

SYNTHESIS, CHARACTERIZATIONS AND BIOLOGICAL APPLICATIONS OF SCHIFF BASE DERIVED FROM O-PHENYLENEDIAMINE AND 2-HYDROXY-1-NAPHTHALDEHYDE AND ITS Mn(II), Co(II), and Zn(II), METAL COMPLEXES

¹Aisha Ahmad, ²Abduljeleel Mohd Abdulazeez, ³Ahmed Aminu, ⁴Balarabe Sarki Sagagi

Department of Chemistry, Kano University of Science and Technology Wudil, Kano State.

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Abstract: Schiff base was synthesized by the condensation of o-phenylenediamine and 2-hydroxy-1-naphthaldehyde. Its metal complexes were also prepared by reacting the Schiff with metal chlorides in ethanol. The Schiff base and its metal (II) complexes were characterized by solubility test, melting and decomposition determination, FTIR, magnetic susceptibility, molar conductance analysis. Solubility test was carried on the Schiff base and the complexes which showed that they are all soluble in ethanol DMSO and DMF, but insoluble in water. From the FTIR result, Azomethine $\nu(\text{C}=\text{N})$ stretching vibration was observed at 1608 cm^{-1} which shifted to 1707 cm^{-1} in manganese (II) complex, 1707 cm^{-1} in cobalt (II) complex, and 1707 cm^{-1} in zinc (II) complexes respectively. Also a broad band was observed in the Schiff base and the complexes at 3108 cm^{-1} which indicate presence of water of crystalliation to the complex structure. The complexes are paramagnetic except for zinc which is diamagnetic, non electrolytic in nature and have high thermal stability. Job's method of continuous variation suggests 1:2 metal to ligand ratio. The antimicrobial studies of the Schiff base and its metal(II) complexes reveals that the metal(II) complexes show better activity when compared to that of the ligand.

Keywords: o-phenylenediamine, 2-hydroxy-1-naphthaldehyde, Ligand, Characterization, Antimicrobial activity.

1. INTRODUCTION

Schiff base metal complexes play a significant role in the development of chelation chemistry. The chelation makes these compounds effective and stereo specific catalyst for oxidation, reduction and hydrolysis, and they also show biological activity and other transformation of organic and inorganic chemistry. (Kawkab, 2012) Transition metal complexes with Schiff base as a ligand have been amongst the widely studied coordination compound in the past few years, since they are found to be widely applicable in many fields. (Dhivya, 2012) It is well known that some drugs have higher activity when administered as metal complexes than as a free ligand, and they have potential applications in many fields such as antibacterial, antiviral, anticancer drugs and electrochemistry. (Kawkab, 2010). In coordination chemistry, phenylenediamine is an important ligand precursor. Schiff base derivatives, like those derived from salicylaldehyde, are excellent chelating ligands. Oxidation of its metal-phenylenediamine complexes affords the diimine derivatives, which are intensely colored and often exist in multiple stable oxidation states. (Nagham et.,al 2019)

There are many applications of phenylene diamine derivatives in bio-field and chemical fields like as a ligands dyes, other applications. Amino acids can act as coordinating agents through their amino (NH_2) and carboxylate (COO^-) groups. For sulfur-containing amino acids, the SH group confers a more versatile coordination activity toward heavy metal ions. The $-\text{SH}$ (sulfhydryl), $-\text{NH}_2$ (amino) and $-\text{COO}^-$ (carboxylate) groups are the possible coordination sites for the complexation processes. Sequestration of toxic heavy metal ions and obtaining safer drugs or antidotes for metal poisoning by complexation is a very promising field. As ligands, amino acids also act as ambidentate so that they can bind through (S,N), (N,O) or (S,O) donor atoms. Due to the acidobasic behaviour, amino acids are considered as ampholytes which means that with the negatively charged $-\text{COO}^-$ group or positively charged $-\text{NH}_3^+$ can behave outwardly as acids or as bases. In an organism, amino acids can be both free and bound. These bound amino acids may be permanently or temporarily incorporated into the proteins or other possible biochemical functional structures. Free amino acids comprise other amino acids generated by modifying the known biogenic amino acids. These are known as biogenic amines, including histamine, dopamine, noradrenaline, ornithine, taurine, or growth factors sarcosine, spermine and spermidine. Determination of free amino acids or biogenic amines is insufficient to understand the metal biochemistry. It needs to deal directly with their own interactions between the metal and amino acids.

