SYNTHESIS, CHARACTERIZATION AND KINETIC STUDIES OF Fe(II) and Cu(II) COMPLEXES OF NICOTINIC ACID HYDRAZIDE

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Abstract: Complexes of nicotinic acid hydrazide [NAH] with M (II) sulphates (M = Fe, and Cu) have been synthesized and characterized by elemental analysis, conductance, magnetic susceptibility and electronic spectral studies. The infrared data suggest that the ligand act as neutral bidentate donors ligating through the carbonyl O and the azomethine N. The magnetic and spectra data indicate a distorted octahedral geometry in all the complexes. Thetemperature effect showed that the reaction rate increased slightly with increase in temperature. The plot of the natural logarithm of the concentration of complexes obtained over time (sec) showed that the reaction had a pseudo first order kinetics. The activation entropy obtained from plots of $\ln(k_{obs}/T)$ vs. $1/T$ of the complexes were -327.314 and -320.347, $J.K^{-1}.mol^{-1}$ for $[Cu(NAH)_2]SO_4.3H_2O$ and $[Fe(NAH)_2]SO_4.3H_2O$, respectively agreeing with an associative mechanism of reaction. The activation enthalpy for $[Cu(NAH)_2]SO_4.3H_2O$ and $[Fe(NAH)_2]SO_4.3H_2O$ were -2.403 and -2.619, respectively. The negative enthalpies were an indication that the reaction was rather exothermic. The activation energies E_a for $[Cu(NAH)_2]SO_4.3H_2O$ and $[Fe(NAH)_2]SO_4.3H_2O$ were -107.361 and -105.038 $kJmol^{-1}$ at 328 K. The lower E_a is an indication that the complexes required lower energy before it crossed over to the product formation state at lower temperature.

Keywords: Hydrazine hydrates, NAH, metal complexes, kinetics, pseudo first order

Introduction
The term "Kinetics" has become a popular term in several field of research such as organic chemistry, industrial chemistry, microbiology, engineering, geochemistry, etc. The term has been studied extensively with several ground breaking findings. While some are useful, others require the contributions from basic inorganic chemical reactions which could serve as a bed rock guiding these findings and more so, the kinetic study of complexes is an aspect beckoning for intensive attention. It is worthwhile to note that works on kinetics mainly describe the correlations between time of a reaction and its concentration. The rate constant, reaction order, and activation energy are mostly determined from every kinetic investigation. It is impossible to draw any conclusions about the reaction mechanism when these parameters are absent. Reactions whose half-times are larger than about 10 seconds are considered slow (Zumdahl, 2009); for such reactions, conventional instrumental methods can be used to follow and measure the process of the interaction of ions with the reagent. Fast reactions whose half-time are less than 10 seconds were studied by very rapid methods of mixing solutions and special measurement technique (Atkins and Paula, 2006). Both fast and slow reactions are of interest for analytical purposes in kinetics.

The study of complex compounds of metals with organic ligands has developed through three stages. At first, intense investigation of new organic reagents for metal ions were carried out. Then researches were directed to the elucidation of the effect of the structure of reagents on their reactivity, taking into account the presence of functional-analytical groups and substituents: simultaneously work on the mechanisms of complex formation in solution and the calculation of different constants was carried out. Recently, the studies on the structure of complex compounds using quantum-chemical methods have been developed. So far the problems of rates of formation, dissociation of metal chelates, and replacement of their ligands or central atoms were mainly considered in special papers or books on coordination chemistry (Lee, 2008). Much attention in theoretical and practical works has been given to kinetic methods of analysis based on the use of catalysed reactions of oxidation and reduction. Zumdahl (2009) has a high reputation in the field for the development of the theoretical fundamentals of this highly selective method. Mark and Rechnitz (2008) also dealt with the applications of catalysed reactions. Apart from the unique nature and the different donating sites of nicotinic acid hydrazides, little information is available regarding the kinetic studies of its metal complexes. Thus, it is pertinent to synthesize a wide variety of Fe (II) and Cu (II) complexes of nicotinic acid hydrazide and carry out the kinetic studies on them using gravimetric method if the information on these complexes will be made more available.

