

Spectral and Thermal Characterization of Mn(II), Ni(II) and Zn(II) Complexes Containing Schiff Base Ligands Towards Potential Biological Application

Abstract

Some metal complexes of Zn(II), Mn(II) and Ni(II) ions with tetradentate N,O coordinating Schiff base ligand [2-bis(2-hydroxybenzylidene)}hydrazinecarboxamide], ($C_{15}H_{13}N_3O_3$) were synthesized. The Schiff base ligand was derived from the condensation of semicarbazide hydrochloride and salicylaldehyde. The overall reactions were monitored by TLC and UV-Visible spectral analysis. All the ligands and metal complexes were isolated from the reaction in the solid form and characterized by IR, UV-Visible, Thermal analysis, Magnetic Susceptibility, Conductivity and some physical measurements. Spectroscopic evidence indicated that the Schiff base was behaved as N, O coordinating chelating agent. Magnetic susceptibility data coupled with electronic spectra suggested that $[ZnC_{15}H_{11}N_3O_3]$ and $[MnC_{15}H_{11}N_3O_3].2H_2O$ complexes are tetrahedral whereas $[NiC_{15}H_{11}N_3O_3].H_2O$ complex is square planar. The conductivity value indicated that all the complexes were non-electrolyte. Thermal analysis (TGA and DTG) data showed the possible degradation pathway of complexes ($C_{12}H_8O_2$, at 200-490 $^{\circ}C$ and $-NH_3O-$, at 400-650 $^{\circ}C$). The Schiff bases and their metal complexes have been shown moderate to strong antimicrobial activity against some pathogenic bacteria.

1. INTRODUCTION

Schiff base and their metal complexes have been extensively studied over the recent years due to their wide variety of biological activities, industrial and pharmaceutical applications [1-5]. Schiff base complexes of transition metal ions have great importance in coordination chemistry. The convenient route of synthesis and thermal stability of Schiff base complexes have contributed significantly for their possible applications. Multidentate ligands are extensively used for the preparation of metal complexes with interesting properties [6-9]. Among these ligands, Schiff bases containing nitrogen and phenolic oxygen donor atoms are of considerable interest due to their potential application in catalysis, medicine and material science [10-13]. Transition metal complexes of these ligands exhibit varying configurations, structural liability and sensitivity to molecular environments. The central metal ions in these complexes act as active sites for pharmacological agent. This feature is employed for modeling active sites in biological systems. Therefore, in view of our interest in synthesis of new Schiff base complexes, which might find application as pharmacological and as luminescence probes, we have synthesized and characterized new transition metal complexes of Schiff base formed by the condensation of semicarbazide hydrochloride and salicylaldehyde.

2. EXPERIMENTAL

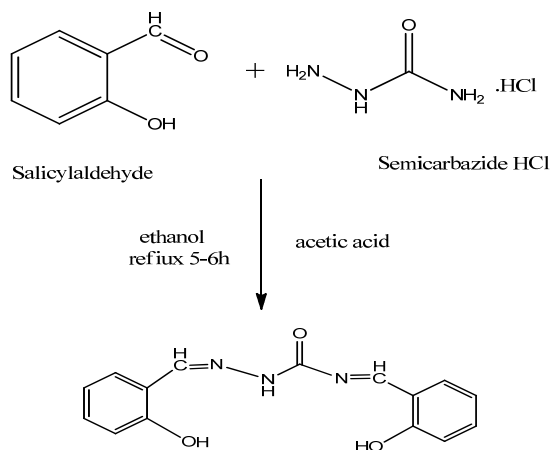
2.1 Materials and Methods

All chemicals and solvents used were commercial products and were used as supplied. All metal(II) salts were used as chloride or sulphate. The solvents such as ethanol, methanol, chloroform, diethyl ether, petroleum ether, DMSO (dimethyl sulfoxide) and acetonitrile were purified by further distillation. The melting point or the decomposition temperature of all the prepared ligand and metal complexes were observed in an electro thermal melting point apparatus model No. AZ6512. Vibrational spectra (IR) were recorded with a NICOLET 310, FTIR spectrophotometer, Belgium, in the range 4000-225 cm^{-1} with a KBr disc as reference. UV-Visible spectra of the complexes in DMSO ($0.5 \times 10^{-3}M$) were recorded in the region 200-800 nm on a Thermoelectron Nicolet evolution 300

UV-Visible spectrophotometer. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance that following the Gouy Method were used to measure the magnetic moment of the solid complexes. The electrical conductance measurements were made at room temperature in freshly prepared aqueous solution (10^{-3} M) and in DMSO using a WPACM35 conductivity meter and a dip-cell with a platinum electrode. Some conductivity were also measured in PTI-18 Digital conductivity meter. The thermogravimetric analyses (TGA) were performed on Perkin Elmer Simultaneous Thermal Analyzer, STA-8000. The purity of the ligand and metal complexes were tested by thin layer chromatography (TLC).

2.2 Synthesis of Schiff bases

Synthesis of Schiff Base [SB]: Semicarbazide hydrochloride (1.12g, 10 mmol) dissolved in absolute ethanol / (30 mL) and distilled water (10 mL). Then salicylaldehyde (2.09 mL, 20 mmol) was added slowly to a constant stirring solution of semicarbazide hydrochloride (1.12 g, 10 mmol) with 2 ml acetic acid and the mixture was refluxed for 4-5h. On cooling, a solid product was formed which was filtered, washed with ethanol, diethyl ether and dried in vacuum over anhydrous CaCl_2 . The synthetic pathway of ligand formation is shown in **Scheme-1** and was monitored by TLC using petroleum ether, ethyl acetate, toluene and methanol solvents. The product was found to be soluble in methanol, chloroform, DMF and DMSO and insoluble in Ethanol, acetone, diethyl ether, Petroleum ether and Isopropanol.

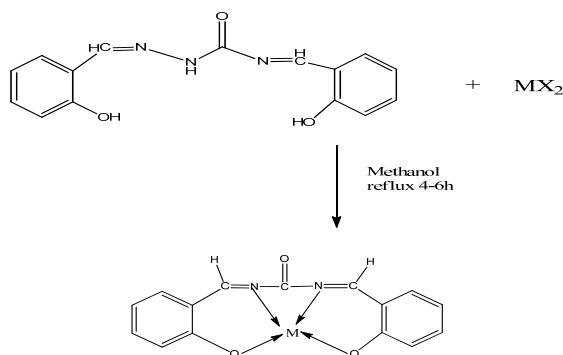


2-bis(2-hydroxybenzylidene)hydrazinecarboxamide [$\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_3$]

Scheme-1: Synthetic pathway of Schiff base ligand [$\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_3$]

2.2. Preparation Procedure of Schiff Base [SB] Metal Complexes:

During complexation reaction a warm methanolic solution 30 mL (0.283 gm, 1mmol) of prepared Schiff base ligand ($\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_3$) was taken in a two necked round bottom flask and kept on magnetic stirring. A warm 10 mL methanolic solution of Manganese(II) chloride tetra-hydrate (0.198 g, 1 mmol)/ Nickel(II) chloride hexa-hydrate (0.238 g, 1 mmol)/ Zinc(II) acetate dihydrate salt was added drop wise and stirred with heating for 4-6 h. On cooling, precipitates were formed which were filtered, washed with ethanol, acetone, and diethyl ether and dried in vacuum desiccators over anhydrous CaCl_2 . The purity of each complex was tested by TLC using petroleum ether, ethyl acetate, toluene and methanol. The complexes were soluble in DMSO and DMF. The synthetic pathway of complexes have presented in **Scheme-2**.