The Schiff bases are considered as privileged ligands' because of their capability to stabilize different metals in various oxidation states and their metal chelates are widely studied owing to the synthetic flexibility, sensitivity and selectivity toward various metal ions (Jayamani .et.al 2014) Aliphatic Schiff bases are relatively unstable and easily polymerizable compared to aromatic Schiff bases because the latter possesses effective conjugation and hence they are more stable in condensation reactions, aldehydes react faster than ketones leading to the formation of Schiff bases because the reaction centres of aldehydes are sterically less hindered than ketones. Moreover, the additional carbon of the ketone less electrophilic compared to the aldehyde.

The coordination compounds of Cd(II), Zn(II) and Pb(II) ions with chemical formula $[\text{ML}(\text{OH})_2(\text{H}_2\text{O})_2]$ in which the primary amine was phenylenediamine have been synthesized and characterized, using elemental analysis, molar conductance, magnetic susceptibility measurements, thermal analysis and some spectral studies were considered as common tools of analysis. All conducted studies support the formation of the chelation phenomena between the positively charged metal ions and the Schiff bases. The reaction of salicylaldehyde with 2-aminophenol or any other amino compounds has been studied in terms of coordination chemistry. The solubility in different chemical solvents gives a lot of indications about the nature of the chelates and can be examined to be electrolytic or non-electrolytic nature. Most bases containing nitrogen atom as well as salicylaldehyde moiety are of significant importance in their chelation or in the other uses. The shad of light of the applications of the Schiff bases give the importance of the natural of the ligands. All isomers of phenylenediamine, can be used in preparation of Schiff bases. The chelation may occur, with one or more metal ions depending on the amount used and the geometrical structure of the bases.

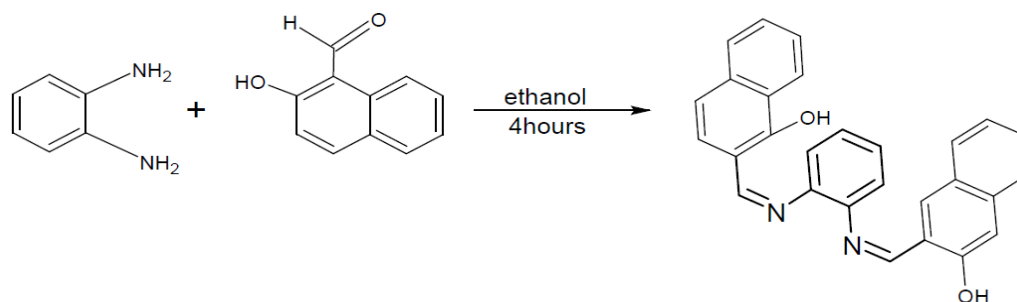
This paper reports synthesis characterizations and antimicrobial studies of a schiff base derived from o-phenylenediamine and 2-hydroxy-1-naphthaldehyde and its manganese (II), cobalt(II), and zinc(II) complexes.

2. MATERIALS AND METHODS

Reagents are of analytical grade purity and were obtained from Sigma Aldrich chemical limited. The glass wares used were washed thoroughly with detergent, rinsed with distilled water and dried in an oven. Melting point and decomposition temperature were determined using Gallen kamp melting point apparatus. Molar conductivity measurement was carried out using Jenway conductivity meter model 4010, while magnetic susceptibility measurement was done on MBS MKI magnetic susceptibility balance at 25°C . IR spectral analysis was carried out using FTIR Cary 630 (Agilent Technology) model in the range of $4000 - 650\text{cm}^{-1}$. Bacterial and fungal isolates were obtained and identified at the Department of Microbiology, Kano University of Science and Technology wudil.

Preparation of the Schiff base

The schiff base ligand were prepared by slow addition of 0.01mole of o-phenylenediamine to a solution of 0.02mole of 2-hydroxyl -1-naphthaldehyde in 40cm^3 of ethanol. The mixture was reflux with vigorous stirring for 3 hours. The product was filtered, re-crystallized with ethanol, and washed with distilled water and dried in desiccators over CaCl_2 for 24hours.



Scheme 3.1.0.: Preparation of Schiff base

Preparation of the Metal Complexes

The metal complex of Schiff base was prepared by the addition of a solution of appropriate metal chloride (1mmol) in an ethanol water-mixture (1:1, 25ml) to the solution of schiff base (0.219g, 2mmol) in the same solvent (25ml). The resulting mixture was stirred under reflux for 1hour upon the complex precipitated and collected by filtration and washed with a 1:1 ethanol-water mixture (Mohamed *et al*, 2005).