Materials and Methods
Reagents/solvents and instrumentation
$FeSO_4.7H_2O$ and $CuSO_4.5H_2O$ were of analytical grade reagents and obtained from commercial sources (Aldrich Chemical Co. and BDH) and used without further purification. Elemental analyses were performed on an Elemental Vario EL III Carlo Erba 1108 analyzer. FT–IR spectra were recorded in KBr medium on a Perkin Elmer RX1 spectrophotometer in wave number $4000 – 400$ cm^{-1}. Electronic spectra indimethylsulphoxide (DMSO) were recorded using Perkin Elmer Lambda – 2B – spectrophotometer. Molar conductance measurements were conducted using 10 – 3M solutions of the complexes in DMSO on Elico – CM 82 Conductivity Bridge at room temperature. Melting point/decomposition temperatures of the ligand and complexes were determined using a Gallenkamp melting point apparatus. The magnetic susceptibilities measurement were taken on a Gouy balance at room temperature using mercuric tetrathiocyanatocobaltate(II) ashecalibrant.

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Preparation of methyl nicotinate (ester)

The ester was prepared using standard method (Madhukar *et al.*, 2011). 12.30 g, [0.1 mole] Nicotinic acid in 30 mL methanol, to which 5 mL conc. H_2SO_4 was added and the reaction mixture was refluxed for 4 h. After thecompletion of the reaction, the precipitate formed was cooled, filtered, re-crystallised from methanol and dried over calcium chloride in a vacuum desiccator. The purity of the synthesised compound was monitored by TLC using silica gel. [% Yield = 80]

Preparationof the hydrazide

The hydrazide was prepared using standard method (Salgın-Gökşen *et al.,* 2007). 14.59 g, [0.29 moles] of hydrazine hydrate was added to 44.01 g, [0.29 moles] of methyl nicotinate in 100 mL of absolute ethanol. Antibumping granules were added to prevent bumping. The mixture was refluxed for six hours, in a 250 mL round bottom flask. It was poured into a beaker which was left overnight to crystallize. The resulting crystals were re-crystallized with minimum quantity of ethanol. The final crystals obtained was allowed to dry over $CaCl_2$ in a vacuum desiccator and weighed. [% Yield = 73]

Preparation of metal complexes

The metal complexes have been prepared by mixing the solution of $CuSO_4.5H_2O$ and $FeSO_4.7H_2O$ to the ethanolic solution of the hydrazide [NAH] in 1:2 molar ratios. The resulting mixture was then refluxed on water bath for about 10 – 15 minutes. A coloured product appeared on standing and cooling the above solution. The complexes were filtered, washed with ether and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. They were further dried in an electric oven.

Kinetic measurements

The kinetic studies were conducted in accordance with the method described by Iorungwa (2014) in order to study the rate of formation of the complexes at varied time intervals. The complexes formed at each 180, 360, 540, 720 and 900 seconds were allowed to cool in an ice bath and the crystals obtained at each time intervals were dried over $CaCl_2$ in the desiccator and weighed. The reactions were carried out at 328, 333, 338, 343, 348 and 353K, respectively.

Results and Discussion

The preparation of the Ester from Nicotinic acid is represented by equation (1)
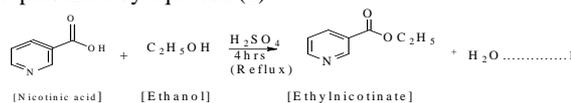
Equation 1: Schematic Diagram for the preparation of the Ester

The preparation of the Hydrazide as ligand from the Ester and hydrazine hydrate is giving in equation (2).
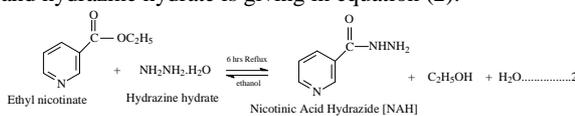
Equation 2: Schematic Diagram for the preparation of Nicotinic Acid Hydrazide

