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Synthesis, Characterization, Kinetics, Thermodynamics and Nematicidal Studies of Sm(III), Gd(III) and Nd(III) Schiff Base Complexes

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ABSTRACT

Schiff base derived from benzaldehyde and ethylenediimine and its Sm(III), Gd(III) and Nd(III) complexes were synthesized. The ligand N, N'-Bis(2-hydroxy-1,2-diphenylethanone)ethylenediamine (N, N'- B_2HDE) and its complexes were characterized by molar conductivity, melting point, solubility test and spectrophotometrically (IR and UV-Vis). The kinetics was studied by determining the rate of formation at different temperatures. The observed rate constants *k* was obtained and used to obtain activation energy (Ea). Thermodynamics parameters showed that activation energy (Ea) obtained for Sm(III) and Gd(III) was 0.452, and 1.196 KJ respectively which were positive (Ea) indicating that, the rate of formation increased with increased temperature. The result of thermodynamic parameters showed that; the ΔG^o of the complexes were -3896.02 KJmol^{-1}and -8201.18KJmol^{-1} which indicated the ability of the studied ligand to form stable complexes, while ΔH^o was 1168 KJmol^{-1} and 2268 KJmol^{-1}, for Sm(III) and Gd(III) respectively. The negative result of the ΔS^o of Sm(III) and Gd(III) was -16.99 KJmol^{-1} and -19.91 KJmol^{-1}respectively. The ligand and its metal complexes were screened for nematicidal activities against a root knot nematode, *Meloidogyne incognita*. The metal complexes revealed better nematicidal activities than ligand. The solubility showed that ligand and its metal complexes were electrolytic nature, soluble in acetone, dimethylsulphoxide, dimethylformaldehyde while the melting point of ligand and complexes was found to be between 120-130 °C. The complexes had molar conductivity of 11.5-12.0 indicating an electrolytic property; The IR spectra coordinated through azomethine nitrogen atom and hydroxyl group. UV-Vis spectrophotometer showed a complexation of the metal and ligand, demonstrating an octahedral geometry for both complexes. Hatching test of the ligand and its metal complexes showed that they behaved radically different from each other. The behaviour of the ligand and its complexes at different time (hours) and concentrations employed showed significant difference in terms of their nematicidal activity against *M. incognita*.

Keywords: Characterization, Kinetics, Nematcidal studies, Synthesis, Thermodynamics

INTRODUCTION

A coordination compound or metal complex can be seen as central metal atom attached with the sheath of ions or molecules (Lee, 1996). The interesting aspects of transition metals are their ability to form coordination compounds. Such compounds are formed between a metal ion and a molecule with one or more unshared electron pairs called a ligand (Chakraborty *et al.*, 2009). A Schiff base is formed from a reaction between an amine and an aldehyde or a ketone. They have been reported to be useful in medicine and catalysis. They are known to exhibit potent antibacterial, antiulcer and analgesic activities (Cleiton *et al.*, 2011). In addition, some Schiff bases show pharmacologically useful activities like anticancer, anti-tuberculosis and antioxidant activities (Prakshash and Adhikari, 2011). Recently, the lanthanide Schiff base complexes have acquired special attention in medicinal and pharmaceutical field since they show excellent biological activities. Some of the lanthanide complexes are used in biomedical analysis as Magnetic Resonance Imaging (MRI) contrast agents (Ashraf *et al.*, 2011). Because of special photophysical and biological properties, lanthanide complexes can be used as biological probes in the areas of clinical chemistry and molecular biology (Gassner *et al.*, 2008). Due to their special electronic configuration, lanthanide complexes have stimulated many research works on the design and synthesis as potential anticancer and antibacterial agents (Mao *et al.*, 2006). Polydentate ligands obtained from Schiff bases, assisted by metal ions, provide highly organized supramolecular metal complexes. Such complexes possess binding sites and cavities for various cations, anions and organic molecules (Dixit *et al.*, 2009).

The versatile nature of the lanthanide Schiff base complexes, make them important contender in catalysis of numerous organic transformations like oxidation of amines to their corresponding oxygen containing derivatives. Some of the Schiff base complexes containing N and O donor atoms are effective stereospecific catalysts for oxidation reduction, hydrolysis, biological activities (Ramasubramanian *et al*., 2012), and other organic and inorganic transformations. These organic transformations are environmentally benign and hence they are highly desirable for the treatment of waste water which contains toxic organic pollutants (Dixit *et al*., 2009). Aniline one of such pollutants is used in the manufacturing of dyes and polymers, which includes rubber, herbicides, pesticides, fungicides, and pharmaceuticals is released into environment from these industries. This research work is aimed at synthesizing, characterizing and monitoring the kinetics, thermodynamics as well as studying the nematicidal properties of the ligand N, N'-Bis(2-hydroxy-1,2-diphenylethanone)ethylenediamine and its complexes with Gd(III), Sm(III) and Nd(III) against the root knot nematode *Meloidogyne incognita* that affects Okra plant (*Abelmoschus esculentus).*

MATERIALS AND METHOD

Materials

Reagents and Solvents

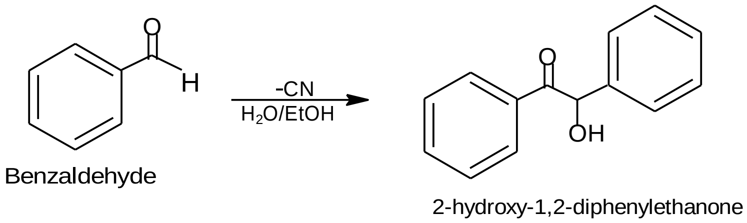
All chemicals used were of analytical grade obtained from commercial source and used without further purification.

