



Metal Complexes of (E) – N¹- (2- hydroxybenzylidene) nicotine hydrazid Schiff Base; Synthesis, Characterisation and Nematicidal Activity

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Abstract

Complexes of Co(II) and Mn(II) were prepared from tridentate Schiff base, (E) – N¹- (2 -hydroxybenzylidene) nicotinohydrazide. The Schiff base ligand was synthesised from nicotinic acid hydrazide and salicylaldehyde. These metal complexes were characterised by elemental analysis, molar conductivity, magnetic susceptibility, thermal analysis, x- ray diffraction, FTIR and UV – visible. The analytical data of these metal complexes showed metal: ligand ratio (1:2). The physicochemical study supports the presence of octahedral geometry in all the complexes. The IR spectral data reveal that the ligand behaves as tridentate with ON donor atom sequence towards central metal ion. The molar conductivity values of the metal complexes suggest their non electrolytic nature. The x ray diffraction data suggests orthorhombic crystal system for these complexes. Thermal behaviour (TGA/DTA) described the general decomposition patterns of the complexes. The ligand and its complexes were screened for their nematicidal activity and the results show that the complexes exhibit promising nematicidal activity. The results reveal that the metal complexes are more potent nematicides than the Schiff base ligand.

Keywords: Metal complexes, Schiff base, spectroscopic, nicotinic acid hydrazide, nematicidal activity.

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1. Introduction

Schiff bases are formed when amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine (C=N) group which is characteristic of Schiff bases with the liberation of water molecule. There has been a substantial increase in the study of the coordination of Schiff bases to transition metals as well as main group organometallics [1, 3]. The breakthrough and progress of pesticides and antibiotics are among the most powerful and successful developments of modern science and technology for the control of contagious diseases. The most amazing advances in medicinal chemistry have been made when coordinating compounds played a significant task in regulating biological systems. Synthesis of Schiff base ligand and their metal complexes having novel structural features possess strange physicochemical properties to have a substantial importance in the biological process [4, 7] and constitute an active area of research in modern coordination chemistry. Schiff base ligands are able to coordinate with various transition metals and to stabilize them in various oxidation states. Schiff base ligand with a variety of donor atoms exhibiting interesting coordination modes towards transition metals [8, 10] and azomethine linkage is responsible for the biological activities. Schiff base metal complexes have a wide variety of applications in many fields including analytical, biological, and inorganic chemistry. These are an important class in medicinal and pharmaceutical fields due to a broad spectrum of biological activities like anti-inflammatory, analgesic, antimicrobial, anticonvulsant, antitubercular, anticancer, antioxidant and anthelmintic. Apart from biological activities, Schiff bases are also used as catalysts, intermediates in organic synthesis, dyes, pigments, polymer stabilizers and corrosion inhibitors [11, 13]. They also show nematocidal activity [14, 16] but could not be exploited to their potential in pest control due to the long period of time required for completion of the reaction and not as stable compounds as they get easily disintegrated when exposed to moisture [17, 18]. To defeat this constraint, their metal complexes have been synthesized which generally show better nematocidal activity than their corresponding ligand. The root-knot nematode species, on the other hand, is the most prevalent and probably the most serious plant-parasitic nematode pest of tropical and subtropical regions throughout the world [19]. They occur as a pest on a wide range of crops and affect the crop quantitatively and qualitatively. Endoparasitic nematodes are more destructive and agriculturally

important than other groups. Many crops are grown as vegetables such as tomato, okra, cucumber, melon, carrot, gourds lettuce and peppers particularly are prone to the nematode. The disease is manifested by the formation of galls in the root accompanied by stunted growth, chlorosis, and loss of vigor of the plant-parasitic [20]. Nematodes, the hidden enemy of the plant has led to the estimated annual yield losses in the world's major crops, hence the need to synthesize more active and ecofriendly Schiff base and its complexes to control their excesses.

2. Materials and methods

All chemical used were received from Sigma- Aldrich and where used as received,

2.1.1 Reagents used

The following chemicals were obtained from Sigma – Aldrich chemical Ltd, and used without further purification.

Nicotinic acid hydrazide, salicylaldehyde, Cobalt (II) sulphates heptahydrates, manganese (II) sulphate monohydrates calcium chloride

2.1.2 Solvents used

Absolute ethanol, Methanol, Dimethylsulfoxide (DMSO), Dimethylformamide (DMF) and Acetone

Equipments used

Routine Laboratory apparatus/equipments such as beakers, conical flasks, test tubes, Desiccators, Thermostatic magnetic stirrer, Weighing balance, Water bath, Reflux and Thermometer

2.2 Preparation of the Schiff base ligand (E) – N¹- (2hydroxybenzylidene) nicotinohydrazide

The Schiff base ligand (E) – N¹- (2 - hydroxybenzylidene) nicotinohydrazide (HNH) was prepared by the method described in the literature [21, 24]. A warm solution of Nicotinic hydrazide [2.7 g, 0.02 Mol] in ethanol was mixed slowly with [2.0 mL, 0.02 Mol] of salicylaldehyde in distilled water. The mixture was reflux for 2 h in 50 mL of absolute ethanol. The yellow solid product obtained were filtered, washed with diethyl ether and recrystallized with minimum quantity of ethanol. The final

crystals obtained was allowed to dry over CaCl_2 in vacuum desiccators and weighed.

2.3 Preparation of metal complexes

The complexes were synthesized by the method reported in the literature [25, 27]. A warm ethanolic solution [0.005 mol] of (E) – N¹- (2 - hydroxybenzylidene) nicotinohydrazide, (HNH) Schiff base ligand was added slowly to the hot ethanolic solution of the corresponding metal salts (sulphate) (0.005 mol) with continuous stirring. The resulting solution was placed on a magnetic stirrer with a constant stirring for about 10 -15 min and left to cool. The crystals obtained was filtered and dried over CaCl_2 in the desiccators and weighed.

2.4 Physical measurements

Elemental analysis (C, H, N and O) was performed using Perkin Elmer CHNO/S analyser. IR spectra of the ligand and their complexes were recorded on Agilent Technology FTIR spectroscopy within the range of 4000 – 650 cm^{-1} using KBr disc. The electronic absorption spectra of the ligand and their complexes using JASCO V-670 spectrophotometer from 250 – 800 nm. Magnetic susceptibilities of the complexes were measured using Guoy balance at room temperature, by making diamagnetic corrections using pascals constant. Thermal studies of the complexes were carried out on Perkin Elmer diamond TGA instrument at a heating rate of 10° C and a nitrogen flow rate of 20 ml/min. The x ray patterns of the complexes were recorded on Xpert pro X – ray diffractometer with $\text{Cu } \alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The diffraction data are integrated on using the trial and error methods.

2.4 Nematicidal activity

Nematicidal activity of the ligand and it complexes was carried out on *Meloidogyne incognita* and it was tested for both hatching and mortality rate.

2.4.1 Isolation of nematodes

The nematode was isolated by the method reported in the literature [28] with slight modification. The nematodes and their egg masses were isolated from the heavily infested Carrot by slicing the carrot into smaller sizes and soak in water for 48 h. The decanted suspension was observed under microscope for

the presence of nematodes and its eggs, the appearance of a thread - like roundworms indicates the presence of nematode. The stock suspension was kept in a refrigerator for the nematicidal activity.

2.4.2 Test for hatching

The suspension containing *M. incognita* was shaken vigorously for 5 min. after adding quickly 500 mL 1% NaOCl, then the suspension was poured quickly through nested 150 and 400 mesh sieves. Eggs that passed through the 400 mesh sieves were recovered by repeated sieving and rinsing. The egg that was retained on the 400 mesh sieves was washed with sufficient quantities of distilled water. From the sieves, eggs were eluted and transferred to 40 mL of water.

A centrifuge tube was two – thirds filled with 20 % sucrose solution and the egg water suspension was centrifuged at 500 g for 5 min. At the junction of sugar solution, a silver layer containing the suspended eggs and egg suspension was removed with the help of a pipette and quickly poured on to a 400 mesh sieve. The eggs retained on the sieve was washed three times thoroughly with distilled water and collected in a beaker.

A total of about 100 eggs of nematode *M. incognita* were used per replicate sample and each treatment was replicated three times. The experiment was conducted at room temperature $30 \pm 2^\circ\text{C}$. The eggs was treated with the complexes dissolved in 50, 100, 150, 200 and 250 $\mu\text{g}/\text{mL}$ for 24 hours and observations in relation to hatching of *Meloidogyne* eggs was noted and Nematicidal properties (NP) in percentage were calculated using the formula:

$$NP(\%) = \frac{HT}{HC} \times 100 \quad (1)$$

2.4.3 Mortality test

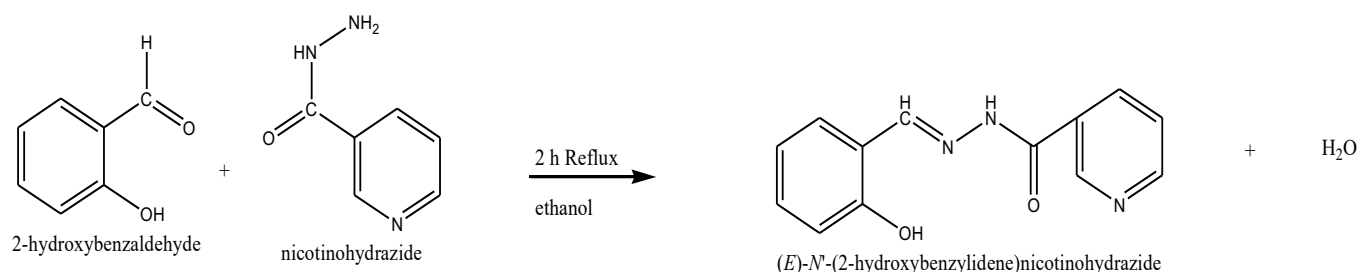
The ligand and its M^{2+} complexes were initially dissolved in dimethyl sulfoxide (DMSO) and then in distilled water to make dilutions of 250, 200, 150, 100 and 50 $\mu\text{g}/\text{mL}$. Experiments were performed under laboratory conditions at $30 \pm 2^\circ\text{C}$. About 100 freshly hatched second stage juveniles were suspended in 5 ml of each diluted compound and incubated. Distilled water with nematode larvae were taken as control. The dead nematodes were observed under an inverted binocular microscope after an incubation of 24 and 48 h. Nematodes were consider dead, if they did not move when probe with a fine

needle [28]. The percentages of mortality were calculated using Microsoft Excel software and the results obtained were recorded.

