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Synthesis, Characterization, Kinetics, Thermodynamic and Antimicrobial Studies of Fe(III), Cu(II), Zn(II), *N,N′*-Bis(2-hydroxy-1,2-diphenylethanone)ethylenediamine Complexes

Moses Saviour Iorungwa*, Raymond Ahulle Wuana, Samuel Terungwa Dafa

Inorganic/Physical Chemistry Research Group Federal University of Agriculture 970001, Makurdi-Nigeria

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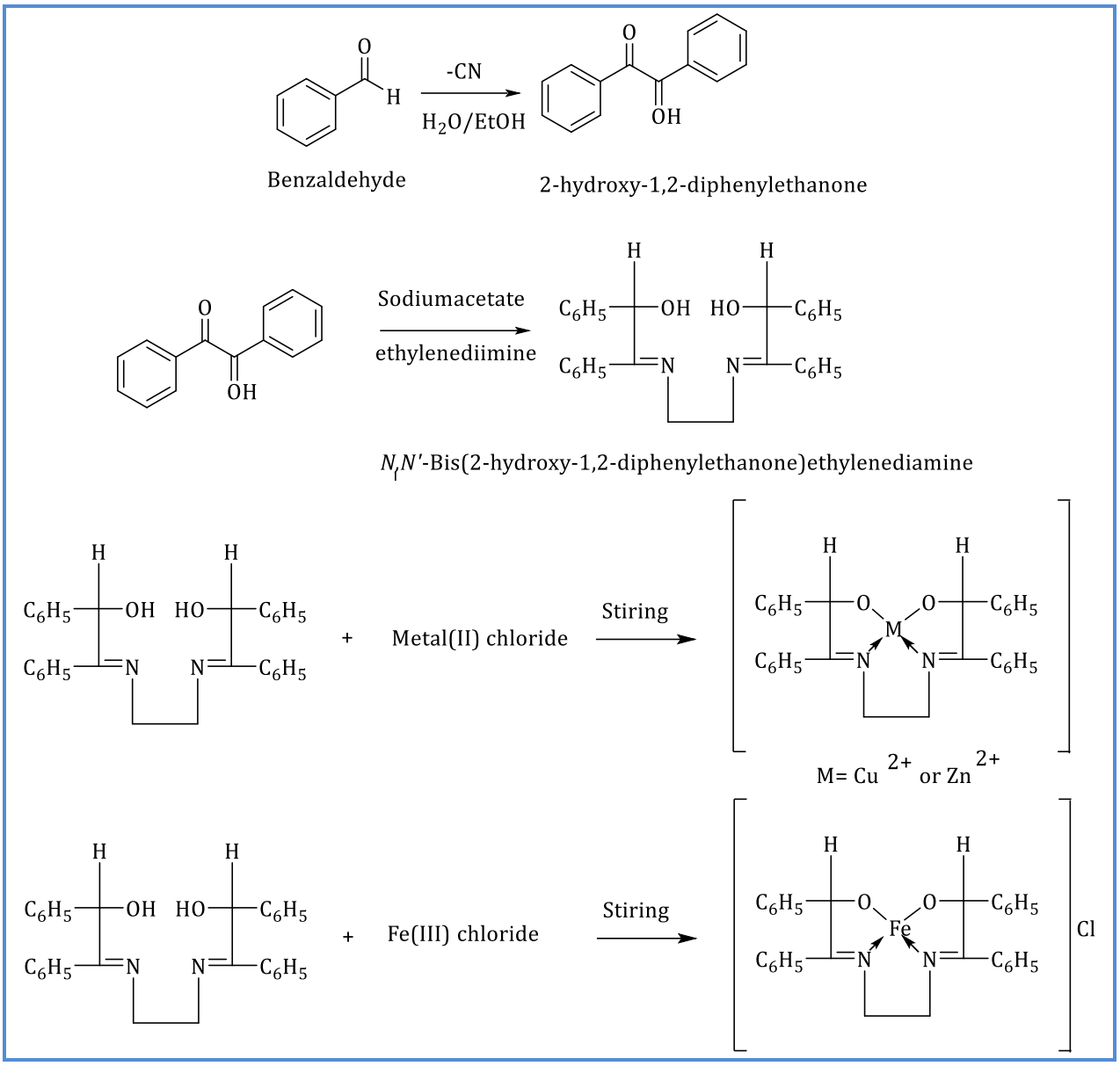
ABSTRACT

Schiff base ligand derived from benzaldehyde and ethylenediimine and its Fe(III),Cu(II) and Zn(II) complexes were synthesized. The ligand *N,N′*-Bis(2-hydroxyl-1,2-diphenylethanone)ethylenediamine(B_2HDE)and its complexes were characterized by molar conductivity, melting point, solubility test and spectrometrically (IR and UV-Vis). The Kinetics of complex formation obtained from a plot lnk_{obs} verses 1/T, thermodynamic parameters were obtained from plots of ln(k_{obs}/T) verses 1/T and antimicrobial activities of the ligand and its complexes were tested. The solubility results showed that B_2HDE and its complexes were soluble in dimethylsulphoxide, dimethylformanide and acetone while the melting point of ligand and complexes showed they are fairly stable. The complexes molar conductivity indicated that they are non-electrolytes. The IR spectra showed a bidented ligand which coordinated through azomethine nitrogen and hydroxyl oxygen atom. UV-Vis results confirmed the complexation of the metal and ligand with a tetrahedral geometry for both complexes and the activation energy (E_a) obtained were positive E_a indicating that, the rate of formation increased with increasing temperature. The kinetic results showed that increase in time and temperature increased the yield of the complexes. The results of thermodynamics parameters showed the formation of an activated complex via an associative pathway. Antimicrobial studies results of complexes were higher than the one found for the free ligand.

*Corresponding author: E-mail: saviour.moses@gmail.com
Department of Chemistry, Federal University of Agriculture, Makurdi, Tel: +234(0)7039189185

Graphical Abstract



Introduction

During recent years, transition metals' complexes of the Schiff base have received a lot of attention because of their potential applications in medicinal and pharmaceutical field [1]. As a result of their stable complex formation with transition metal ions and azomethine linkage (C=N) taking part in the complex formation process, these complexes are seen as a model compound and play an active role in the development of coordination chemistry [2]. The azomethine nitrogen atom has lone pair electron, which has significant ability to complex with different metal ions, given rise to potential biochemical applications [3]. Metal complexes of nitrogen-oxygen chelating agent derived from

carbonyl and amino Schiff base have certain uses in biological, clinical, analytical and pharmaceutical area [4].