The apparatus and instrument used include: Barnstead electro thermal BI9100 melting point apparatus with digital thermometer, pH/Conductivity series 510 conductivity meters, Carry 630 FT-IR spectrophotometer, Shimadzu 1800UV-Visible spectrophotometer, SB160 heat-stirrer, PW 184 weighing balance, 98-1-B temperature regulating heating mantle, and OV/100/F ovum.

METHODS

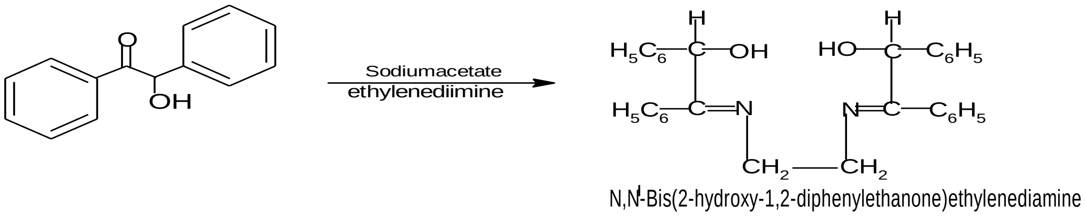
Synthesis of 2-hydroxy-1, 2, diphenylethanone

The Schiff base 2-hydroxy-1, 2, diphenylethanone was synthesized as reported by Iorungwa *et al.* (2019) and as represented in scheme 1. Exactly 65 mL of ethyl alcohol was added to a 500 mL round bottom flask, followed by 47.5 mL of benzaldehyde and a solution of 5 g of sodium cyanide in 50 mL water. Few anti bumping granules were introduced into the flask. A condenser was attached and the mixture was refluxed on a steam bath for 30 minutes. The round bottomed flask and its contents was cooled in an ice-bath. The products were filtered and washed with cold water, dried and recrystallized from 40 mL of hot ethanol. The crystals were dried at 50 ^{o}C and weighed.



Scheme 1: Synthesis of N, N'-Bis (2-hydroxy-1,2-diphenylethanone)ethylendiamine ligand (N,N'-B$_2$HDE)

The synthesis of N, N'-Bis (2-hydroxy-1, 2, diphenylethanone) ethylenediamine Ligand was done as described by Iorungwa *et al*. (2019). To a methanolic solution of 2-hydroxy-1, 2, diphenylethanone (2.12 g) and ethylenediamine (0.6 mL), 4 g of anhydrous sodium acetate was added and the mixture was refluxed for an hour. The hot solution was poured into ice-cold water upon yellow precipitate of the Schiff base was separated; filtered, washed with water; dried and recrystallized from ethanol. The equation of the synthesis is as in Scheme 2.



Scheme 2: Synthesis of N, N'-Bis (2-hydroxy-1, 2, diphenylethanone) ethylenediamine

Synthesis of N,N'-Bis(2-hydroxy-1,2-diphenylethanone)ethylenediamine Sm(III) Complex

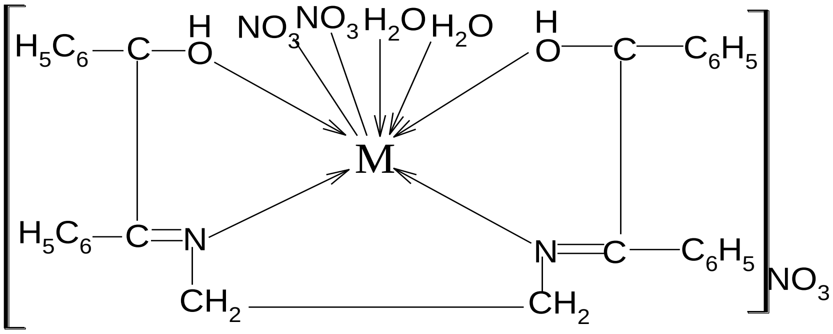
The method for the synthesis of N,N'-Bis(2-hydroxy-1,2,diphenylethanone)ethylenediamine Sm(III) complex was done as described by Evans *et al.* (2002). An accurate weight (1.792 g, 4.00 mmol) of N,N'-Bis(2-hydroxyl -1,2,diphenylethanone)ethylenediamine in hot ethanol (65 °C) was mixed with (1.777 g, 4.00 mmol) of $N_3O_9Sm.5H_2O$ in 25 mL of ethanol and the mixture was stirred for 2 h using magnetic stirrer. The precipitate obtained was filtered off, washed with hot ethanol, ether and dried under vacuum at 70 °C. The expected equation for the reaction is as given in equation (1).

$$N_3OS_9m.5H_2O+B_2HDE \longrightarrow [Sm(B_2\,HDE)\,(NO_3)_2.2H_2O)]\,NO_3 \qquad (1)$$

The same procedure was followed for the synthesis of Gd(III) and Nd(III) complexes as given in equations 2 and 3 respectively.

$$GdN_3O9.6H_2O+B_2HDE \longrightarrow [Gd\,(B_2HDE)\,(NO_3)_2.2H_2O]\,NO_3 \qquad (2)$$

$$N_3NdO_9.6H_2O+B_2HDE \longrightarrow [Nd\,(B_2HDE)\,(NO_3)_2.2H_2O]\,NO_3 \qquad (3)$$



M = Sm(III), Nd(III) and Gd(III)

Scheme 3: Proposed general structure of the metal complex

CHARACTERIZATION OF LIGAND AND COMPLEXES

Solubility test

The prepared Schiff base alongside its complexes was added to 10 mL portions of each of the solvents (distilled water, methanol, ethanol, chloroform, dimethylsulfoxide, dimethylformanide and acetone) and was shaken vigorously.