Scheme-2: Synthesis pathway of Schiff base metal complex, $[MC_{15}H_{11}N_3O_3]$,

Where, M = Mn(II), Ni(II), Zn(II)

3. CHARACTERIZATION OF THE LIGAND AND COMPLEXES

3.1 Melting point

Melting point gives an approximate idea about the nature of the complexes and can suggest whether it is covalent or ionic. The melting points or decomposition temperature of all the prepared metal complexes were observed with an electro thermal melting point apparatus and shown in **Table-1**.

Table-1: Physical and analytical data of the Schiff base and metal complexes.

Compounds/Mol. Formula	Molecular Weight	Color	Yield (%)	Decomposition temperature ($^{\circ}C$)	μ_{eff} in B.M.
[SB] [C ₁₅ H ₁₃ N ₃ O ₃]	283	White	78	210	-
[Zn(SB)] [ZnC ₁₅ H ₁₁ N ₃ O ₃]	346.38	Yellowish white	75	245	0.43
[Mn(SB)] [MnC ₁₅ H ₁₁ N ₃ O ₃].2H ₂ O	371.94	Pale Yellow	71	>300	5.62
[Ni(SB)] [NiC ₁₅ H ₁₁ N ₃ O ₃].H ₂ O	357.69	Green	65	>300	1.55

3.2 Characterizations by conductivity

The molar conductivities were obtained using the formula

$$\Lambda = \frac{1000}{C} \times \text{Cell constant} \times \text{observed conductivity.} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

Where, Λ =molar conductance, C= concentration

The molar conductance has calculated from the measured specific conductance at room temperature by using the above equation. To determine the molar conductivity, we have used Horiba conductivity meter B173 in which cell constant is fixed. So, the observed conductivity is the specific conductance. The experimental results are shown in **Table 2**. From the above table data it is showed that all the complexes are non-electrolyte in nature.

Table- 2: Data for the determination of Molar conductivity.

Name of Complex	Observed conductivity (ohm ⁻¹ cm ² mol ⁻¹)	Molar conductance Λ $= (1000/c)$ $\times \text{specific conductance}$ $\text{Scm}^2\text{mol}^{-1}$
[Zn(SB)] [ZnC ₁₅ H ₁₁ N ₃ O ₃]	2	2
[Ni(SB)] [NiC ₁₅ H ₁₁ N ₃ O ₃].H ₂ O	3	3
[Mn(SB)] [MnC ₁₅ H ₁₁ N ₃ O ₃].2H ₂ O	2	2

Where, [SB]= [C₁₅H₁₃N₃O₃]

3.3. Characterizations by magnetic susceptibility

Measurement of magnetic susceptibility: The measurements of magnetic susceptibilities were made at about constant temperature; Curie-law was used and was calculated from the following equation.

$$\mu_{\text{eff}} = 2.83 \sqrt{\chi_{\text{m}}^{\text{corr}} \cdot T} \quad \text{B.M.} \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

Thus μ_{eff} obtained is known as effective magnetic moment. The observed values of effective magnetic moment (μ_{eff}) of the complexes at room temperature are given in **Table 1**. From the above data it is showed that the Zn(II) and Ni(II) complexes are diamagnetic and Mn(II) complex is paramagnetic in nature.

3.4: IR spectra of Schiff Base ligand-(SB) and its metal complexes:

a. IR spectra of Schiff Base ligand [C₁₅H₁₃N₃O₃]:

. An absorption band of Schiff base ligand showed at 1627 cm⁻¹, which is assigned as azomethine, $\nu(\text{HC}=\text{N})$ linkage [14]. The band indicated the formation of the Schiff base complex. An absorption band at 3494 cm⁻¹ observed due to $\nu(\text{-OH})$ stretching present [15]. The band at 3153 cm⁻¹ was assigned as $\nu(\text{-NH-})$ and was supported by the presence of $\delta(\text{NH}_2)$ deformation bands around 1600–1500 cm⁻¹. The strong band at 1697 cm⁻¹ assigned for $\nu(\text{C}=\text{O})$ attributed that the bond for amide group in the Schiff base ligand [16-17]. The IR characteristic bands were given in **Table 3**

b. IR spectra of Zn(II) complex [ZnC₁₅H₁₁N₃O₃]:

In Zn(II) complex the absorption frequency of ligand shifted to the lower absorption frequency at 1619 cm⁻¹ suggested that CH=N group was coordinated to metal atom [14,18-22]. This may be explained based on a drift of the lone pair density of the azomethine nitrogen towards the metal atom [23, 24], indicating that coordination occurred through the nitrogen of the (C=N) groups. The –OH band was also shifted to the lower absorption frequency at 3437 cm⁻¹ is due to the co-ordination of –OH groups as a deprotonated phenolic oxygen with the metal in the complex and $\nu(\text{-NH-})$ shifted to the region 3339 cm⁻¹ in the complex (figure-2) may be assigned to N–H stretching vibrations due to complex formation. Further conclusive evidence of the coordination of Schiff base with metals was the IR absorption spectra of complex at 524 cm⁻¹ assigned as $\nu(\text{M–O})$ bond and at 307 cm⁻¹ assigned as $\nu(\text{M–N})$ bond in which –OH and HC=N group co-ordinate with metal atom [25,26].

c. IR spectra Ni(II) complex [NiC₁₅H₁₁N₃O₃].H₂O :

In Ni(II) complex the absorption band of ligand was shifted to the lower absorption frequency at 1615 cm^{-1} suggested that $\text{CH}=\text{N}$ group was also coordinated to metal atom. This may be explained based on a drift of the lone pair density of the azomethine nitrogen towards the metal atom, which indicate that the coordination occurred through the nitrogen of the ($\text{C}=\text{N}$) groups. The $-\text{OH}$ absorption band was also shifted to the lower absorption frequency at 3434 cm^{-1} due to the co-ordination of $-\text{OH}$ groups as deprotonated phenolic oxygen with the metal in the complex and $\nu(\text{NH}-)$ shifted to the region 3335 cm^{-1} assigned to $\text{N}-\text{H}$ stretching vibrations due to complex formation. Further conclusive evidence of the coordination of Schiff base with metals was the absorption of complex at 529 cm^{-1} assigned as $\nu(\text{M}-\text{O})$ bond and at 376 cm^{-1} assigned as $\nu(\text{M}-\text{N})$ bond.