Antimicrobial Activity

The antibacterial activity of the Schiff base ligand and its metal complexes was carried out by using bacterial isolates of *Staphylococcus aureus*, and *Escherichia coli*. Ciprofloxacin was used as the standard antibacterial drug. The antifungal activities were tested against two pathogenic fungi; *Candida albicans*, and *Aspergillus fumigatus*, using disc diffusion method. Ketoconazole was used as standard fungicide and DMSO was used as a negative control. The suspension of each microorganism was smeared on the surface of the solidified Muller-Hinton Agar (MHA) already poured into petri dishes. The Schiff base and the metal Complexes were separately dissolved in DMSO so as to have four distinct concentrations (100µg/disc, 50µg/disc, 25µg/disc and 12.5 µg/disc) through serial dilution and placed on the surface of the culture media, incubated at 37°C for 24 hours.

Activities were determined by measuring (mm) the diameter of the zone of inhibition and compared with a standard drug (Khan *et al.*, 2014).

3. RESULTS AND DISCUSSION

The reaction between o-phenylenediamine and 2-hydroxy-1-naphthaldehyde yielded Schiff base ligand which is a white crystalline solid with the percentage yield of 82% and melting point temperature of 135°C. (Table1). The interaction between Schiff base and metal (II) salt of (manganese, cobalt and zinc) formed complexes with different colours. (Table 1) The colours may be due to charge transfer or nature of the ligand.

The decomposition temperature Mn(II), Co(II) and Zn(II) complexes fall in the range of 201°C, 188°C and 214°C respectively. (Table 1) these temperatures are relatively high indicating the good thermal stability of the complexes due to the formation of large rings.

The Schiff base and its metal complexes are soluble in some common organic solvents such as methanol, acetone, Dimethylsulfoxide (DMSO), Dimethylformamide (DMF), and chloroform, slightly soluble in ethanol and insoluble in water. (Table 2)

The molar conductance values obtained in (Table 3) ranges from 6.60, 4.73 and 3.42 Ohm-1cm²mol⁻¹ for Co(II), Mn(II) and Zn(II) complexes respectively, indicating non electrolytic nature of the complexes as reported by Dhivya *et al.*, 2012. The values obtained from magnetic susceptibility measurement of the Co(II) and Mn(II) complexes at room temperature shows that the complex is paramagnetic due to positive values, while Zn(II) complex is diamagnetic due negative value. (Table 4)

All the complexes were found to be hydrated due to the presence of broad peak around 3108cm⁻¹ in the IR spectra of the complexes, indicating water of hydration. (Table 5) shows the percentage of water of crystallization in the complexes. where Mn(II) complex was found to be 4.2%, Co(II) complex 7.3% and Zn(II) 5.1%. Jobs method of continuous variation was used to confirm the metal ligand reacting ratio. From the Job's plot giving in figures 1,2 and 3, the number of coordinated ligand was determined which indicate a 1:2 metal ligand ratio for the two metal complexes.

Table 6 shows the important IR bands in the ligand and its complexes. The IR spectrum of the ligand does not exhibit any band corresponding to a free primary diamine or a free keto group which suggest the complete condensation of the amino groups with the keto groups. The ligand showed absorption peak at 1608cm^{-1} that is assignable to azomethine and confirms the formation of the ligand. Upon complexation, the peak shifted towards the frequencies of 1707cm^{-1} , 1707cm^{-1} and 1707cm^{-1} for Co(II), Mn(II), and Zn(II) complexes respectively.

Aromatic $\nu(\text{C}=\text{C})$ value appears around 1608cm^{-1} which shifted to 1637cm^{-1} in Co (II), 1637cm^{-1} in Mn (II), and 1687cm^{-1} in Zn (II) complexes respectively. In the case of metal complexes, the appearance of bands in the region of $739\text{-}748\text{ cm}^{-1}$ and $648\text{-}683\text{ cm}^{-1}$ corresponds to the M-N and M-O vibrational frequencies respectively. And also 739 cm^{-1} and 748 cm^{-1} which were absent in the spectra of the ligand indicates the metal to nitrogen bond (Bharat *et al.*, 2015). Similarly 648cm^{-1} and 683cm^{-1} which were also not found in the spectra of the ligand indicates the coordination of the diamine to the respective metal ions.