3. Results and discussion

3.1. Formation of Schiff base ligand

The Schiff base ligand is one of the most widely used ligand due to the ease of formation and remarkable versatility, and therefore they have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals.



Equation for the preparation of the schiff base ligand

The Schiff base ligand (E) – N¹- (2 - hydroxybenzylidene)nicotinohydrazide (HNH) was prepared in good condition and it was characterised by elemental analysis, melting point, UV visible, FTIR, magnetic susceptibility and molar conductance. The percentage yield of the Schiff base ligand was calculated to be 74 %, this is an indication that it has a very good yield. When tested for nematicidal activity, it proved to be active though, its metal complexes showed more activity compare to the free ligand.

3.2 Formation of the Complexes

All the complexes precipitated as powders and were insoluble in most common solvents except ethanol; this could be as a result of their polymeric nature [29] :



Where M = Co²⁺ and Mn²⁺ n = 1, 2, 4, 5 and 6 R = C₅H₄N, R¹ = C₆H₅O

3.3 Physicochemical Characteristics of Ligand and Complexes

The analytical data for the ligand and its complexes were highlighted in Table 1 and are in good agreement with the data required by the general composition of the Schiff base ligand and its metal complexes. The complexes obtained are insoluble in distilled water, methanol and ethanol but soluble in DMF and DMSO. Attempts to grow a single crystal of the complexes were unsuccessful. The molar conductance values on Table 1 were too low. Hence the complexes may be regarded as non electrolyte and it implies that, the compounds are coordination compounds and their absence of ion is because the ligands (ions) are part of the coordinate structure of the complexes [30]. Thus, they exhibit weak ionic (non-electrolytic) character [31].

Melting point of a substance is the temperature at which the solid substance melts to liquid states. It is usually a measure to determine the purity of a substance since small quantity of impurities widens the melting points. In this present study, the melting points of ligand and complexes were determined and the results presented in Table 1 show the melting point range of 205 °C - 245 °C.

Electronic Absorption Spectra Data and Magnetic Data for Ligand and the Complexes

The electronic spectra and the magnetic moment support the stereochemistry of the complexes. The spectra of transition metal complexes depend on the transition of unpaired electrons from the ground state to an excited state. Most of the transition metal complexes are coloured and the colour is observed due to d-d transition in the visible region. The atomic overlap in metal ligand bond allows d – electrons to penetrate from the central atom to the ligand [32]. The electronic spectra of Mn(II) complex in DMSO show bands at 12837, 15432 and 20576 assignable to ${}^6A_{1g}(F) \rightarrow {}^4T_{1g}(F)(v_1)$, ${}^6A_{1g}(F) \rightarrow {}^4T_{2g}(F)(v_1)$ and charge transfer respectively. The observed magnetic moment 5.32 B. M was found in Mn (II) complex which in addition to the electronic spectra data suggest the possibility of an octahedral geometry for Mn (II)

In the case of Co(II) complexes exhibits three bands at 8467, 16304 and 25260 cm^{-1} assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(v_1)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(v_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)(v_3)$ respectively. These transitions and observed magnetic moment of 4.65 indicate high spin octahedral geometry of the complex [33]

Table 1: Analytical and physical properties of the complexes

Complexes	Colour	Yield (%)	m.p. °C	Molar conductance (ms/cm)	Elemental analysis found (calcd)				
					C	H	N	M	SO ₄ ²⁻
C ₁₃ H ₁₁ N ₃ O ₂	Light	85	205	0.02	64.93	4.66	17.68	-	-
	Yellow				(64.73)	(4.56)	(17.43)		
C ₂₆ H ₂₄ N ₆ O ₉ SMn	Yellow	75	235	0.51	47.64 (47.93)	3.76 (3.69)	12.68 (12.90)	8.21 (8.43)	14.55 (14.75)
C ₂₆ H ₂₄ N ₆ O ₉ SCo	Orange	76	245	0.82	47.44 (47.64)	3.26 (3.66)	12.38 (12.83)	9.23 (9.20)	14.22 (14.65)

Table 2: Electronic absorption spectra data and Magnetic Data for ligand and the Complexes

Compound	μ_{eff} (B.M)	Absorption cm^{-1}	Assignment	Geometry
$\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$	-	24330	Charge transfer	Octahedral
$\text{C}_{26}\text{H}_{24}\text{N}_6\text{O}_9\text{SMn}$	5.32	12837	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{v}_1)$	Octahedral
		15432	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{v}_2)$	
		20576	Charge transfer	
$\text{C}_{26}\text{H}_{24}\text{N}_6\text{O}_9\text{SCo}$	4.65	8467	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\text{v}_1)$	Octahedral
		16304	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\text{v}_2)$	
		25260	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(\text{v}_3)$	

Infrared Spectra of the Ligand and Metal (II) Complexes

The data of the FT - IR spectra of the ligand and its metal complexes are listed in Table 3 (Figure 1-3). The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in the complexes. Characteristic peaks in the spectra of the ligand and complexes were considered and compared. The band in the spectra of the ligand at 1644 cm^{-1} have been assigned to $\nu(\text{C}=\text{O})$. These bands were lowered by 22 to 45 cm^{-1} ($1599 - 1622 \text{ cm}^{-1}$) on the metal complexes indicating the involvements of the carbonyl group in the bonding to metal [34]. The imino group i.e $\nu(\text{C}=\text{N})$ band at 1614 cm^{-1} for the free ligand which are found to be shifted to lower frequency region around ($1599 - 1540 \text{ cm}^{-1}$) on complexes suggest the involvement of the nitrogen atom of the $\nu(\text{C}=\text{N})$ azomathine nitrogen in the bonding with the metal (II) ions [35]. A high intensity band was present around 1357 cm^{-1} region in the spectrum of the ligand, which was assign to phenolic $\nu(\text{C}-\text{O})$ vibrations and shift towards lower frequency region around $1298 - 1272 \text{ cm}^{-1}$ on complexion and it indicative of bonding through phenolic oxygen [36].

The appearance of broad band at 3141 cm^{-1} in the Schiff base ligand may be due to $\nu(\text{OH})$ and the broadening of the same was also due to intermolecular H - bonding between OH groups. These bands were missing in the metal complexes indicating that the phenolic character of the ligand has been lost upon complexation [37]. The various observation bands in the regions around 1156 cm^{-1} may be assigned to SO_4^{2-} [38]. In the FT-IR spectra, the band due to N- H stretching in the free ligand occurs in the 3476 cm^{-1} region which may be due to hydrogen bonding probably of the type $\text{NH}\dots\text{N}$ type in the ligand which account for the appearance of the $\nu[\text{N}-\text{H}]$ band around $3443 - 3052 \text{ cm}^{-1}$ in the complexes. The stretching $\nu(\text{NH})$ of the ligand is not much altered in the spectra of the complexes

indicating the nonparticipation of nitrogen atom of NH_2 . Hence it is concluded that the compound (HNH) acted as a neutral tridentate ligand [39]. The $\nu(\text{M-N})$ stretching bands were not observed in the spectrum of the ligand but observed in the spectrum of the complexes around $764 - 724 \text{ cm}^{-1}$ probably because there is no (M-N) coordinated in the ligand [40]. Similarly, there is no $\nu(\text{M-O})$ stretching band in the ligand because, there was no metal coordinated to oxygen meanwhile observed in the spectrum of the complexes around $969 - 925 \text{ cm}^{-1}$, this is in line with the study of [34].