Melting point determination

Each sample of the Schiff base with the metal complexes were put in separate capillary tubes and each were inserted into the heating block and were heated one after the other and the temperature at which each of the sample melt was read from the digital screen.

Molar Conductivity Measurement

The molar conductivities of the complexes were obtained from acetone using pH/Conductivity series 510 conductivity meters (Iorungwa *et al.*, 2019).

Kinetic and Thermodynamic Studies

The kinetic study of the complexes was done by mixing an accurate amount (1.792 g, 4.0 mmol) of N, N'Bis (2-hydroxy-1,2-dephenylethanone) ethylenediamine, dissolved in 20 mL of absolute ethanol with 4.0 mmol of Samarium (III) nitrate hexahydrate ($N_3O_9Sm.6H_2O$) salt and the mixture was stirred 1900 rpm while heating at temperatures of 40, 50, 60, and 70 ^{0}C, this was maintained for the required time of 10, 20, 30 and 40 minutes. The crystals formed were filtered, dried and weighed. The various weight obtained were analyzed to ascertain the yield in mole. The graph of semi-log of yield in mole against time was plotted to obtain observed rate constants which were in turned used to plot Ink_{obs} vs. 1/T to obtain activation energy (Ea) and In(k_{obs}/T) vs. 1/T to obtain thermodynamic parameters(Iorungwa *et al.*, 2014; Iorungwa *et al.*, 2019).

Nematicidal activity of Schiff base and metal complexes

The nematicidal studies were conducted using Schiff bases and their metal complexes against *Meloidogyne incognita* (root knot nematode). The compounds were tested for hatching and mortality of root knot nematode at four different concentrations alongside with control.

Raising of root knot nematodes

Roots were collected from Akaaior farm along Naka road in Makurdi, Benue state. The roots of the infected okra(*Abelmoschus estculentus*) plants were cut into 1-2cm sections crushed using ceramic pistol and mortar. The eggs were collected on a 38µm sieve and washed in a beaker. The egg suspension was poured onto an extraction tray and juveniles were collected.

Hatching of nematodes

Fresh egg masses of *Meloidogyne incognita* were collected from stock culture maintained on okra (*Abelmoschus estculentus*) root tissues and kept in water for egg hatching. The eggs suspensions were poured on a cotton wool filter paper and incubated at room temperature to obtain freshly hatched juveniles (J2). About 25 egg masses were picked and placed in 10.00 mL of 30, 15, 7.5 ppm concentrations of ligand the metal complexes to monitor the hatching within 12 hours. A regular time interval of 4, 8 and 12 hours were employed in monitoring the hatched larvae of the nematodes, which the number of unhatched nematodes was observed and recorded within the time exposure. These were observed under an inverted binocular microscope. This method adopted is as described elsewhere (Ekta, 2013).

Mortality test of nematodes

For mortality, 25 eggs collected from pure culture were taken into different concentrations of the ligand and its metal complexes. The number of sacrificed nematodes was observed with the time interval of 4, 8, and 12 hrs respectively. These were observed under an inverted binocular microscope. After 12 hours of exposure, revived juveniles were counted and sacrificed nematodes were confirmed. Nematodes were considered sacrificed when they could not move.

RESULTS AND DISCUSSIONS

The results of the physicochemical properties of the ligand and complexes are presented in Tables 1 to 7. Table 1 shows some physical constants for the ligand and its complexes, while Table 2 presents the solubility test results while Tables 3 and 4 show the result of some of the spectral absorption values of both the ligand and its metal complexes, while Tables 5 to 7 presents their kinetics and thermodynamic properties respectively.

Figures 1 to 5 presents the spectral information of the ligand and its metal complexes. Figure 6 to 11 reveals the nematicidal behaviour of the Schiff base ligand and its metal complexes at various concentrations and time of exposure.

The physical appearance of the compounds was noted by visual observation. The reaction between N, N'-Bis(2-hydroxy-1,2-diphenylethanone)ethylenediamine and Sm(III), Gd(III) and Nd(III) ions formed metal complexes which are powdered solids and coloured with a proposed general structural formula as given in Scheme 3. The complexes were found to melt in the temperature range of 120-130°C which shows a fairly stable complex compound. The compounds were found to be insoluble in water and common organic solvents but are soluble in acetone, dimethysulphoxide (DMSO) and dimethylformaldehyde (DMF). The molar conductivity of the complexes was found to be in the range of 11.5-12.0 showing their electrolytic nature of the complexes.

Table 1: Some Physical Properties of the Ligand and the Metal Complexes

Compound	Colour of crystal	Melting point (°C)	Molar Conductivity (ohm^{-1}cm^{2}mol^{-1})
N, N'- B$_2$HDE	Yellow	120 - 121	
Sm(III) N, N'- B$_2$HDE	White	130 – 132	11.5
Gd(III) N, N'- B$_2$HDE	Yellow	129 - 130	11.9
Nd(III) N, N'- B$_2$HDE	Yellow	122 - 123	12.0

Table 2: Solubility Data of the Ligand and Complexes in Difference Solvent at Room Temperature

Compound	Distilled Water	Acetone	Ether	Chloroform	DMSO	DMF
N, N'- B$_2$HDE	INS	S	S	S	S	S
Sm(III) N, N'- B$_2$HDE	INS	S	SS	S	S	S
Gd(III)(N, N'- B$_2$HDE	INS	S	S	S	S	S
Nd(III) N, N'- B$_2$HDE	INS	S	S	S	S	S