The broad band in the region $3108\text{-}3048\text{cm}^{-1}$ is accorded to $\nu(\text{O}-\text{H})$ stretching vibrations, a feature indicating the presence of water of coordination in the complexes.

Table 1: Physical properties of Ligand and its metal (II) Complexes

| Compounds | Colour | Percentage Yield | Melting Point | Decomposition Temperature |
|---------------------|--------|------------------|---------------|---------------------------|
| Ligand | White | 82 | 135 | |
| [CoL ₂] | White | 71 | – | 188 |
| [MnL ₂] | Dark | 66 | – | 201 |
| [ZnL ₂] | White | 72 | – | 214 |

Where; L= C₂₈H₁₈N₂O₂ M.P = Melting Point, D. Temp.= Decomposition Temperature

Table 2: Solubility Test of Schiff base Ligand and its Metal Complexes

| Complexes | Distilled water | Ethanol | Methanol | Acetone | Chloroform | DMF | DMSO |
|---------------------|-----------------|---------|----------|---------|------------|-----|------|
| Ligand | IS | S | SS | SS | IS | S | S |
| [CuL ₂] | IS | S | S | IS | IS | S | S |
| [MnL ₂] | IS | S | S | IS | IS | S | S |
| [ZnL ₂] | IS | S | S | IS | IS | S | S |

L= C₂₈H₁₈N₂O₂

KEY: S – Soluble

IS – Insoluble

SS – Slightly Soluble

Table 3: Conductivity Measurement Data of 10⁻³ M Metal(II) Complexes in DMSO

| Complexes | Electrical Conductivity (ohm ⁻¹ cm ⁻¹)×10 ⁻⁶ | Molar Conductance (ohm ⁻¹ cm ² mol ⁻¹) |
|---------------------|---|---|
| [CoL ₂] | 19.82×10^{-6} | 6.60 |
| [MnL ₂] | 14.20×10^{-6} | 4.73 |
| [ZnL ₂] | 10.28×10^{-6} | 3.42 |

L= C₂₈H₁₈N₂O₂

Table 4: Magnetic susceptibility Measurement of the complexes

| Complex | X _g (ergG ⁻² g ⁻¹) | X _m (ergG ⁻² mol ⁻¹) | μ _{eff} (B.M) |
|---------------------|--|--|------------------------|
| [CoL ₂] | 3.137×10^{-10} | 2.726×10^{-8} | 3.7 |
| [MnL ₂] | 3.08×10^{-11} | 2.676×10^{-8} | 4.9 |
| [ZnL ₂] | -4.218×10^{-10} | -3.667×10^{-7} | - |

Table 5: Percentage of Water of Crystallization

| Complexes | initial weight (g) | weight loss (g) | %water of crystallization |
|-----------------|--------------------|-----------------|---------------------------|
| Co (ii) Complex | 0.3 | 0.022 | 7.3 |
| Mn (ii) Complex | 0.3 | 0.014 | 4.2 |
| Zn (ii) Complex | 0.3 | 0.016 | 5.1 |

Table 6: Selected infrared spectral data of the Schiff base and its metal (ii) complexes

| Compound | u(OH) cm ⁻¹ | u(C=N) cm ⁻¹ | u(C-N)cm ⁻¹ | u(M- N)cm ⁻¹ | u(M-Cl)cm ⁻¹ |
|---------------------|------------------------|-------------------------|------------------------|-------------------------|-------------------------|
| Ligand | 3108 | 1608 | 1443 | - | - |
| [CoL ₂] | 3082 | 1707 | 1451 | 743 | 683 |
| [MnL ₂] | 3048 | 1707 | 1424 | 743 | 648 |
| [ZnL ₂] | 3108 | 1707 | 1383 | 739 | 683 |

The antimicrobial activity of the Schiff base and its metal complexes were tested against bacterial strains (*Staphylococcus aureus* and *Escherichia coli*) and fungal isolates (*Candida Albican* and *Aspergillus flavus*). The diameter of the inhibition zones were measured and recorded as shown in Table 7 and 8. The results of the tests indicated moderate antimicrobial activity against the tested microorganisms when compared with the standards (Ciprofloxacin and Ketoconazole), and this activity decreases with decreasing concentration. And also the metal complexes showed higher activity than free ligand, due to the effect of metal ions on the normal metabolic function of the cell.

