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Original Article

Synthesis, characterization and antimicrobial studies on Mn(II), Fe(II), Co(II) complexes of schiff base derived from 3-Formylchromone and Benzohydrazide

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ABSTRACT

Schiff base formed by condensation of 3-formylchromone and benzohyrazide and its metal(II) complexes of Mn(II), Fe(II), and Co(II), have been prepared and characterized by conductivity measurement, magnetic susceptibility, IR Spectra, atomic absorption spectroscopy, elemental analysis, as well as melting point/decomposition temperature and solubility test. The melting point of the Schiff base (165 ^{0}C) and decomposition temperatures of the complexes (185-198)^{0}C indicating their thermal stability. The molar conductivity measurement determined are in the range (10.54-23.10) $\Omega^{-1}cm^{2}mol^{-1}$ revealing that all the complexes are non-electrolytic in nature. IR spectra of the Schiff base showed a band at 1633cm^{-1} which assigned to ʋ(-C=N-) stretching vibration. This band was observed downfield in the range (1603 -1655) cm^{-1} in the spectra of the metal(II) complexes revealing that the Schiff base formed metal complexes with the metal ions. The gram magnetic susceptibility measurements of the complexes showed that all the complexes except that of Zinc are paramagnetic and have tetrahedral geometry. The elemental analysis suggested a metal to ligand ratio of 1:1. The Schiff base and its metal complexes have been screened for their antimicrobial activity against four pathogens. Some compounds were active, while others are not active against the isolates

1. Introduction

Schiff bases were discovered by a German chemist, Hugo Schiff in 1864 [1]. Schiff bases are versatile ligands which are synthesized from the condensation of a primary amine with carbonyl compounds [2]. The oxygen atom in the carbonyl group (>C=O) is replaced by a nitrogen atom to give an imine group (>C=NR where R≠ H). In this definition, Schiff base is synonymous with azomethine, although some restrict the term to secondary aldimines in which the carbon atom is bonded to hydrogen [3]. The Schiff bases of aliphatic aldehydes are relatively unstable and can readily be polymerized, while those of aromatic aldehyde, having an effective conjugation system, are more stable [4]. They are widely used for industrial purposes and also exhibit a broad range of biological activities. Aromatic aldehydes and aliphatic or aromatic ketones give stable azomethine moiety. So far, modifications of the Schiff bases have proven highly efficient with improved potency and lesser toxicity [5]. In a broad sense, Schiff bases have the general formula ($R^1R^2C=NR^3$) where R^1, R^2 and R^3 are alkyl, aryl, cycloalkyl or heterocyclic groups while R3 cannot be. Schiff bases may act as mono-, di-, tri-, or tetra dentate ligands depending on the number of coordinating atoms present in the molecule and can form generally five or six -membered chelate rings upon reaction with a metal ion [6]. Moreover, If they contain additional functional groups like –OH, –NH_2 or –SH, the resulting Schiff bases

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can serve as mixed-donor ligands that can participate in bi-, tri-, tetra- and higher coordination modes [7]. Transition metal Schiff base complex compounds are well known for almost two centuries; for example, Ettling in 1840 as cited in [8] isolated a dark green crystalline product from the reaction of cupric acetate, salicyladehyde and aqueous ammonia. However, there was no comprehensive and systematic study until when Pfeiffer and associates in 1931 as cited in [9], reported a series of complexes derived from Schiff bases of salicylaldehyde and its substitution products.Transition metals are known to form Schiff base complexes; this is because the Schiff base possesses a lone pair of an electron that can donate to the empty orbital of the transition metal. These metals are involved in many biological processes which are essential to life processes. The metals can coordinate with O or N-terminals from proteins in a variety of models and play a crucial role in the conformation and function of biological macromolecules [10]. Transition metal centers are particularly attractive moieties for reversible recognition of nucleic acids research because they exhibit well-defined coordination geometries. Besides, they often show distinct electrochemical or photo physical properties, thereby increasing the functionality of the binding agent [7]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications [11]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions [12]. In this study the Schiff base of 3-formylchromonehydrazide was synthesized from 3-formylchromone and benzohydrazide and its metal(II) complexes were prepared. The Schiff base and metal complexes were further characterized and their antibacterial and antifungal effect was also determined.

