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

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Received: May 15, 2016 Accepted: August 08, 2016

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 carboxyl O and the azomethine N. The magnetic and spectra data indicate a distorted octahedral geometry in all the complexes. The temperature 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 \( \ln(\text{rate})/\text{T} \) vs. 1/T of the complexes were -327.314 and -320.347, J.K\(^{-1}\).mol\(^{-1}\) for [Cu(NAH)\(_2\)SO\(_4\).3H\(_2\)O and [Fe(NAH)\(_2\)SO\(_4\).3H\(_2\)O, respectively agreeing with an associative mechanism of reaction. The activation enthalpy for [Cu(NAH)\(_2\)SO\(_4\).3H\(_2\)O and [Fe(NAH)\(_2\)SO\(_4\).3H\(_2\)O 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\(_2\)O and [Fe(NAH)\(_2\)SO\(_4\).3H\(_2\)O 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 is 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\(_2\)O and CuSO\(_4\).5H\(_2\)O 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.
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. H₂SO₄ was added and the reaction mixture was refluxed for 4 h. After the completion 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]

Preparation of 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 standing and cooling the above solution. The complexes were filtered, washed with ether and dried under reduced pressure over anhydrous CaCl₂. The purity of the reaction mixture was refluxed for 4 h. After the completion of the reaction, the precipitate formed was cooled, filtered, washed with ether and dried under reduced pressure over anhydrous CaCl₂ in a vacuum desiccator. The final crystals obtained was allowed to dry over CaCl₂ in a vacuum desiccator and weighed. [% Yield = 73]

Preparation of metal complexes
The metal complexes were prepared by mixing the solution of CuSO₄·5H₂O and FeSO₄·7H₂O 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 CaCl₂ in a desiccator. They were further dried in an electric oven.

Kinetic measurements

Table 1: Elemental analysis of the ligand and metal complexes

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% M</th>
<th>% SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₇N₂O</td>
<td>52.50</td>
<td>5.10</td>
<td>5.25</td>
<td>30.63</td>
<td>30.23</td>
</tr>
<tr>
<td>C₁₂H₁₄O₇S₄Cu</td>
<td>52.11</td>
<td>5.25</td>
<td>30.23</td>
<td>13.03</td>
<td>12.79</td>
</tr>
<tr>
<td>C₁₂H₁₄O₇S₄Fe</td>
<td>52.63</td>
<td>5.14</td>
<td>17.36</td>
<td>11.83</td>
<td>11.99</td>
</tr>
</tbody>
</table>

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 Scm²M⁻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

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Molecular form</th>
<th>Color</th>
<th>Form wtg</th>
<th>M.p. °C</th>
<th>Mol. Cond. S cm⁻²Mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAH</td>
<td>C₆H₇N₂O</td>
<td>White</td>
<td>137.14</td>
<td>161</td>
<td>0.01</td>
</tr>
<tr>
<td>[Cu(NAH)₃]SO₄·3H₂O</td>
<td>C₁₂H₁₄O₇S₄Cu</td>
<td>Blue</td>
<td>487.823</td>
<td>219</td>
<td>0.19</td>
</tr>
<tr>
<td>[Fe(NAH)₃]SO₄·3H₂O</td>
<td>C₁₂H₁₄O₇S₄Fe</td>
<td>Brown</td>
<td>480.125</td>
<td>146</td>
<td>0.80</td>
</tr>
</tbody>
</table>

The kinetic studies were conducted in accordance with the method described by loringwia (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 CaCl₂ 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)

\[
\text{Ethyl nicotinate} + \text{Hydrazine hydrate} \rightarrow \text{Ester + Hydrazine} \quad (1)
\]

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).

\[
\text{Ethyl nicotinate} + \text{Hydrazine hydrate} \rightarrow \text{Nicotinic Acid Hydrazide (NAH)} \quad (2)
\]

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)

\[
\text{MSO₄.nH₂O + RCONHNH₃ \rightarrow [M(RCONHNH₃)₃]SO₄.nH₂O + nH₂O} \quad 3
\]

Where: M = Cu²⁺ and Fe²⁺

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

The data of the FT - IR spectra of the ligand and its metal complexes are listed in Table 3. The FT-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 ν(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 ν(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 complexation which
suggest the involvement of the nitrogen atom of the \( \text{u(C=N)} \) azomethine nitrogen in the bonding with the metal (II) ions (Manjulata, 2003).

The stretching vibrations of the sulphate ion \( \text{u(SO}_4^{2-} \) are observed to have a sharp singlet band at 1102 - 1032 \text{cm}^{-1} indicating that \( \text{SO}_4^{2-} \) was involved in the inner sphere coordination since the stretching vibrations of the sulphate ion are usually observed as a sharp singlet around 1100 \text{cm}^{-1} and a medium band around 680 \text{cm}^{-1} (Raman and Ravichandran, 2002). The appearance of broad band at 3368 – 3404 \text{cm}^{-1} in the complexes have been assigned to \( \text{u(OH)} \) 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 \text{cm}^{-1} attest for the distorted vibration of \( \text{u(OH)} \) 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 \text{cm}^{-1} region which may be due to hydrogen bonding probably of the type NH...N type in the ligand which account for the appearance of the \( \text{u[N-H]} \) band around 3233 - 3258 \text{cm}^{-1} in the complexes. The stretching \( \text{u(NH)} \) of the ligand is not much altered in the complexes. Hence it is concluded that the compound (NAH) act as a neutral bidentateligand (Sonmez and Sekerel, 2002). The \( \text{u(M-N)} \) stretching bands are not observed in the spectrum of the ligand but are observed in the spectrum of the complexes probably because, there is no \( \text{M-N} \) coordinated in the ligand (Waeel, 2013). Similarly, there is no \( \text{u(M-O)} \) 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 \( ^3\text{B}_1\text{g} \rightarrow ^1\text{A}_1\text{g} \) 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**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \mu_{\text{B.M}} )</th>
<th>( \lambda_{\text{max}} )</th>
<th>Assignment</th>
<th>Geom.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NAH)_2SO_4.H_2O</td>
<td>1.873</td>
<td>311 \text{nm}</td>
<td>( ^3\text{B}_1\text{g} \rightarrow ^1\text{A}_1\text{g} )</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Fe(NAH)_2SO_4.H_2O</td>
<td>2.867</td>
<td>287 \text{nm}</td>
<td>( ^3\text{T}_2\text{g} \rightarrow ^3\text{E}_g )</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>