Table 7: Antibacterial Screening of the ligand and its complexes

| Complexes | Concentration (ug/ml)/ Zone of inhibition (mm) | | | | | | | |
|---------------------|--|----|----|------|-------------------------|----|----|------|
| | <i>Staphylococcus Aureus</i> | | | | <i>Escherichia Coli</i> | | | |
| | 100 | 50 | 25 | 12.5 | 100 | 50 | 25 | 12.5 |
| Ligand | 17 | 15 | 12 | 10 | 20 | 16 | 11 | 9 |
| [CoL ₂] | 22 | 18 | 15 | 13 | 18 | 16 | 13 | 11 |
| [MnL ₂] | 25 | 22 | 19 | 16 | 20 | 19 | 17 | 14 |
| [ZnL ₂] | 17 | 15 | 11 | 10 | 19 | 16 | 14 | 9 |
| Standard | 30 | | | | 28 | | | |

L = Ligand, C₂₈H₁₈N₂O₂

Standard = Ciprofloxacin

Table 8: Antifungal sensitivity test of the Schiff base and its metal (ii) complexes

| Complexes | Concentration (ug/ml)/ Zone of inhibition (mm) | | | | | | | |
|---------------------|--|----|----|------|------------------------------|----|----|------|
| | <i>Candida Albican</i> | | | | <i>Aspergillus fumigatus</i> | | | |
| | 100 | 50 | 25 | 12.5 | 100 | 50 | 25 | 12.5 |
| Ligand | 24 | 21 | 18 | 14 | 20 | 16 | 11 | 9 |
| [CoL ₂] | 19 | 16 | 14 | 10 | 18 | 14 | 11 | 9 |
| [MnL ₂] | 23 | 20 | 18 | 15 | 22 | 19 | 16 | 12 |
| [ZnL ₂] | 16 | 17 | 10 | 8 | 18 | 15 | 12 | 10 |
| Standard | 35 | | | | 34 | | | |

L = Ligand, C₂₈H₁₈N₂O₂

Standard = Ketoconazole

4. CONCLUSION

The Schiff base and its metal complexes of Mn(II), Co(II), and Zn(II) have been synthesized and studied by various analytical techniques. Job's method of Continuous variation shows that the metal-ligand ratio in all the complexes is 1:2. All the complexes are non-electrolytes in DMSO solvent. The decomposition temperature of the metal (II) complexes

indicated that complexation has taken place. Based on magnetic susceptibility data, Mn(II) and Co(II) Schiff base complexes are paramagnetic while Zn(II) complex is diamagnetic. The antimicrobial studies of the Schiff base and its metal(II) complexes reveals that the metal(II) complexes show better activity when compared to that of the ligand.

Based on the analytical and spectral studies, we propose octahedral geometry to all the complexes.

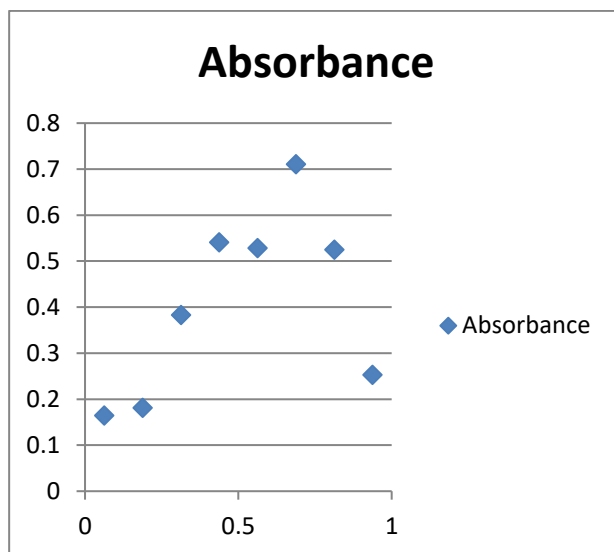


Fig.1: Zn²⁺ ion absorbance against mole fraction.