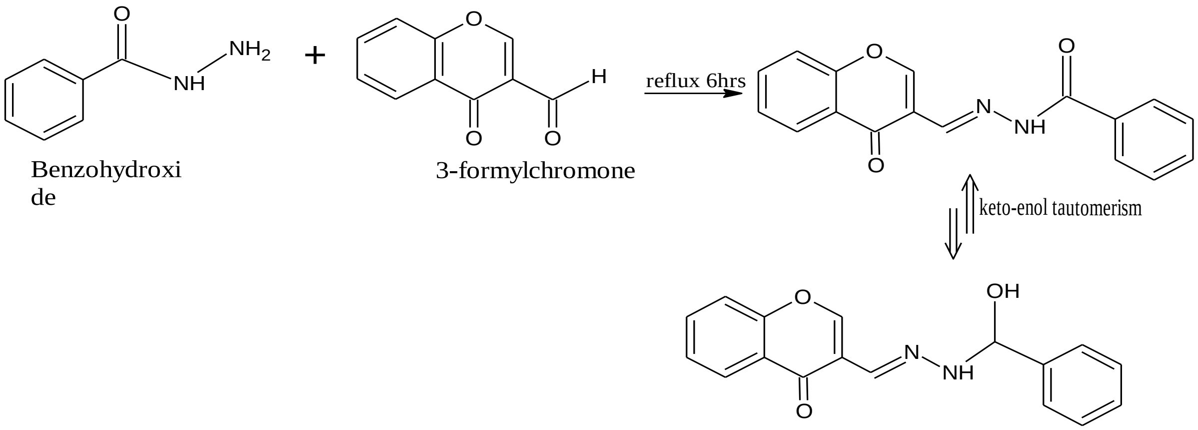
2. Material and Methods

2.1 Chemicals, Reagents and Apparatus

All reagents used in this work were of analytical grade and were used without further purification. All weighing was carried out on an electric Metler balance model H_3OAR. All glass wares were washed thoroughly with detergent and rinsed thoroughly with distilled water and dried in an oven at 110°C before use.

2.2 Synthesis of the Schiff base Ligand

The ligand was prepared according to the adopted method of Jessica *et al*. [14] Benzohydrazides (25.0 mmol, 3.404g), 3-formylchromone (25.0 mmol, 4.354g), and a few drops of acetic acid were dissolved in 50 mL of ethanol, and the mixture was stirred and refluxed for 6 h. The resulting mixture was collected and cooled on ice-cold water, then it was concentrated and dried in dried in a desiccator over $CaCl_2$ for a week [13].



Scheme 1: Synthetic pathway of the ligand.

2.3 Synthesis of the metal (II) Schiff Base Complexes

About 20 mmol of metal (II) salt dissolved in $50cm^3$ methanol was added gradually to 20 mmol(5.842g) of the ligand, dissolved in DMF. The reaction mixture was heated under reflux for 8 hours. The resulting precipitates were filtered, washed with methanol and hexane then diethyl ether and finally air-dried. The complexes were kept in desiccators over anhydrous calcium chloride [13].

2.4 Physical measurements

IR spectra of the Schiff base and its metal complexes were recorded on FTIR Carry Agilent Technologies model 630 spectrophotometer at 4000 - 650 cm^{-1} region in KBr powder. C, H and N were estimated by using elemental analyzer Perkin-Elmer model 240. Jenway 4010 conductivity meter was used in conductivity measurement using DMSO as solvent. SMP10 STUART melting point apparatus was used to obtained Melting point and decomposition temperature. Magnetic measurements of the complexes were performed on Gouy's balance at room temperature.

2.5 Antibacterial and Antifungal Test

The synthesized ligand and their metal complexes were screened for antimicrobial activity against the following isolates*; Staphylococcus aureus, Escherichia coli, Candida albican and Aspergillusfluvus*. A double dilution formula was used to make concentrations of 4000µg/ml, 2000µg/ml, 1000µg/ml and 500µg/ml. A sterilized forcep was then used to place the prepared disc of the ligand and complexes on the already inoculated agar plate at various interval and then inoculated at 37^{o}C for 24 hrs for bacteria and 48 hrs for fungi [15]. The inhibition zone of the ligand and complexes were then measured (in diameter) around the disc and compared with the standard. (Amoxicilin capsule and Nystatin drug for bacteria and fungi respectively).