The reaction of the metal (II) salts and the hydrazide [NAH] to form the complexes can be represented by the general equation (3)

$$MSO_4.nH_2O + RCONHNH_2 \rightarrow [M(RCONHNH_2)_2.SO_4.nH_2O + nH_2O \ .... \ 3$$

Where: M = Cu^{2+} and Fe^{2+}

Equation 3: Reaction of metal (II) sulphates with hydrazide [NAH]

Table 1: Elemental analysis of the ligand and metal complexes

Molecular formula	Mol.wgt	Elemental analysis									
		% C		% H		% N		% M		% SO_4^{2-}	
		Cald	Found	Cald	Found	Cald	Found	Cald	Found	Cald	Found
$C_6H_7N_3O$	137.14	52.50	52.11	5.10	5.25	30.63	30.23	–	–	–	–
$C_{12}H_{20}N_6O_9SCu$	487.82	29.53	29.30	4.10	4.01	17.21	17.14	13.03	12.79	19.68	19.52
$C_{12}H_{20}N_6O_9SFe$	480.13	29.99	29.77	4.17	4.11	17.50	17.69	11.63	11.53	19.99	19.85

All the metal complexes are coloured, solid and stable towards air or moisture at room temperature. They decompose on heating at high temperature, insoluble in most organic solvents except ethanol. Analytical data of the compounds, together with their physical properties are consistent with proposed molecular formula given in Table 1 and 2. All the metal complexes have 1:2 (metal:ligand) stoichiometry. The molar conductance in DMSO of the complexes is 0.19 and 0.80 Scm^2Mol^{-1} for Fe (II) and Cu (II) complexes of (NAH), respectively. These indicate that the complexes are non – electrolytic.

Table 2: Physical constants for ligand and complexes

Complexes	Molecular form	Color	Form wgt	M.p °C	Mol. Cond. S cm^2Mol^{-1}
N A H	$C_6H_7N_3O$	White	137.14	161	0.01
[Cu(NAH)$_2$]SO$_4$.3H$_2$O	$C_{12}H_{20}N_6O_9SCu$	Blue	487.823	219	0.19
[Fe(NAH)$_2$]SO$_4$.3H$_2$O	$C_{12}H_{20}N_6O_9SFe$	Brown	480.125	146	0.80

Table 3: FTIR spectra bands of ligand and complexes

| S/N | Molecular formula | FTIR inKBr pellets (cm^{-1}) | | | | | | | |
		C=N	N–N	N–H	C=O	M–O	M–N	SO$_4^{2-}$	H$_2$O
1	$C_6H_7N_3O$	1549	1337	3219	1655	–	–	–	–
2	[Cu(NAH)$_2$]SO$_4$.3H$_2$O	1555	1368	3258	1638	483	398	1032	3404
3	[Fe(NAH)$_2$]SO$_4$.3H$_2$O	1431	1351	3233	1643	458	407	1102	3390

FT-IR Spectra

The data of the FT - IR spectra of the ligand and it metal complexes are listed in Table 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 1655 cm^{-1} have been assigned to υ(C=O). This band was lowered by 7 to 17 cm^{-1} on the complexes, indicating the involvement of the carbonyl group in the bonding to metal (Nwabueze and Salawu, 2012). The imino group; i.e υ(C=N) band at 1549 cm^{-1} for the free ligand and 1431 - 1555 cm^{-1} for the metal complexes which are found to be shifted to lower frequency region to 6±118 cm^{-1} on complexion which

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suggest the involvement of the nitrogen atom of the υ(C=N) azomathine nitrogen in the bonding with the metal (II) ions (Manjulata, 2003).