Due to the demand of new metal-based antibacterial and antifungal compounds, metal organic chemistry is becoming an emerging area of research [5]. A survey of the literature reveals that several work has been carried out on the synthesis, characterization and antimicrobial of the Schiff base complexes but few work have been done on their kinetic and thermodynamics which is the study of their rate of formation and the stability.

This work covers the synthesis, characterization, kinetic, thermodynamics and antimicrobial activity of *N*,*N'*-bis(2-hydroxy-1,2,diphenylethanone)ethylenediamine complexes of some transition metals namely: Fe^{3+}, Cu^{2+} and Zn^{2+}. This is in promotion of the sustained interest in the use of the transition metal complexes in the treatment of human diseases against the backdrop of the alarming problem of multi-drugs resistant microorganism world over.

Experimental

Materials

Reagents and solvents

The used reagents and solvents were ethyl alcohol, distilled water, benzaldehyde, sodium cyanide, ethylenediamine, zinc(II)chloride (BHD), iron(III)chloride (BHD), copper(II)chloride (BHD), sodium hydroxide, methanol, sodium acetate, ammonia, ether, dimethyl sulphoxide (DMSO), *N,N'*-dimethylformamide (DMF), nutrient agar, potato dextrose agar (PDA), acetone, salmonella shigella agar (SSA). All the chemicals were of analytical grade with sigma Aldrich. These chemical were used immediately as they arrived.

Apparatus and instrument

The used apparatus and instruments include Barnstead electro thermal BI9100 melting point apparatus with digital thermometer, pH/conductivity series 510 conductivity meters, ProRaman-L-785-B1S FT-IR spectrophotometer, carry 630 FT-IR spectrophotometer, Shimadzu 1800 UV-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 method for the synthesis of 2-hydroxy-1,2-diphenylethanone was done [6]. Exactly 65 mL of ethyl alcohol was added to a 500 mL round bottom flask, 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 then 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. These were filtered with cold water, dry and then recrystallize from 40 mL of hot ethanol. The crystal was dried at 50 °C and weighed.

Synthesis of *N,N'*-bis(2-hydroxy-1,2-diphenylethanone)ethylendiamine ligand (*N,N'*-B_2HDE)

The method for the synthesis of *N,N'*-bis(2-hydroxy-1,2-diphenylethanone)ethylendiamine ligand was done as described in the previous research [6]. 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 where upon yellow precipitate of the Schiff base was separated, filtered, washed with water; dry and recrystallized from ethanol.

Synthesis of *N,N'*-bis(2hydroxy1,2,diphenylethanone)ethylenediamine metal complex

The method for the synthesis of *N,N'*-bis (2-hydroxy-1,2-diphenylethanone)ethylenediamine metal complexes was done as described elsewhere [7]. An accurate weight (4.00 mmole) of *N,N'*-bis (2-hydroxyl-1,2-diphenylethanone)ethylenediamine in hot ethanol (65 °C) was mixed with (4.00 mmole) of metal chloride in 25 mL of ethanol and the mixture was placed on SB160 heat-stirrer and was stirred for 2 hours using magnetic stirrer. The precipitate obtained were filtered off, washed with hot ethanol, ether and dried under vacuum at 70 °C.

Characterization of ligand and complexes formed

Solubility Test

The prepared Schiff base alongside their complexes was added to 10 mL portions of each of the solvents (distilled water, methanol, ethanol, dimethyl sulfoxide, *N,N'*-dimethylformamide and acetone) and was shaken vigorously. The entire solute dissolved to give a homogenous mixture after shaking the sample (S). However some sample was slightly soluble (SS) and some were insoluble (INS).

Melting point determination

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

The molar conductivity measurement

The molar conductivities of the Schiff base along with the respective complexes were obtained from DMSO using pH/conductivity series 510 conductivity meters.

Infrared and electronic spectra data

The infrared spectra data of the synthesized Schiff base alongside the complexes was obtained by using carry 630 FT-IR spectrophotometer for the Schiff base ligand while proRamman-L-785-B1S FT-IR spectrophotometer was used for the complexes. The prepared ligand along with the complexes was placed on the slide which was placed on the sample chamber of the spectrophotometer so that the distance between the slide and the lens should be about 7 mm apart. The spectrophotometer was instructed to scan the sample and suitable peaks were obtained. The ultraviolet spectral of the prepared Schiff base along with the complexes was obtained using acetone as solvent from Shimadzu 1800 UV-visible spectrophotometer.

Kinetic and thermodynamic data of complexes

An accurate weight of 4.0 mmole of *N*,*N*'-bis(2-hydroxyl-1,2-diphenylethanone)ethylenediamine in a hot ethanol (65 °C) was mixed with 4.0 mmole of the metal salt in 25 mL of the ethanol and the mixture was placed on a SB160 heat-stirrer. The stirrer was set at the required rpm and the mixture was heated at temperatures of 30, 40, 50, 60 and 70 °C, this was maintained for the required time. The obtained precipitates were filtered and washed with hot ethanol, ether and dried under vacuum at 70 °C and weighed. The various obtained weights 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 constant which was in turned used to plot $\ln K_{obs}$ *vs*. 1/T to obtained activation energy (E_a) and $\ln(K_{obs}/T)$ *vs*. 1/T to obtained thermodynamic parameters.

Antimicrobial studies

The antimicrobial studies were done in the microbiology laboratory of University of Agriculture, Makurdi using the agar-well diffusion technique.

Test for zone of inhibition (bacteria)

The bacteria culture media was done as described elsewhere with slight modifications [8]. A stock solution of the antimicrobial agent was prepared by dissolving 1 g of the substance in 10 mL of 20% dimethyl sulphuroxide (DMSO) to give a stock solution of 100 mg/mL. One mL of the broth inoculums (microbial specie inoculated in normal saline and incubated 24 hrs) was dispensed into a sterile Muller Hinton agar (Himedia, India) was poured into the plate and mixed properly (pour-

plate method) and allowed to gelled. A sterile cork borer, 6 mm in diameter was used to bore wells on the plate and 20 µL of the stock antimicrobial agent was dispensed into the wells and labeled properly. The plates were allowed to stand for 30 minutes to allow the antimicrobial agent diffuse into the agar. The plates where packed, wrapped and incubated at 37 °C for 24 hrs and room temperature for 72 hrs for bacteria and fungi respectively. After incubation, the zone of inhibition was then measured in mL [8].

