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Synthesis, Characterization and TGA Studies of Co (II), Ni (II) and Zn (II) Complexes of 3-(2-(4-hydroxy-3-methoxy benzylidene) hydrazinyl)-2H-benzo[b] [1, 4] oxazin-2-one Schiff Base.

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ABSTRACT

Co (II), Ni (II) and Zn (II) complexes of the Schiff base 3-(2-(4-hydroxy-3-methoxy benzylidene) hydrazinyl)-2H-benzo[b] [1,4]oxazin-2-one (HMB-HBO) were synthesized and characterized by elemental analysis, molar conductivity, IR, LC-MS, magnetic susceptibility, thermogravimetry, electron absorption spectra and powder X-ray diffraction. The ligand HMB-HBO is forming polymeric octahedral complexes with ONO donor atoms with all the metals studied.

Keywords: magnetic susceptibility, thermogravimetry, ONO donor atoms, octahedral.

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INTRODUCTION

Schiff bases play an important role in coordination chemistry as they form stable complexes with most of the transition metal ions readily [1]. A literature survey reveals that a Schiff base containing poly functional groups can coordinate with transition metal ions forming metal complexes. Many biologically important Schiff bases have been reported in the literature possessing, antifungal [2], antibacterial [3], antimicrobial, anti-inflammatory, anti-HIV, anticonvulsant and antitumor activities [4]. Benzoxazines are an important class of N-containing heterocyclic compounds which exhibit a wide range of biological activity including plant resistance factor against microbial diseases and insects, potassium channel modulators, anti-rheumatic and antihypertensive activity [5] and are key moieties for the synthesis of pharmaceutical agents.

Benzoxazines and their Schiff bases are found to be biologically active but, their metal complexes have received less attention in spite of their high metal chelating properties and applications.

Hence importance was given to study these systems and in the present research article we have described the synthesis and characterization of the Co(II), Ni(II) and Zn(II) metal complexes of the Schiff base 3-(2-(4-hydroxy-3-methoxy benzylidene) hydrazinyl)-2H-benzo[b] [1,4]oxazin-2-one (HMB-HBO) which were characterized by IR, UV-Vis, mass, elemental analysis, thermal studies and magnetic susceptibility methods. The metal complexes of the Schiff base HMB-HBO may show enhanced biological activity which may have their importance in the field of medicinal chemistry.

MATERIALS AND METHODS

Analytical grade organic solvents were purchased from Merck (India) and metal chlorides from SD Fine chemicals. IR spectra were recorded using KBr discs in the region $4000 - \approx 400 \text{ cm}^{-1}$ on Bruker optics Germany TENSOR 27 FTIR instrument and Far IR spectrum was recorded using IR Prestige-21 Shimadzu spectrophotometer in the region $750 - \approx 250 \text{ cm}^{-1}$. UV-3600 Shimadzu UV-Vis-NIR spectrometer was used to record Solid UV spectra. Elemental analysis was performed using Thermo Finnigan Flash EA 1112 elemental analyzer. The metal contents were analyzed using a Shimadzu AA-6300 Atomic absorption spectrophotometer. Using Elico digital conductivity meter (model CM-180) electrical conductivity measurements were recorded with a dip type cell calibrated with KCl solution using freshly prepared DMSO solutions ($1 \times 10^{-3} \text{ mol.L}^{-1}$). On a Shimadzu Japan LCMS-2010 A spectrometer the mass spectrum was recorded. Faraday magnetic susceptibility millibalance model-7550 was used to record magnetic moments of the complexes at room temperature with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as standard. The diamagnetic corrections were performed by using Pascal's constants and temperature independent paramagnetic corrections were computed. By thermogravimetric analysis (TGA) studies using TGA Q 5000 V3.13 build 261 instrument the presence of water was established. Differential scanning calorimetric (DSC) studies were done to know the m.p. of the complexes using DSC Q 1000V9.9 build 303 instrument. Powder XRD was recorded on a Rigaku Miniflex diffractometer in the range of 5° to $80^\circ 2\theta$ values.