3. Results and Discussion

3.1. Physical Properties of the Schiff base and its Metal (II) Complexes

The Schiff base and its metal (II) complexes were prepared in good yield, the physical properties of the synthesized Schiff base and its metal complexes were analyzed and presented in table 1. The percentage yield of the Schiff base was 92 % while that of the complexes were 89, 78 and 80 %. The Schiff base was pale yellow crystal while the Mn(II), Fe(II) and Co(II) complexes were dark brown, dark green and green respectively. It was found that the melting point of the Schiff base is 165^{O}C and the decomposition temperature of the metal (II) complexes are 190, 185 and 198^{O}C, this is an indication of thermal stability. The molar conductance of the metal complexes are 10.54, 17.40 and 23.10 $\Omega^{-1}cm^{2}mol^{-1}$ for Mn(II), Fe(II) and Co(II) complexes. These low values of their molar conductance due to their non-electrolytic nature as reported by [16]. The effective magnetic moments of the complexes were also calculated. The magnetic moment of Mn(II), Fe(II) and Co(II) complexes are 5.9, 5.3, 4.1 B.M, indicate that all the complexes are paramagnetic in nature [17].

Table 1: Physical Properties of the Schiff base and its Metal (II) Complexes

Compounds	**Colour**	**% yield**	**M.P (^{O}C)**	**D. Temp (^{O}C)**	(B.M.)	**M.L(Ω^{-1} cm^{2} mol^{-1})**
Ligand	paleYellow	92	165	-	-	-
MnL(H_2O)(oAc)].5H_2O	Dark brown	89	-	190	5.9	10.54
[FeL(H_2O)(oAc)].4H_2O	Dark green	78	-	185	5.3	17.40
[CoL(H_2O)(oAc)].H_2O	Green	80		198	4.1	23.10

3.2. Solubility Test

Water and some common organic solvents were used to determine the solubility of the Schiff base and its metal (II) complexes. From the result of solubility test presented in table 2, it can be seen that, the Schiff base and its metal complexes were soluble in dimethylsulfoxide (DMSO) and Methanol, slightly soluble in ethanol and (DMF) and insoluble in petroleum ether and water.

Table 2: Solubility test of the Schiff base and its metal (II) complexes

Compound	Water	Ethanol	methanol	CCl_4	DMF	DMSO	Chloroform	P.Ether
Ligand	IS	S	S	IS	SS	S	SS	IS
[MnL(H_2O)(oAc)].5H_2O	IS	SS	S	IS	S	S	SS	IS
[FeL(H_2O)(oAc)].4H_2O	IS	SS	S	SS	SS	S	IS	IS
[CoL(H_2O)(oAc)].H_2O	IS	SS	S	SS	SS	S	S	IS

3.3 Elemental Analysis

The elemental analysis of the Schiff base and its metal (II) complexes were determined and presented in table 3. The calculated and excremental values were found to be in good agreement. The elemental analysis data of the Schiff base suggested the formation of $C_{17}H_{12}N_2O_3$, while that of the complexes revealed the formation of [MnL(H_2O)(oAc)].5H_2O, [FeL(H_2O)(oAc)].4H_2O and [CoL(H_2O)(oAc)].H_2O. The complexes are formed in 1:1 metal-ligand ratio. It also revealed the presence of acetate ion as a ligand.

Table 3. Elemental Analysis Data of the Schiff base and its Metal (II) Complexes

Compound	C Excremental (calculated)	H Excremental (calculated)	N Excremental (calculated)
Ligand	70.36 (69.86)	4.06 (4.14)	9.66 (9.58)
$[MnL(H_2O)(oAc)].5H_2O$	43.21 (44.45)	4.04 (5.10)	6.59 (5.46)
$[FeL(H_2O)(oAc)].4H_2O$	38.47 (45.99)	3.70 (4.87)	7.30 (5.65)
$[CoL(H_2O)(oAc)].H_2O$	49.16 (51.25)	3.43 (4.07)	7.56 (6.29)