d. IR spectra of Mn(II) complex $[\text{MnC}_{15}\text{H}_{11}\text{N}_3\text{O}_3]\cdot 2\text{H}_2\text{O}$:

In Mn(II) complex the absorption frequency of ligand was shifted to the lower frequency at 1611 cm^{-1} suggested that $\text{CH}=\text{N}$ group was also coordinated to metal atom [19,27-28]. This may be explained based on a drift of the lone pair density of the azomethine nitrogen towards the metal atom, indicating that coordination occurred through the nitrogen of the ($\text{C}=\text{N}$) groups. The $-\text{OH}$ band was also shifted to the lower absorption frequency at 3439 cm^{-1} is due to the co-ordination of $-\text{OH}$ groups as a deprotonated phenolic oxygen with the metal in the complex and $\nu(\text{NH}-)$ shifted to the region 3337 cm^{-1} in the complex may be assigned to $\text{N}-\text{H}$ stretching vibrations due to complex formation. Further conclusive evidence of the coordination of Schiff base with metals was the absorption of complex at 524 cm^{-1} assigned as $\nu(\text{M}-\text{O})$ bond and at 314 cm^{-1} assigned as $\nu(\text{M}-\text{N})$.

3.5 Characterization by UV-visible spectra

a. Electronic spectra of the ligand and complexes

The electronic spectrum of ligand exhibits high intense absorption peaks at 270 nm and 310 nm which have been assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively. The UV-Vis spectra of the complex showed the presence of three strong absorption bands in the UV-Vis region at 265, 295 and 365 nm. The UV spectra of the ligand at 270 nm and at 305 nm are shifted in the Zn(II) complex. This confirmed the coordination of ligand to metal center²⁸. The peak at 265 nm is attributed to $\pi \rightarrow \pi^*$ transition and the peak at 295 nm is assigned to $n \rightarrow \pi^*$ transition due to lone pair of electrons of an azomethine nitrogen and an antibonding p orbital. The presence of an absorption band at 365 nm in the case of the complex assigned as a ligand-to-metal charge transfer (LMCT). Since the zinc ion has d^{10} configuration and the observed absorption spectra of Zn(II) complex could be assigned the absence of any d-d electronic transitions the Zn(II) complex is diamagnetic in nature. However, taking into account the spectrum and the magnetic moment value, the configuration of the Zinc(II) ion, a tetrahedral geometry [29,30] could be assumed for its complex. The UV-Vis spectra of Mn(II) complex at 265 nm and 295 nm are assigned as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively. The UV-Vis spectra of Mn (II) complex displayed absorption at the 320 nm, 390 nm assigned to the ligand field and charge transfer transitions. The metal complexes also exhibited d-d transition in the visible region of their spectra. The band at 440 nm is attributed to (d-d) transition of type ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$ [31]. The magnetic moment of Mn(II) Complex is 5.62 B.M. The assigned spectrum transition and magnetic moment value indicate the tetrahedral structure of manganese (II) complex. The UV-Vis spectra of Ni(II) complex displayed absorption at 295 nm and 320 nm are assigned to the ligand to metal charge transfer transition (Figure-1). The band at 340 nm and 400 nm is attributed to (d-d) transition of type ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ [32, 33]. The magnetic moment of Ni(II) complex is 1.55 B.M. The assigned spectrum transition and magnetic moment value indicate the square planar structure of Ni(II) complex. All the obtained electronic spectral data of ligand and complexes are shown in Table-3.

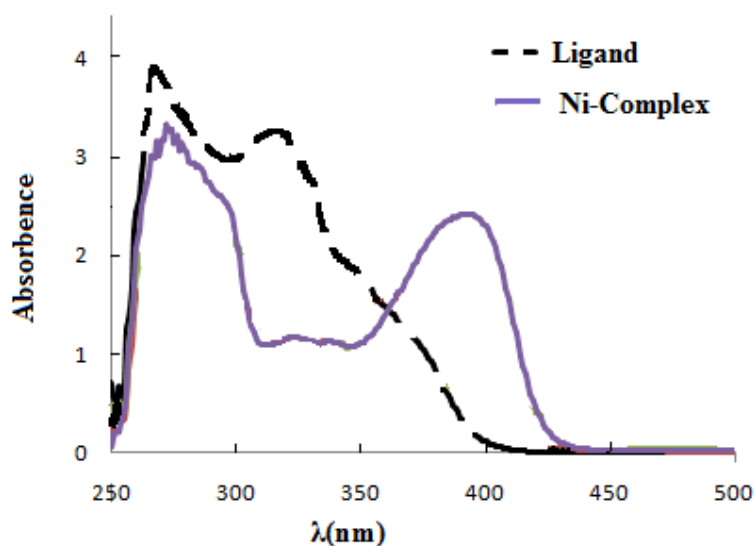


Figure-1: Electronic spectra of Ligand $[C_{15}H_{13}N_3O_3]$ & Complex $[NiC_{15}H_{11}N_3O_3].H_2O$

Table-3: The electronic spectral data Schiff base and its metal complexes.

Ligand/Complex	$\lambda(nm)$	Wave number cm^{-1}	Assignment
[SB] [$C_{15}H_{13}N_3O_3$]	270	37037	$\pi \rightarrow \pi^*$
	305	32258	$n \rightarrow \pi^*$
[Zn(SB)] [$ZnC_{15}H_{11}N_3O_3$]	265	37735	$\pi \rightarrow \pi^*$
	295	33898	$n \rightarrow \pi^*$
	365	27397	Charge transfer (C.T)
[Mn(SB)] [$MnC_{15}H_{11}N_3O_3$].2H ₂ O	265	37735	$\pi \rightarrow \pi^*$
	295	33898	$n \rightarrow \pi^*$
	320	31250	Charge transfer(C.T)
	390	25641	Charge transfer(C.T)
	440	22727	${}^6A_1 \rightarrow {}^4T_2$
[Ni(SB)] [$NiC_{15}H_{11}N_3O_3$].H ₂ O	275	36363	$n \rightarrow \pi^*$
	295	33898	Charge transfer(C.T)
	320	31250	Charge transfer(C.T)
	340	29411	Charge transfer(C.T)
	400	25000	d-d

