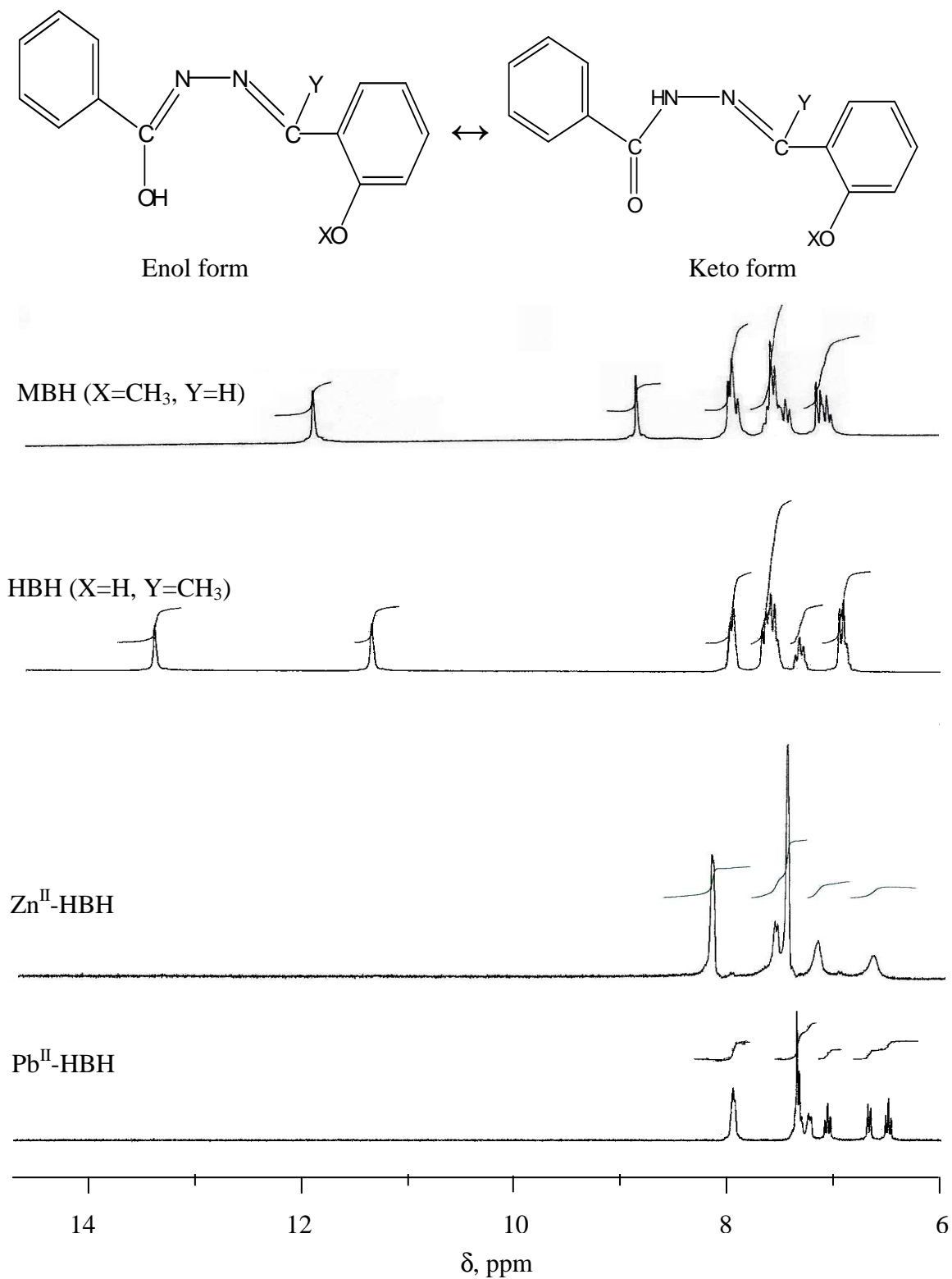


Fig. 1.  $^1\text{H}$  NMR spectra of ligands (HBH, MBH) along with diamagnetic Zn<sup>II</sup> and Pb<sup>II</sup>-HBH complexes.

#### *Preparation of solid complexes*

All the isolated solid complexes (Table 1) were prepared by mixing equimolar amounts of ligands and metal(II) acetates [M = Cu(II), Cr(III), Mn(II), Co(II), Ni(II), Zn(II) and Pb(II)] in 100 cm<sup>3</sup> ethanol. Fe(III) chloride was utilized in case of separating the iron complex. The reaction mixture was refluxed on hot plate for 3 h. Colored microcrystalline solids were isolated by concentrating the solutions to their halves and then filtered on hot. The obtained complexes were washed repeatedly with hot ethanol and finally dried in oven at 80 °C for 24 h. The complexes retain their colors for long time, insoluble in water and petroleum ether, and soluble in DMF and DMSO.