3.4 FTIR Analysis

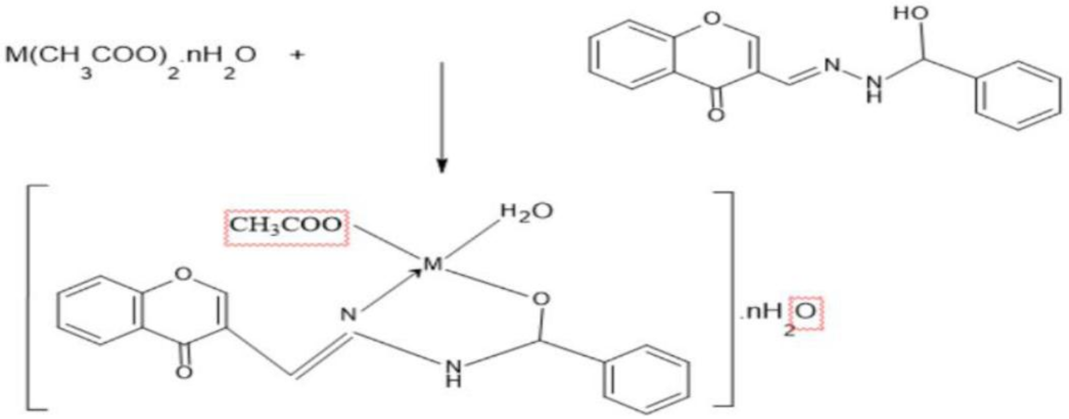
The FTIR spectral data of the ligand showed a band at 1633cm^{-1}, which is assigned to v(C=N) stretching vibration, this band was observed downfield in the range (1581-1655)cm^{-1} in the complexes compounds, which indicated the involvement of the –C=N of the ligand in coordination to the metal ions [18]. Furthermore, the spectra of M (II) complexes showed bands in the range (3204 – 3365)cm^{-1} which are assigned to v(OH) stretching frequencies, suggesting that they have water of crystallization[19]. The bands in the spectra of the complexes in the ranges (638-768)cm^{-1} and (444 - 519)cm^{-1}. Are attributed to v(M-N) and v(M-O) stretching frequencies respectively, indicating coordination of the Schiff base to the respective metal ions [20]. Additional band in the range (816-969)cm^{-1} was also observed in the complexes which were assigned to coordinated water [21].

Table 4. Infrared spectral data of the Schiff base and its metal (II) complexes

Compound	υ(C=N)cm-1	υ(M-N)cm-1	υ(M-O)cm-1	υ(OH/H2O) cm-1	υ(OH) cm-1
Ligand	1633	-	-	-	
[MnL(H2O)(oAc)].5H2O	1655	712	504	3204	816
[FeL(H2O)(oAc)].4H2O	1618	757	444	3212	905
[CoL(H2O)(oAc)].H2O	1603	768	519	3365	868

3.4 Antimicrobial and antifungal Activity

Activity was determined by measuring the diameter (mm) of zones Inhibition (IZ) showing complete inhibition. In order to clarify any participating role of DMSO as control in the biological screening, separate studies were carried out with the solutions alone of DMSO and they showed no activity against any bacterial strains. In vitro *antifungal* activity of all the compounds was studied [22, 23]. The result of antimicrobial activity of the Schiff base and its metal complexes is presented in table 5. The Schiff base and its metal (II) complexes were screened for their antibacterial activities against the selected bacteria isolates of *Staphylococcus aureus* and *Eschirichia coli* by disc diffusion method. It was found that metal complexes have more effect in inhibiting the microbial growth. This may be due to the interaction of the metal complexes with lipoproteins of the cell. Therefore the metal complexes may restrict the normal functioning of the microbial cell. Furthermore, their higher stability at higher temperature may also allow to use them as a potential antimicrobial agent. Similar result was also recorded in table 6 for antifungal activity shown by selected fungi isolates of *Aspergillus fluvus,* and *Candida albican*.