EXPERIMENTAL

Synthesis of metal complexes

The Schiff base HMB-HBO was prepared by a three-step process involving the synthesis of 1,4-Benzoxazine-2, 3-dione and 3-Hydrazino-1, 4-benzoxazine-2-one (HBO). [6]

HMB-HBO (3.11 g, 0.01 M) was dissolved in hot DMSO 20 mL to which [(0.005 M) 1.18 g Co (II), 1.18 g Ni (II) and 0.68 g Zn (II)] divalent metal chlorides were added slowly and stirred in a round bottom flask. 10 % methanolic ammonia solution was added to each mixture to maintain pH $\sim 7-8$. The mixture was then boiled under reflux until it became clear and continued heating (4-5 h) until the products precipitated out. The bright colored metal complexes were separated, filtered and washed successively with small amounts of distilled water, methanol and petroleum ether and dried in vacuum. Purity of the metal complexes was tested by TLC using different solvent mixtures.

RESULTS AND DISCUSSION

Yield of the complexes: Co (II) – 75 %, Ni (II) – 72 %, Zn (II) – 68 %.

The complexes are dark in color, stable to air and moisture and are insoluble in most of the polar and non-polar solvents, but are sparingly soluble in DMSO.

The m.p. of Co (II), Ni (II) and Zn (II) complexes are 296.9 °C, 295.74 °C and 293.74 °C respectively.

Elemental analysis of metal complexes

The analysis of metal, carbon, hydrogen, nitrogen and chloride reveal the following formulae- $\text{CoC}_{32}\text{H}_{29}\text{N}_6\text{O}_{9.5}$, $\text{NiC}_{32}\text{H}_{29}\text{N}_6\text{O}_{9.5}$ and $\text{ZnC}_{32}\text{H}_{28}\text{N}_6\text{O}_9$ which is given in Table 1. Analytical data reveals a metal to ligand ratio as 1:2 in all the complexes. The complexes do not have any chloride ions. Hence it is assumed that ligand is acting as monobasic system towards these metal ions.

Table 1: Analytical data and physical properties of HMB-HBO complexes

Complex with Emp. Formula	Mol. wt.	Color	Elements (found) % Calc.				$\Lambda_m / \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
			M	C	H	N	
$[\text{Co}(\text{L})_2] \cdot 1.5\text{H}_2\text{O}$ $\text{CoC}_{32}\text{H}_{29}\text{N}_6\text{O}_{9.5}$	708	Dark Brown	8.32 (8.14)	54.23 (52.91)	4.09 (4.09)	11.86 (11.75)	7.4
$[\text{Ni}(\text{L})_2] \cdot 1.5\text{H}_2\text{O}$ $\text{NiC}_{32}\text{H}_{29}\text{N}_6\text{O}_{9.5}$	707	Dark Brown	8.29 (8.20)	54.20 (54.07)	4.06 (4.08)	11.83 (11.77)	4.0
$[\text{Zn}(\text{L})_2] \cdot \text{H}_2\text{O}$ $\text{ZnC}_{32}\text{H}_{28}\text{N}_6\text{O}_9$	705	Yellow	9.31 (9.15)	54.46 (53.26)	3.97 (3.96)	11.91 (12.01)	3.2

Conductivity measurements

The conductivity measurements were carried out in freshly prepared $1 \times 10^{-3} \text{ mol. L}^{-1}$ DMSO solutions. The molar conductance values are shown in Table 1. The conductivity data show negligible molar conductance values (3 to 8 $\text{mho cm}^2 \text{ mol}^{-1}$), indicating that all the complexes are non-electrolytes [7, 8].

Thermal Analysis

Representative thermo grams (TGA & DSC) of Co (II) complex are given in Figs. 1&2. The heating rates were controlled at $10 \text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere and the weight loss was measured from the ambient temperature to $350 \text{ }^\circ\text{C}$. The TGA, DTG and DSC data of all the complexes are listed in Table 2.

Table 2: Thermo analytical results of HMB-HBO metal complexes.

Complexes	TGA $t / ^\circ\text{C}$	DTG	Wt. loss, %		Assignment	DSC $t / ^\circ\text{C}$
			Calc.	Found		
Co(II) Complex	42.5– 67.5	48	3.71	3.42	Single step loss of 1.5 lattice H_2O .	69.43, 296.9, 310, 330 $^\circ\text{C}$.
Ni(II) Complex	40 – 80	61	3.71	3.45	Single step loss of 1.5 lattice H_2O .	69.28, 295.7, 345 $^\circ\text{C}$.
Zn(II) Complex	35 – 62.5	50	2.55	2.72	Single step loss of 1 lattice H_2O .	293.74 $^\circ\text{C}$.