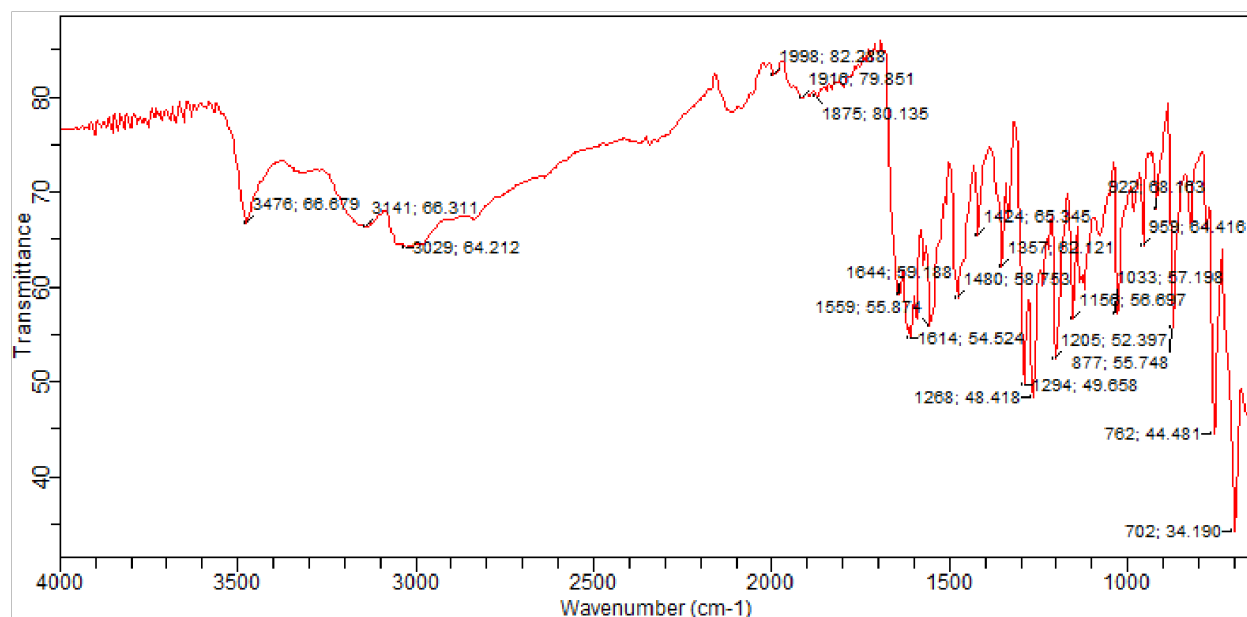


Fig 1: FT – IR of the HNH Schiff base

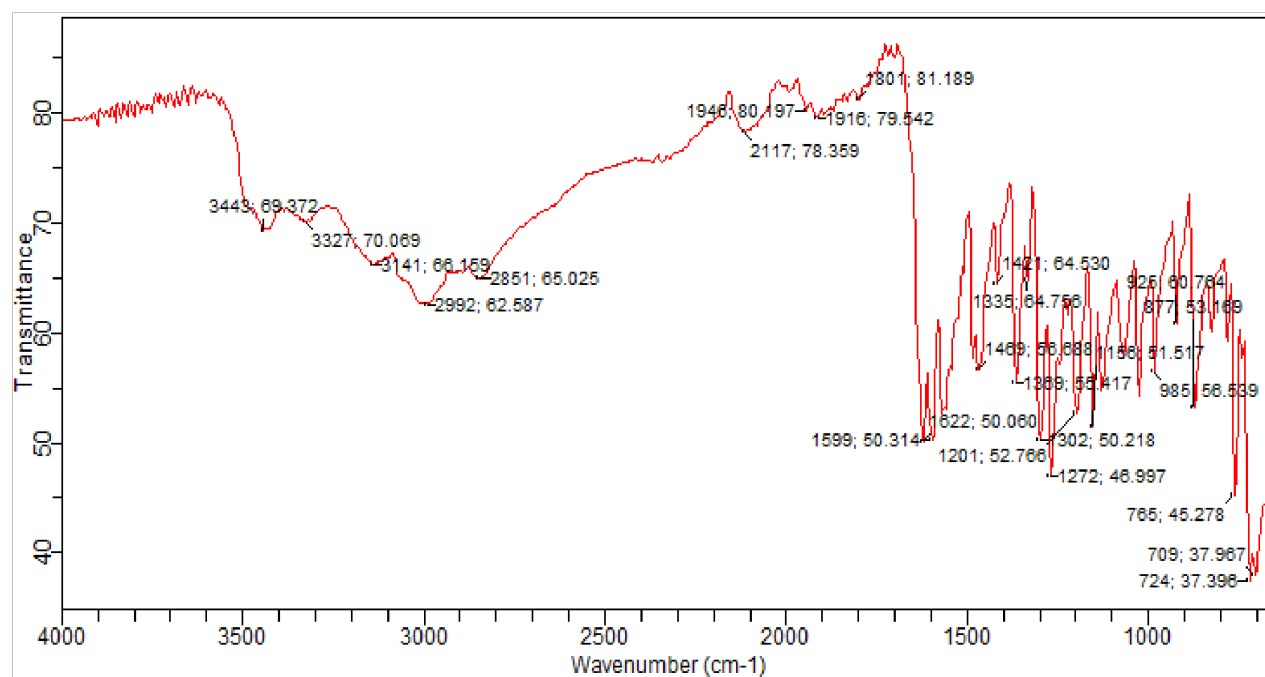


Fig 2: FT – IR of $[\text{Mn}(\text{HNH})_2]\text{SO}_4\cdot\text{H}_2\text{O}$

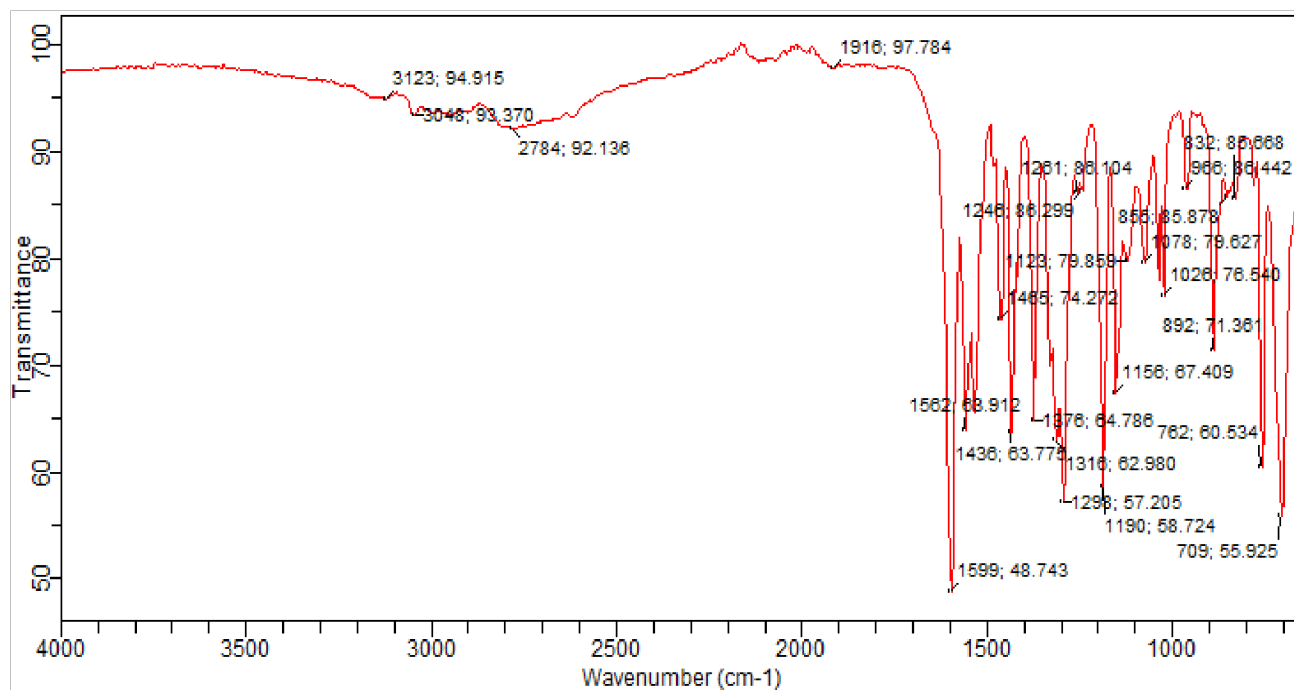


Fig 3: FT – IR of $[\text{Co}(\text{HNH})_2]\text{SO}_4\cdot\text{H}_2\text{O}$

Table 3: The Relevant Infrared Spectra Data for the Ligand and Complexes

Molecular formulae	FTIR in KBR pellets (cm^{-1})								
	C=N	N-N	N-H	C=O	M-O	M-N	SO_4^{2-}	(O-H)	C-O
HNH	1614	1357	3476	1644	-	-	-	3141	1357
Mn- HNH	1599	1369	3443	1622	925	724	1156	-	1272
Co- HNH	1562	1316	3123	1599	969	764	1156	-	1298

Thermal activity study (TGA)

Thermogravimetric analyses (TGA) of the Complexes are used to (i) get information about thermal stability of these new complexes, (ii) decide whether the water molecules (if present) are inside or outside the coordination sphere of the central metal ion, and (iii) suggest a general scheme for thermal decomposition of these complexes. In the present study, heating rate was suitably controlled at $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere, and the weight loss was measured from the ambient temperature up to 950.00°C . The thermograms are shown in Figure 4 - 7 data are provided in Table 4 and the weight losses for each complex were calculated within the corresponding temperature ranges. The thermogram of the Mn(II)-HNH complex within the temperature range of $30 - 550^\circ\text{C}$. Whereas the Co(II) – HNH shows four 4 decomposition steps within the temperature range $30 - 650^\circ\text{C}$.

The thermal dehydration of the compound $[\text{Mn}(\text{HNH})_2]\text{SO}_4\cdot\text{H}_2\text{O}$ take place in three stages. In the first

stage of the thermal dehydration of the complex takes place in a single step that is between 30 - 280 °C with mass loss of 3.01 % (calcd 2.70 %) corresponding to loss of one molecule of water. The maximum rate of mass loss was indicated by DTA peak at 65°C.