3.6 Thermo Gravimetric Analysis

Thermo gravimetric analysis (weight changes) was performed for complexes in the temperature range from room temperature up to 800°C using Nitrogen as inert gas. The heating rate was suitably controlled at 30°C min⁻¹. The data obtained strongly supported the proposed structure of the complexes. The TGA and DTG data of complexes in different temperature ranges are listed in **Table-4**

a. For $[\text{ZnC}_{15}\text{H}_{11}\text{N}_3\text{O}_3]$ Complex: The decomposition of Zn(II) complex was occurred in three main steps. The data from the TGA and DTG curve clearly showed that the metal complex was stable up to 200°C , indicating absence of hydrated and coordinated water [34]. Then Where, the 1st step involves the major fragmentation of part $\text{C}_{12}\text{H}_8\text{O}_2$ (calculated 53.25%, experimental 52.12% weight) of the complex at temperature range $200\text{--}490^\circ\text{C}$. In 2nd step occurred around $490\text{--}640^\circ\text{C}$ (calculated 21.09%, experimental 20.32% weight) due to decomposition of $\text{-NH}_3\text{O-}$ and in 3rd step the complex is completely decomposed and removed as Zn/ZnO at above 650°C ^{14,35}. The TGA and DTG curve is shown in figure-2.

b. For $[\text{MnC}_{15}\text{H}_{11}\text{N}_3\text{O}_3]\cdot 2\text{H}_2\text{O}$ Complex: The TGA and DTG curve showed that the Mn(II) complex was decomposed in four steps. At 1st steps in the temperature range $150\text{--}220^\circ\text{C}$ (calculated 8.91 %, experimental 20.32% weight) which can be attributed to the elimination of two hydrated water molecules [35]. The 2nd step involves the removal of $\text{C}_{12}\text{H}_8\text{O}_2$ (calculated 56.75%, experimental 56.28% weight) at temperature range $270\text{--}460^\circ\text{C}$. The part of complex $\text{-NH}_3\text{O-}$ was decomposed between temperature range $460\text{--}650^\circ\text{C}$ (calculated 22.24%, experimental 23.14% weight) at 3rd Step of decomposition. In 4th step the complex is completely decomposed and removed as Mn/MnO at above 700°C [36, 37]. The TGA and DTG curve is shown in figure-3.

c. For $[\text{NiC}_{15}\text{H}_{11}\text{N}_3\text{O}_3]\cdot \text{H}_2\text{O}$ Complex: The Ni(II) Complex was decomposed in four steps. The TGA and DTG curve showed that complex was decomposed at 1st steps in the temperature range $70\text{--}150^\circ\text{C}$ (calculated 4.98 %, experimental 5.05% weight) which can be attributed to the elimination of one hydrated water molecules. The 2nd step involves the removal of $\text{C}_{12}\text{H}_8\text{O}_2$ (calculated 53.75%, experimental 54.17% weight) at temperature range $240\text{--}400^\circ\text{C}$. The part of complex $\text{-NH}_3\text{O-}$ was decomposed between temperature range $460\text{--}650^\circ\text{C}$ (calculated 22.55%, experimental 21.20% weight) at 3rd Step of decomposition. In 4th step the complex is completely decomposed and removed as Ni/NiO at above 600°C . The TGA and DTG curve is shown in figure-4.

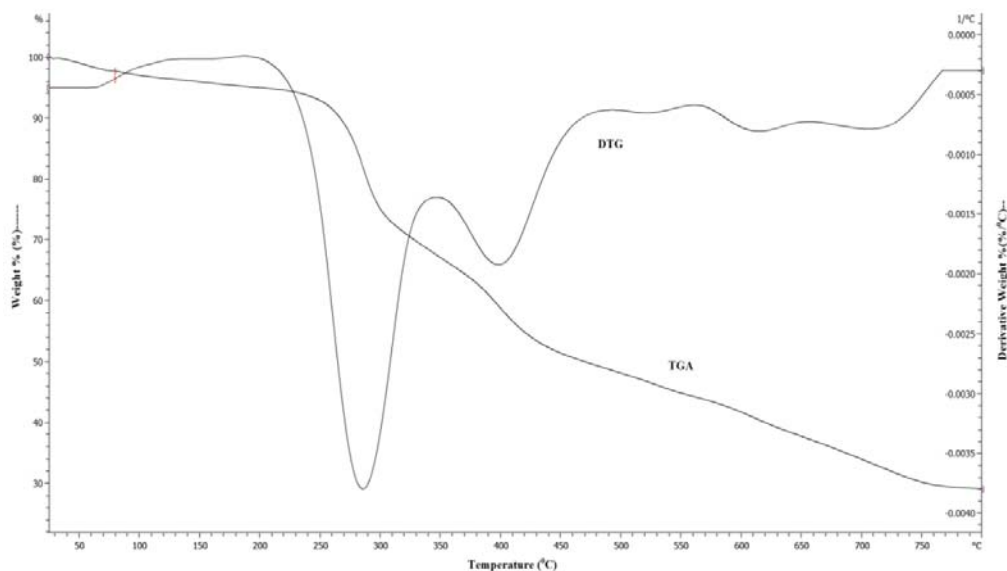


Figure-2: TGA Band DTG curve of Complex $[\text{ZnC}_{15}\text{H}_{11}\text{N}_3\text{O}_3]$

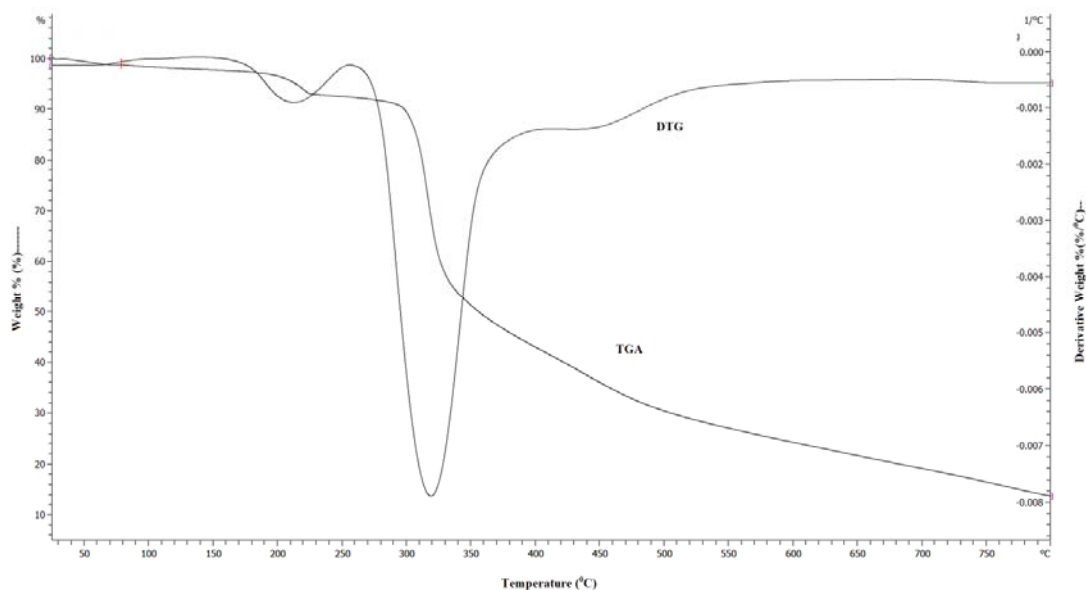


Figure-3: TGA Band DTG curve of Complex $[\text{MnC}_{15}\text{H}_{11}\text{N}_3\text{O}_3] \cdot 2\text{H}_2\text{O}$