The stretching vibrations of the sulphate ion υ(SO_4^{2-}) are observed to have a sharp singlet band at 1102 - 1032 cm⁻¹ indicating that SO_4^{2-} was involved in the inner sphere coordination since the stretching vibrations of the sulphate ion are usually observed as a sharp singlet around 1100 cm⁻¹ and a medium band around 680 cm⁻¹ (Raman and Ravichandran, 2002). The appearance of broad band at 3368 – 3404 cm⁻¹ in the complexes have been assigned to υ(OH) which was associated with coordinated or solvent water molecules which is indicative of the presence of water molecules in the complexes and supporting band in the range of 611 – 951 cm⁻¹ attest for the distorted vibration of υ(OH) band and this implies that water molecules held by a crystal lattice is present in the complexes (Venkatesa *et al.,* 2000). In the FT-IR spectra the band due to N– H stretching in the free ligand occurs in the 3219 cm⁻¹ region which may be due to hydrogen bonding probably of the type NH…N type in the ligandwhich account for the appearance of the υ[N-H] band around 3233 - 3258 cm⁻¹ in the complexes. The stretching υ(NH) of the ligand is not much altered in the spectra of the complexes indicate the non participation of nitrogen atom of NH_2. Hence it is concluded that the compound (NAH) act as a neutral bidentateligand (Sonmez and Sekerel, 2002) The υ(M-N) stretching bands are not observed in the spectrum of the ligsnd but are observed in the spectrum of the complexes probably because, there is no (M-N) coordinated in the ligand (Waeel, 2013). Similarly, there is no υ(M-O) stretching band in the ligand because, there is no metal coordinated to oxygen (Salawu and Aliyu, 2012).

Electronic absorption spectra

Electronic absorption spectra of the ligand and their transition metal complexes in the UV-Visible range 200–800 nm were recorded on ultraviolet visible spectrophotometer in ethanol using a 1 cm quartz cell. The absorption bands for the complexes will help to give an idea of their structure. The absorption spectra and magnetic moments of the metal complex are given in Table 4. The diffuse electronic spectrum of Cu^{2+} complex shows two broad bands around 305 nm and 311 nm. The first band may be due to a $^2B_1g \rightarrow {^1A_1g}$ transition while the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu^{2+} metal complex. The higher value of the magnetic moment of the Cu^{2+} complex supports the same (Silverstein *et al.*, 1981). When the complexes are compared with the free ligands, there was a shift in frequency.

Table 4: Electronic and Magnetic data for the complexes

Compounds	μ_{eff}(B.M)	λ_{max}(nm)	Assignment	Geom.
$Cu(NAH)_2SO_43H_2O$	1.873	311 305	$^2B_1g \rightarrow {^1A_1g}$	Octahedral
$Fe(NAH)_2SO_43H_2O$	2.867	287	$^5T_1g \rightarrow {^5Eg}$	Octahedral

Table 5: Solubility of the ligand and metal complexes in some selected solvents

Ligand/complexes	Distilled water	Ethanol	Methanol	Acetone	DMSO	DMF
N A H	N S	S	S S	S S	S S	S S
[Cu(NAH)₂]SO₄.3H₂O	N S	S	N S	N S	N S	N S
[Fe(NAH)₂]SO₄.3H₂O	N S	S	N S	N S	N S	N S

S = Soluble, SS = Slightly Soluble, NS = Not Soluble

Solubility test for the ligand and complexes

The solubility test for the ligand and the complexes were carried in different solvents and the result in Table 5 showed that both the ligand and the complexes were insoluble in most organic solvent except ethanol. This may be due to the polymeric nature of the complexes (Salawu and Aliyu, 2012).

Kinetic Measurements

After monitoring the reaction at the temperature of 328 K, the reactions were further considered at higher initial temperatures of 333, 338, 343, 348 and 353 K. The reactions were observed to be faster as temperature of the reaction was increased. Most of the reactions were observed to be completed at a temperature of about 353 K and at a time of 360 seconds. A plot of the natural logarithm of the concentration of the complexes against time was made (Figs. 1 and 2) and it showed that the reaction had a pseudo first order dependence on the complexes formed. The observed rate constants (k_{obs}) were obtained from the slopes of the plots (Figs. 1 and 2).