Scheme 2: Structure of complexes. M=Mn(II),Fe (II),Co (II)

Table 5. Antibacterial activity on the schiff base and its metal (II) complexes

Isolates	Compound	Zone of Inhibition (mm)/Concentration (μg/cm^3)				Control(mm)Amoxicillin 500mg
		4000	2000	1000	500	
Staphylococcus aureus	Ligand	15	12	9	-	31
	$[MnL(H_2O)(oAc)].5H_2O$	15	12	10	8	
	$[FeL(H_2O)(oAc)].4H_2O$	19	16	14	9	
	$[CoL(H_2O)(oAc)].H_2O$	18	15	13	9	
Escherichia coli	Ligand	10	8	-	-	26
	$[MnL(H_2O)(oAc)].5H_2O$	13	12	9	-	
	$[FeL(H_2O)(oAc)].4H_2O$	12	9	8	-	
	$[CoL(H_2O)(oAc)].H_2O$	14	13	9	-	

Table 6. Antifungal activity on the schiff base and its metal (II) complexes

Isolates	Compound	Zone of Inhibition (mm)/Concentration (μg/cm^3)				Control(mm) Nystatin 200mg
		4000	2000	1000	500	
Candida albicans	Ligand	14	12	10	8	30
	$[MnL(H_2O)(oAc)].5H_2O$	16	12	10	8	
	$[FeL(H_2O)(oAc)].4H_2O$	15	12	9	-	
	$[CoL(H_2O)(oAc)].H_2O$	21	19	16	14	
Aspergillusfluvus	Ligand	16	12	8	-	40
	$[MnL(H_2O)(oAc)].5H_2O$	17	15	13	10	
	$[FeL(H_2O)(oAc)].4H_2O$	20	17	14	11	
	$[CoL(H_2O)(oAc)].H_2O$	20	16	14	10	

4. Conclusion

The Schiff base and its metal (II) complexes were synthesized and characterized. The non-electrolytic nature of the complexes were revealed by conductivity measurement data. The elemental analysis data suggest 1:1 metal to ligand ratio. The infrared data indicated that the Schiff base ligand was coordinated to the central metal ion via the azomethine nitrogen and phenolic oxygen atoms after deprotonation. The solubility tests carried out showed that the ligand and both of its metal (II) complexes were soluble in methanol and dimethylsulphoxide, slightly soluble in dimethylformamide and ethanol and insoluble in water and petroleum ether. The ligand and its metal (II) complexes were tested for antimicrobial and antifungal activity against some bacteria and fungi isolates. Both of the complexes were found to be more active against the bacteria *and* fungi than the Schiff base. From the analytical and spectral data, it can be concluded that the synthesized complexes are stable with probably following structures. Scheme 2:

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5. Supplemented data

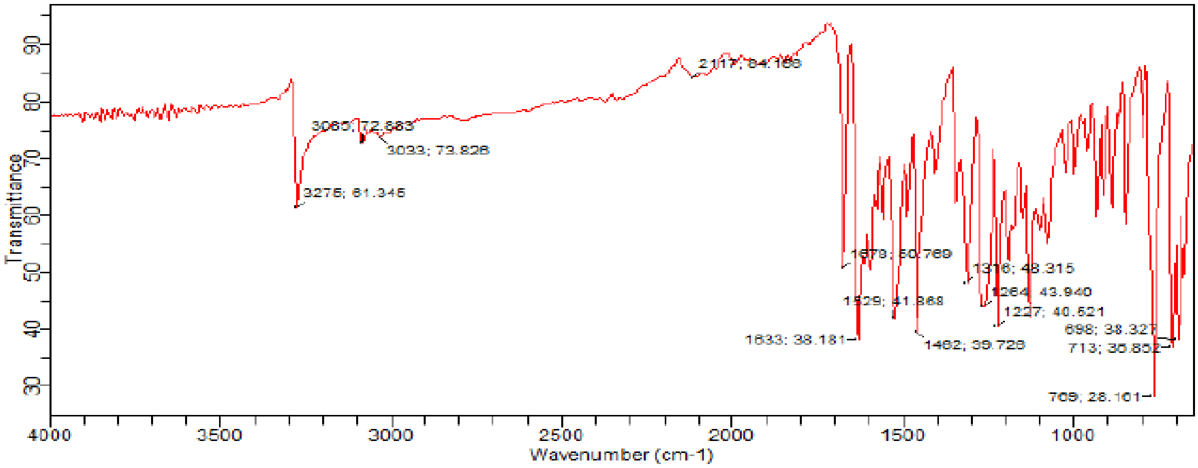

Fig. 1 FTIR of the 3-formylchromonehydrazone

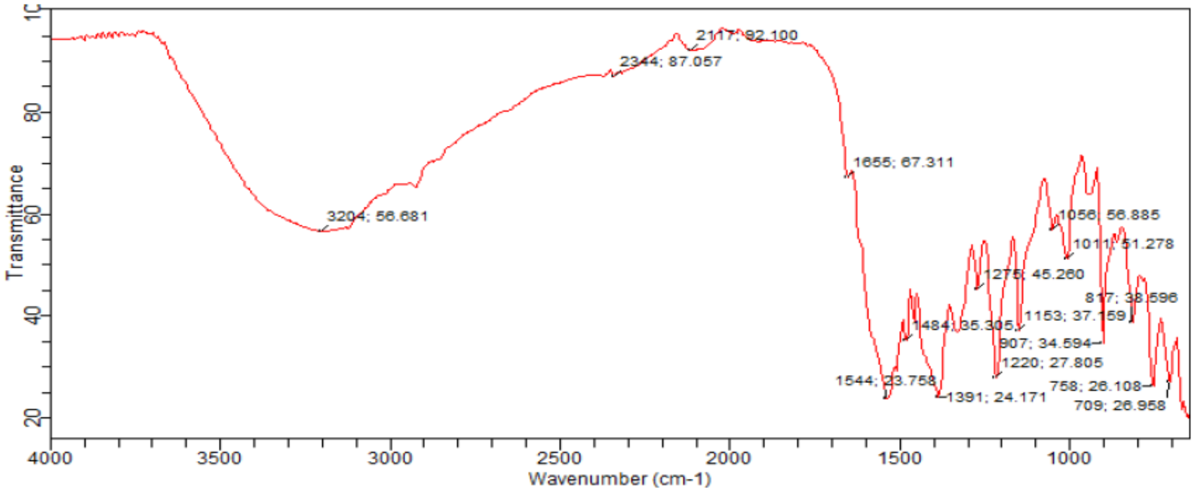