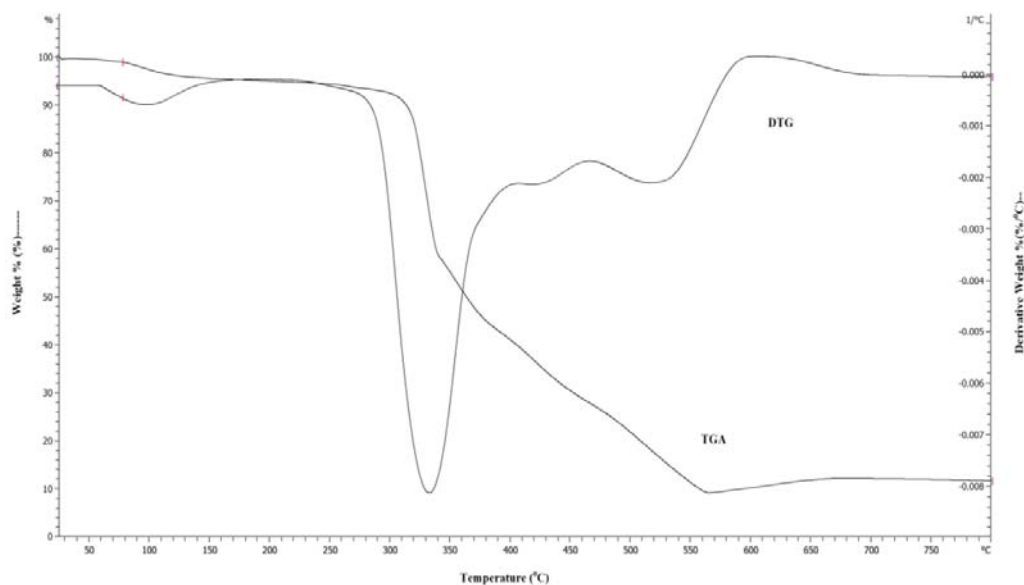


Figure-4: TGA Band DTG curve of Complex $[\text{NiC}_{15}\text{H}_{11}\text{N}_3\text{O}_3] \cdot \text{H}_2\text{O}$

Table-4: Thermal data of Zn (II), Mn (II), and Ni(II) complexes.

Complexes	Steps	Temperature Range/ °C	DTG peak/ °C	TG mass loss% calc./found	Assignments
$[\text{C}_{15}\text{H}_{11}\text{ZnN}_3\text{O}_3]$	1 st	200-490	285	53.25/53.12	$\text{C}_{12}\text{H}_8\text{O}_2$
	2 nd	490-640	600	21.09/20.32	$-\text{NH}_3\text{O}-$
	3 rd	>650		24.56/23.50	Zn/ZnO

$[C_{15}H_{11}MnN_3O_3].2H_2O$	1 st 2 nd 3 rd 4 th	130-220 270-460 460-650 >700	200 320	8.91/9.82 56.75/56.28 22.24/23.14 12.44/12.27	2H ₂ O C ₁₂ H ₈ O ₂ -NH ₃ O- Mn/MnO
$[C_{15}H_{11}NiN_3O_3].H_2O$	1 st 2 nd 3 rd 4 th	70-150 240-400 400-530 >600	100 335 520	4.98/5.05 53.77/54.17 22.55/21.20 19.27/20.88	H ₂ O C ₁₂ H ₈ O ₂ -NH ₃ O- Ni/NiO

4. Antibacterial activity

The prime objective of performing the antibacterial screening is to determine the susceptibility of the pathogenic microorganism to test the compound which, in turn is used to selection of the compound as a therapeutic agent. The free Schiff base ligand and their metal complexes were screened for their antibacterial activity against strains the *Bacillus cereus* ATCC25923, *Streptococcus agelactiae*, *Escherichia coli* ATCC 25922, *Shigella dysenteriae*. The compounds were tested at a concentration of 30 µg/0.01 mL in DMSO solution using the paper disc diffusion method with Kanamycin as standard [38]. The susceptibility zones were measured in diameter (mm) and the result are listed in **Table 5**. The susceptibility zones were the clear zones around the discs killing the bacteria.

Table 5: Antibacterial activities of the compounds.

Bacterials strains	Zone of inhibition, diameter in (mm)			
	$[ZnC_{15}H_{11}N_3O_3]$ (10µg/disc)	$[MnC_{15}H_{11}N_3O_3].2H_2O$ (10µg/disc)	$[NiC_{15}H_{11}N_3O_3].H_2O$ (10µg/disc)	Kanamycin (30µg/disc)
Gram positive				
<i>Bacillus cereus</i>	11	13	08	26
<i>Staphylococcus agelactiae</i>	14	09	12	26
Gram negative				
<i>Escherichia coli</i>	13	10	12	26
<i>Shigella dysenteriae</i>	16	11	13	26

5. Conclusion

The foregoing observations suggest that $[ZnC_{15}H_{11}N_3O_3]$ and $[MnC_{15}H_{11}N_3O_3].2H_2O$ complexes are tetrahedral whereas $[NiC_{15}H_{11}N_3O_3].H_2O$ complex is square planar. All the complexes were non-electrolyte. Thermal analysis (TGA and DTG) data showed the possible degradation pathway of complexes (C₁₂H₈O₂, at 200-490 °C and -NH₃O-, at 400-650 °C). All these Schiff bases and their metal complexes have been screened for their antibacterial activities. The complexes showed good antibacterial activity compared to the ligands. This may be explained due to enhanced lipophilic property of the central metal ion as a result of chelation with the ligand moieties.