#### *Agar diffusion well method to determine antimicrobial activity*

The synthesized compounds were screened for their antimicrobial activity against eight different test organisms having environmental and clinical importance. The microorganism's inoculums were uniformly spread using sterile cotton swab on a sterile Petri dish Malt agar (for fungi) and nutrient agar (for bacteria). 100 µL of each sample was added to each well (10 mm diameter holes cut in the agar gel, 20 mm apart from one another). The systems were incubated for 24-48 h at 37 °C (for bacteria) and at 28 °C (for fungi). After incubation, microorganism's growth was observed. Inhibition of the bacterial and fungal growth were measured in mm. Tests were performed in triplicate [15]. Minimal inhibitory concentration (MICs) of nickel complex (Ni<sup>II</sup>-HBH) was determined by dissolving the nickel specimen in DMSO and using different concentrations (0.001-0.078 mg/L). The minimal inhibitory concentration (MICs) was determined after incubation period.

## RESULTS AND DISCUSSION

All the analytical, physical and spectroscopic data of the hydrazones and their corresponding metal complexes are given in Tables 1- 2. Comparison of the analyses for both calculated and found percentages indicates that the compositions of the isolated solid complexes are coincided with the proposed formulae.

#### *IR Spectra*

The positions of the significant IR bands of hydrazones as well as their metal complexes are summarized in Table 2. The IR spectra of the free ligands (HBH and MBH) exhibit strong absorptions at 3100-3300, 1620-1700, 1580-1620 and 700-800 cm<sup>-1</sup> assignable to  $\nu(\text{NH})$ ,  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{N})$  and the out of plane deformation of the aromatic ring, respectively. The observation of the (C=N) band ascertains the formation of the azomethine linkage and thus the requested hydrazones. The appearance of both  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{O})$  with unnoticeable the  $\nu(\text{OH})_{\text{enolic}}$  suggest the keto form of ligands in the solid state (Fig. 1). However, in solution and in the presence of metal ions, the ligands may exist in equilibrium with the tautomeric enol form (Fig. 1). The observation of a broad but weak bands in the 2000-1700 cm<sup>-1</sup> region for HBH in addition to the band at 2764 cm<sup>-1</sup> ( $\nu_{\text{OH}}$ ) is taken as an evidence for the formation of stable six membered ring of intermolecular hydrogen bonding of the type -CH=N...OH [16]. The positions of other bands assigned to  $\nu(\text{CH})_{\text{aromatic, aliphatic}}$  and  $\delta(\text{NH})_{\text{amide III}}$  are demonstrated in Table 1.

The IR spectral data for the complexes indicate that HBH may acts as bi- or tridentate ligand towards the investigated metal ions while MBH behaves as tridentate with Ni(II) and Cu(II). The following evidences support this criteria (Table 2) where: (1) The obscure of the bands related to the H-bonding in the free HBH ligand indicates the involvement of the phenolic hydroxyl and/or azomethinic nitrogen in coordination. Worthy mention, the negative shift of the azomethine group to lower wavenumber asserts the involvement of this group in bonding [12]. Besides, the splitting in the vibrational stretching C=N band which sometimes remarked in some chelates substantiates the presence of two dissimilar azomethine groups [17]. (2) Disappearance of both  $\nu$ ,  $\delta(\text{NH})$  by chelation indicates that the ligands coordinate in enolic form. (3) Unnoticeable of the  $\nu(\text{OH})_{\text{phenolic}}$  in case of some HBH complexes reflects the deprotonation of this group during the coordination as in case of Cu(II), Ni(II), Zn(II) and Pb(II)-HBH species. The negative shift noticed in the  $\nu$ ,  $\delta(\text{NH})$  band associated with Ni(II)-HBH refers to the existence of NH...OH<sub>2</sub> hydrogen bond as shown in its chemical structure, Fig. 3. (4) Appearance of  $\nu$ ,  $\delta(\text{NH})$  and  $\nu(\text{OH})$  along with a shift in the  $\nu(\text{C}=\text{O})$  for Mn(II)-HBH affirms the coordination of HBH ligand via its keto and enol sides. Moreover, a strong broad absorption at 3384 cm<sup>-1</sup> for Ni(II)-HBH complex suggests the presence of water. (5) The negative shift for  $\delta(\text{C}-\text{OMe})$  related to MBH ligand (1294 cm<sup>-1</sup>) by 13-15 cm<sup>-1</sup> upon chelation with Cu(II) (1281 cm<sup>-1</sup>), and Ni(II) (1279 cm<sup>-1</sup>) ions points to the bonding of metal ions with methoxy group providing octahedral structures as suggested by the electronic investigation shown later. (6) Finally, the persistence of new bands attributed to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  supports the formation of the complexes.