Fig. 1: A plot of ln[Cu(NAH)₂]SO₄.3H₂Ovs time (secs) for various temperatures

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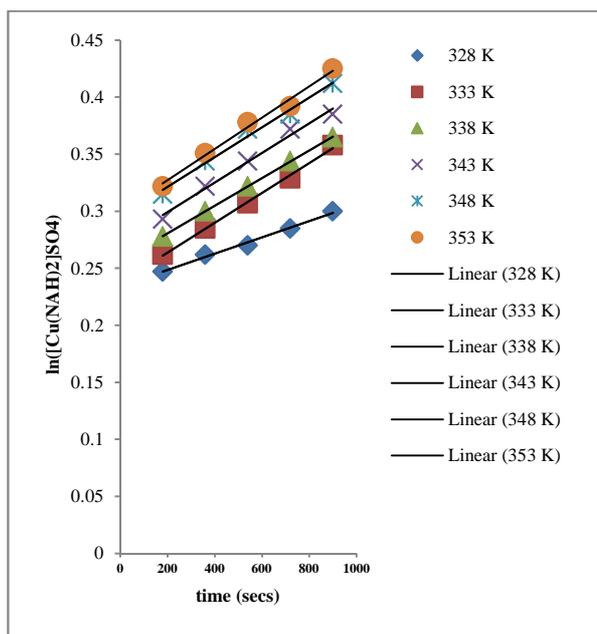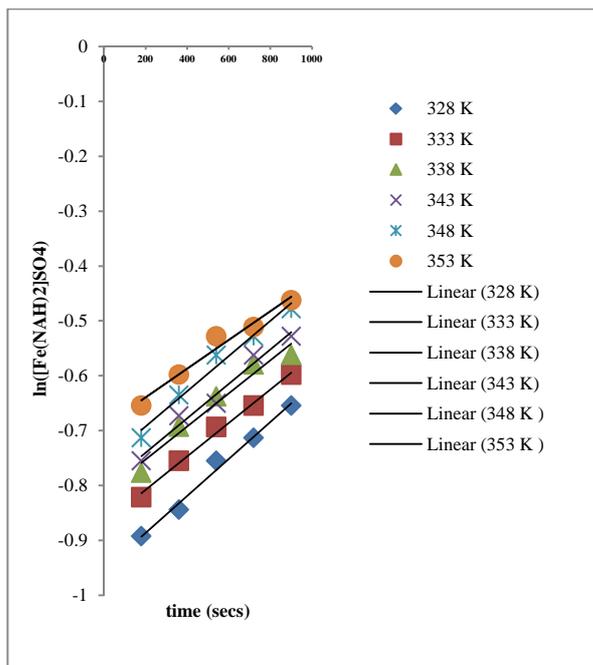
Fig 2: A plot of ln[Fe(NAH)₂]SO₄.3H₂O VS time (secs) for various temperatures

$$\text{Fig 2: A plot of } \ln[Fe(NAH)_2]SO_4.3H_2O \text{ VS time (secs) for various temperatures}$$
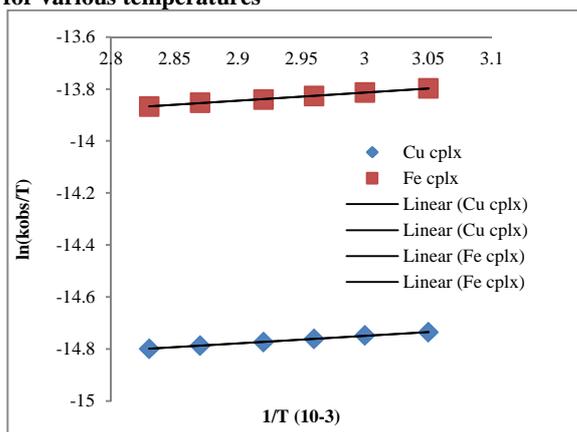
Fig. 3: Show the plot of $\ln(k_{obs}/T)$ vs $1/T$

The data in Table 6 was used to plot a graph of $\ln[Cu(NAH)_2]SO_4.3H_2O$ against time (Fig. 1), the straight line graph is an indication that the reaction had a pseudo first order dependence on the complexes formed. The data in Table 7 was used to plot a graph of $\ln[Fe(NAH)_2]SO_4.3H_2O$ against time (Fig. 2), the straight line graph observed is an indication that the reaction had a pseudo first order dependence on the complexes formed. The results in Tables 6 and 7 show that, the rate of formation of the complexes increases with increase in time. These results agreed with the earlier studies (Chulsung *et. al.,* 2007).