References

- [1]. Md. Saddam Hossain, H.M.Tariqul Islam, Md. Nuruzzaman Khan, Abinash Chandro Sarker, Nasiruddin, Md.Ashrafal Alam, C M Zakaria, Md. Kudrat-E-Zahan, 2018. A Short Review

- on Antimicrobial Activity Study on Transition Metal Complexes of Ni Incorporating Schiff Bases, *Biological Sciences*, (1), 135-145.
- [2]. Md. Saddam Hossain, Pijush Kanti Roy, C M Zakaria, Md. Kudrat-E-Zahan, 2018. Selected Schiff base coordination complexes and their microbial application: A review, *International Journal of Chemical Studies*, 6(1), 19-31.
- [3]. Md. Saddam Hossain, C M Zakaria, Md. Kudrat-E-Zahan, 2018. Metal Complexes as Potential Antimicrobial Agent: A Review. *American Journal of Heterocyclic Chemistry*, 4(1), 1-21.
- [4]. Md. Saddam Hossain, Md. Abdul Mannan, F.K. Camellia, A.K.B. Zaman, C.M. Zakaria, Md. Kudrat-E-Zahan. 2017. Isoniazid Containing Metal Based Drugs as Potential Antimicrobial Agent: A Short Review, *Science Journal of Chemistry*, 5(5): 62-70.
- [5]. Md. Saddam Hossain, C.M. Zakaria, Roushoun Ali, Md. Kudrat-E-Zahan, 2017. Selected Pharmacological Applications of 1st Row Transition Metal Complexes: A review, *Clinical Medicine Research*, 6(6): 177-191.
- [6]. Angela Kriza, Lucica Viorica Ababei, Nicoleta Cioatera, Ileana Rău And Nicolae Stănică, 2010. Synthesis And Structural Studies Of Complexes Of Cu, Co, Ni And Zn With Isonicotinic Acid Hydrazide And Isonicotinic Acid (1-Naphthylmethylene)Hydrazide, *J. Serb. Chem. Soc.*, 75 (2): 229–242.
- [7]. P. K. Das, N. Panda, N. K. Behera. 2016. Synthesis, Characterization and Antimicrobial Activities of Schiff Base Complexes Derived from Isoniazid and Diacetylmonoxime, *IJSET - International Journal of Innovative Science, Engineering & Technology*, 3(1): 42-54.
- [8]. Anil Kumar M R, Shanmukhappa S, Rangaswamy B E, Revanasiddappa M. 2015. Synthesis, Characterization, Antimicrobial Activity, Antifungal Activity and DNA Cleavage Studies of Transition Metal Complexes with Schiff Base Ligand, *International Journal of Innovative Research in Science, Engineering and Technology*, 4(2): 60-66.
- [9]. O' Boyle N M, Tenderholt A L & Langer K M. 2008. cclib: a library for package-independent computational chemistry algorithms *J Comput Chem.*, 29, 839.
- [10]. K.D. Karlin, Z. Tyeklar, *Bioinorganic Chemistry of Copper*, Chapman&Hall: New York, 1993, 101-109
- [11]. V. Arun, N. Sridevi, P.P. Robinson, S. Manju, K.K.M. Yusuff. 2009. "Ni(II) and Ru(II) Schiff base complexes as catalysts for the reduction of benzene" *J. Mol. Catal. A: Chem.*, 304(1-2), 191-198.
- [12]. K.C. Gupta, A.K. Sutar. 2008. Catalytic activities of Schiff base transition metal complexes, *Coord. Chem. Rev.*, 252: 1420-1450.
- [13]. R. I. Kureshy, N. H. Khan, S. H. R. Abdi, P. Iyer and S. T. Patel. 1999. Chiral Ru(II) Schiff base complexes catalysed enantioselective epoxidation of styrene derivatives using iodosyl benzene as oxidant II, *J. Mol. Catal.*, 150(1-2): 175-183.
- [14]. Md. Saddam Hossain, C M Zakaria, Md. Kudrat-E-Zahan and B Zaman. 2017. Synthesis, Spectral and Thermal Characterization of Cu(II) Complexes with Two New Schiff Base Ligand towards Potential Biological Application. *Der Chemica Sinica*, 8(3): 380-392.
- [15]. Joshua A. Obaleye, Johnson F. Adediji, and Matthew A. Adebayo. 2011. Synthesis and Biological Activities on Metal Complexes of 2,5-Diamino-1,3,4-thiadiazole Derived from Semicarbazide Hydrochloride. *Molecules*. 16(7): 5861-5874.
- [16]. S. Janarthanan, Y.C. Rajan, P.R. Umarani, D. Jayaraman, D. Premanand and S. Pandi. 2010. Synthesis, growth, optical and thermal properties of a new organic crystal semicarbazone of p-anisaldehyde (SPAS). *Indian Journal of Science and Technology*; 3(8): 885-889.
- [17]. Abbas A. Salih Al-Hamdani, Muhamnd A. Mahmoud, Shaimaa. R. Bakir. 2013. Synthesis, Structural Studies of Some New Transition Metals Complexes of Semicarbazide hydrochloride Schiff Base Derivatives. *Baghdad Science Journal*, 10(3): 583-596.
- [18]. G. Sahni, M.P. Swamy, O.P. Joshi and V.B. Rana. 1976. *Proceeding of the Convention of Chemists Bangalore*, p. 30.