Minimum inhibitory concentration (MIC) and minimum bactericidal or fungicidal concentrations (MBC/MFC)

The MIC was carried out based on the method described by [8] using agar-dilution techniques. Varying concentrations of the antimicrobial agent were prepared in an agar by mixing different proportions of the Muller Hinton agar and the stock solution of the antimicrobial agent. The following combinations were done 6 mL: 6 mL, 3 mL: 9 mL, 1.5 mL: 10.5 mL and 0.75 mL: 11.25 mL of antimicrobial agent and Mueller Hinton agar respective thereby giving the following percentage concentrations 50% , 25%, 12.5% and 6.25%, respectively. The organisms were spot-inoculated on all the concentrations and incubated. After 24 hr and 72 hr for bacteria and fungi incubation, the plates were checked for growth. The minimum concentration at which the organism completely inhibited was recorded as the minimum bactericidal or fungicidal concentration (MBC/MFC) while the minimum concentrations at which the organism was not inhibited but did not expand beyond the spot of inoculation was recorded as the MIC.

Result and Discussion

Physical properties results of ligand and its complexes

The reaction between *N*,*N'*-bis(2-hydroxyl-1,2-diphenylethenone)ethylenediamine and iron(III), copper(II) and zinc(II) ions produced metal complexes which are crystalline and colored. The complexes were found to melt in the temperature range of 132-134 °C showing a fairly stable complex compounds (Table 1). The complex compounds were insoluble in water and common organic solvents but soluble in acetone, dimethyl sulfoxide (DMSO) and *N*,*N*'-dimethylformamide (DMF) (Table 2) the molar conductivity of the complexes was found to be the range of 8.3-8.7 showing their non-electrolytic nature of the complexes.

Table 1. Physical properties of synthesized ligand with its complexes

Compound	Colour of crystal	Melting point (°C)	Molar conductivity ($S.m^2.mol^{-1}$)
N,*N'*-B_2HDE	Yellow	136.00	-
Fe(III)*N*,*N*'-B_2HDE	Brown	133.00	8.50
Cu(II)*N*,*N*'-B_2HDE	Green	132.00	8.30
Zn(II)*N*,*N*'-B_2HDE	Yellow	134.00	8.70

Table 2. Solubility data of the ligand along with the complexes in various room temperature

Compound	Distilled water	Methanol	Ethanol	D.M. F.	Acetone	D. M. S. O.
N,N'-B_2HDE	INS	SS	SS	S	S	S
Fe(III)*N,N'*-B_2HDE	INS	SS	SS	S	S	S
Cu(II)*N,N'*-B_2HDE	INS	SS	SS	S	S	S
Zn(II)*N,N'*-B_2HDE	INS	SS	SS	S	S	S

Key: S = Soluble, SS = Slightly soluble and INS = Insoluble

IR spectra results of ligand and its complexes

The infrared (IR) spectra of the complexes were recorded in the range of 0 cm^{-1}, 4000 cm^{-1} using proRaman-L-785-B1s FTR-IR and that of ligand in the range of 650 cm^{-1}, 4000 cm^{-1} using carry 630 FT-IR machine. The ligand molecules consist of a band at 3377 cm^{-1}. This confirmed the presence of hydroxyl (OH) in the ligand. This band disappeared in the IR spectrum of the metal complexes confirming the deprotonation of the OH and involvement of the OH in complexation. The strong band of the ligand at 1677 cm^{-1} is due to $C=NH^+$ group which shift to lower frequencies of 1638 cm^{-1}, 1675 cm^{-1} and 1650 cm^{-1} for Fe(III), Cu(II) and Zn(II) complex respectively. This confirmed the formation of C=N metal bond. The metal-oxygen bond appear at 558 cm^{-1}, 556 cm^{-1} and 575 cm^{-1} for Fe(III), Cu(II) and Zn(II) respectively which support the formation of M-O and the metal-nitrogen band appeared at 422 cm^{-1} for Fe(III) and Zn(II) complexes and 420 cm^{-1} for Cu(II) complex which support the formation of M-N bond. Thus complexation of the Fe(III), Cu(II) and Zn(II) ion is through the deprotonated hydroxyl group and the azomethine nitrogen [2-4].

Table 3. Important infrared bands (cm^{-1}) of the ligand and its metal complexes

Compound	√(C-H)	√(C-C)	√(C=N)	√(O-H)	√(M-O)	√(M-N)
N,N'-B_2HDE	2937	1092	1677	3377	_	_
Fe(III)*N,N'*-B_2HDE	2876	1006	1638	_	558	422
Cu(II)*N,N'*-B_2HDE	2876	1008	1675	_	556	420
Zn(II)B_2HDE	2876	1010	1650	_	575	422