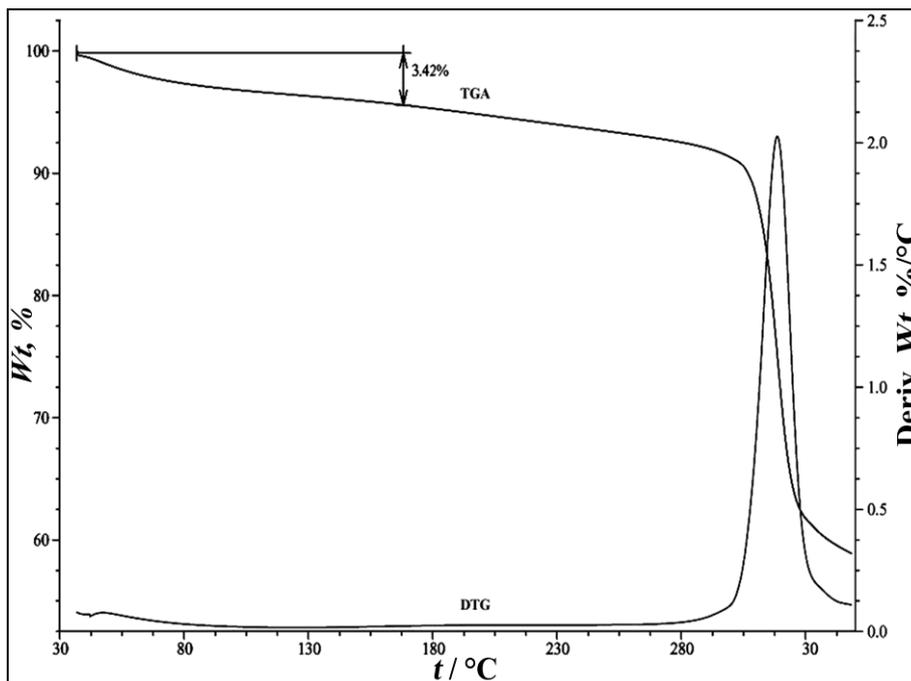


Fig 1: TGA of Co (II) complex of HMB-HBO

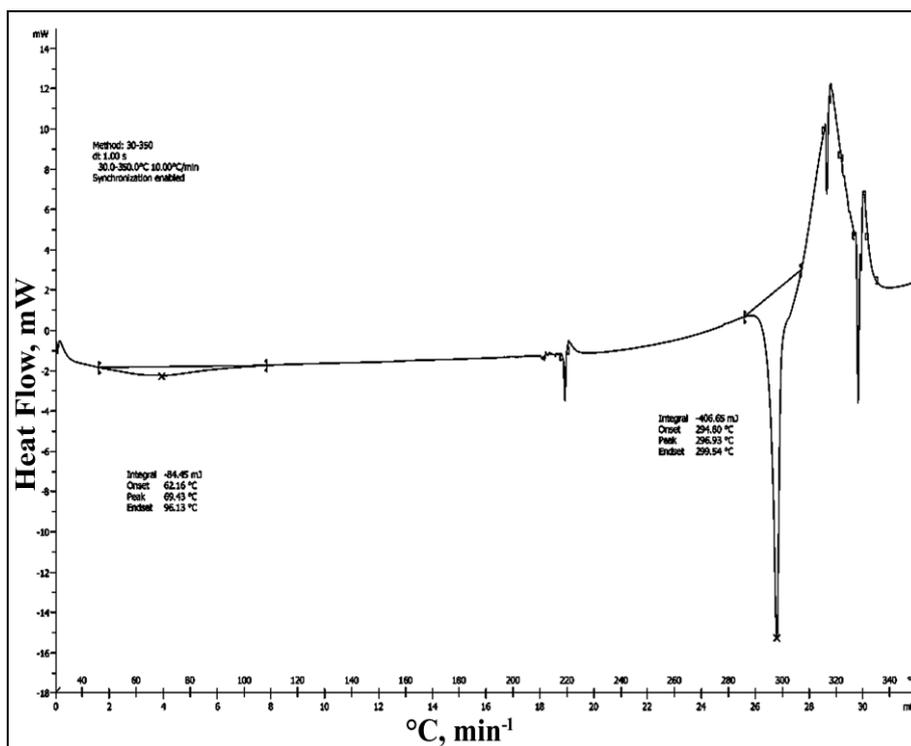


Fig 2: DSC of Co (II) complex of HMB-HBO

The TGA data of Co (II) complex shows a small decrease in weight at a low range of temperature 42.5-67.5 °C which is found to be 3.42 % close to the calculated value (3.71 %) in a single step process associated to loss of 1.5 moles of lattice water [9, 10, 11]. The DTG of the complex shows a very small, broad peak at 48 °C and other at 317 °C which is very sharp, corresponding to loss of water followed by further decomposition of the complex. DSC result of the Co (II) complex shows decomposition of water molecule (small endothermic peak) under an air flux at 69.43 °C. The DSC exhibits a very sharp intense peak at 296.93 °C which is due to its