Fig 2. FTIR of Mn (II) complex

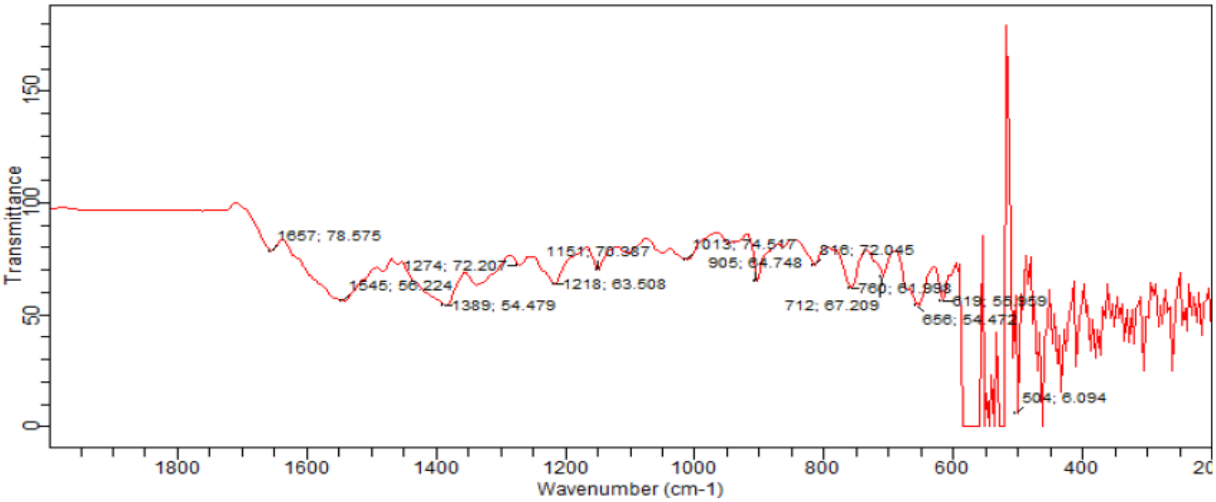

Fig 3. Lower region FTIR of Mn(II) complex

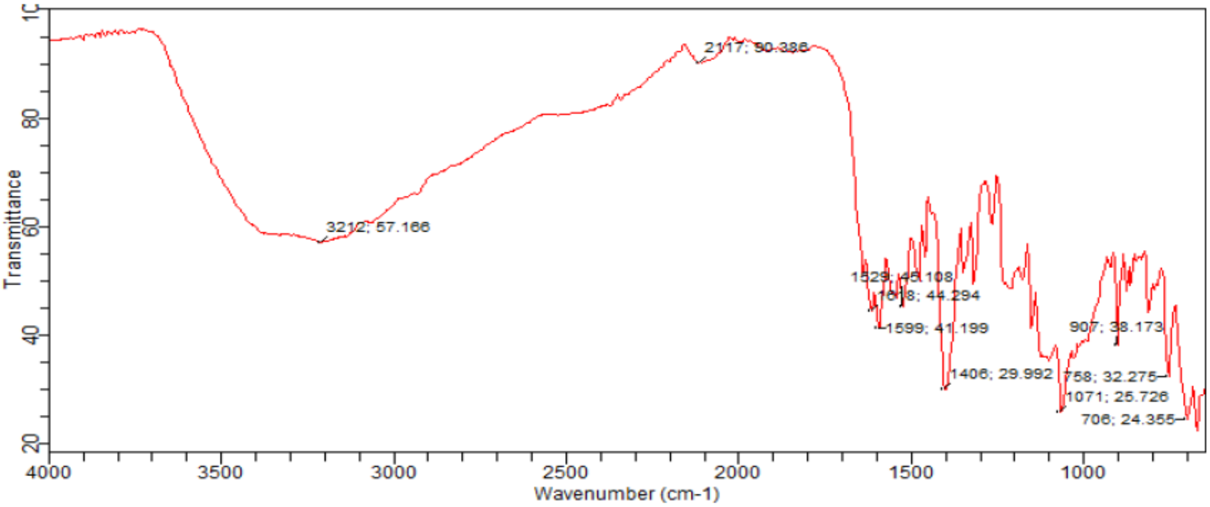

Fig 4. FTIR of Fe (II) complex

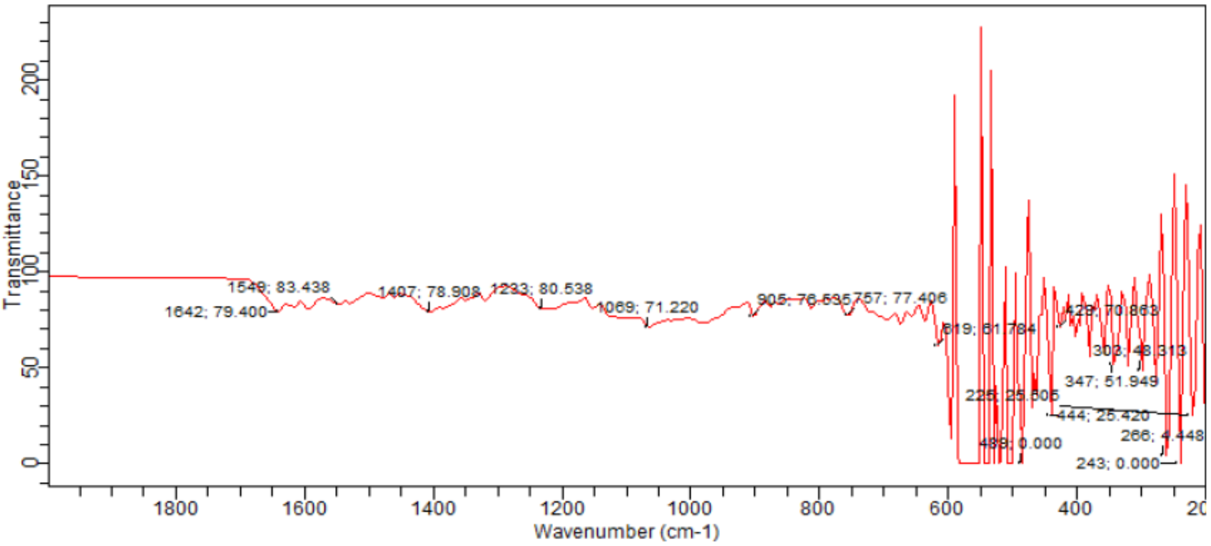