#### *<sup>1</sup>H NMR Spectra*

The assignments of the main signals in <sup>1</sup>H NMR spectra of the HBH, MBH and diamagnetic Pb<sup>II</sup>, Zn<sup>II</sup>-HBH complexes are given in Fig. 1 and Table 1. <sup>1</sup>H NMR spectra of hydrazones exhibit three signals with integration (1:1:3) at (11.3, 13.4, 2.5) and (11.9, 8.8, 3.9) ppm, downfield of TMS, and assigned to the protons of (-NH, -OH, -CH<sub>3</sub>) and (-NH, -CH=N, -CH<sub>3</sub>) for HBH and MBH, respectively [14,18]. The much higher frequency of the OH

signal in case of HBH compared with that reported in literature is most probably due to the intermolecular hydrogen bonding established between the hydrogen atom of the orthohydroxyl group and the azomethinic nitrogen (OH...N type) as previously provided by the IR data. Comparing the  $^1\text{H}$  NMR spectrum of the hydrazone HBH with that of the corresponding Zn(II), and Pb(II) complexes, namely  $[\text{Zn}(\text{L}_1\text{-1H})]_2$  and  $[\text{Pb}(\text{L}_1\text{-1H})]_2$ , demonstrates that no signal is recorded for a phenolic OH nor NH as in the case of the HBH hydrazone. This foundation gives a clue for the departure of the  $-\text{CH}=\text{N}\dots\text{HO}$  H-bond and deprotonation of both ortho and enolic hydroxyl groups. The signals attributed to the aromatic protons for all samples were observed within 6-8.4 ppm with slightly change in their positions.

#### *Optical absorption and magnetic investigation*

The assignments of the observed electronic absorption bands of the free ligands accompanied with their solid complexes as well as the geometry and magnetic data of the chelates are shown in Table 2. and Fig. 2 [14, 19-22].

It is clear that HBH and MBH hydrazones exhibit six bands assignable to  $n\rightarrow\pi^*(\text{C}=\text{O})$ ,  $n\rightarrow\pi^*(\text{C}=\text{N})$ ,  $\pi\rightarrow\pi^*(\text{C}=\text{O})$ ,  $\pi\rightarrow\pi^*(\text{C}=\text{N})$ ,  $\pi\rightarrow\pi^*(o\text{-substituted phenyl ring})$  and  $\pi\rightarrow\pi^*(\text{phenyl ring})$ [14]. The electronic spectra of the metal chelates suggest different environments around the metal ions.

**For HBH complexes:** The results revealed that Cu(II) complex is square planar, Mn(II) complex showed intense bands assigned to a tetrahedron and Co(II), Ni(II), Cr(III), Fe(III) complexes are most probable to be octahedral. The Zn(II) and Pb(II) complexes are diamagnetic as expected and no d-d bands are observed owing to the filling of d sub shell by 10 electrons ( $d^{10}$  configuration). The electronic spectra of Zn(II) and Pb(II)-HBH complexes exhibited only M $\rightarrow$ L charge transfer bands. These complexes are assumed as tetrahedral depending their analytical and spectral IR data. Worthy mention, Zn(II) occurs largely in four coordination as tetrahedral complexes whereas the octahedral complexes of zinc are not very stable [20, 23].

**For MBH complexes:** The electronic spectra of Cu(II) and Ni(II) complexes refer to the formation of octahedral structures as previously confirmed by IR spectroscopy.

The values of magnetic moments (Table1) of metal complexes under study also support the proposed stereochemistry derived from the electronic data. The results give two different behaviors: (i) the complexes  $\text{Cu}^{\text{II}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  of HBH ligand have 1, 5, 5, 5, 1 and 2 unpaired electrons, respectively, showing a paramagnetic nature. Further, complexes of  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  with MBH have 1 and 2 unpaired electrons, respectively, reflecting the paramagnetic nature else. (ii) The complexes of  $\text{Zn}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$ -HBH were found to be contain no unpaired electrons showing a diamagnetic behavior. Perhaps, the lower  $\mu_{\text{eff}}$  values for  $\text{Cu}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$  and  $\text{Co}^{\text{II}}$ -HBH than the expected spin-only values established from the distortion from the idealized symmetry and/or the great approaching of two metal ions to each other especially with formation of phenolic and/or enolic bridges. The metal ions may be close to each other by which the M-M interaction gives rise to incomplete quenching of the spin moments of the ions. This means that the supposition of two metal ions in the molecular structure is not excluded and the obtained  $\mu_{\text{eff}}$  values may be considered in a good agreement with the proposed dimeric structures as published in some papers [22, 24].