melting. It also exhibits two peaks at 310 °C and 330 °C which are usually associated with further decomposition of the complex.

TGA curve of Ni (II) complex shows single step decomposition with a small weight loss of 3.45 % at 40-80 °C which is in match with the calculated value (3.71 %) indicating loss of 1.5 moles of crystalline water. The two peaks from DTG of this complex are seen at 61 °C and 318 °C which are short and broad, sharp and high intense which are due to loss of water and decomposition of the complex respectively. DSC of this complex exhibits decomposition of water molecule which is observed as a small, broad endothermic peak at 69.28 °C. It also exhibits a very sharp intense peak at 295.74 °C which is corresponding to its m.p. A small peak above 340 °C is confined to its decomposition.

TGA of Zn (II) complex showed an indication of loss in mass of about 2.72 % (cal.2.55 %) at a lower temperature of 35-62.5 °C which corresponds to loss of 1 lattice water molecule in single step, which is evident from the respective DTG showing a short broad peak at a lower temperature of 50 °C. Further decomposition of the complex may be observed at higher temperature. DSC analysis of Zn (II) complex exhibits a very sharp and intense endothermic peak at 293.74 °C which is corresponding to the m.p. of the complex.

Infrared Spectroscopy

The main IR bands and the assignments of the ligand and the complexes are listed in Table 3, Fig.3.

Table 3: Characteristic infrared frequencies of HMB-HBO complexes

Compound	ν / cm^{-1}							New bands
	-OH	-NH	C=O	C=N (free)	C=N (ring)	C-O	N-N	
HMB-HBO	3501	3238	1656	1603	1512	1210	958	—
Co(II) complex	3710-3200 (b)		1588		1515	1288	968	784,491,445,261.
Ni(II) complex	3710-3200 (b)		1590		1515	1287	963	1028, 783,491,448, 384.
Zn(II) complex	3720-3240 (b)		1588		1513	1286	963	1028,782,490,445, 298.

Comparison of the IR spectrum of free ligand with that of each metal complex suggests single possible mode of chelation. The IR spectrum of free ligand showed sharp bands at 3501, 3238 cm^{-1} for phenolic OH and NH stretching respectively. The IR spectrum of all the complexes showed the presence of a broad trough in the region of 3000-3720 cm^{-1} which can be attributed to a combination of OH (of coordinated or lattice water) and NH stretching vibrations [12, 13]. As the complexes are isolated in neutral/weakly basic media the deprotonation of phenolic group is confirmed. The deprotonation of phenolic OH and participation of phenolic oxygen in M-O bond formation is further confirmed by the upward shift of C-O (phenolic) by 76-78 cm^{-1} in all the complexes [14] which may be attributed to the drift of electron density from oxygen to the metal ions resulting in greater ionic character of the C-O bond and a consequent increase in C-O stretching vibration [15, 16]. The presence of lattice water in all the complexes is supported from thermal analysis. Two strong bands noticed at 1656 cm^{-1} and 1603 cm^{-1} attributed to lactone C=O and C=N (free) showed a negative shift (shifted to lower stretching vibration) by merging together in all the complexes to (1588-1590 cm^{-1}) indicating the involvement of both carbonyl oxygen and free azomethine nitrogen [17-19] in metal bonding which is further confirmed by a positive shift to higher stretching of N-N by 5-10 cm^{-1} in all the complexes [20, 21] which may be attributed to the loss of repulsive forces of the lone pair on the nitrogen atom [22]. The infrared spectra show no change in C=N (ring) stretching in all the three complexes which confirms its non-participation in chelation.