Fig 5. Lower region FTIR of Fe(II) complex

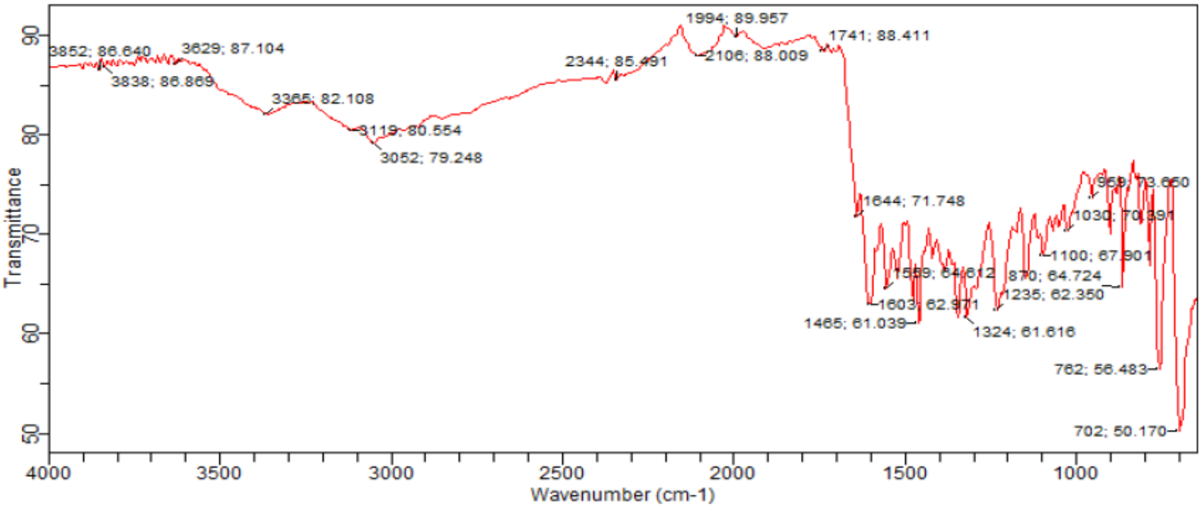

Fig 6. FTIR of Co (II) complex

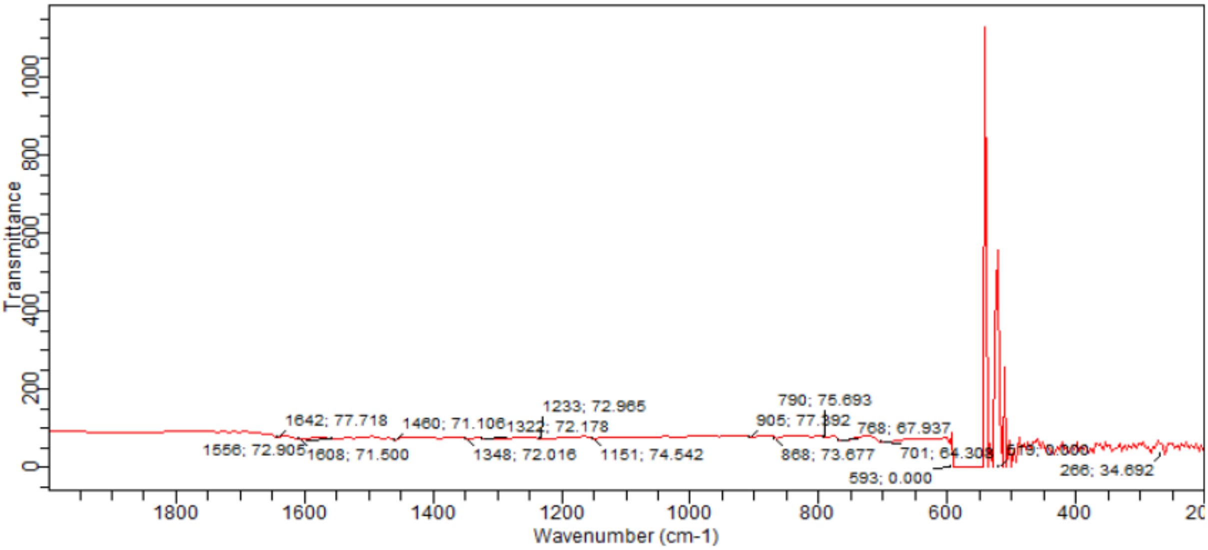

Fig 7. Lower region FTIR of Co (II) complex