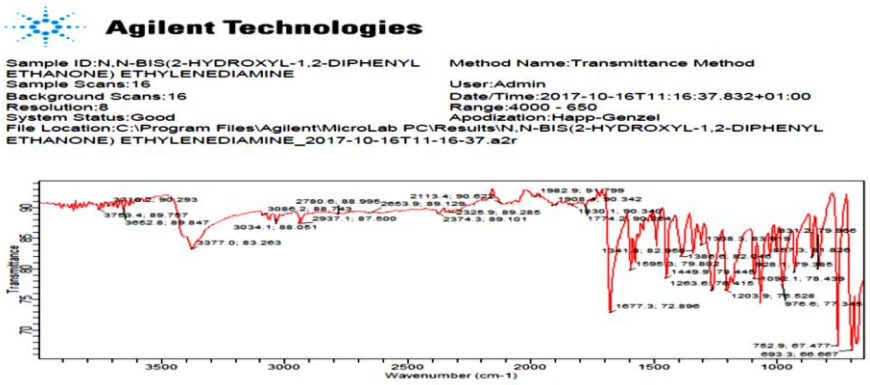


Figure 1a. IR Spectra of *N,N`*-B_2HDE

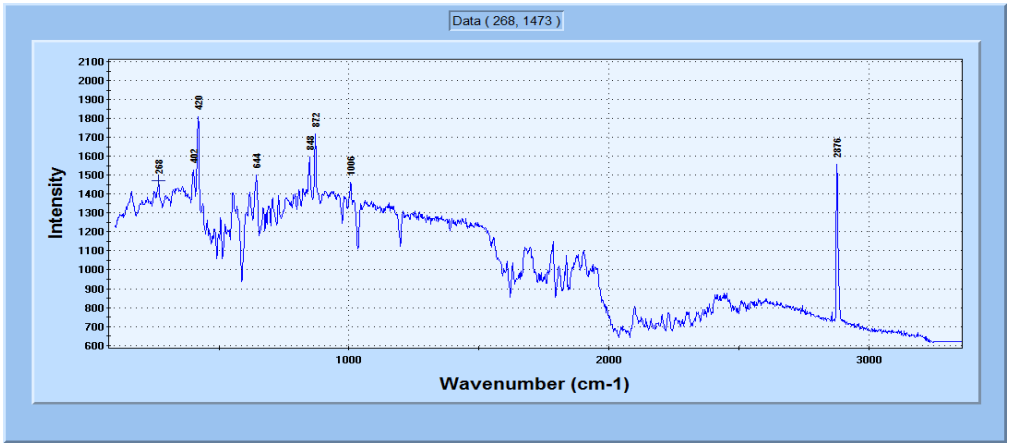


Figure 1b. IR spectra of Fe(III)*N*,*N*`-B_2HDE

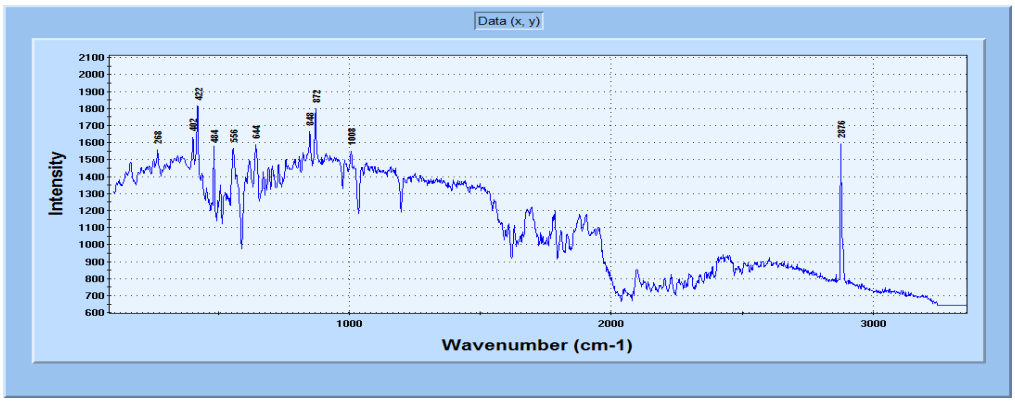


Figure 1c. IR spectra of Cu(II)*N*,*N*`-B_2HDE

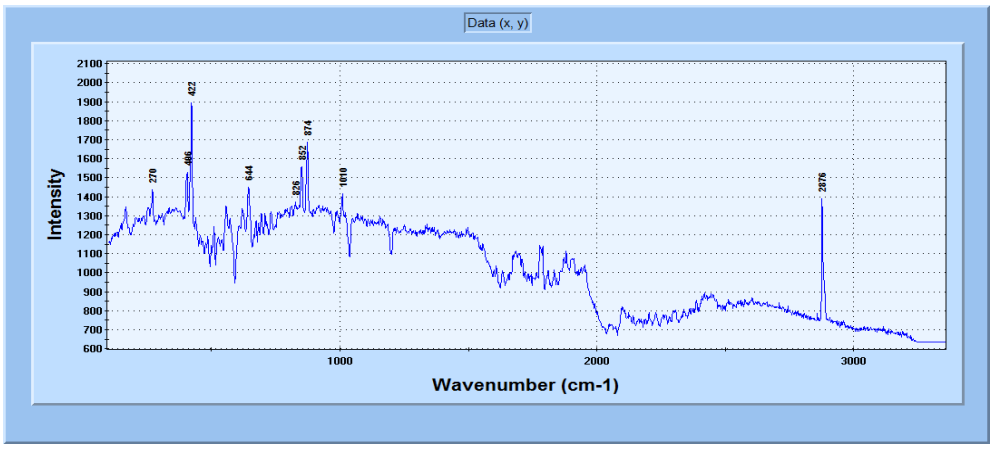


Figure 1d. IR spectra of Zn(II)*N*,*N*`-B_2HDE

The electronic spectra result of the ligand and its complexes

The electronic spectra of the free ligand (*N*,*N*'-B_2HDE) showed band at 218.50 nm as assigned to the n→δ* transition within the azomethine (CH=N) group [9], 232 nm was assigned to n→Π* transition

within the benzene ring of the ligand and 325.5 nm was assigned to Π→Π* transition within which it is assigned to Π→Π* transition within the azomethine (CH=N) group. The complex of Zn(II) exhibited band at 239 nm as assigned to n→Π* transition of the benzene ring and 326 nm was assigned to charge transfer between the ligand Zn(II) ion. The electronic spectra of Fe(III) complex exhibited band at 192 nm as assigned to n→δ* transition within the azomethine (CH=N) group, 213 nm was assigned to n→Π* transition of OH group, 257-292 nm assigned to Π→Π* within the azomethine and the electronic spectra of Cu(II) complex shows band at 240 nm assigned to n→Π* transition of azomethine (CH=N) group. Hence, the electronic spectra of the free ligand when compared to the complex using the various transitions show a shift from higher to lower frequencies therefore confirming the complexation.

Table 4. Electronic spectral data of the ligand (*N,N'*-B_2HDE) and its complexes

Compounds	Absorbance	λ (nm)	Band(cm^{-1})	Assignment	Geometry
N,N'-B_2HDE	0.019 0.364 2.171	218.5 232.0 325.5	45,767 43,104 30,722	$n \rightarrow \delta^*$ $n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	
Zn(II)*N,N'*-B_2HDE	4.00 1.522	239.0 326.0	41,841 30,675	$n \rightarrow \Pi^*$ $L \rightarrow M$	Tetrahedral
Fe(III)*N,N'*-B_2HDE	1.818 2.545 2.651	192.0 235.0 327.0	52,083 42,255 30,581	$n \rightarrow \delta^*$ $n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	Tetrahedral
Cu(II)*N,N'*-B_2HDE	1.818 2.527	240.0 328.5	41,667 30,441	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	Tetrahedral