**Table 1. Analytical, physical and spectroscopic data of the hydrazones and their related metal complexes.**

Compound	M.p (°C), Color	Found(Calcd.)%				<sup>1</sup> H-NMR Chemical shift (δ, ppm)	M <sup>r</sup> Found(Calcd.)	μ <sub>eff.</sub> <sup>a</sup> B.M.
		C	H	N	M			
HL <sub>1</sub> =HBH	192 off white	70.26 (70.84)	5.32 (5.56)	11.65 (11.02)	-	11.3(NH, s), 13.4(OH, s), 2.5(CH <sub>3</sub> , s), 6.8-8(aromatic protons, m)	254 (254.3)	
[Cu(L <sub>1</sub> -1H) <sub>2</sub> ]	206 green	57.20 (57.04)	4.56 (4.16)	8.91 (8.87)	19.4 (20.1)			0.8
[Cr(L <sub>1</sub> ) <sub>3</sub> ]	>300 Chocolate brown	66.04 (66.56)	4.68 (4.80)	10.12 (10.35)	5.9 (6.4)			3.9
[Mn(HL <sub>1</sub> ) <sub>3</sub> -1H](OAc)	>300 Brown	62.12 (62.61)	5.51 (5.16)	8.91 (8.94)	6.3 (6.3)			5.7
[Fe <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> . 4Cl]	>300 Violet	47.56 (47.39)	3.77 (3.45)	7.89 (7.37)	14.2 (14.7)			4.3
[Co <sub>2</sub> (L <sub>1</sub> ) <sub>4</sub> ]	>300 Dark brown	63.51 (63.70)	4.85 (4.64)	9.32 (9.90)	9.52 (10.4)			0.6 <sup>d</sup>
[Ni <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].(OAc) <sub>2</sub> . 2H <sub>2</sub> O	>300 Pale green	48.82 (48.04)	4.63 (4.47)	7.21 (6.59)	14.4 (13.8)			2.9
[Zn(L <sub>1</sub> -1H) <sub>2</sub> ]	>300 Pale yellow	56.08 (56.71)	4.01 (3.81)	8.26 (8.82)	21.0 (20.6)	2.5(CH <sub>3</sub> , s), 6.5-8.2(aromatic protons, m)		Diamg.
[Pb(L <sub>1</sub> -1H) <sub>2</sub> ]	>300 Yellow	39.91 (39.20)	3.18 (2.61)	6.82 (6.12)	45.9 (45.1)	2.4(CH <sub>3</sub> , s), 6.4-8.0(aromatic protons, m)		Diamg.
HL <sub>2</sub> =MBH	200 Bridal white	70.61 (70.84)	5.82 (5.56)	11.60 (11.02)	-	11.9(NH, s), 8.8(CH=N, s), 3.9(-OCH <sub>3</sub> , s), 6.5 - 8 (aromatic protons, m) <sup>c</sup>	254 <sup>c</sup> (254.3)	
[Cu(L <sub>2</sub> ) <sub>2</sub> ]	>220 Dark brown	63.51 (63.20)	3.99 (3.91)	9.32 (9.83)	9.4 (9.4)			1.9
[Ni(L <sub>2</sub> ) <sub>2</sub> ]	>280 Green	54.51 (54.16)	3.99 (3.94)	9.26 (9.91)	9.1 (8.8)			2.9

<sup>a</sup> Values measured per one metal ion, <sup>b</sup> solvent is DMSO, <sup>c</sup> these values have been quoted from Ref. [14], <sup>d</sup> the much lower value is most probable due to the low spin state and spin cross criteria..

Table 2. Significant IR and electronic absorption data of hydrazones and their metal complexes

Compound	v(OH) phenolic	v(NH)	v(C=O)	v(C=N)	v(CH) aromatic	v(CH) aliphatic	$\delta$ (NH)	v(OAc)	Solvent (MeOH/H <sub>2</sub> O)	vM-O/M-N	$\lambda_{max}$ , nm (assignments)	Structure
HL <sub>1</sub> =HBH	2764	3218	1650	1606	3056	2930	1251	-	-	-	388 (n→π*, C=O), 370 (n→π*, C=N), 360 (π→π*, C=O), 355 (π→π*, C=N), 348 (π→π*, o-substituted phenyl ring), 335 (π→π*, phenyl ring)	