In the second stage which occurs in the temperature range of 281 – 500°C with DTA peak observed at 285°C, this range corresponds to the decomposition of $C_{26}H_{22}N_3SO_4$ and the observed mass loss was recorded as 72.30 % (86.34 %). The third stage was the decomposition of MnO residue in the temperature above 501 °C and DTA peak at 580°C. The observed mass loss recorded was 10.89 (11.47 %). The overall mass loss observed was 86.21 % and it was compared with theoretical mass loss value which was found to fall within the range.

Table 4: Thermal analysis of Metal (II) Complexes

Name of complexes	TGA range (°C)	DTA (°C)	Stage	Mass loss found (Calc)	Assignment
Mn(HNH) ₂ .SO ₄ .H ₂ O	30 – 280	65	I	3.01 (2.70)	Dehydration of H ₂ O
Mn(C ₁₃ H ₁₁ N ₃ O ₂) ₂ SO ₄ .H ₂ O	281 - 500	285	II	72.30 (86.34)	C ₂₆ H ₂₂ O ₃ N ₆ SO ₄
	>501	580	III	10.9 (10.89)	MnO Residue
Co(HNH) ₂ SO ₄ .H ₂ O	30 – 180	35	I	2.8 (2.75)	Dehydration of H ₂ O
Co(C ₁₃ H ₁₁ N ₃ O ₂) ₂ SO ₄ .H ₂ O	181 - 260	200	II	62.20 (65.19)	C ₂₀ H ₁₇ O ₂ N ₃ SO ₄
	261- 400	270	III	20.0 (20.61)	C ₆ H ₅ N ₃
	> 401	455	IV	10.0 (11.44)	CoO Residue

The thermal dehydration of the compound [Co(HNH)₂]SO₄H₂O takes place in four stages. The first stage account for a mass loss of 2.8% (2.75%) was attributed to the loss of one molecule of water takes place between 30 – 180 °C. The maximum rate mass loss was indicated by the DTA peak at 35°C.

The remaining complex begins to decompose from temperature range of 181 - 260°C. This range corresponds to decomposition of C₂₀H₁₇O₂N₃SO₄ with DTA peaks observed at 200°C which clearly shows that at least unstable intermediates are also formed during this degradation stage. The observed mass loss was 62.2 % (calcd 65.19 %). The third stage was decomposition of C₆H₅N₃O in temperature range of 261°C - 400°C with the DTA peak observed at 270°C. The observed mass loss was 20.0 % (calcd 20.61 %). The overall mass loss observed was 97.2 % and it was compared with theoretical mass loss value. The end product was estimated to be CoO which decomposed above 401°C with observed mass loss of 2.2 % (calcd 2.73 %) and the observed mass loss and calculated mass were overall equal. On the basis of all spectral data; elemental analysis, FTIR, electronic spectra, and thermal analysis, the suggested structures of the complexes are shown in [Figure 10](#).

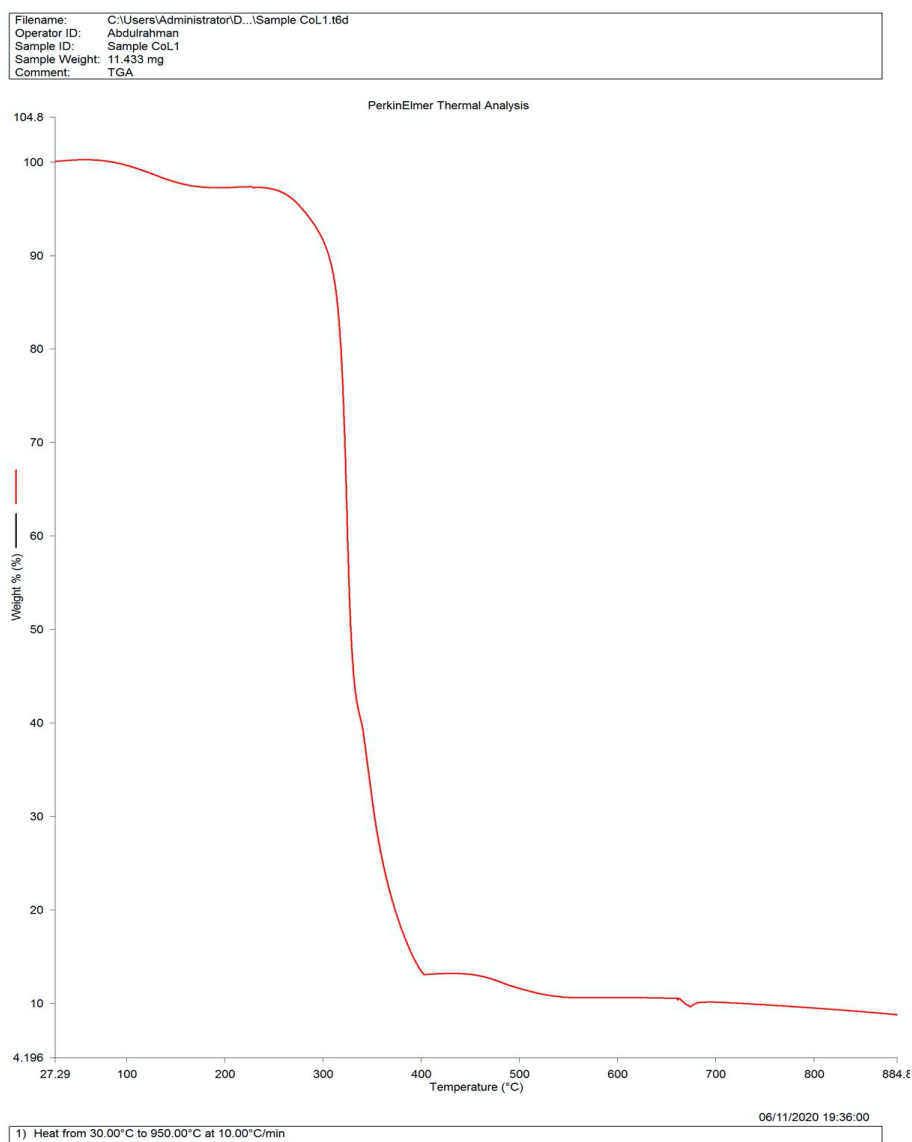


Figure 4: TGA graph of $[\text{Co}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$

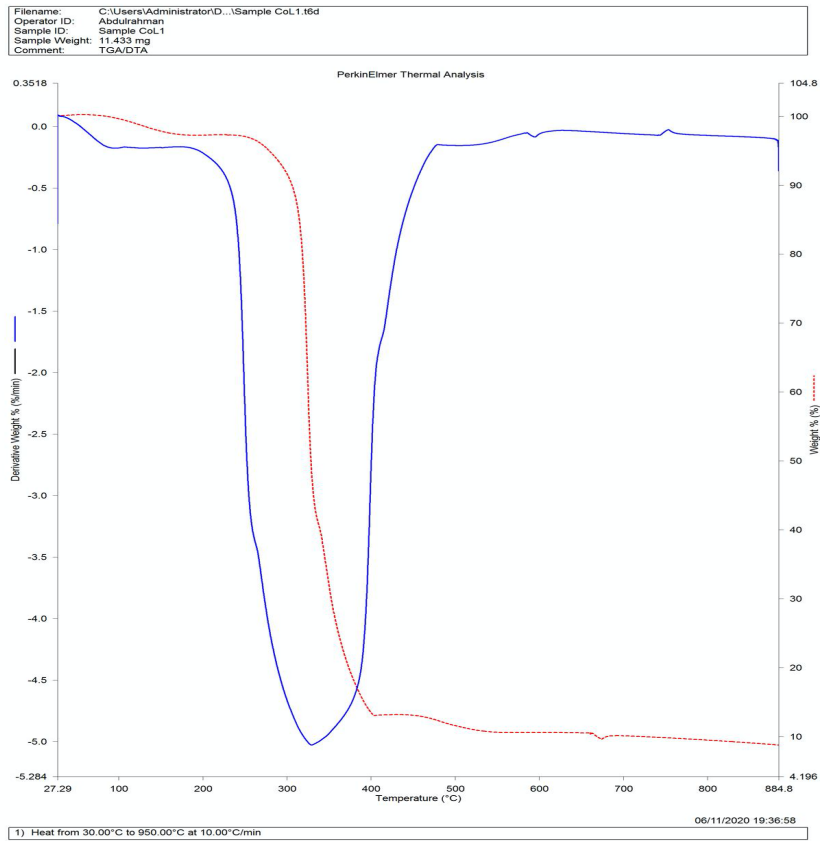


Figure 5: DTA graph of $[\text{Co}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$