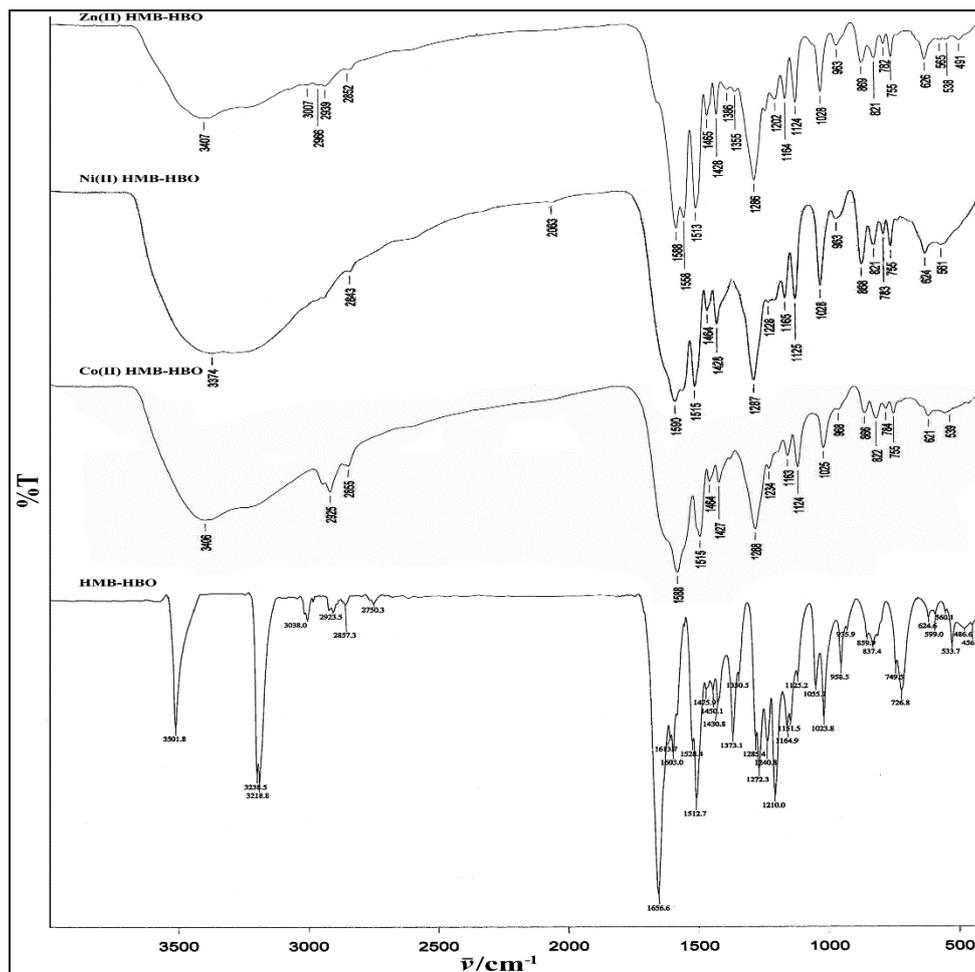


Fig 3: IR Spectrum of HMB-HBO complexes.

Thus all the IR data suggests that all the metals are bound to the Schiff base through the phenolic oxygen, carbonyl oxygen, and free azomethine nitrogen. The low region of the spectra revealed the presence of medium intensity bands- Co (II) - 491, 445 cm^{-1} , Ni (II) - 491, 448 cm^{-1} and Zn (II) - 490, 445 cm^{-1} due to (M-N) and (M-O) vibrations respectively [23]. Thus the IR data proves the existence of ONO donor sequence around all the metal ions under investigation.

Magnetic moment

The observed magnetic moment values are shown to be subnormal than expected which are given in Table 4.

The Co (II) complex has shown a spin only magnetic moment of 2.99 μ_B which is lower than the expected value (4.7-5.2 μ_B) of spin free d^3 system. The Ni (II) complex exhibits effective magnetic moment of 1.11 μ_B which is slightly lower than the expected (2.5-3.5 μ_B) spin free d^2 system. The Zn (II) complex shows no d-d bands as is expected for a d^{10} system and was found to be diamagnetic in nature.