Key: S= soluble, SS= slightly soluble, INS= Insoluble

The infrared spectra of all the complexes and the ligand were recorded in the range of 0 cm^{-1} - 4000 cm^{-1}) and the ligand in the range of 34400 cm^{-1}- using Carry 630 FT-IR machine. The important IR frequencies of the ligand and its Gd (III), Sm (III) and Nd (III) complexes are presented in Table 3. In order to study the binding mode of the ligand to metal ions, the IR spectrum of the ligand was compared with the spectra of the metal complexes. A strong band was observed for the ligand around 1677 cm-^{1}, characteristic of the azomethine (C=N) stretching vibration. In the metal chelates, the band characteristic of the azomethine group was shifted to around 1674 cm-^{1} from 1677 cm-^{1} in the ligand, suggesting coordination of the azomethine nitrogen atom to the metal ion (Tyagher, 2020). The spectrum also showed a broad band in the region 3377 cm-^{1} which may be due to υ(OH) and the broadening of the same was due to intermolecular H-bonding between OH groups. These bands were missing in the metal complexes indicating that the OH character of the ligand has been lost upon complexation. The various absorption bands in the region 1092-1071.22 cm-^{1} may be assigned to υ(C-C) aromatic structure. Vibrations in the regions around 752.9-606.87 cm-^{1} have been assigned to υ(M-O) and 693.3-503.71 cm-^{1} υ(M-N) bands. The bands may be due to the established coordination of the ligand to the respective metal ions in each complex compound. These agreed with the result obtained elsewhere (Ekta, 2013; Tyagher, 2020).

Table 3: Important Infrared bands (cm^{-1}) of the Ligand and its Metal Complexes

Compound	**υ(C-H)**	**υ(C-C)**	**υ(C=N)**	**υ(O-H)**	**υ(M-O)**	**υ(M-N)**
N, N'- B$_2$HDE	2933	1092	1677	3377	752.9	693.3
Sm(III) N, N'- B$_2$HDE	2930.97	1074.18	1672.81	—	502.03	384.11
Gd(III) N, N'- B$_2$HDE	2929.17	1069.79	1673,89	—	500.74	385.15
Nd(III) N, N'- B$_2$HDE	2926.22	1071.16	1674.80	—	606.87	503.71