Cu <sup>II</sup> -HBH	-	-	-	1599	3062	2924	-	-	-	484/417	619 ( <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub> , <sup>2</sup> B <sub>2g</sub> , <sup>2</sup> E <sub>g</sub> )	Square planar
Cr <sup>III</sup> -HBH	3420	-	-	1599	3057	2924	-	-	-	455/420	665, 615 ( <sup>4</sup> A <sub>2g</sub> → <sup>2</sup> T <sub>1g</sub> , <sup>2</sup> E <sub>g</sub> ), 572 ( <sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>2g</sub> ), 523 ( <sup>4</sup> A <sub>2g</sub> → <sup>2</sup> T <sub>2g</sub> (F)), 468, 414 ( <sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (F))	Octahedral
Mn <sup>II</sup> -HBH	3417	3218	1650/1634	1599	3056	2924	1253	1536	-	480/419	618, 457, 439, 425 ( <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G), <sup>2</sup> T <sub>2g</sub> (G), <sup>4</sup> E <sub>g</sub> (G), <sup>4</sup> A <sub>1g</sub> (G))	Octahedral
Fe <sup>III</sup> -HBH	3414	-	-	1619, 1596	3057	2924	-	-	-	548/420	619 ( <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> ) <sup>a</sup> , 480 (L→Fe)CT	Octahedral
Co <sup>II</sup> -HBH	3419	-	-	1600, 1620	3060	2924	-	-	-	480/466	930 ( <sup>4</sup> A <sub>2</sub> (F) → <sup>4</sup> E <sub>2</sub> (F), 698 ( <sup>4</sup> A <sub>2</sub> (F) → <sup>4</sup> A <sub>2</sub> (P)), 554 ( <sup>4</sup> A <sub>2</sub> (F) → <sup>4</sup> E <sub>2</sub> (P), 456 (Co→L, CT)	Trigonal bipyramidal
Ni <sup>II</sup> -HBH	-	3205br	1630	1620/1599	3071	2926	1219	1540	-/3384	487/420br	915 ( <sup>3</sup> A <sub>2g</sub> → <sup>2</sup> T <sub>2g</sub> (P)), 638 ( <sup>3</sup> A <sub>2g</sub> → <sup>2</sup> T <sub>1g</sub> (F)), 420 ( <sup>3</sup> A <sub>2g</sub> → <sup>2</sup> T <sub>1g</sub> (P))	Octahedral
Zn <sup>II</sup> -HBH	-	-	-	1600	3064	2920	-	-	-	471/418	638, 420 (Zn→L, CT)	Tetrahedral
Pb <sup>II</sup> -HBH	-	-	-	1593	3055	2921	-	-	-	539/460	638, 420 (Pb→L, CT)	Tetrahedral
HL <sub>2</sub> =MBH	-	3188	1643	1606	3028	2950	1252	-	-	-	387 (n→π*, C=O), 365 (n→π*, C=N), 357 (π→π*, C=O), 348 (π→π*, C=N), 334 (π→π*, o-substituted phenyl ring), 324 (π→π*, phenyl ring)	
Cu <sup>II</sup> -MBH	-	-	-	1599, 1616	3052	2950	-	-	-	537/447	692 (d <sub>xy</sub> , d <sub>z</sub> <sup>2</sup> and (d <sub>xz</sub> , d <sub>yz</sub> ) → d <sub>x<sup>2</sup>-y<sup>2</sup></sub> , σ*(L <sub>2</sub> ))	Distorted octahedral
Ni <sup>II</sup> -MBH	-	-	-	1598, 1610	3020	2948	-	-	-	533/446	930 ( <sup>3</sup> A <sub>2g</sub> → <sup>2</sup> T <sub>2g</sub> (P)), 582 ( <sup>3</sup> A <sub>2g</sub> → <sup>2</sup> T <sub>1g</sub> (F)), 410 ( <sup>3</sup> A <sub>2g</sub> → <sup>2</sup> T <sub>1g</sub> (P))	Octahedral

