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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF METAL(II) COMPLEXES WITH SCHIFF BASE DERIVED FROM 2-AMINOPHENOL AND 2-HYDROXY-6-METHOXY-3-QUINLINECARBOXALDEHYDE

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ABSTRACT
Schiff base derived from 2-aminophenol and 2-hydroxy-6-methoxy-3-quinolinecarboxaldehyde and its Co(II) and Ni(II) complexes were synthesized and characterized by elemental analysis, melting point and decomposition temperature, molar conductivity, IR spectral analysis, AAS analysis, solubility test, and magnetic susceptibility. The FTIR spectral data of the Schiff base determined showed a band at 1622cm^{-1} which was assigned to the v(C=N), a feature of azomethine group. The same band was observed to shift to lower frequencies 1577 and 1599cm^{-1} in the complexes suggesting coordination of the Schiff base with the respective metal (II) ions. Molar conductance values 14.58 and 12.65Ω^{-1}cm^{2}mol^{-1}show that the metal complexes were non-electrolytic in nature. The magnetic susceptibility of the complexes were determined and the gram magnetic susceptibility of the complexes were found to be positive, revealing that they are paramagnetic. The elemental analysis of the complexes for C, N and H determined suggested (1:1) metal to ligand ratio. The result of the antimicrobial studies showed that, the metal (II) complexes exhibited higher antibacterial and antifungal activity than the Schiff base but lower than the reference drugs *Amoxicillin* and *Ketoconazole* used as control in all cases.

Keywords: Schiff base ligand, complex, antibacterial and antifungal studies

INTRODUCTION

Schiff base is a compound containing an imine or azomithine group, (-N=CH-). It is a condensation product of aldehyde or ketone with primary amine and was first reported in 1864by a German chemist Hugo Schiff (liyu, 2018; Yahyazadeh, 2013).Schiff base is a very important structure for synthetic organic chemistry.These compounds are usually characterized by an imine functional group (–N=CH-), that helps us to clarify the mechanism, racemization and transamination interaction in biological system (Chaudry, 2012). Azomithune nitrogen in the Schiff base, is of considerable chemical and biological importance, not only provides binding sites for metal ions but also makes attachments with various substrate of bio-molecules like proteins and amino acids in biological systems and that of diseases-causing germs (Chaudary, 2012) These compounds play an important role in medicinal fields because of their wide spectrum of biological activities. Many of them have antimicrobial and anticancer effect as biologically important compounds (Zoubi, 2013). A part from their biological effect, they are used in many fields such as pigments, dyes, fungicidal, corrosion inhibitors, analytical chemistry, polymer stabilizers, agrochemical, ion exchange, electrical conductivity catalysis, nonlinear optics and magnetism (Emriye, 2016; Arulmurugan *et al.*, 2010). Schiff base is changeable molecule and can be bi- or tridentate ligands capable of producing very stable complexes with transition metals like nickel, iron, cobalt, copper, vanadium etc (Aliyu, 2018) Most of the metal chelates have higher antibacterial and antifungal activities than the individual ligands(Emriye, 2016). The biological implementations and chelating ability of metal complexes have attracted a significant concern. Transition metal complexes have been widely studied due to their various biological applications in pharmacological areas. These complexes were reported to have antitumor, anti-inflammatory, antioxidan, antimalarial, andantimicrobial activities (Savithra and Revanasiddappa, 2018; Qin *et al.*, 013; Wang, *et al*., 2012). Metal complexes with N, O as their donor atoms are very noticeable because of their important biological activities like anticancer, and herbicidal activity. In this study the schiff base of 3-[(2-hydroxy-phenylimino)-methyl]-6-methoxy -quinolin2-ol was synthesized from 2-aminophenol and 2-hydroxy-6-methoxy-3-quinlinecarboxaldehyde and its divalent metal complexes were prepared. The ligand and metal complexes were further characterized and their antimicrobial activity was also determined.

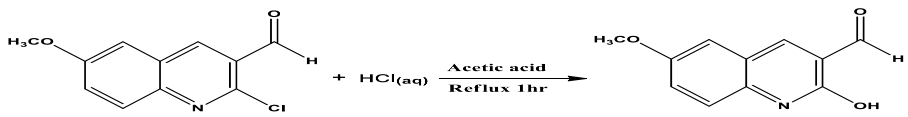
MATERIALS AND METHODS

Chemicals, Reagents and Apparatus

All the reagents and chemicals used in this research work were of analytical grade and used without further purification. All weighing were carried out using an electric balance model AB54. The IR spectral analysis was recorded using Cary 630 FTIR Agilent Technologies. Conductivity measurement was carried out in DMSO solvent using Jenway 4010 conductivity meter. Melting point and decomposition temperature measurements were obtained with a SMP10 STUART melting point apparatus. Elemental Analysis was conducted at Micro Analytical Centre OEA labs, United Kingdom, using CE Instrument (Thermo) EA1110 Elemental Analyser. The antimicrobial activity of ligand and metal complexes were tested *in vitro* against bacteria *taphylococcus, aureus,Escherichia coli* and *klebsiela pneumonia* by paper disc plate method and compared with known antibiotics,Gentamycin. For the fungicidal activity, compounds were screened *in vitro* against *Aspergillus fumigates, Aspergillus flavus* and *Aspergillus Niger* by the same method which compared with Ketaconazole. The antimicrobial activity studies were carried out at the Department of Microbiology, Bayero University, Kano.