Table 4: Magnetic and electronic spectral data of HMB-HBO complexes

Complex	$\mu_{\text{eff}} / \mu_{\text{B}}$	UV-Vis ν/cm^{-1}	Assignment	$(\nu_2)/(\nu_1)$	B cm^{-1}	10Dq cm^{-1}	β
Co(II) Complex	2.99	6253 12019 26881	${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$ ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$	1.92	514.8	5766	0.53
Ni(II) Complex	1.11	7102 12048 29498	${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{2\text{g}}(\text{F})$ ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})$ ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$	1.69	441.6	4946	0.42
Zn(II) Complex	Dia	–	–	–	–	–	–

Electronic Spectroscopy

The high intensity bands noticed at 49261-45045, 36231 and 28011 cm^{-1} of Co (II), 49504-45454, 35714, 28900 cm^{-1} of Ni (II) complexes corresponding to the transitions $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ of benzene, benzoxazine and free azomethine groups have seem to be shifted to a longer wavelength compared to ligand, whereas $n\text{-}\pi^*$ of phenolic and lactone carbonyl group chromophore (31152, 30395 cm^{-1} of Co (II)) and (31746, 30581 cm^{-1} of Ni (II)) showed decrease in absorption and ring azomethine suffered no change (29154 cm^{-1}) in both Co (II) and Ni (II) complexes indicating its non-involvement, finally confirming formation of the expected HMB-HBO metal complexes. Spectrum is shown in Fig.4 and selective electronic spectral bands are given in Table 4. The electronic spectrum of Co (II) complex shows three bands assignable to d-d transitions at 6253 cm^{-1} (ν_1), 12019 cm^{-1} (ν_2) and other characteristic band at 2688 cm^{-1} (ν_3). The observed transitions are assigned to ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$, ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ and ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$ in the ascending order of frequency. These are consistent with octahedral geometry for Co (II) complexes with $\nu_2/\nu_1 = 1.92$, which is within the range of 1.9-2.2 further confirming the proposed geometry. The electronic spectrum of Ni (II) complex exhibits three bands at 7102, 12048, 29498 cm^{-1} assignable to three spin allowed transitions ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{2\text{g}}(\text{F})$ (ν_1), ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})$ (ν_2), ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$ (ν_3) respectively which are in accordance with octahedral geometry around Ni(II) complex [24, 25]. The ratio ν_2/ν_1 is 1.69 which is also in support of the expected structure. The ligand field parameters 10Dq and B have been calculated for Co (II) and Ni (II) complexes, which suggest that the metal-ligand bond in the complexes is covalent. The Racah interelectron repulsion parameter (B) and nephelauxetic parameter suggests a strong ligand field and metal-ligand covalency [26]. Since no bands are observed for Zn (II) complex, on the basis of analytical, conductance and other spectral data obtained octahedral geometry has been assigned for it.

Powder X-Ray Diffraction Studies

Single crystals of the complexes under investigation could not be prepared and hence powder diffraction data were obtained for structural characterization. The X-ray diffractogram of the ligand and the complexes was recorded in the range 5° to 80° 2θ values, which are shown in the Fig.5. The XRD pattern indicates that the ligand and its complexes have crystalline patterns with various degrees of crystallinity. The extra peaks observed in the complexes compared to the ligand prove the coordination of metal ion forming the metal complexes [27].

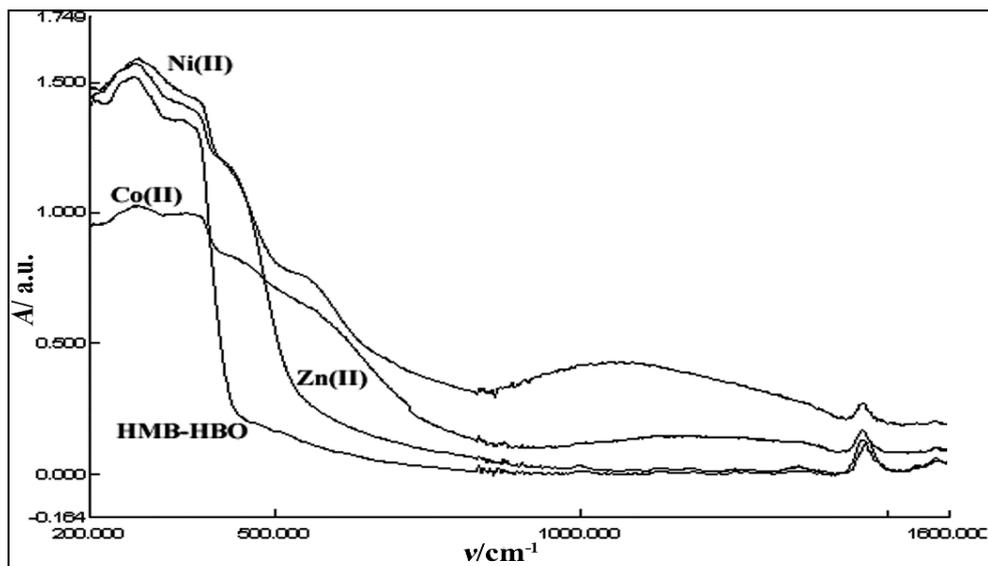


Fig 4: Electronic Spectra of HMB-HBO and its complexes.