<sup>a</sup> The widening of this band suggest an octahedral geometry around the Fe(III) ion where the tetrahedral Fe(III) complexes such as FeX<sub>4</sub> (X=halogens) generally characterized by fairly narrow bands.

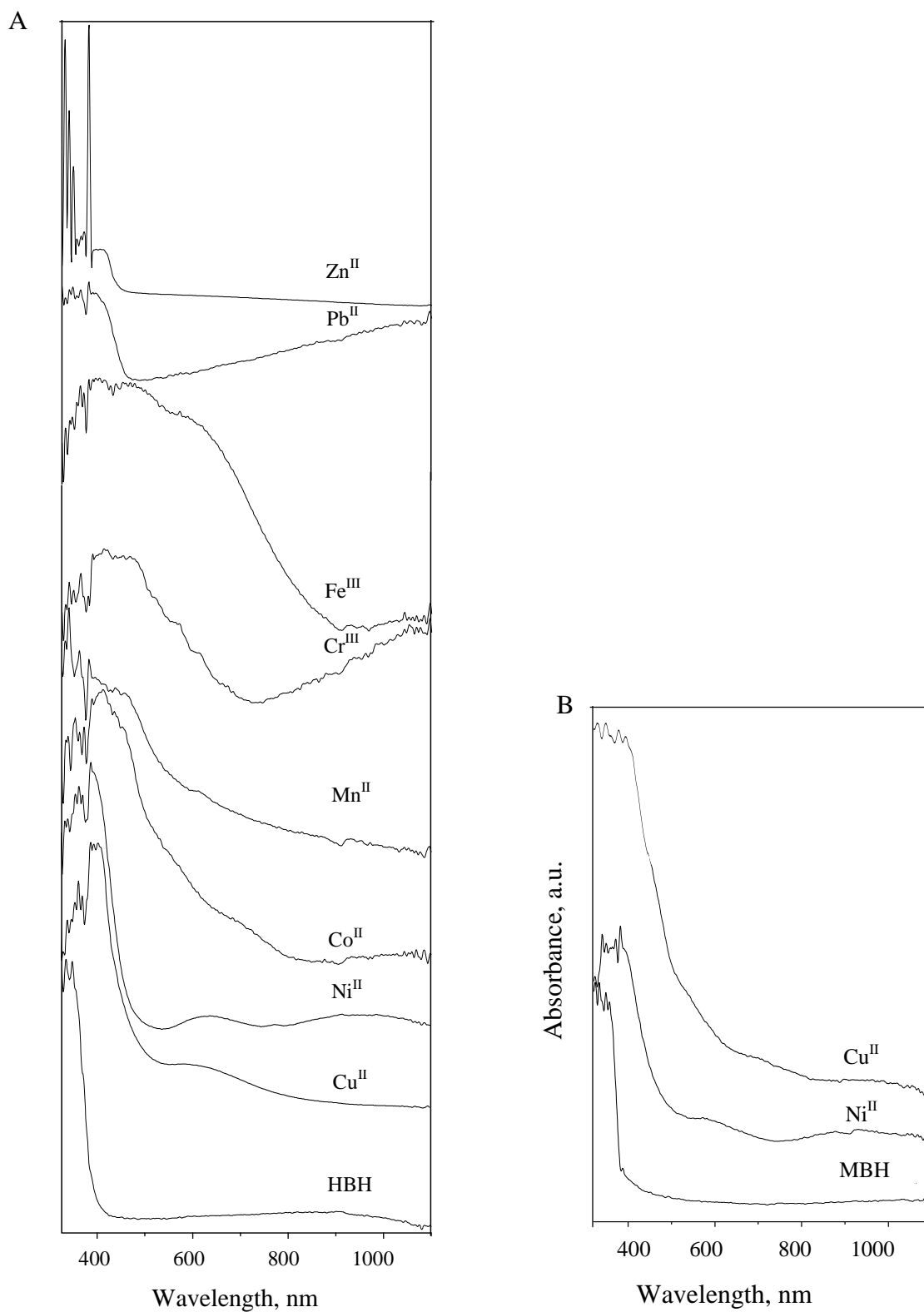


Fig. 3. Electronic spectra of (A) HBH accompanied with its chelates and (B) MBH along with its chelates.



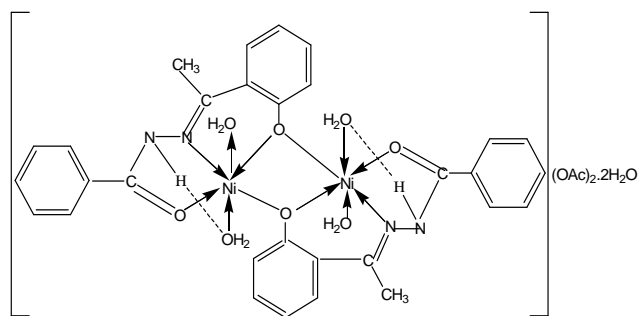
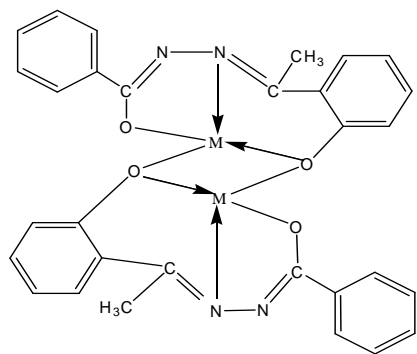
*Thermal studies*

The thermal decomposition studies (TG) on most of synthesized solid complexes, M-HBH [M = Cu(II), Mn(II), Fe(III), Co(II), Ni(II), Zn(II) and Pb(II)] and M-MBH [M = Cu(II), Ni(II)] have been carried out. The TG curves up to 800 °C for these complexes showed 2-3 stages of decompositions except Ni(II)-HBH and Zn(II)-HBH which showed 5 and 2 decomposition steps, respectively. The thermogravimetric data reveal that: (1) The first decomposition stage for complexes begins at 230-375 °C and the decomposition process is ended by the formation of (found/calculated)%: (i) metal oxides (MO): Mn(II) (9.1/8.1), Fe(III)(10.1/9.5), Ni(II)(9.8/8.8), Zn(II)(12.2/12.8)-HBH. Cu(II) and Ni(II)-MBH are (14.8/14.0) and (11.4/11.2), respectively; (ii) carbonate: Pb(II)-HBH (30.0/29.1); (iii) mixture of metal and metal oxide (M+MO): Co(II)-HBH (12.1/11.9) and finally (iv) metal: Cu-HBH (9.0/10.0). The resulting metal associated with the last two compounds is eventuated by the reduction of metal oxide by carbon. (2) According to Nikolaev *et al* [25], water eliminating below 150 °C can be considered as free crystal water and water eliminating near 150 °C may be due to its coordination to the metal ion. Taking this fact into account, All the samples have not any crystal or coordinated solvent (methanol or water) except Ni(II)-HBH,  $[\text{Ni}_2(\text{L}_1)_2(\text{H}_2\text{O})_4](\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , which showed two weight loss stages at 50-175 and 175-225 °C. The first mass loss corresponds to loss of two lattice water molecules (4.2% theoretical against to 4.5% found) however the second mass loss step indicates the removal of four coordinated water molecules (8.5% theoretical against to 8.5% found). Interestingly, the higher melting points for HBH complexes (>300 °C) coincide with the postulating dimeric or unusual compositions (i.e., high molecular weight) formulas. Based on the initial decomposition temperature, the thermal stability order for the investigated complexes is found to be  $\text{Mn}^{\text{II}}\text{-HBH} < \text{Zn}^{\text{II}}\text{-HBH} < \text{Cu}^{\text{II}}\text{-MBH} < \text{Ni}^{\text{II}}\text{-MBH} < \text{Fe}^{\text{III}}\text{-HBH} < \text{Co}^{\text{II}}\text{-HBH} = \text{Pb}^{\text{II}}\text{-HBH} < \text{Cu}^{\text{II}}\text{-HBH} < \text{Ni}^{\text{II}}\text{-HBH}$ . Noteworthy, Ni<sup>II</sup>-HBH which recorded the higher thermal stability revealed an upper biological activity that add a characteristic property for this specimen.