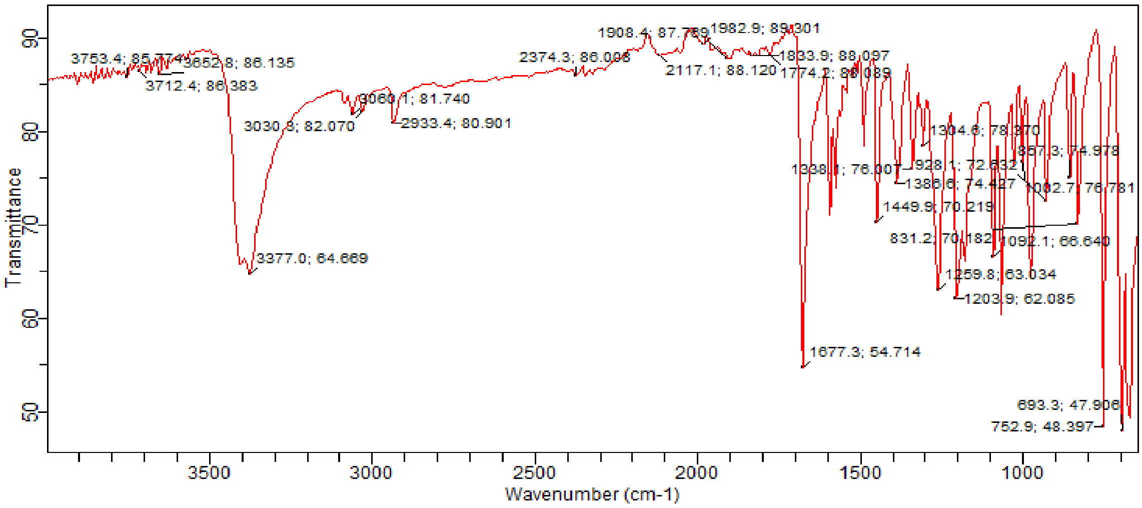


Figure 1: **IR Spectra of N,N'-B$_2$HDE**

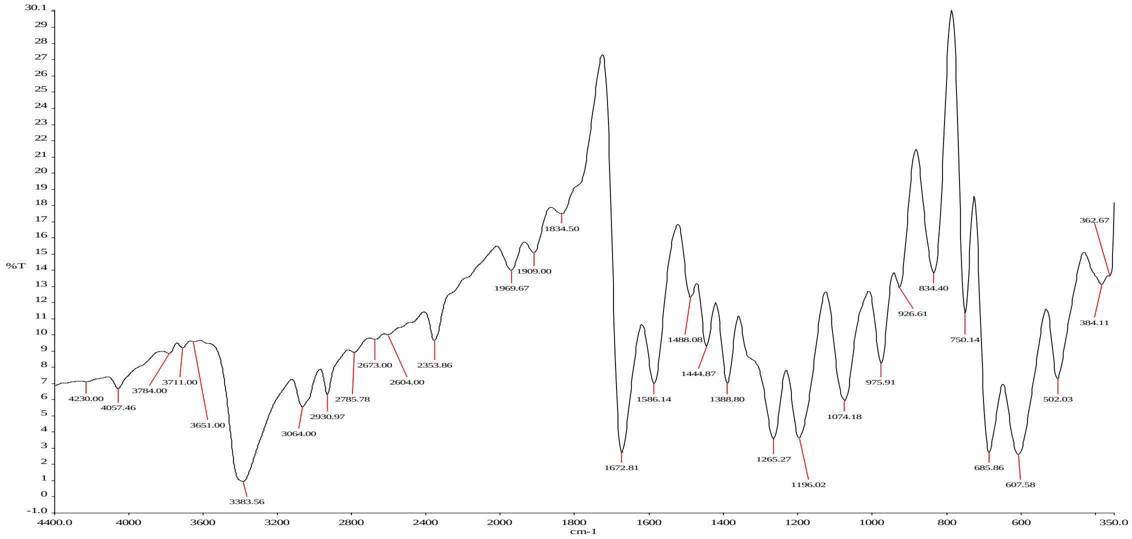


Figure 2: IR Spectra of Sm(III)-N,N'-B$_2$HDE

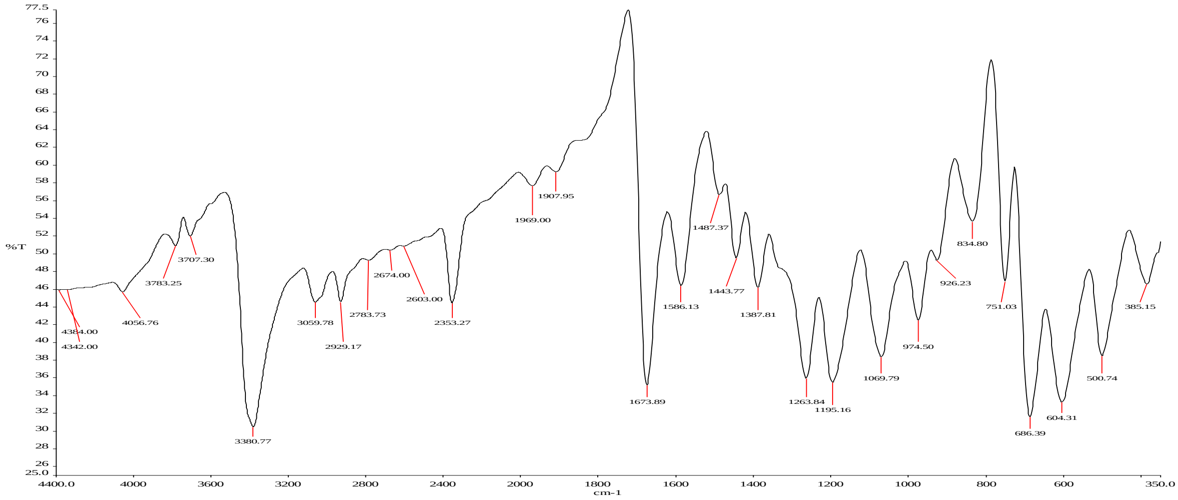


Figure 3: IR Spectra of Gd(III)-N,N'-B$_2$HDE

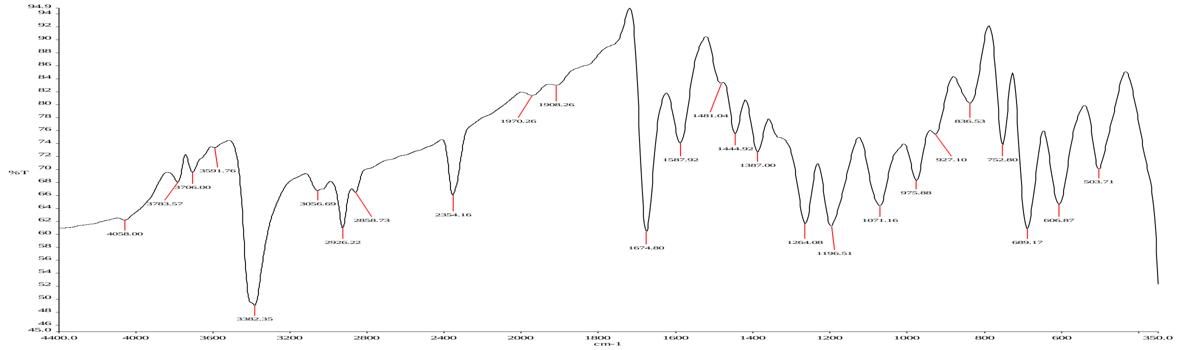


Figure 4: IR Spectra of Nd(III)-N,N'-B$_2$HDE

The UV-visible absorption spectra of the ligand and its metal complexes Gd (III), Sm (III) and Nd (III) were recorded in acetone at room temperature. The values of the absorption wavelength and its band assignments are listed in Table 3 and spectral data for the ligand and its metal complexes is shown in Table 4. The absorption of the ligand is characterized by three main absorption bands at 270, 325 and 385 nm. The band appearing at lower energy is attributed to n-π* transition of conjugation between the lone pair of electrons of *p* - orbital of N atom in azomethine group and conjugated to π bond of the benzene ring (Youssef, 2008). The bands appearing at higher energy are attributed to π-π* of the benzene ring and π-π* transition of the azomethine group (Guo *et al*., 2006). The UV-visible absorption spectra of all the metal complexes show similarities, which indicates similarity in their structures and generally show the characteristic bands of the free ligands with some changes both in frequencies and intensities. Upon complexation, the absorption bands of the complexes are to some extent shifted to shorter wavelength (Blue shift) compared to those of the ligand. These modifications of the shifts and intensity of the absorption bands indicates the coordination of the ligand to the metal ion. In general, the lanthanide ions do not appreciably contribute to the spectra of their complexes, since *f-f* transitions are Laporte forbidden and very weak in nature (Lee, 1996; Chempakam *et al*., 2011). It was observed that the Sm (III) and Gd (III) complexes have high absorbance when compared to other complexes. This is due to the difference in their molar absorptivity of the complexes that cause the spectrum to become more intense which is referred to as hyperchromic shift and the decrease in absorbance is referred to as a hypochromic shift (Sinelshchikova, *et al*., 2011). There is a variety of factors that can cause these changes. One of the factors is found in a process known as solvatochromism (Sinelshchikova, *et al*., 2011). It can also be due to the solvent polarizability as well. Basically, it is the change in the colour of a material, as a function of the dielectric properties of the solvent.