- [19]. Parulverma And Pankaj Srivastava. 2010. Synthesis, Structural Characterization And Biological Screening Of Manganese(II) Complexes Deriv Ed From Schiff Bases Containing Semicarbazone, Asian Journal Of Chemistry, 22(6):4234-4238.
- [20]. Laila Arjuman Banu, Islam, M.S. Abdul Alim al-Bari, M. and Md. Kudrat-E-Zahan. 2015. Synthesis and characterization with antibacterial, antifungal, cytotoxicity Studies on the Co (ii), Ni (ii) and Cu (ii) complexes of tridentate ONO coordinating Schiff bases and heterocyclic amines. International journal of recent advances in multidisciplinary research; (01): 0145-0148
- [21]. Md. Saddam Hossain, Md.Ashraful Islam, C. M. Zakaria, M.M.Haque, Md. Abdul Mannan, Md. Kudrat-E-Zahan. 2016. Synthesis, Spectral and Thermal Characterization with Antimicrobial Studies on Mn(II), Fe(II), Co(II) and Sn(II) Complexes of Tridentate N,O Coordinating Novel Schiff Base Ligand. JCBPS; Section A, 6(4): 041-052.
- [22]. Parul Verma and Pankaj Srivastava, Synthesis. 2010. Structural Characterization and Biological Screening of Manganese(II) Complexes Derived from Schiff Bases Containing Semicarbazone. Asian Journal of Chemistry, 22(6): 4234-4238.
- [23]. Dharam Pal Singh and Ramesh Kumar, 2007. Trivalent metal ion directed synthesis and characterization of macrocyclic complexes, J. Serb. Chem. Soc., 72 (11): 1069–1074.
- [24]. D. P. Singh, Monika Kamboj, Krishan Kumar, Kiran Jain, Chetan Sharma, and K. R. Anej, 2011. Synthesis, Spectroscopic Studies and Biological Screening of 18-Membered Octaazamacrocyclic Complexes Derivedfrom Acetylacetone and Thiocarbohydrazide, Russian Journal of Inorganic Chemistry, 56(9):1396–1401.
- [25]. Md. Saddam Hossain, Shudepta Sarker, A. S. M. Elias Shaheed, Md. Mamun Hossain, Abdul Alim-Al-Bari, Md. Rabiul Karim, C. M. Zakaria, Md. Kudrat-E-Zahan, 2017. Thermal and Spectral Characterization of Cr(III), Co(II) and Cd(II) Metal Complexes Containing Bis-Imine Novel Schiff Base Ligand Towards Potential Biological Application, Chemical and Biomolecular Engineering, 2(1): 41-50.
- [26]. Z. H. Chohan, A. Munawar, and C. T. Supuran, 2001. Transition Metal Complexes of Some Schiff Bases Synthesis Characterization and Antibacterial Studies. Metal based drugs, 8(3): 137-145.
- [27]. Rehab K. Al-Shemary, Ahmed T. Numan , and Eman Mutar Atiyah. 2016. Synthesis, characterization and antimicrobial Evaluation of mixed ligand complexes of Manganese(ii), cobalt(ii), copper(ii), nickel(ii) and Mercury(ii) with 1,10 phenanthroline and a Bidentateschiff base. Eur. Chem. Bull; 5(8):335-338.
- [28]. N. K. Gondia, J. Priya, S. K. Sharma, 2017. Synthesis and physico-chemical characterization of a Schiff base and its zinc complex. Res Chem Intermed; 43:1165–1178.
- [29]. Majumder, A., Rosair, G.M., Mallick, A., Chattopadhyay, N. and Mitra, S., 2006. Synthesis, Structures and Fluorescence of Nickel, Zinc and Cadmium Complexes with the N, N, O tridentate Schiff Base N-2- pyridyl methyldene-2-hydroxyphenylamine. Polyhedron; 25: 1753-1762.
- [30]. Shayma a. Shaker. 2010. Preparation and Spectral Properties of Mixed-Ligand Complexes of VO(IV), Ni(II), Zn(II), Pd(II), Cd(II) and Pb(II) with Dimethylglyoxime and N-Acetyl glycine. E-Journal of Chemistry, 7: 580-586.
- [31]. Iniaya G. E., Olanrele O. S., Iorkpiligh T. I. 2015: Synthesis, Structure Characterization and Antimicrobial Activity of Manganese (II) and Copper (II) Complexes of Isatinphenylhydrazone. The International Journal Of Science & Technoledge. 3(8): 229-233.
- [32]. Md. Kudrat-E-Zahan, M. S. Islam, and Md. Abul Bashar. 2015. Synthesis, Characteristics, and Antimicrobial Activity of Some Complexes of Mn(II), Fe(III) Co(II), Ni(II), Cu(II), and Sb(III) Containing Bidentate Schiff Base of SMDTC1. Russian Journal of General Chemistry, 85(3): 667–672.
- [33]. Hunasekatte G Bheemanna, Virupaiah Gayathri and Nadur M. Nanje Gowda . 2014. Synthesis and spectral studies on Co (II), Ni(II) and Cu(II) complexes with 1,2- bis(N-methylbenzimidazolyl) benzene .IOSR Journal of Applied Chemistry (IOSR-JAC), 7(4): 17-22.

- [34]. Damian C. Onwudiwe and Peter A. Ajibade. 2012. Thermal Studies of Zn(II), Cd(II) and Hg(II) Complexes of Some N-Alkyl-N-Phenyl-Dithiocarbamates. *Int. J. Mol. Sci.*, 13: 9502-9513
- [35]. S. Achut Munde, Amarnath N. Jagdale, Sarika M. Jadhav and K.Trimbak Chondhekar, 2010. Synthesis, characterization and thermal study of some transition metal complexes of an asymmetrical tetradentate Schiff base ligand *J.Serb. Chem. Soc.*, 75(3):349–359
- [36]. M. Šumar Ristović, D. M. Minić, V. Blagojević, K. Anđelković. 2014. Kinetics of Multi-Step Processes of Thermal Degradation of Co(II) Complex With N-Benzyloxycarbonylglycinato Ligand. *Deconvolution of DTG Curves*, *Science of Sintering*, 46:37-53.
- [37]. Ahlam Jameel Abdulghani, Rasha Khuder Hussain. 2015. Synthesis and Characterization of Schiff Base Metal Complexes Derived from Cefotaxime with 1H-indole-2,3-dione (Isatin) and 4-N,N-dimethyl-aminobenzaldehyde. *Open Journal of Inorganic Chemistry*, 5:83-101.
- [38]. Abdel-Rahman, L. H.; Abu-Dief, A. M.; El-Khatib, R. M.; Abdel-Fatah, S. M., 2016. Some new nano-sized Fe(II), Cd(II) and Zn(II) Schiff base complexes as precursor for metal oxides: Sonochemical synthesis, characterization, DNA interaction, in vitro antimicrobial and anticancer activities *Bioorganic Chemistry* 69:140–152.

Supplementary materials

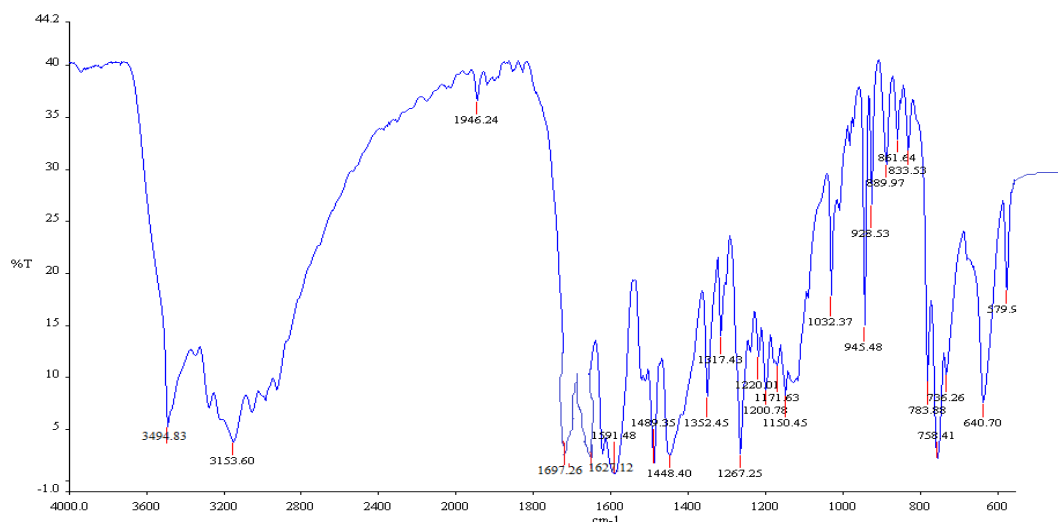


Figure: IR spectra of Schiff Base Ligand [C₁₅H₁₃N₃O₃]