In the light of the forgoing results, the coordination cores of the metal complexes associated with HBH and MBH hydrazones can be represented by Fig. 3. In Comparison of MBH species with that of analogous HBH, perhaps the incapability to separate synonymous metal complexes other than Cu(II) and Ni(II)-MBH comes from two reasons. (1) The less basicity of the methoxy group (OMe in MBH) than phenolic hydroxyl group (OH in HBH). The OH group can easily do deprotonation that compensates the positive charges on metal ion and thus facilitates the metal-ligand interaction by which a lot number of complexes may be got. (2) The steric effect that results from a slightly larger size of MBH compared with HBH (Fig. 1). In fact, the ability of Cu(II) and Ni(II) ions to form complexes with MBH comes from high stability of these complexes in accordance with a known Irving-Williams series.

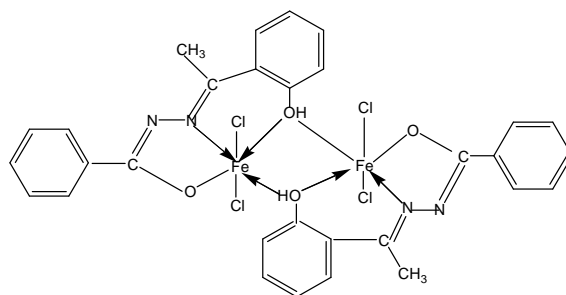
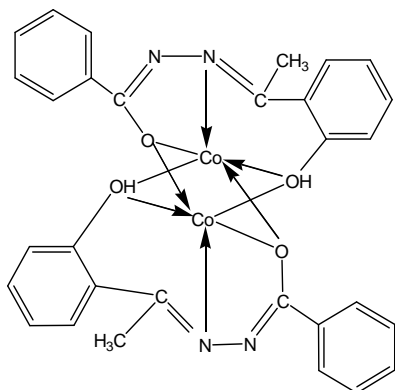
*Antimicrobial investigations*

Antimicrobial activities of the prepared compounds and their complexes were evaluated against two Gram-positive bacteria strains (*Staphylococcus aureus* and *Bacillus subtilis*), two Gram-negative strains (*Pseudomonas aeruginosa* and *Escherichia coli*) and four fungi strains (*Aspergillus fumigates*, *Penicillium italicum*, *Syncephalastrum racemosum* and *Candida albicans*). The activity was tested by a disc-diffusion method. The prepared compound MBH exhibited no effect on Gram-positive and negative bacteria as well as the tested fungi, while the second compound HBH gave a little effect. Perhaps the lower activity of the original ligand HBH arises from its lower concentration but as known for aromatic compounds, upraise their concentrations is undesirable owing to their expected toxicity and chemical influences. The results also indicated that the metal complexes was more effective than original compound. This result is in agreement with those of Kupeman and Carreiro [26] and Ajani [10]. It should be mentioned that there was no antifungal activities in the cases of MBH with either Cu<sup>II</sup> or Ni<sup>II</sup>. However, the same complexes exhibited a medium effective against two or one Gram-positive bacteria in the cases of Cu<sup>II</sup> and Ni<sup>II</sup>, respectively. The results also illustrated that compound of HBH with Cu<sup>II</sup> can induce great inhibition for two tested fungi (*Aspergillus fumigates* and *Syncephalastrum racemosum*), whereas the same compound with Co<sup>II</sup> or Zn<sup>II</sup> exhibited a slight inhibition of *Syncephalastrum racemosum* only (see Table 3). As concerns antibacterial activities, HBH with any of the tested metals was a quit effective against all tested Gram-positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*). Interestingly, Ni<sup>II</sup>-HBH was found to induce complete inhibition of all tested fungi and bacteria compared to the other compounds. Accordingly, The activity (MICs) of Ni<sup>II</sup>-HBH against bacteria and fungi was determined and given in Table 4. The final result may give a promising approach for using such compound in the future as a diverse range of applications due to its simple synthesis, high potent antibacterial and antifungal agent and its low concentrations in MICs. Doubtless, nickel can enhance the hydrazone inhibition (HBH) against several microorganisms.