Table 6: Shows the values of the natural logarithm of [Cu(NAH)₂]SO₄.3H₂O at different time interval

Time(s)	1n[Cu(NAH)₂]SO₄.3H₂O at varied temp.					
	328K	333K	338K	343K	348K	353K
180	0.247	0.262	0.278	0.293	0.315	0.322
360	0.262	0.285	0.300	0.322	0.344	0.351
540	0.270	0.307	0.322	0.344	0.372	0.378
720	0.285	0.329	0.344	0.372	0.385	0.392
900	0.300	0.358	0.365	0.385	0.412	0.425

Table 7: Shows the values of the natural logarithm of [Fe(NAH)₂]SO₄.3H₂O at different time interval

Time(s)	1n[Fe(NAH)₂]SO₄.3H₂O at varied temp.					
	328K	333K	338K	343K	348K	353K
180	–0.892	–0.821	–0.777	–0.755	–0.713	–0.654
360	–0.844	–0.755	–0.693	–0.673	–0.635	–0.598
540	–0.755	–0.693	–0.638	–0.650	–0.562	–0.528
720	–0.713	–0.654	–0.580	–0.562	–0.528	–0.511
900	–0.654	–0.598	–0.562	–0.528	–0.478	–0.462

Table 8: Shows the k_{obs} derived from the plot of ln[Cu(NAH)₂]SO₄.3H₂O against time for varied temperature

Temp. (K)	k_{obs} (10^{-4})	k_{obs}/T (10^{-7})	$1n(k_{obs}/T)$	$1/T$ (10^{-3})
328	1.306	3.983	–14.736	3.09
333	1.310	3.934	–14.748	3.00
338	1.312	3.574	–14.843	2.96
343	1.315	3.819	–14.778	2.92
348	1.317	3.767	–14.792	2.87
353	1.319	4.051	–14.881	2.83

Table 8 presents the observed rate constants obtained from the plot of the natural logarithm of the complexes against time (secs). It was observed in Table 8 that as the temperature was kept at 328 K, the rate of formation of $[Cu(NAH)_2]SO_4.3H_2O$ was 1.306×10^{-4} but when the temperature was increased to 333 K, the rate increased to 1.310×10^{-4}. Further increase in temperature to 338, 343, and 353 K show a significant increase in the observed rate constant (k_{obs}) to 1.312×10^{-4}, 1.315×10^{-4}, 1.317×10^{-4} and 1.319×10^{-4}, respectively. It was observed in table 9 that as the temperature was kept at 328 K, the rate of formation of $[Fe(NAH)_2]SO_4 3H_2O$ was 3.337×10^{-4} but when the temperature was increased to 333 K, the rate increased to 3.340×10^{-4}. Further increase in temperature to 338, 343, and 353 K show a significant increase in the observed rate constant (k_{obs}) to 3.343×10^{-4}, 3.347×10^{-4}, 3.349×10^{-4} and 3.351×10^{-4}, respectively. These regular variations in the observed rate constants as the temperatures were increased are suggestive of the fact that the rate of formation of the complexes depended highly on the temperatures. This fact is in agreement with research findings made by Xu and Gu (2005).