**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 \( k_{\text{obs}} \) were obtained from the slopes of the plots (Figs. 1 and 2).

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

<table>
<thead>
<tr>
<th>Ligand/complexes</th>
<th>Distilled water</th>
<th>Ethanol</th>
<th>Methanol</th>
<th>Acetone</th>
<th>DMSO</th>
<th>DMF</th>
</tr>
</thead>
</table>

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

**Fig. 1:** A plot of ln([Cu(NAH)_2SO_4.H_2O] vs time (secs) for various temperatures
Fig 3: A plot of ln[Fe(NAH)$_2$SO$_4$.3H$_2$O] VS time (secs) for various temperatures

Table 7: Shows the values of the natural logarithm of [Fe(NAH)$_2$SO$_4$.3H$_2$O] at different time interval

<table>
<thead>
<tr>
<th>Time(s)</th>
<th>ln[Fe(NAH)$_2$SO$_4$.3H$_2$O] at varied temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>328K</td>
<td>0.307</td>
</tr>
<tr>
<td>333K</td>
<td>0.285</td>
</tr>
<tr>
<td>338K</td>
<td>0.285</td>
</tr>
<tr>
<td>343K</td>
<td>0.285</td>
</tr>
<tr>
<td>348K</td>
<td>0.285</td>
</tr>
<tr>
<td>353K</td>
<td>0.285</td>
</tr>
<tr>
<td>Linear (328 K)</td>
<td>Linear (333 K)</td>
</tr>
</tbody>
</table>

Fig 2: A plot of ln[Fe(NAH)$_2$SO$_4$.3H$_2$O] VS time (secs)

Table 8: Shows the rate constants obtained from the plot of ln[Fe(NAH)$_2$SO$_4$.3H$_2$O] against time for varied temperature

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$k_{obs}$ (10$^{-4}$)</th>
<th>$k_{obs}$/T (10$^{-5}$)</th>
<th>ln($k_{obs}$/T)</th>
<th>1/T (10$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>328</td>
<td>1.300</td>
<td>3.293</td>
<td>-14.736</td>
<td>3.09</td>
</tr>
<tr>
<td>333</td>
<td>1.310</td>
<td>3.934</td>
<td>-14.748</td>
<td>3.00</td>
</tr>
<tr>
<td>338</td>
<td>1.312</td>
<td>3.574</td>
<td>-14.843</td>
<td>2.96</td>
</tr>
<tr>
<td>343</td>
<td>1.315</td>
<td>3.819</td>
<td>-14.778</td>
<td>2.92</td>
</tr>
<tr>
<td>348</td>
<td>1.317</td>
<td>3.767</td>
<td>-14.792</td>
<td>2.87</td>
</tr>
<tr>
<td>353</td>
<td>1.319</td>
<td>4.051</td>
<td>-14.881</td>
<td>2.83</td>
</tr>
</tbody>
</table>

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 [Fe(NAH)$_2$SO$_4$.3H$_2$O] was 1.300 x 10$^{-4}$ but when the temperature was increased to 333 K, the rate increased to 1.310 x 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 x 10$^{-4}$, 1.315 x 10$^{-4}$, and 1.319 x 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$_2$O] was 3.337 x 10$^{-4}$ but when the temperature was increased to 333 K, the rate increased to 3.340 x 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 x 10$^{-4}$, 3.347 x 10$^{-4}$, 3.349 x 10$^{-4}$, 3.351 x 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 energy was therefore computed from the slopes of another plot of ln($k_{obs}$/T) against 1/T (Fig. 3). This is in accordance with the Elovitz and Fish (1994) equation:

$$\frac{ln(k_{obs})}{T} = ln(k_{b}h) + \frac{\Delta H}{T} + \frac{\Delta S}{T}$$

**Where**

- $T$ is the temperature in Kelvin
- $k_{b}$ is Boltzmann’s constant ($1.38 \times 10^{-23}$ J/K)
- $h$ is plank constant ($6.63 \times 10^{-34}$ Js), and
- $R$ is the molar gas constant ($8.314$ J/K/mol)

The activation energy was therefore computed from the relationship:

$$E_{a} = \frac{\Delta H}{T} - \frac{\Delta S}{T}$$
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. 

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (kJ/mol/K)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(NAH)$_2$SO$_4$.3H$_2$O</td>
<td>2.403</td>
<td>327.314</td>
<td>107.361</td>
</tr>
<tr>
<td>Fe(NAH)$_2$SO$_4$.3H$_2$O</td>
<td>2.619</td>
<td>320.247</td>
<td>105.038</td>
</tr>
</tbody>
</table>

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

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$^{3+}$ 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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