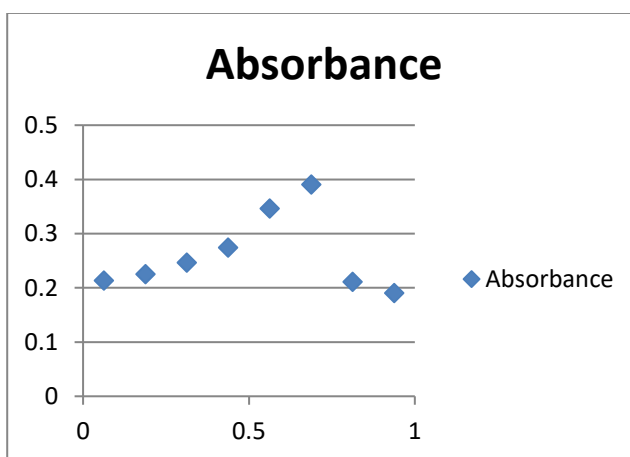


Fig. 2: Co²⁺ ion absorbance against mole fraction

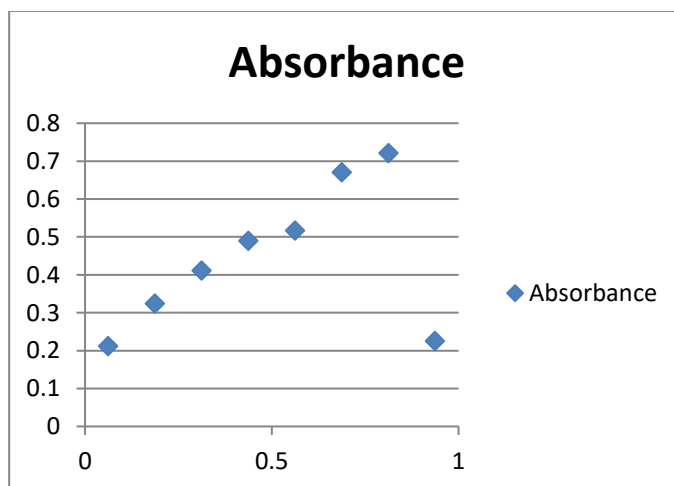
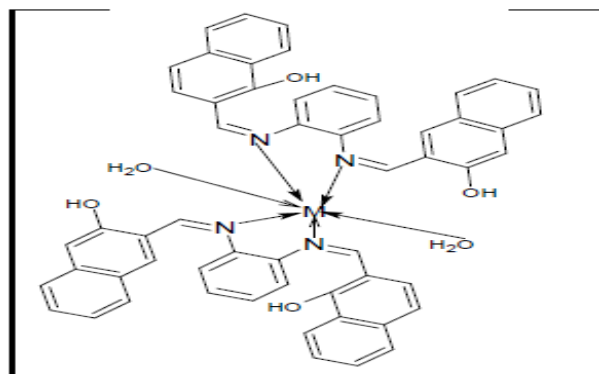


Fig.3: Mn²⁺ ion absorbance against mole fraction



Proposed Structure of the complexes.
M= Co, Mn, and Zn.

REFERENCES

- [1] Bharat, A M, Pratik, N. D and Pratik, B. T (2015).Synthesis of Schiff base and their transition metal complexes, characterization and application.*International Journal of Science, Technology and Management*, 04(1):642-652.
- [2] Dhivya, D.P., Akila, E., Usharani, M. and Rajavel, R. (2012). Synthesis spectra and biological activity of mixed ligand Schiff base complexes derived from salicylaldehyde. *Internal journal of pharmacy & Technology*. 4(1): 4067-4078.
- [3] Dr. Nagham Mahmood Aljamali, Mohammed Alaa Abdulzahra, Dr.Mithaq Saeed Mohamad,
- [4] Widad Hashim Yahya Almuhana, Muna Abbas Hadi. (2019) International Journal of Innovations in Scientific Engineering. Review on Phenylene diamine (Preparation, Reactions,Biological Applications, Bio-Uses).
- [5] Jayamani A, Thamilarasan V, Sengottuvelan N, Manisankar P, Kang SK, et al. (2014) Synthesis of mononuclear copper(II) complexes of acyclic Schiff's base ligands: spectral, structural, electrochemical, antibacterial, DNA binding and cleavage activity. *Spectrochim Acta A Mol Biomol Spectrosc* 122: 365-374.
- [6] Khan, S,A, Asiri, A.M., Kumar, S. and Sharma, K. (2014). Green synthesis, antimicrobial activity and computational study of Pyrazoline Pyrimidine derivatives from 3(3,4-dimethoxyphenyl-1-(2,5-dimethylthiophen-3- yl)-propenone. *European Journal of Chemistry*,5:85-90.
- [7] Kawkab, A. and Al-Ali, H. (2010). Synthesis, characterization and study of electrical properties of Fe(III) and Al(III) of Schiff base. *Journal of inorganic chemistry* 2(3):1-11
- [8] Mohamed, G.G., Omar, M.M. and Hindy, A.M. (2006). Metal Complexes of Schiff Bases: Preparation, Characterization, and Biological