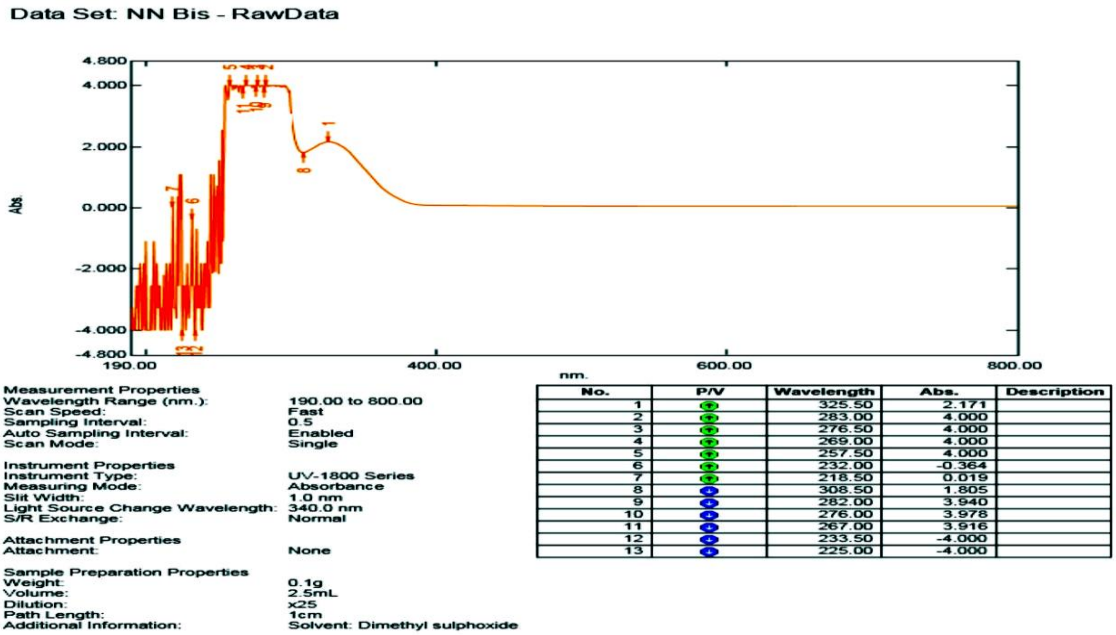
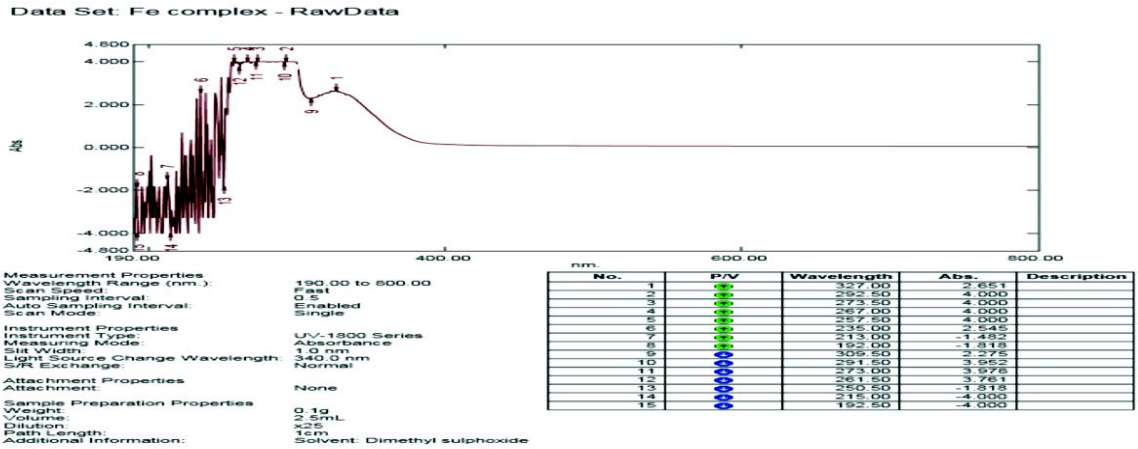
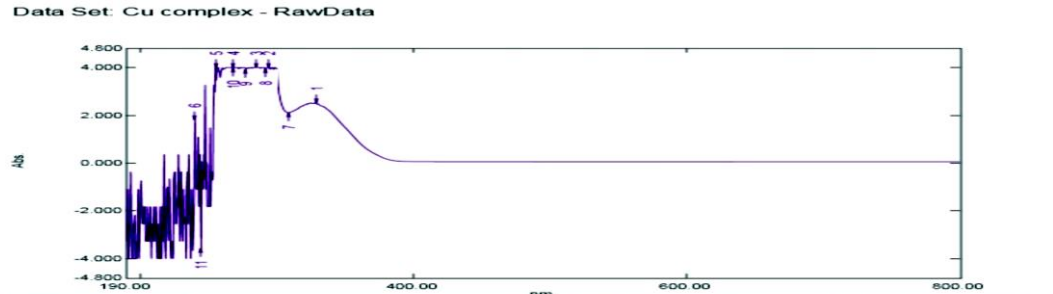


Figure 2a. Electronic spectra of *N,N`*-B_2HDE



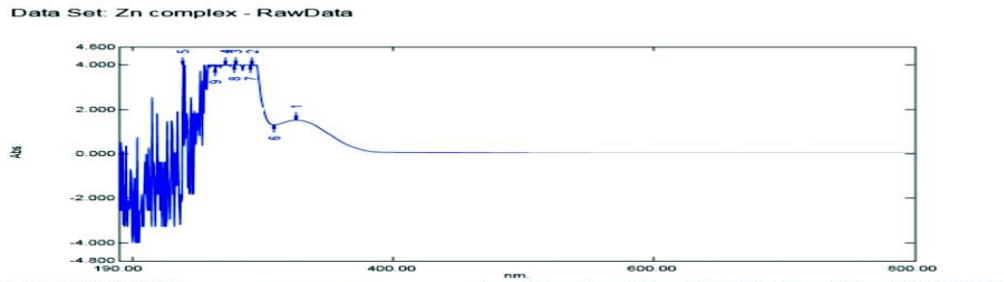
No.	P/V	Wavelength	Abs.	Description
1		327.00	2.651	
2		292.50	4.000	
3		273.50	4.000	
4		267.00	4.000	
5		257.50	4.000	
6		235.00	2.545	
7		213.00	-1.482	
8		192.00	-1.818	
9		309.50	2.275	
10		291.50	3.952	
11		273.00	3.975	
12		261.50	3.761	
13		250.50	-1.818	
14		315.00	-4.000	
15		192.50	-4.000	

Figure 2b. Electronic spectra of Fe(III)*N,N`*-B_2HDE



No.	P/V	Wavelength	Abs.	Description
1		328.50	2.527	
2		293.50	4.000	
3		285.00	4.000	
4		268.50	4.000	
5		255.00	4.000	
6		240.00	1.818	
7		309.00	2.105	
8		291.50	3.939	
9		277.50	3.931	
10		266.00	3.966	
11		244.50	-3.581	

Figure 2c. Electronic spectra of Cu(II)*N,N`*-B_2HDE



No.	P/V	Wavelength	Abs.	Description
1		326.00	1.522	
2		291.50	4.000	
3		279.00	4.000	
4		271.00	4.000	
5		239.00	4.000	
6		308.50	1.296	
7		290.50	3.973	
8		276.00	3.989	
9		263.50	3.831	

Figure 2d. Electronic spectra of Zn(II)*N,N`*-B_2HDE

Kinetic studies of the complexes

The kinetic studies investigated the effects of temperature on the amount of metal complex formed at various times. The plots of semi-log of the yield of metal complexes in mole against time showed an increase in the rate constant of the formation of complexes which indicate an 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 $\ln k_{obs}$ versus 1/T Figure 4.