For each of the complexes another plots of $\ln(k_{obs}/T)$ against $1/T$ was made, this was in accordance with Elovitz and Fish, (1994). The graph was found to be linear with very nice regression coefficient (Fig. 3). The activation enthalpies and entropies ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) was obtained from the slopes and intercepts of another plot of $\ln(k_{obs}/T$ against $1/T$ (Fig. 3). This is in accordance with the Elevoitz and Fish (1994) equation;

$$\ln(k_{obs}/T) = \ln(kb/h) + \Delta S/R - \Delta H/RT \quad \text{…………4}$$

Where
T is the temperature in Kelvin
K_b is Boltzman's constant (1.38×10^{-23} J/k)
h is plank constant (6.63×10^{-14} Js), and
R is the molar gas constant (8.314 J/K/mol)
The activation energy was therefore computed from the relationship;

$$E_a = \Delta H - T\Delta S \quad \text{…………………5}$$

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Table 9: Shows the rate constant k_{obs} derived from the plot of ln[Fe(NAH)$_2$]SO$_4$.3H$_2$O against time for varied temperature

Temp. (K)	k_{obs} (10^{-4})	k_{obs}/T (10^{-7})	ln(k_{obs}/T)	1/T (10^{-3})
328	3.337	10.170	–13.798	3.05
333	3.340	10.030	–13.813	3.00
338	3.343	9.8910	–13.827	2.96
343	3.347	9.7580	–13.840	2.92
348	3.349	9.6240	–13.853	2.87
353	3.351	9.4930	–13.868	2.83

Table 10: Activation data for the complexes formed at 328 K

Complexes	$-\Delta H^{+}$ (kJ/mol)	$-\Delta S^{+}$ (kJ/mol)	$-E_a$ (kJ/mol)
Cu(NAH)$_2$SO$_4$.3H$_2$O	2.403	327.314	107.361
Fe(NAH)$_2$SO$_4$.3H$_2$O	2.619	320.247	105.038

It was observed from (Table 10) that the thermodynamic studies of the complexes show that [Cu(NAH)$_2$]SO$_4$.3H$_2$O and [Fe(NAH)$_2$]SO$_4$.3H$_2$O had negatives entropies. The negative value of the entropies is a suggestive that the reactions follow associative mechanisms. The activation entropy is often used as an indicator of the configuration of the activated complex (Iorungwa *et al*, 2014). The activation energies E_a for [Cu(NAH)$_2$]SO$_4$.3H$_2$O and [Fe(NAH)$_2$]SO$_4$.3H$_2$O at 328 K were observed. The lower E_a is an indication that the complexes required lower energy before it crossed over to the product formation state at lower temperature. Mean while the enthalpy values for [Cu(NAH)$_2$]SO$_4$.3H$_2$O and [Fe(NAH)$_2$]SO$_4$.3H$_2$O were also presented in Table 10.

From all the available data, the probable structures for the complexes have been proposed as shown in Scheme 1;
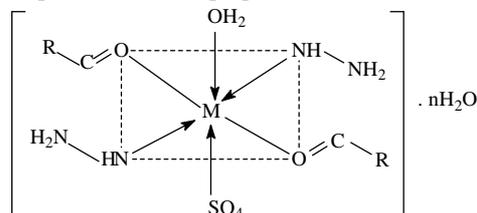
Scheme 1: Proposed structures for 1:2 Octahedral geometry; **where:** M = Fe (II) and Cu (II) and R = C$_6$H$_5$N

Conclusion

The complexes were recognized to be non electrolytic. The FT-IR spectra of the ligand and the metal complexes show a clear evidence of formation of the complexes, the Uv spectra of the complexes recognized that the complexes were octahedral complexes. The magnetic moment for Fe^{2+} indicates that the complex is a high spin type paramagnetic while the magnetic moment for Cu^{2+} complex was also found to be within the expected value. The kinetic results show that the rate of formation of the complexes increases with increase in time and temperature for all the complexes formed. Judging from their observed rate constant (k$_{obs}$) when a plot of the natural logarithm of the concentration of the complexes against 1/T was plotted, it was seen that for all the complexes, there was regular variations in the rate of formation of the complexes as the temperatures were increased the observed rate constants equally increased, that was a suggestive of the fact that the rate of formation of the complexes depend on temperature. The thermodynamic parameters show a lower activation complex E_a for all the complexes formed which is an indication that the complexes required lower energy before it crossed over to the product formation state at lower

temperature. Also the negative value of the entropies is a suggestive that the reactions follow associative mechanisms. The negatives values of the enthalpy implying that the reaction is rather exothermic.

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