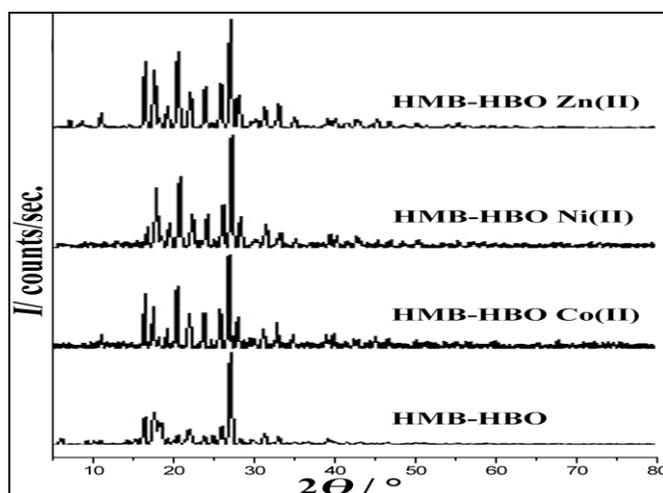


Fig 5: Powder XRD spectra of HMB-HBO and its complexes

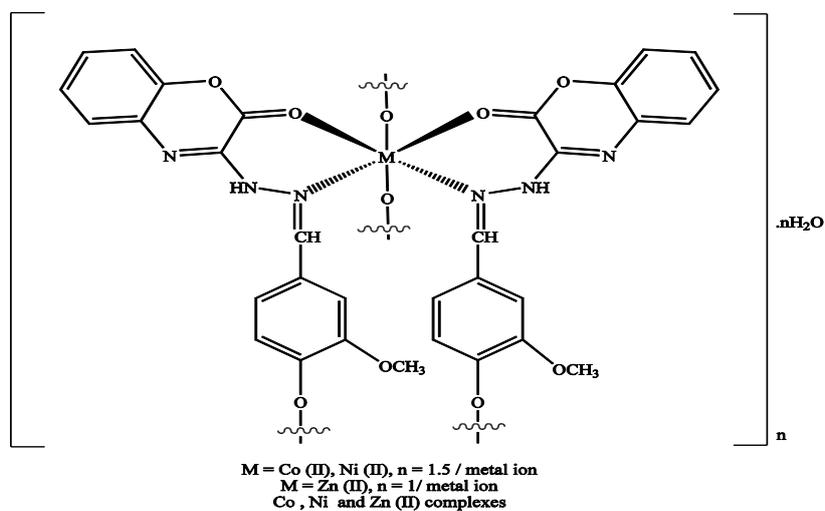


Fig 6: Structure of HMB-HBO complexes

CONCLUSION

In the present work Co (II), Ni (II) and Zn (II) metal complexes of the Schiff base 3-(2-(4-hydroxy-3-methoxy benzylidene) hydrazinyl)-2H-benzo[b] [1,4]oxazin-2-one (HMB-HBO) have been synthesized and characterized. Analytical data showed that the ligand is acting as monobasic system towards all metal ions studied. Conductivity data showed that all the complexes are non-electrolytic in nature. Thermal studies (TGA) showed the presence of lattice water molecules in all the complexes and (DSC) showed endothermic peaks corresponding to their melting points. IR data proved the presence of ONO donor sequence around all the metal ions. Magnetic moment values of all the complexes are subnormal than the expected values. The electronic spectrum of Co (II) complex showed three bands assignable to d-d transitions which are consistent with octahedral geometry, Ni (II) complex exhibits three bands assignable to octahedral geometry and Zn (II) complex is assigned an octahedral geometry on the basis of analytical, conductance and other spectral data. The powder XRD pattern indicates crystalline patterns with various degrees of crystallinity for both the ligand and its complexes.

Thus, based on the analytical data, conductivity, thermal analysis, spectral and magnetic susceptibility data, it is concluded that HMB-HBO is forming polymeric octahedral complexes with ONO donor atoms with all the metals studied. The proposed structure of the complexes is represented in Fig.6.

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