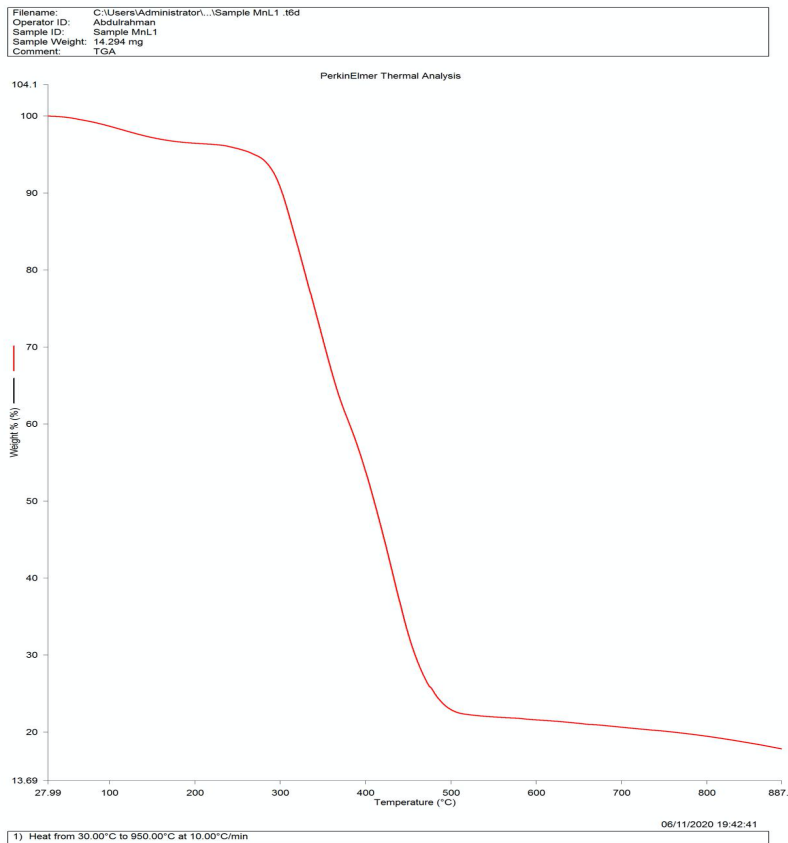


Figure 6: TGA graph of $[\text{Mn}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$

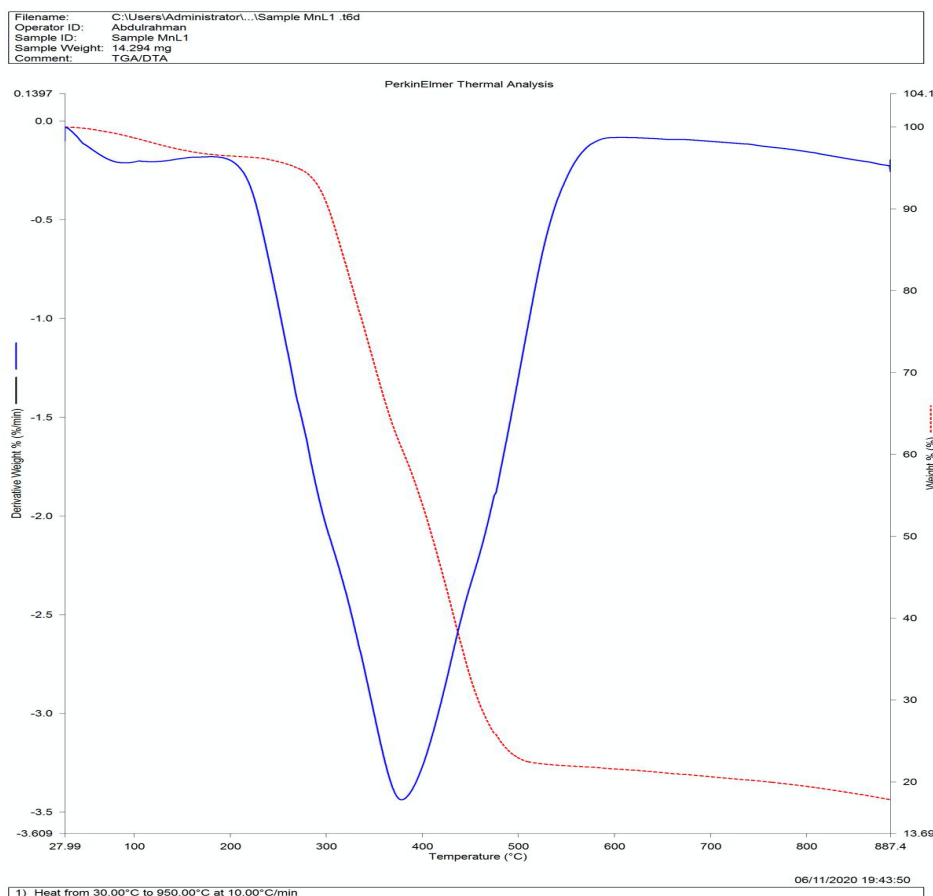


Figure 7: DTA graph of $[\text{Mn}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$

Powder XRD Studies of the complexes

The X – ray diffraction patterns of the metal complexes are given in Figure 14 - 19. Single crystals of the complexes could not be obtained from any solvents because of their insolubility in most organic solvents; hence the powder diffraction data were obtained for structural characterization. The powdered XRD patterns of the complexes were recorded in the range $2\theta = 10 - 50^\circ\text{C}$, they show sharp crystals line peaks indicating its crystalline nature. Phase and unit cell parameters were found using trial and error methods. All the complexes show orthorhombic crystal system. The unit cell parameters of all complexes are as follows; Co- HNH: $a = 8.74\text{Å}$, $b = 16.97\text{Å}$, $c = 8.614\text{Å}$ and $V = 1277.12 \text{Å}^3$; Mn-HNH: $a = 7.64\text{Å}$, $b = 6.51 \text{Å}$, $c = 3.38 \text{Å}$ and $V = 168.11\text{Å}^3$. The crystallite sizes of the complexes were calculated from Scherer's formula [41] :

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad 4$$

Where λ is the wavelength of the X ray radiation, β is the full width at half maximum of diffraction line and θ is the diffraction angle. Using the full width at half maximum intensity of the patterns, the average crystallite sizes of the crystals are given as 11.65 and 11.40 for Co(II), Mn(II) complexes

respectively, suggesting that the complexes are in nanocrystalline phase. The calculated and observed x ray diffraction data is given in Table 5 – 6.

Table 5: X - Ray Diffraction Studies of [Co(HNH)₂]SO₄.H₂O Complex

S/No.	d- spacing (Å ^o)		2θ Values		Δ2θ	Hkl
	Observed	calculated	Observed	Calculated		
1	9.58670	9.57711	9.2251	9.2231	0.0020	(100)
2	8.61464	8.60335	10.2687	10.2697	-0.0010	(001)
3	5.06307	5.05697	17.5166	17.5164	0.0002	(200)
4	4.80090	4.79422	18.4845	18.4846	-0.0001	(020)
5	4.29124	4.28601	20.6992	20.6925	0.0067	(201)
6	4.02348	4.01862	22.0934	22.0923	0.0011	(211)
7	3.47706	3.47282	25.6202	25.6204	-0.0002	(220)
8	3.38420	3.38013	26.3358	26.3354	0.0004	(202)
9	3.23156	3.22760	27.6037	27.6040	-0.0003	(122)
10	2.91783	2.91429	30.6407	30.6407	0.0000	(300)
11	2.71162	2.70828	33.0351	33.0356	-0.0005	(320)
12	2.38759	2.38472	37.6759	37.6755	0.0004	(400)

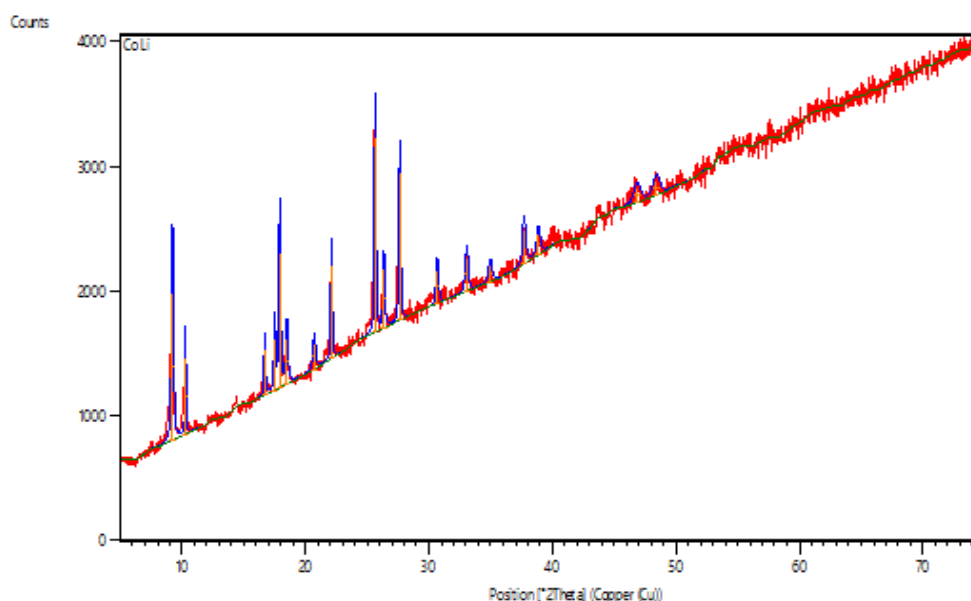


Figure 8: Powder XRD pattern of [Co(HNH)₂]SO₄.H₂O

Nematicidal Activity of Schiff base Ligand and their Metal Complexes

The nematicidal studies were conducted using the Schiff base ligand and its complexes against

Meloidogyne incognita (root knot nematode). The compounds were tested for hatching and mortality of root knot nematode at five different concentrations along with control. The observations were taken for five days and corrected percentage mortality was calculated.