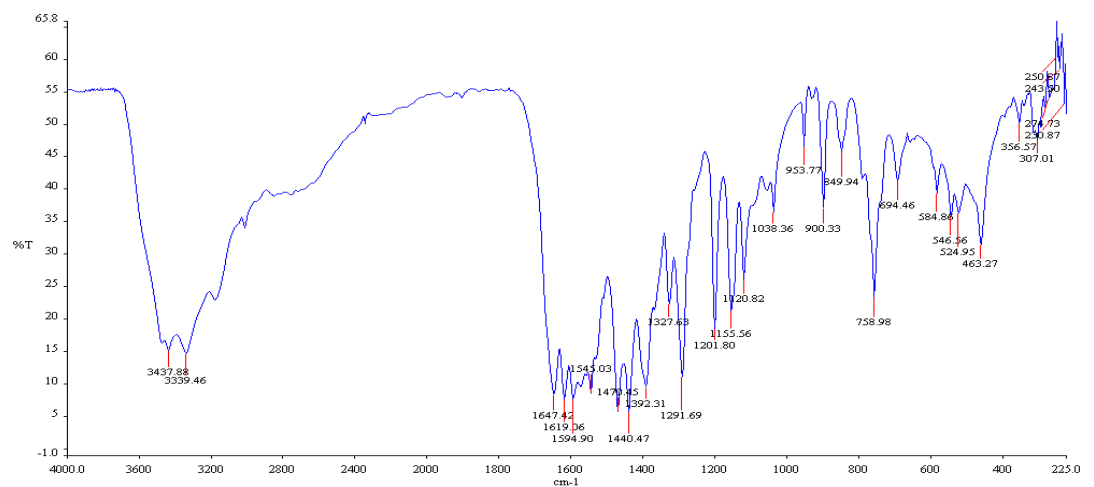


Figure: IR spectra of Zn(II) Complex $[ZnC_{15}H_{11}N_3O_3]$

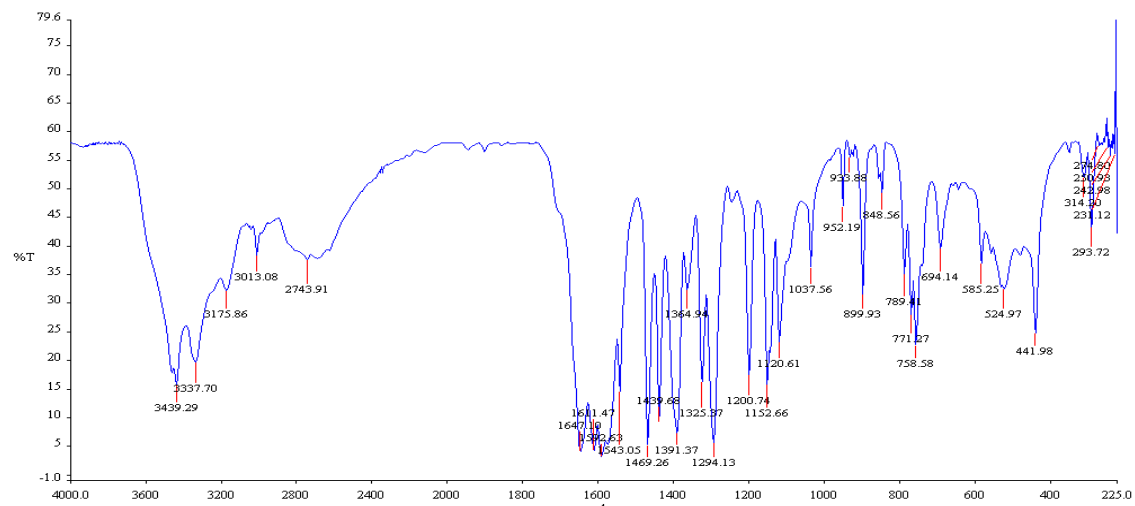


Figure: IR spectra of Mn(II) Complex $[MnC_{15}H_{11}N_3O_3].2H_2O$

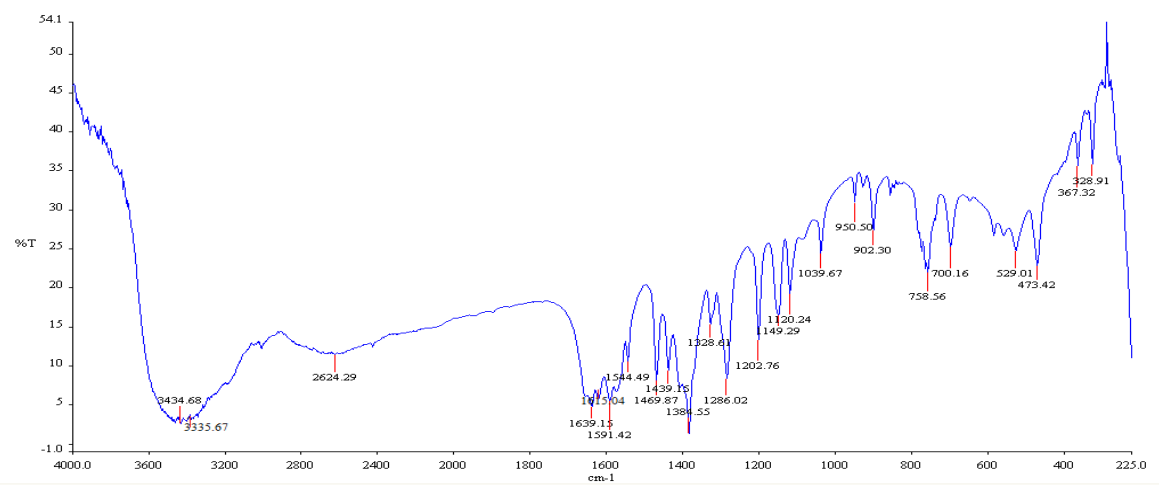


Figure: IR spectra of Ni(II) Complex $[NiC_{15}H_{11}N_3O_3].H_2O$

Table : Selected IR spectral data of Schiff base Ligand and their metal complexes

395

Ligand/complex	IR(cm^{-1})				
	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{HC=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
[SB] [C ₁₅ H ₁₃ N ₃ O ₃]	3494	3153	1627		
[ZnC ₁₅ H ₁₁ N ₃ O ₃]	3437		1619	307	524
[NiC ₁₅ H ₁₁ N ₃ O ₃].H ₂ O	3434		1615	376	529
[MnC ₁₅ H ₁₁ N ₃ O ₃].2H ₂ O	3439		1611	314	524

396

397