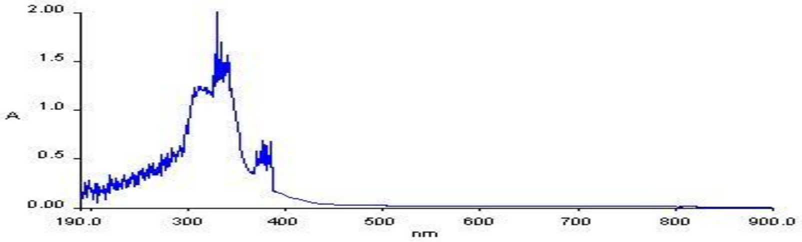


Figure 5: Electronic Spectra of N, N'- B_2HDE

Table 4: Electronic Spectral Data of the Ligand and its Metal Complexes

Compound	**λ (nm)**	**Assignment**	**Geometry**
N, N'- B_2HDE	270 325	n-π* π-π*	
Sm(III) N, N'- B_2HDE	221 320	n-π* π-π*	octahedral
Gd(III) N, N'- B_2HDE	240 321	n-π* π-π*	octahedral
Nd(III) N, N'- B_2HDE	230 321	n-π* π-π*	octahedral

The effects of temperature on the quantity of metal complex formed at various time was studied and results obtained from the plots of semi-log of the yield of metal complexes in mole against time which did showed inconsistent increase in the observed rate constant of the formation of complexes but signify a little increase in the amount of complexes formed as temperature and time increased. The activation energy (E_a) of various complexes was determined from the slope of the plots of lnk_{obs} versus l/T.

Generally, the rate of formation of complexes depends on the temperature at which it is run. As the temperature increases, the molecules of reactants move faster and consequently collide more often. The proportion of collisions that overcome the activation energy for the formation increases with temperature. Hence, allows for the complexes to be formed.

Thermodynamic parameters such as enthalpy (ΔH°) change of activation during the formation of the complexes were evaluated.

The values of ΔH° and ΔS° were determined from the slope and intercept of the plots of In $(\frac{kobs}{T})$vs$\frac{1}{T}$. The value of ΔG° were calculated from Equation (4). The plots were used to compute the values of thermodynamic parameters (Iorungwa *et al.*, 2014).

$$\Delta G° = \Delta H° - T\Delta S° \quad (4)$$

The values of the enthalpy change of activation (ΔH°), the entropy change of activation (ΔS°) and the Gibbs free energy of activation (ΔG°) found in this work were 1168 kJmol^{-1}, -16.99 kJmol^{-1} and -3,896.02 kJmol respectively for Sm(III)N,N'-B_2HDE and 2268 kJmol^{-1} , -19.91 kJmol^{-1} and -8,201.18 kJmol^{-1} for Gd(III)N,N'-B_2HDE. The large negative values for the activation entropy are suggestive of an associative mechanistic pathway for the complex formation process. This is in agreement with the result obtained elsewhere (Mocanu *et al.*, 2010; Iorungwa *et al.*, 2014; 2019).

The negative values of ΔG° showed the ability of the studied ligand to form stable complexes which was spontaneous in nature. The positive value of enthalpy change of formation (ΔH°) of the complexes implies that the energy content of the complex were more than that of the reactants. The complex was more stable. The reaction was there endothermic. However, the large negative values of the activation entropy (ΔS°) is suggestive of an associative mechanistic pathway for the complexation process (Iorungwa *et al.*, 2014).

Table 5: Rate constant observed at various temperature of Sm(III) N, N'- B$_2$HDE complex

S/N	T(K)	k_{obs} (10^{-6})	k_{obs}/T(10^{-7})	In$k_{obs/T}$	Ink_{obs}	1/T(K^{-3})
1	303	6.00	1.980	-13.132	-9.721	3.300
2	313	5.00	1.597	-13.347	-9.903	3.195
3	323	5.00	1.548	-13.379	-9.903	3.096
4	333	5.00	1.502	-13.409	-9.903	3.003
5	343	4.00	1.166	-13.662	-10.127	2.915

Table 6: Rate constant observed at various temperature of complex Gd(III) N, N'- B$_2$HDE

S/N	T(K)	k_{obs} (10^{-6})	$k_{obs/T}$(10^{-7})	In$k_{obs/T}$	Ink_{obs}	1/T(K^{-3})
1	303	5.00	1.650	-13.315	-9.903	3.300
2	313	2.00	1.597	-11.045	-8.517	3.195
3	323	5.00	1.548	-13.379	-9.903	3.096
4	333	5.00	1.502	-13.409	-9.903	3.003
5	343	6.00	1.749	-13.256	-9.722	2.915