Table 6: X - Ray Diffraction Studies of $[\text{Mn}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$ Complex

S/No.	d- spacing (Å°)		2θ values		$\Delta 2\theta$	hkl
	Observed	Calculated	Observed	Calculated		
1	7.6478	7.6389	11.5710	11.5705	0.0005	(100)
2	6.5146	6.5067	13.5927	13.4678	0.1249	(010)
3	5.0565	5.0565	17.5395	17.5180	0.0215	(110)
4	4.8576	4.8516	18.2638	18.2640	-0.0002	(111)
5	3.8017	3.7970	23.4003	23.4003	0.0000	(200)
6	3.3622	3.3582	26.5114	26.5106	0.0008	(210)
7	3.2742	3.7970	27.2369	27.2363	0.0006	(121)
8	3.0276	3.0239	29.5042	29.5045	-0.0003	(211)

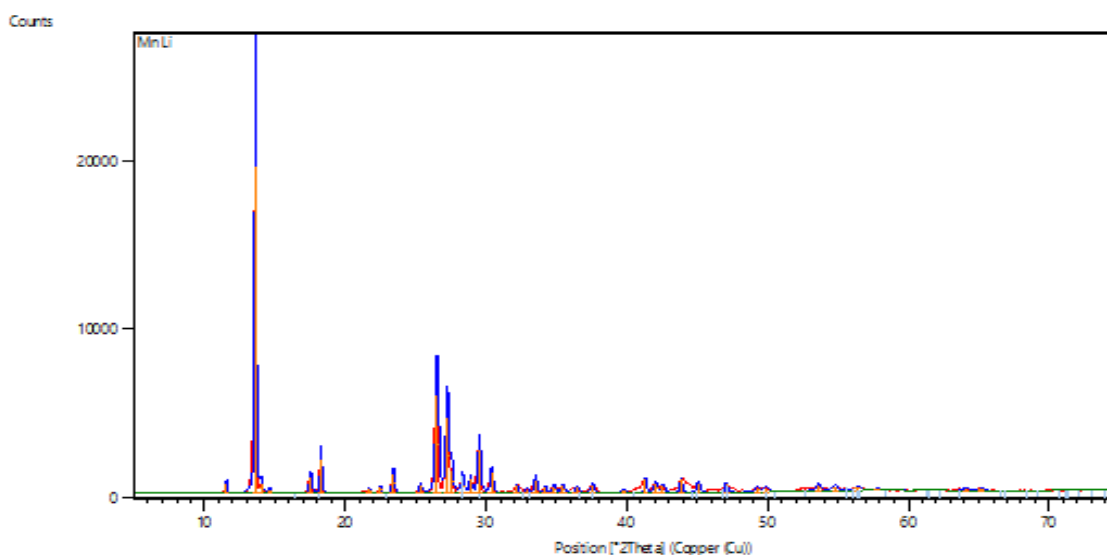


Figure 9: Powder XRD pattern of $[\text{Mn}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$

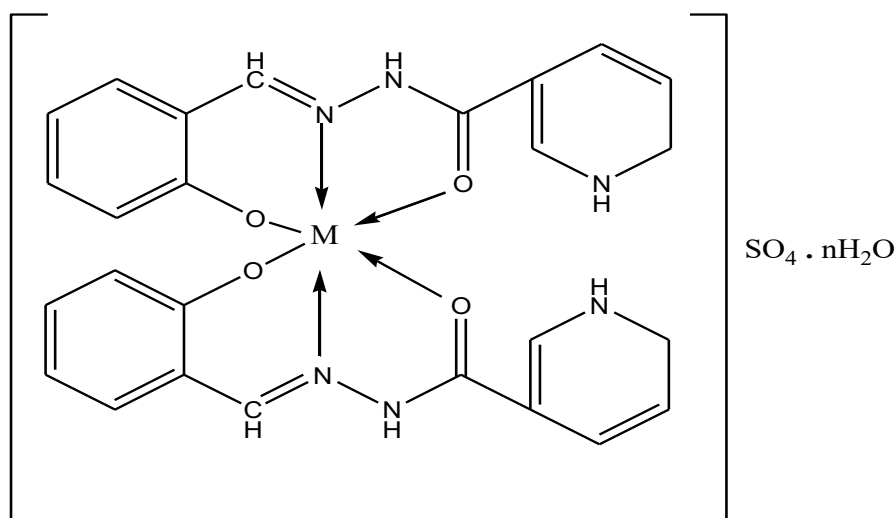


Figure 10: Proposed Structure for 1:2-Octahedral Complexes where M = Co(II) and Mn(II)

Effect of duration of exposure of Schiff base ligand and its complexes on hatching of root knot nematode at different concentrations

After monitoring the reaction at varied concentration of 250, 200, 150, 100 and 50 ppm for five days, the percentage hatching of root knot nematode in Schiff base ligand and its metal complexes were observed to increase with decrease in concentration and increase in number of days of exposure. Figure 12 shows the percentage hatching values of $[\text{Mn}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$ at different concentrations and at different time interval of time. At 250 ppm concentration of $[\text{Mn}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$ the hatching percentage of the root knot nematode was 9.1 percent after 24 hours of exposure but increased to 30.4 percent on the fifth day of exposure of the compound. Similarly at 200 ppm the hatching percentage was 12.4 after 24 hours of exposure and it increased to 38.4 percent on the fifth day of exposure of the compound. Also, at 150 ppm the hatching percentage was 15.2 percent after 24 h of exposure of the compound and the hatching percentage later increased to 41.1 percent on the fifth day of exposure of the compound. At 100 ppm the hatching percentage was 19.7 percent after 24 h of exposure of the compound which later increased to 43.8 percent on the fifth day after exposure of the compound.

Also, at 50 ppm the hatching percentage was observed to be 25.5 percent after 24 h which enhanced to 48.0 percent after exposure of the compound.

Figure 13 shows the percentage hatching value of root knot nematode at different concentration of $[\text{Co}(\text{HNH})_2]\text{SO}_4 \cdot \text{H}_2\text{O}$ and at different time interval of time. At 250 ppm, the hatching percentage after 24 h of exposure was 3.0 percent but increased to 11.0 percent on the fifth day. Similarly at 200 ppm the hatching percentage was 6.0 after 24 h of exposure and it is increased to 16.4 percent on the fifth day of exposure of the compound. Also, at 150 ppm the hatching percentage was 7.6 percent after 24 h of exposure of the compound and later increases to 23.3 percent on the fifth day of exposure of the

compound. At 100 ppm the hatching percentage was 9.1 percent after 24 h of exposure of the compound which later increased to 26.7 percent on the fifth day after exposure of the compound. Also, at 50 ppm the hatching percentage was observed to be 10.7 percent after 24 h which enhanced to 34.3 percent after exposure of the compound.

Figure 11 shows the percentage hatching value of root knot nematode at different concentration of HNH and at different time interval of time. At 250 ppm, the hatching percentage after 24 h of exposure was 4.60 percent but increased to 23.3 percent on the fifth day. Similarly at 200 ppm the hatching percentage was 7.7.0 after 24 h of exposure and it is increased to 25.3 percent on the fifth day of exposure of the compound. Also, at 150 ppm the hatching percentage was 10.6 percent after 24 h of exposure of the compound and later increases to 34.3 percent on the fifth day of exposure of the compound. At 100 ppm the hatching percentage was 13.7 percent after 24 h of exposure of the compound which later increased to 38.4 percent on the fifth day after exposure of the compound. Also, at 50 ppm the hatching percentage was observed to be 16.7 percent after 24 h which enhanced to 43.2 percent after exposure of the compound. A plot of the percentage hatching of the root-knot nematode against duration was made (Figures 11-13) and it shows that hatching at different concentrations increases with increase in time of exposure. This is in agreement with the result obtained by [28]. The hatching observed in the control (Distilled water) were higher, almost 100 percent hatching in the control, this shows that the complexes were able to inhibit the growth of the nematodes though, the compound become less effective with increase in number of days. Also, higher concentrations were found to be more effective than lower concentration for hatching of root-knot nematode.