Figure 3a, 3b and 3c. showed the semi-log plots of Fe(III), Cu(II) and Zn(II), *N*,*N*'-B_2HED yield in mole with time at different temperatures. The three plots showed an increased in the observed rate constants of the formation of the three complexes as temperature increases. This means the rate of formation of these complexes depends on the temperature at which it is run. As the temperature increases, the molecules of reactants move faster and therefore collide more frequently. The molecules also carry more kinetic energy. Thus, the proportion of collisions that overcome the activation energy for the formation increases with temperature. This, therefore, allows for the complexes to be formed faster [10].

Figure 4. showed the semi-log plots of the observed rate constant of Fe(III), Cu(II) and Zn(II), *N*,*N*'-B_2HED against temperature inverse ($\ln K_{obs}$ *vs.* 1/T). The values of activation energy (E_a) obtained from the plots were 12.450, 11.902 and 19.223k Joules for Fe(III), Cu(II) and Zn(II), *N*,*N*'-B_2HED respectively which were positive activation energy (E_a) indicating that, the rate of the formation increases with increasing temperature and the "apparent" rate constant of the overall formation-defined by Arrhenius behavior will increased as temperature is increased and is a signal that the formation of the complexes has no complex mechanism and the relative higher activation energy of zinc explained the small yield of zinc complex at some temperature because only a very small fraction of collision would have enough energy to overcome activation energy [11].

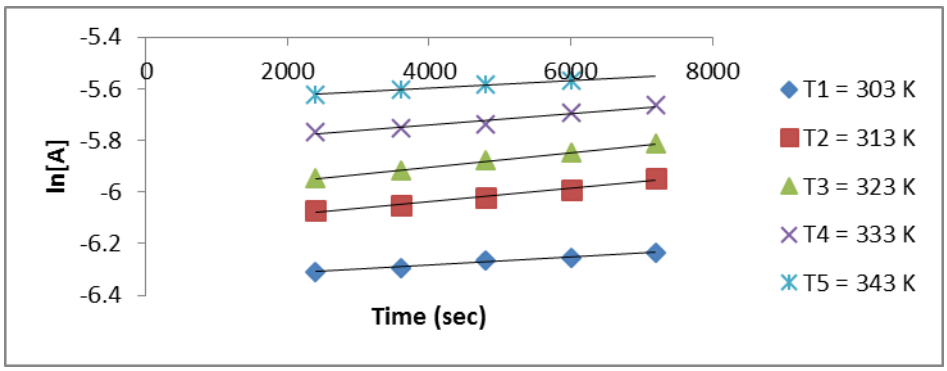


Figure 3a. Semi-log plots of Fe(III), *N*,*N*'-B_2HDE yield at different temperatures

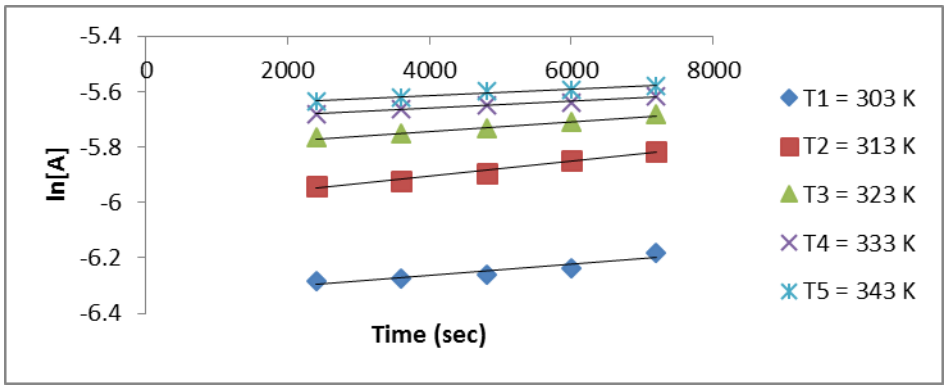


Figure 3b. Semi-log plots of Cu(II)-*N*,*N*'-B_2HED yields with time at different temperature

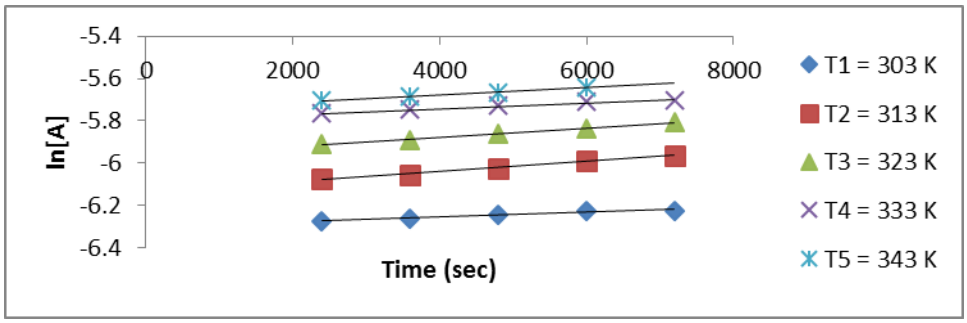


Figure 3c. Semi-log plots of Zn(II)-*N*,*N*'-B_2HED yield with time at different temperatures