Table 7: Thermodynamics Parameters for Formation of Sm(III) and Gd(III) N, N'- B$_2$HDE Complexes

Complex	ΔH^o (kJmol^{-1})	ΔG^o (kJmol^{-1})	ΔS^o (kJmol^{-1})	Ea (kJmol^{-1})
Sm(III) N, N'-B$_2$HDE	1168	-3,896.02	-16.9900	0.45243
Gd(III) N, N'-B$_2$HDE	2268	-8,201.18	-19.9100	1.28699

NEMATICIDAL STUDIES OF LIGAND AND ITS COMPLEXES

Hatching of root knot nematode at different concentrations

The hatching values of root knot nematode of different compounds at different concentrations and at different intervals of exposure were studied and presented in Figures 8 to 10. Generally, the amount of unhatched nematodes was found to decrease as the time of exposure increased for both the ligand and all the metal complexes. And this was found to be more effective than the metal complexes. In case of metal complexes Gd (III), Sm(III), metal complex showed a steady decrease in the hatching as the time of exposure increased. While Nd(III) was found to be less effective from other metal complexes. Generally, it was found that at lower concentrations hatching was more effective as maximum hatched count was observed in Schiff base ligand. This observation is in agreement with other findings (Ekta, 2013; Ugama, 2019).

Mortality of root knot nematode at different concentrations

The mortality values of root knot nematode of different compounds at different concentrations and at different intervals as shown in Figures 9 to 11. Nematode mortality attributed to the Schiff base was found to be less effective compared to the mortality attributed to the metal complexes. This is as a result of the synergistic effect arising from complexation between the ligand and the metals (Lee, 1996; Nallaswamy *et al*., 2001). As the time of exposure increased there was a decrease in mortality rate recorded. At higher concentrations there was increase in mortality rate of the nematodes. While at low concentrations there was decrease in the mortality rate. These metal complexes were found to be more toxic to root knot nematode as compared to the Schiff base ligand at higher concentrations.

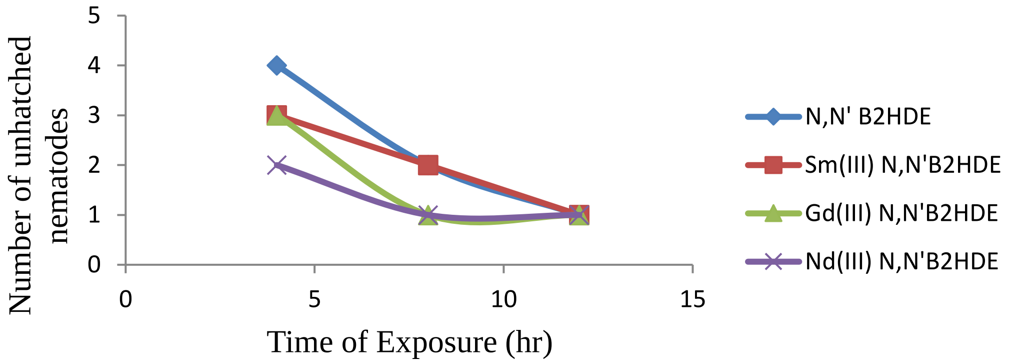


Figure 6: Unhatched nematodes against time of exposure at concentration of 30ppm

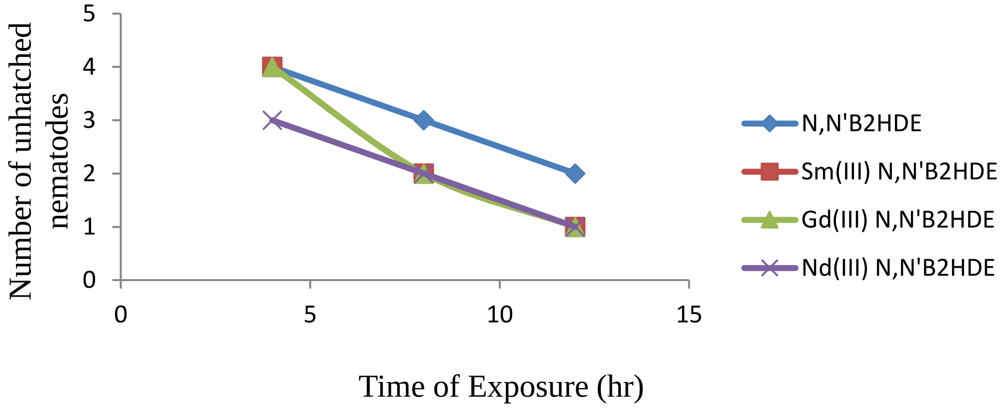


Figure 7: Unhatched nematodes against time of exposure at concentration of 15ppm

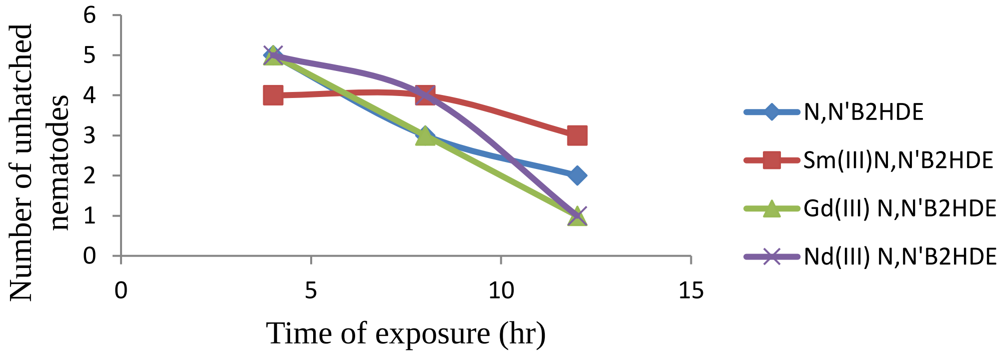


Figure 8: Unhatched nematodes against time of exposure at concentration of 7.5ppm