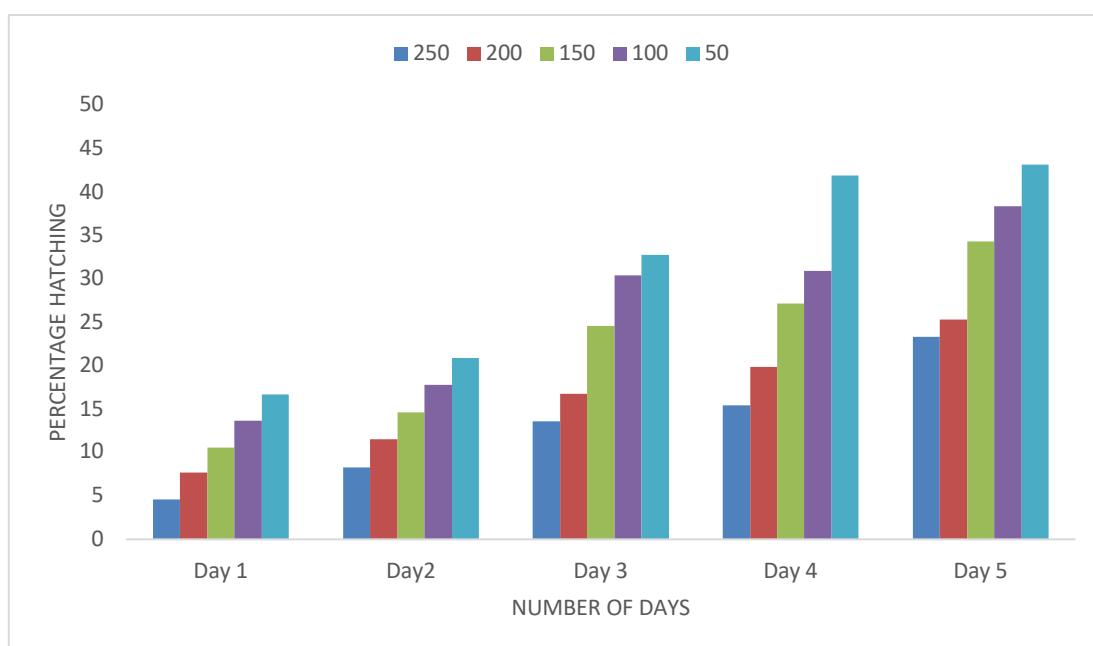


Figure 11: Percentage of Nematodes hatching in-HNH Schiff base Ligand

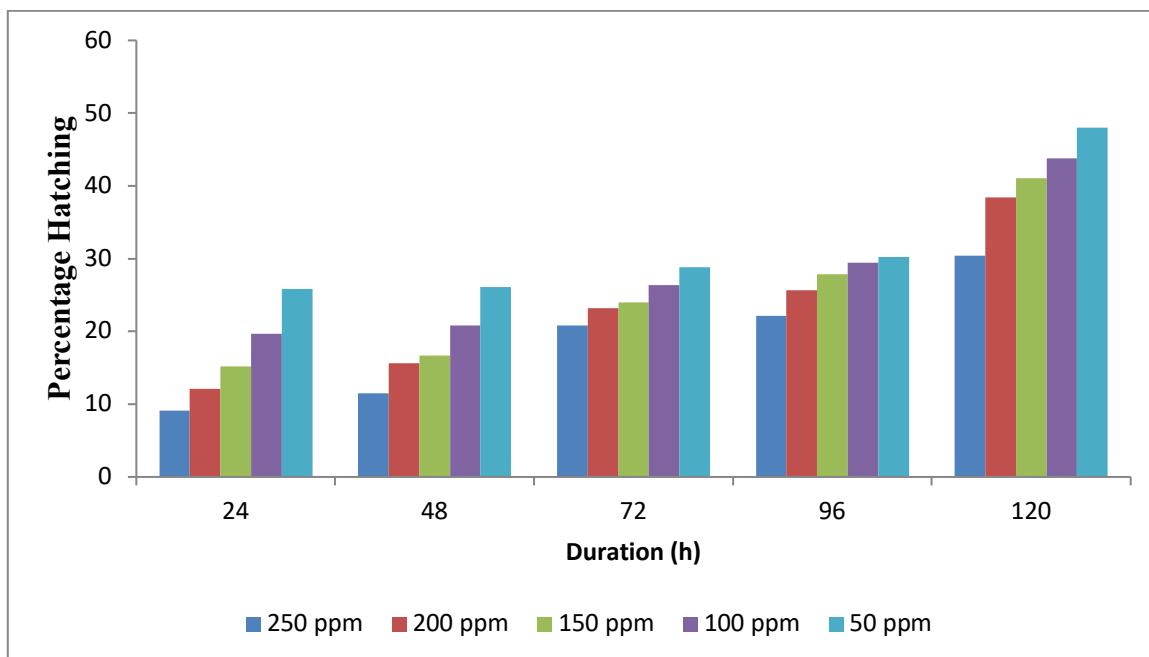


Figure 12: Percentage of Hatching of Nematodes in Mn-HNH Complex

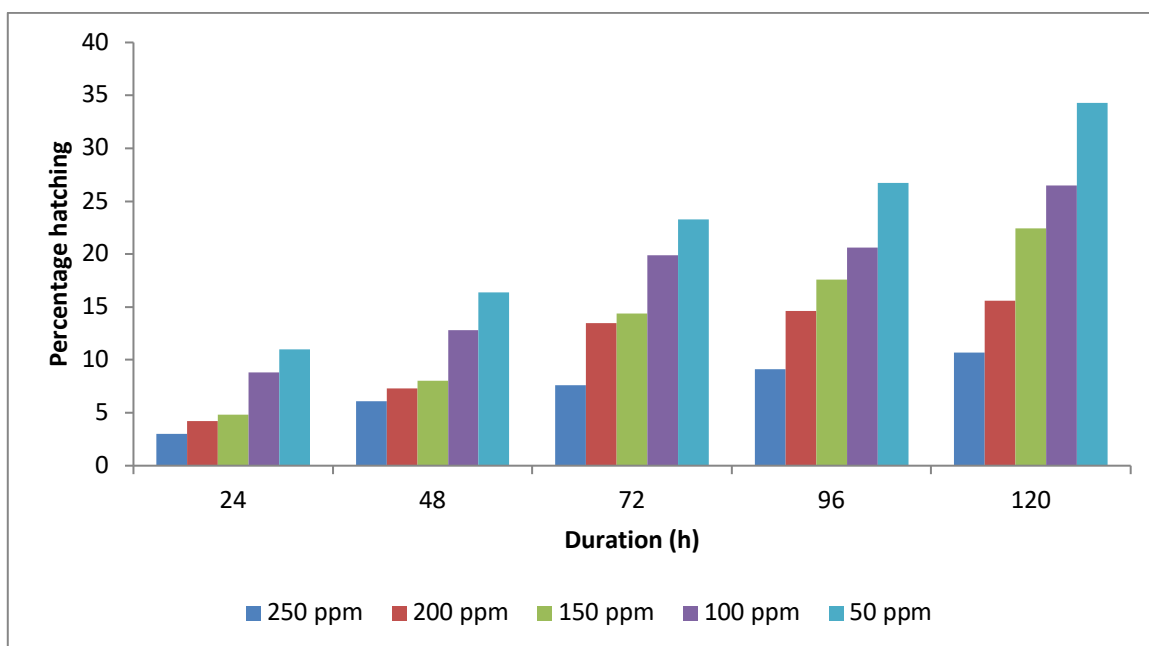


Figure 13: Percentage of Hatching of Nematodes in Co-HNH Complex

Effect of Schiff base and its complexes on mortality of root knot nematode

The percentage mortality of root knot nematode in Schiff base and its complexes are shown in [Figures 14-16](#). The bio efficacy activity studies of the Schiff base ligand and its complexes were carried out at five different concentrations ranging from 250 ppm to 50 ppm for five days were observed and the percentage mortality were recorded.

The percentage mortality of 32.8, 26.9, 23.2, 17.7 and 14.6 percent were observed at 250, 200, 150, 100, and 50 ppm concentrations respective after 24 h in Mn-HNH complex. On the second day (48 h)

percentage mortality of 41.4, 33.1, 26.6, 21.3 and 18.1 percent were recorded at different concentrations ranging from 250 to 50 ppm respectively. On the third day (72 hours) the percentage mortality of 51.1, 42.2, 32.6, 25.3 and 22.9 percent were recorded at different concentrations of 250, 200, 150, 100 and 50 ppm respectively. On the fourth day percentage mortality of 77.5, 63.9, 49.5, 38.3, and 34.8 percent were observed at 250, 200, 150, 100 and 50 ppm concentration respectively.

On the fifth day of the treatment the percentage mortality of 82.5, 68.4, 50.7, 43.7 and 36.2 were observed at 250, 200, 150, 100 and 50 ppm concentrations respectively. There was an increase in the corrected percentage mortality from the second day to the fifth day of exposure; consequently, the corrected percentage mortality was high at 250 ppm concentration and lowest at 50 ppm concentration. There was no mortality observed in the control (Distilled water), this is a confirmation that the complexes were able to kill the nematode at varied concentration. This shows that a complex at lower concentration was not exerting enough toxic influence on the nematodes. Therefore implies that the percentage mortality increases with increases in concentration and time of application of Mn-HNH complex.

The percentage mortality of Co-NHN complex against *M. Incognita* is shown in Figure 14. The percentage mortality of 31.6, 20.4, 15.1, 11.9 and 11.3 percent were observed at 250, 200, 150, 100 and 50 ppm concentrations respectively in 24 h. On the Second day (48 h) the percentage mortality of 46.6, 29.8, 21.3, 20.2 and 17.5 were observed at 250, 200, 150, 100 and 50 ppm concentrations respectively. On the fourth day (72 h) Percentage Mortality of 65.3, 43.6, 41.5, 30.7 and 27.0 percent were observed at 250, 200, 150, 100 and 50 ppm Concentrations respectively.