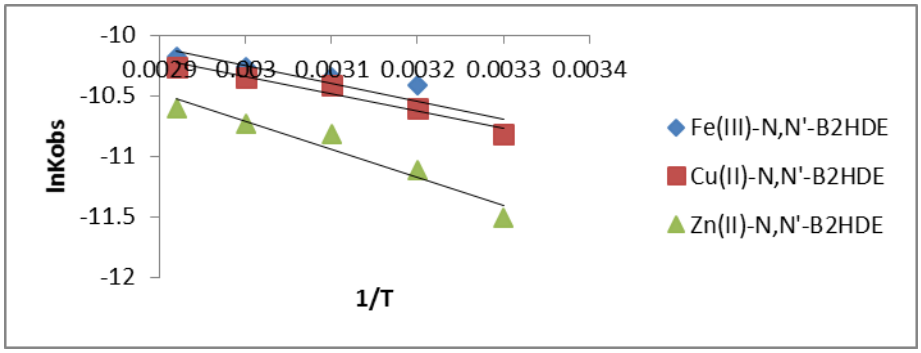


Figure 4. Plots of lnK_{obs} versus 1/T for formation of Fe(III), Cu(II) and Zn-*N*,*N*'-B_2HDE complexes

Thermodynamics studies of the complexes

Thermodynamics parameter such as enthalpy (ΔH^o), entropy (ΔS^o) change of activation during the formation of the complexes can be evaluated from the following equation:

$$\ln\left(\frac{kobs}{T}\right) = \ln\left(\frac{kb}{h}\right) + \frac{\Delta S^\circ}{R} - \frac{\Delta H}{RT} \qquad (1)$$

$$\Delta G^\circ = \Delta H^\circ - T_a\,\Delta S^\circ \qquad (2)$$

Where K_{obs} = observed reaction rate constant, T = temperature (K), T_a = the absolute temperature at which reaction can occur, Kb =Boltzmann constant, h = Planck constant, R = gas constant ($Jmol^{-1}K^{-1}$), ΔG^o=the Gibbs free energy of activation ($kJmol^{-1}$), ΔH^0=the enthalpy of activation ($kjmol^{-1}$) and ΔS^o= the entropy of activation ($kJmol^{-1}$).

The values of ΔH^o and ΔS^o were determined from the slope and intercept of the plots of $\ln\left(\frac{Kobs}{T}\right)$ verses $\frac{1}{T}$ Figure 5. The values of ΔG^o were calculated from the equation 2. The plots were used to compute the values of thermodynamics parameter.

The values of the enthalpy change of activation (ΔH^o), the entropy change of activation (ΔS^o) and the Gibbs free energy of activation (ΔG^o) found in this work were -16.75 k $Jmol^{-1}$, 1.017 $kJmol^{-1}$ and -324.97 $kJmol^{-1}$ for Fe(III), *N*,*N*`-$B_2$HDE while -9.877 $kJmol^{-1}$, 1.000 $kJmole^{-1}$ and -312.880 $kJmol^{-1}$ for Cu(II)*N*,*N*`-B_2HDE and -9.245 $kJmol^{-1}$, 0.998 $kJmol^{-1}$ and -311.639 $kJmol^{-1}$ for Zn(II)*N*,*N*`-B_2HDE.

The negative values of ΔG^o showed the ability of the studied ligand to form a stable complex since the complex had less potential energy as the formation of the complexes is spontaneous in nature. The negative value of enthalpy change of formation (ΔH^o) of the complexes implies that the enthalpy is the driving force for the formation of the complexes. However, the positive values of entropy (ΔS^o) shows that entropy is responsible for the complexation process [11].

The values for overall stability (logβ) were 56.014, 53.980 and 53.716 for Fe(III), Cu(II) and Zn(II)-*N*,*N*'-B_2HDE respectively which indicate that the complexes were stable with Fe(III)-*N*,*N*'-B_2HDE having overall stability which was higher than Cu(II) and Zn(II) complexes. This is as a result of the size of charge on Fe(III). When the metal ion size is decreased, the surface charge density increases as the ionic radius decreases. This means more effective attractive force for the ligand applied which lead to an increase in the size of logβ [13].

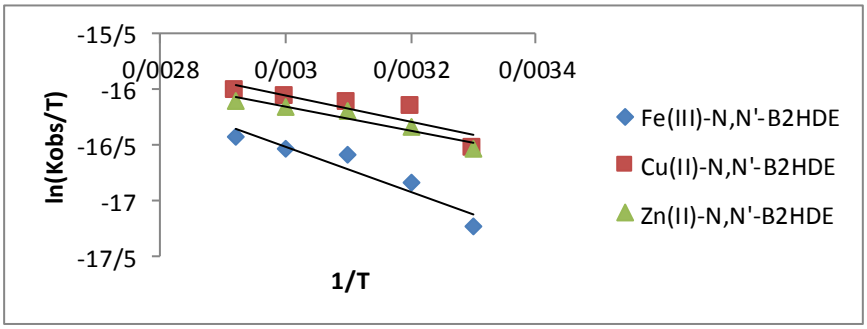


Figure 5. Plots of ln(K_{obs}/T) verses 1/T for formation of Fe(III), Cu(II) and Zn(II)-*N*,*N*'-B_2HDE complexes

Table 5. Thermodynamic parameters for formation of Fe(III), Cu(II) and Zn(II)-*N*,*N*'-B_2HED complexes

Complex	ΔH^o (kJmol^{-1})	ΔG^o (kJmol^{-1})	ΔS^o (kJmol^{-1})	Logβ	Ea (kJ)
Fe(III)-*N*,*N*'-B_2HED	-16.745	-324.970	1.017	56.014	12.450
Cu(II)-*N*,*N*'-B_2HED	-9.877	-312.880	1.000	53.930	11.902
Zn(II)-*N*,*N*'-B_2HED	-9.245	-311.639	0.998	53.716	19.223

Antimicrobial studies

The main objective of performing the antimicrobial screening was to determine the susceptibility of the pathogenic microorganisms such as the lower concentration in which the prevented visible growth of microorganism and lower concentration that killed the microorganism to the tested compound, in turn, was used for selection of the compound as a therapeutic agent. The Schiff base and its complexes were tested for antimicrobial activity against four strain of bacteria (gram positive; *Staphylococcus aureus* and gram negative; *Escherichia coli, Salmonella typhi* and *Klebsiella pneumonia* and three fungal such as *Candida albicans, Trichophyton rubbim* and *Microporum canis.* The susceptibility of the strain of microorganism towards the ligand and the complexes was judged by measuring the size of inhibition in diameter (mm). The minimum inhibitory concentration and the minimum bactericidal or fungicidal concentration test was carried out to determine the minimum concentration at which the organism did not die and expand beyond the spot of inoculation and the concentration at which the organism died which was recorded as minimum inhibitory concentration (MIC) and minimum bactericidal or fungicidal concentration using agar-dilution method respectively.

The susceptibility zones were measured in diameter (mm) and the result are listed in Table 6. The susceptibility zones where the clear zones around the well killing the bacteria.