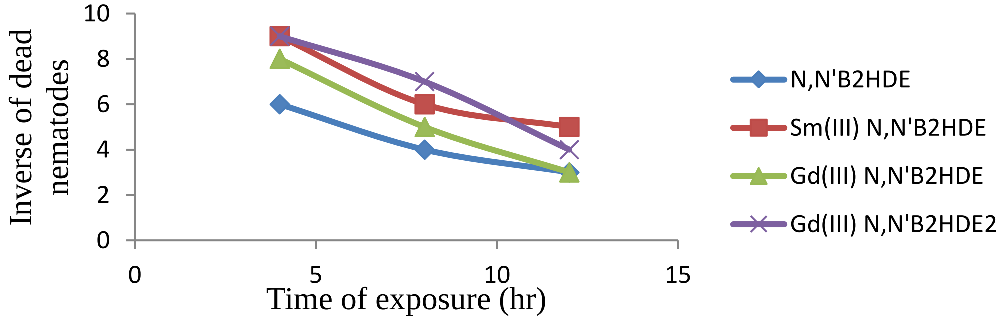


Figure 9: Inverse of dead nematodes against time of exposure at concentration of 30ppm

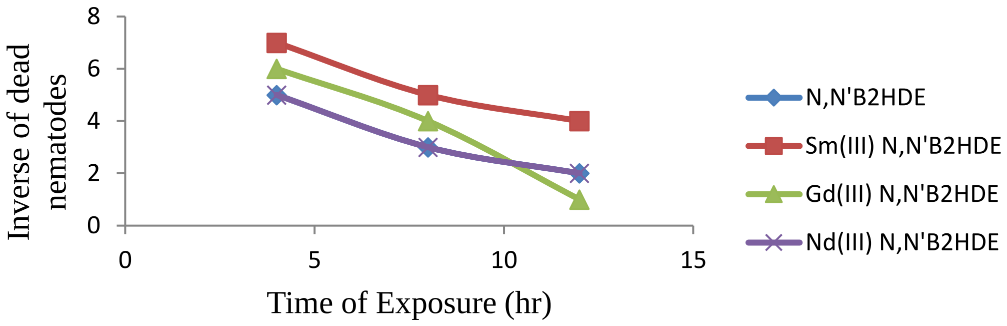


Figure 10: Inverse of dead nematodes against time of exposure at concentration of 15ppm

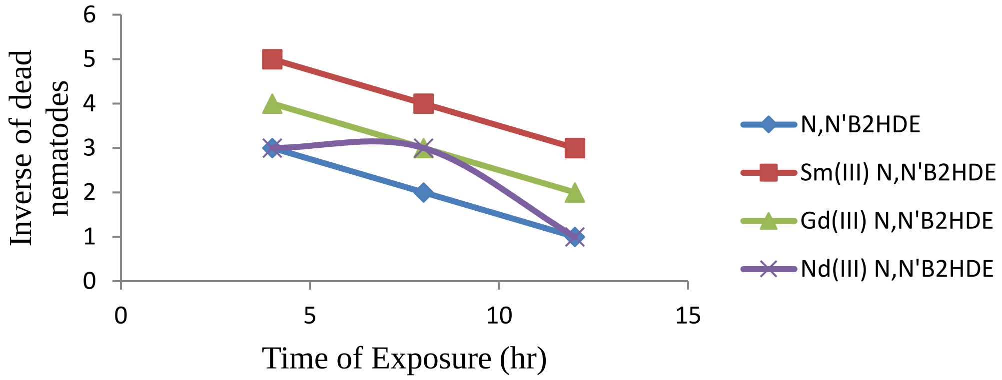


Figure 11: Inverse of dead nematodes against time of exposure at concentration of 7.5ppm

CONCLUSION

The ligand and its metal complexes were synthesized and characterized. Kinetics and thermodynamics studies were carried out on the synthesized compounds. IR studies showed the chelation of Sm(III), Gd(III) and Nd(III) ion through the protonation of hydroxyl group and azomethine nitrogen. In the electronic spectra of the ligand when compared to the complexes via various transition showed a shift to lower frequency side on co-ordination with metal ion. In the studies of kinetics an increase in the amount of complexes formed when time and temperature were increased. The thermodynamics parameters revealed the negative value of ΔG^o showed the ability of the studied ligand to form stable complexes was spontaneous in nature. The positive value of enthalpy change of formation (ΔH^o) of the complexes implies that the energy content of the complex were more than that of the reactants. The complex was more stable. The reaction was there endothermic. However, the large negative values of the activation entropy (ΔS^o) suggested an associative mechanistic pathway for the complexation process. In the present studies, all the synthesized compounds had shown nematicidal activity against root knot nematode by inhibiting egg hatch and causing larval mortality of second stage juveniles and the nematicidal activity of these compounds was found to be dose and time dependent. J2 Stage nematodes and their egg masses were obtained from the heavily infested okra roots for studies. The mortality was noted after every 4 hours intervals until a complete mortality rate was observed. All the compounds showed complete mortality at 30.00 ppm whereas the compounds at low concentrations showed less mortality. The results indicated that mortality increased with increase in concentration of the compound but mortality decreased as the time of exposure increases.

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