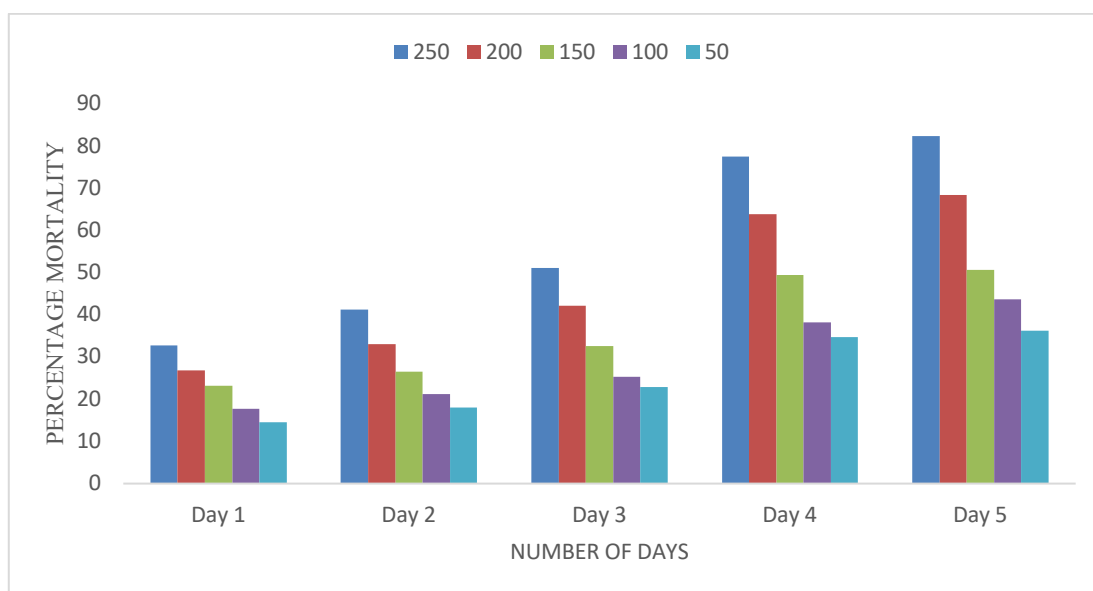


Figure 14: Percentage Mortality of Nematodes in Mn-HNH at Different Concentration

On the fifth day of treatments the percentage mortality of 92.6, 69.5, 66.7, 52.1 and 47.2 were observed at 250, 200, 150, 100 and 50 ppm respectively. There was a slow increase in the percentage mortality

from the second day to fifth day of exposure. Consequently, the percentage mortality was high at 250 ppm concentration and lower at 50 ppm concentration. This showed that Complex at low Concentration was not exerting toxic influence on nematode. That showed that the corrected percentage mortality increased with increase in concentration and time of application of Co-HNH.

Percentage mortality of HNH complex against *M. Incognita* is shown in Figure 16. The nematocidal activity of the (HNH) Schiff base ligand was observed for five days at different concentration ranging from 250 ppm to 50 ppm. Percentage mortality of 12.0, 10.0, 7.1, 7.0 and 5.0 percent were observed after 24 h at concentrations of 250, 200, 150, 100 and 50 ppm respectively. On the second day, the percentage mortality of 12.7, 8.5, 8.1, 5.9 and 5.4 percent were recorded at different concentration of 250, 200, 150, 100 and 50 ppm respectively. Also, the percentage mortality of 31.0, 21.1, 18.6, 10.3 and 13.1 were observed after 72 h of exposure in 250, 200, 150, 100, and 50 ppm concentrations respectively. On the fourth day of exposure, the percentage mortality of 71.3, 49.1, 43.7, 35.3 and 29.1 were observed in 250, 200, 150, 100 and 50 ppm concentrations respectively. On the fifth day of the treatment, the percentage mortality of 83.2, 60.1, 47.0, 40.1 and 34.1 were observed at 250, 200, 150, 100 and 50 ppm concentrations respectively. There was an increase in the corrected percentage mortality from the second day to the fifth day of exposure; consequently, the corrected percentage mortality was high at 250 ppm concentration and lowest at 50 ppm concentration. There was no mortality observed in the control (Distilled water), this is a confirmation that the complexes were able to kill the nematode at varied concentrations. This shows that complexes at lower concentration were not exerting enough toxic influence on the nematodes. These imply that the percentage mortality increases with increases in concentration and time of application of (HNH). This fact is in agreement with the research finding made by Eka *et al.* [42].

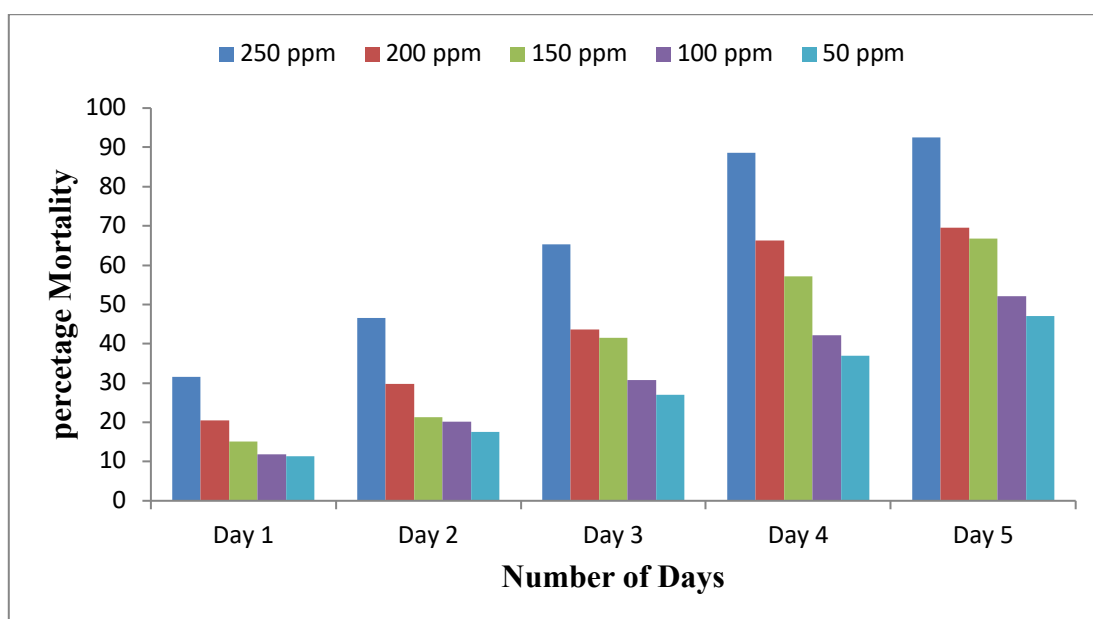


Figure 15: Percentage of Mortality of Nematodes in Co-HNH

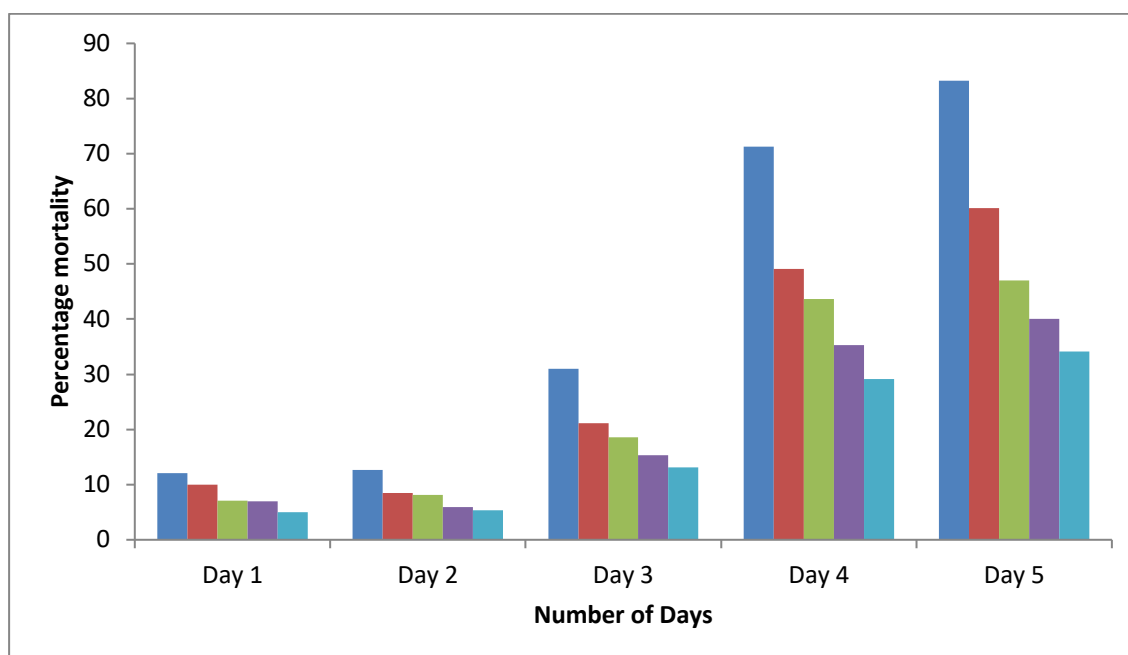


Figure 16: Percentage Mortality of Nematodes in HNH Ligand at Different Concentration

Conclusion

In summary, a series of metal II complexes of Schiff base (E) – N¹- (2 - hydroxybenzylidene) nicotinohydrazide have been prepared and characterized using physical and various spectroscopic techniques. The results of the FTIR spectra of the ligand and the complexes showed clear evidence of formation of the complexes, the UV spectra of the complexes supported by the magnetic moment revealed that the ligand coordinate in a tridentate manner to the metal ions and the complexes are rather octahedral in nature hence, an octahedral geometry has been proposed for all the complexes. From the thermograms, the numbers of lattice water molecules present in the complexes were calculated and an orthorhombic system has been proposed for all the complexes. The powder XRD pattern revealed that the crystals are of orthorhombic systems and it satisfy the condition $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$ for a typical orthorhombic crystal system. The Schiff base and the complexes showed effective nematicidal activity, the complexes appear to be more effective nematicide than the Schiff base ligand.

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