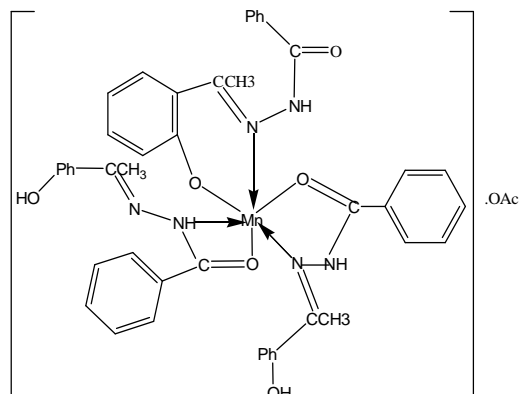
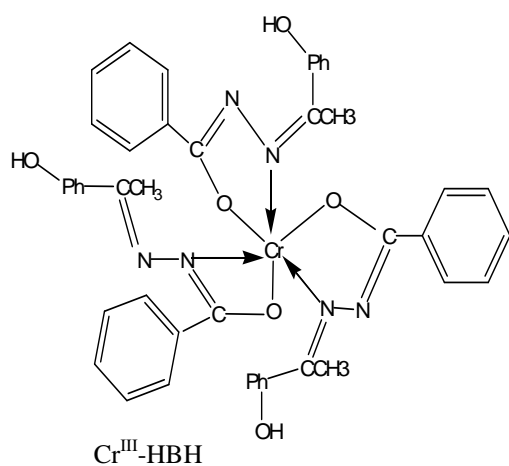
$M^{II}$ -HBH,  $M = Cu^{II}, Pb^{II}$  and  $Zn^{II}$

$Ni^{II}$ -HBH



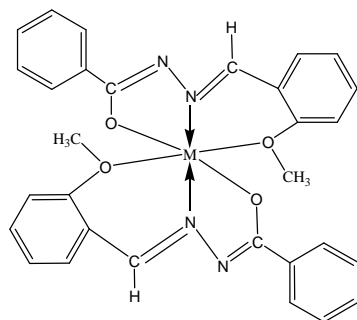
$Co^{II}$ -HBH

$Fe^{III}$ -HBH



$Cr^{III}$ -HBH

$Mn^{II}$ -HBH



$Cu^{II}$  and  $Ni^{II}$ -MBH

Fig. 2. Coordination cores of the HBH and MBH complexes.

**Table 3. Antimicrobial screening activity of hydrazones (HBH and MBH) and their corresponding complexes.**

Sample label Microorganism	HBH									MBH		ST.	
	HBH	Cu <sup>II</sup>	Cr <sup>III</sup>	Mn <sup>II</sup>	Fe <sup>III</sup>	Co <sup>II</sup>	Ni <sup>II</sup>	Zn <sup>II</sup>	Pb <sup>II</sup>	MBH	Cu <sup>II</sup>		Ni <sup>II</sup>
<i>Aspergillus fumigatus</i>	0	12	0	0	0	0	<b>21</b>	0	0	0	0	0	<b>24</b>
<i>Penicillium italicum</i>	0	0	0	0	0	0	<b>17</b>	0	0	0	0	0	<b>19</b>
<i>Syncephalastrum racemosum</i>	0	13	0	0	0	7	<b>14</b>	8	0	0	0	0	<b>21</b>
<i>Candida albicans</i>	0	0	0	0	0	0	<b>16</b>	0	0	0	0	0	<b>19</b>
<i>Staphylococcus aureus</i>	8	10	7	6	6	8	<b>13</b>	11	10	0	12	10	<b>15</b>
<i>Pseudomonas aeruginosa</i>	0	0	0	0	0	0	<b>7</b>	0	0	0	0	0	<b>11</b>
<i>Bacillus subtilis</i>	8	18	7	0	16	9	<b>19</b>	12	9	0	10	0	<b>22</b>
<i>Escherichia coli</i>	0	0	0	0	0	0	<b>21</b>	0	0	0	0	0	<b>27</b>

St. = Reference standard Terbinafin was used as a standard antifungal agent while chloramphenicol was used as a standard antibacterial agent.

Well diameter: 6.0 mm... (100 ul of each concentration was tested). 0 = zone of (mm) inhibition reflecting no inhibition of growth.

**Table 4. MICs of Ni<sup>II</sup>-HBH against bacteria and fungi.**

Organism	MICs, mg/mL
<i>Aspergillus fumigatus</i>	0.001
<i>Penicillium italicum</i>	0.004
<i>Syncephalastrum racemosum</i>	0.009
<i>Candida albicans</i>	0.002
<i>Staphylococcus aureus</i>	0.004
<i>Pseudomonas aeruginosa</i>	0.078
<i>Bacillus subtilis</i>	0.001
<i>Escherichia coli</i>	0.001

## CONCLUSION

The results obtained in this work verified that number of arylhydrazones complexes attributed to o-hydroxyacetophenone and o-methoxybenzaldehyde have been synthesized successfully. The compositions and coordination cores of these complexes can be established on the basis of a battery of different physicochemical techniques. The mode of binding of the arylhydrazones under investigation is mainly depends on the substitute in the ortho-position of the phenyl ring. The persistence of a basic group in the ortho- position of phenyl ring e.g. phenolic OH may facilitate its coordination with the metal cation upraising the number of coordination sites. This is very conspicuous in the separation of numerous solid complexes in case of o-hydroxyacetophenone benzoylhydrazone. Biological studies of hydrazones and their complexes revealed a high antimicrobial activity for some of these samples showing the possibility of using as an antimicrobial to overcome some diseases. Virtually, inhibition of organic compound e.g. hydrazone against fungi and bacteria can be stimulated by coordinating it with transition metal ion as noticed in case of Ni<sup>II</sup>-HBH.

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