The Schiff base and the complex exhibited varying degrees of inhibitory effects on the growth of the tested microorganism species. As observed, the free Schiff base was moderately active against the microorganism species while the antimicrobial activity of the Schiff base became more pronounced when it is chelated to the metal ions (complexes), it was noted that the Cu(II) complex is more active as compared to Fe(III) and Zn(II) complex. In conclusion, the biological activity of the complexes follows the order; Cu(II)>Fe(III)>Zn(II)>Schiff base ligand. In addition, the data showed that *Escherichia coli, Salmonella typi* and *Klebsiella pneumonia* was inhibited to a greater degree by the Cu(II) and Fe(III) complexes and the three complexes showed no activity against fungal except the moderate activity against *Candida albicans*. Therefore the complexes prepared with *N*,N`-Bis(2-hydroxl-1,2-diphenylethanone)ethylenediamine could reasonably be used for the treatment of

some common disease caused by *E. coli, S. typhi* and *K. pneumonia* while they cannot be used to treat diseases caused by fungal like *Tricholphytum rubrum* and *Microsparum canis.*

The higher the activity of the complexes compared to free ligand may be attributed to chelation [15] which reduced polarity of the metal ion by partial sharing of the positive charge with donor atoms of the ligands. This increases the lipophilic character, favouring the permeation through lipid layers of the microorganism membrane [16].

The minimum inhibitory concentration (MIC) results for each microorganism are given in Table 7. It is clearly evident from the table that efficacy of the ligand and the complexes depends on the microorganism. For instance *Staphylococcus aureus* the only gram positive required a low concentration of the ligand and the complexes (MIC on average 12.50 mg/mL) to prevent the visible growth of *S. aureus* and *Salmonella typhi, Escherichia coli* and *Klebsiella pneumonia* which are the gram negative required a lower concentration of the ligand and the complexes (MIC on average 12.50±25.00 mg/mL) to prevent their visible growth while the fungal; *Candida albican, Trichophyton rubbrum*and, *Microsporum canis* required concentration of the ligand and complexes (MIC on average 12.00±50.00 mg/mL) to prevent their visible growth.

The minimum bactericidal concentration/fungicidal concentration (MBC/MFC) for each organism is given in Table 7- 8. The MBC/MFC values showed that *Klebsiella pneumonia* required a lower concentration of the ligand and the complexes (MBC on the average 12.50±50.00 mg/mL) to be dead, *Salmonella typhi, Escherichia coli* and *Staphylococcus aureus* required a lower concentration of the ligand and the complexes (MBC on average 25.00±50.00 mg/mL) to be dead while the ligand and its complexes has death activity against fungal except Cu(II) complexes that can inhibit *Candida albicans* at a lower concentration of 50 mg/mL [17].

In conclusion, the ligand and the complexes tested against the bacterial and fungal required a lower concentration in the range of 12.50±50.00 mg/mL to terminate the bacteria and there was no activity against fungal except Cu(II) complex for *Candida albicans*.

Table 6. Zone of inhibition of the ligand along with its complexes

Compound	S.T	E.C	K.P	S. A	C. A	T. K	M. C
N,*N*'-B_2HED	8	10	12	8	7	NA	NA
Fe(III)*N*,*N*'-B_2HDE	11	9	13	9	8	NA	NA
Cu(II)*N*,*N*'-B_2HDE	13	16	14	11	9	NA	NA
Zn(II)*N*,*N*'-B_2HDE	9	11	8	10	8	NA	NA

Key: S.T = *Salmonella typhi,* E.C = *Escherichia Coli,* K.P = *Klebsielli pneumonia,* S.A =*Staphylococcus aureus,* C.A = *Candida albicans,* T.K = *Trichophytum rubbrum,* M. = *Microsporum canis* and NA= No activity.

Table 7. Minimum inhibitory concentration of ligand along with its complexes (mg/mL)

Compound	S.T	E. C	K.P	S.A	C. A	T.R	M.C
N,*N*'-B_2HDE	12.50	25.00	12.50	12.50	25.00	50.00	50.00
Fe(III)*N*,*N*'-B_2HDE	25.00	25.00	12.50	12.50	25.00	50.00	50.00
Cu(II)*N*,*N*'-B_2HDE	12.50	12.50	12.50	12.50	25.00	50.00	50.00
Zn(II)*N*,*N*'-B_2HDE	25.00	25.00	25.50	12.50	25.00	50.00	50.00

Table 8. Minimum bacteriocidal/fungicidal Concentration of the ligand along with its complexes (mg/mL)

Compound	S.T	E.C	K.P	S.A	C.A	T.R	M.C
N,*N*'-B_2HDE	25.00	25.00	25.00	25.00	50.00	_	_
Fe(III)*N*,*N*'-B_2HDE	50.00	25.00	25.00	25.00	50.00	_	_
Cu(II)*N*,*N*'-B_2HDE	25.00	12.50	25.00	12.50	50.00	_	_
Zn(II)*N*,*N*'-B_2HDE	50.00	25.00	50.00	25.00	50.00	_	_

Conclusion

In conclusion, the ligand and its Fe(II), Cu(II) and Zn(II) complexes were synthesized, characterized, kinetic and thermodynamics studies were carried out, the complexes were tested for their antimicrobial activities and the efficacy of the complexes was also tested. The IR result revealed that the chelation of Fe(III), Cu(II) and Zn(II) ion was through the deprotonated hydroxyl group and the azomethine nitrogen thus indicating the bidentated nature of the ligand. The electronic spectra of the free ligand when compared to complexes using various transitions showed a shift from lower to higher frequencies which confirmed the chelation of the ligand and metal ions. The kinetic studies revealed an increase in the amount of complexes formed when time and temperature were increased and the activation energy obtained showed that the rate constant of the formation increases with increasing the temperature. Thermodynamic parameters of complexation were determined from the temperature dependency of the observed rate constant. The negative value of ΔG^o of the complexes showed the ability of the studied ligand to form stable complexes and the process tend to proceed spontaneously. The obtained negative values of ΔH^o showed that enthalpy is the driving force for the formation of the complexes. However, the positive values of ΔS^o indicate that the entropy was responsible for the complexation process and the overall stability results showed that, the complexes were stable. The result of antimicrobial studies showed ligand possess moderate activity and metal complexes possess significant activities against different bacteria which might be due to chelation of the ligand and metals ions as there were no activities against different strain of fungal except *Candida albican* and the antimicrobial efficacy of the various complexes was determined. The result showed higher efficacy against the bacteria while there was no efficiency against fungal except for *Canida albican.*

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