Synthesis of the 2-hydroxy-6-methoxy-3-quinlinecarboxaldehyde

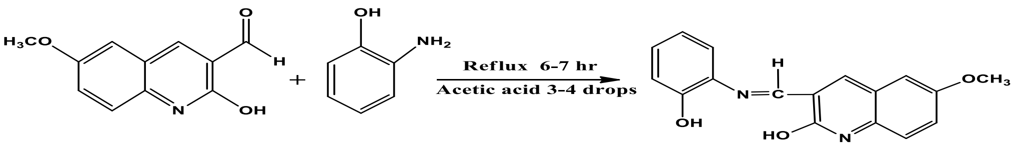
2-chloro-6-methoxy-3-quinolinecarboxaldehyde (2.4g, 0.01mol) was added to aqueous hydrochloric acid (35ml, 4mol) and the resulting solution was refluxed on water bath for about 1 hour. The resulting mixture was then cooled to room temperature. 2-hydroxy-6-methoxy-3-quinlinecarboxaldehyde was filtered, washed thoroughly with cold ethanol followed by diethyl ether into yellow cotton-like (Siddappa and Chandrakant, 2012).



Scheme 1: Synthesis of 2-hydroxy-6-methoxy-3-quinlinecarboxaldehyde

Synthesis of the Schiff base

The Schiff base was prepared by condensation of 2-hydroxy-6-methoxy-3-quinlinecarboxaldehyde (0.01mol) with 2-aminophenol (0.01mol) in ethanol and refluxing on water bath for six to seven (6–7) hours in the presence of a few drops of acetic acid. The reaction mixture was thereafter cooled to room temperature and then the ligand was filtered, washed thoroughly with cold ethanol followed by diethyl ether to get a pure sample (Siddappa and Reddy, 2012).



Scheme : Formation of 3-[(2-Hydroxy-phenylimino)-methyl]-6-methoxy -quinolin-2- ol

Preparation of the metal (II) Schiff Base Complexes

To the hot solution of 3-[(2-Hydroxy-phenylimino)-methyl]-6-methoxy -quinolin-2- ol(0.001mol) in ethanol (35ml), a hot ethanolic solution of respective metal (II) chlorides (0.001mol) in ethanol (15ml) was added. The resulting solution was refluxed on a water bath for 4 - 5 hours to get a clear solution. Excess sodium acetate (0.5g) was added to the reaction mixture to adjust the pH (7 to 8) of the solution and the refluxing was continued further for 2 hours. The resulting reaction mixture was then decomposed by pouring into distilled water (100ml) with constant stirring. A yellow complex was obtained. This was allowed to settle and separated out by filtration, washed with distilled water, then with hot ethanol and cold diethyl ether and dried in vacuum over phosphorus pentoxide (Siddappa and Reddy, 2012).

Antibacterial Activity Test

The method used by Jorgensen (Jorgensen, and Turnidge, 2003) was used in antibacterial test, in which the schiff base and its metal(II) complexes were assayed by ager disc diffusion method using cultures of *Escherichia coli, salmonella typhi and staphylococcus aureus*. The samples were separately dissolved in dimethylsulfoxide (DMSO) to have three different concentrations (1000, 2000 and 3000) µg/disc. Each of these was separately placed on the surface of the culture media before incubation at 37°C for 24 hrs. The diameter of zone of inhibition produced by the ligand and its metal(II)complexes was compared with the standard drug, amoxicillin capsule.

Antifungal Activity Test

The *in vitro* antifungal activity of the Schiff base and its Co(II) and Ni(II) complexes were assayed using three fungal isolates *Aspergillus flarus, Aspergillus niger* and *Mucor indicus* using different concentrations (1000, 2000 and 3000)µg/disc by Disc Diffusion Technique. Potato Dextrose Ager (PDA) was used to prepare the culture media and incubated at room temperature for seven days. The results obtained were compared with the activity of Ketoconazole (200mg) as a standard antifungal drug and DMSO as negative control (Jorgensen, 2003).

RESULTS AND DISCUSSION

Physical Properties of the Schiff Base and its Metal(II) Complexes

The Schiff base and its Co(II) and Ni(II) complexes were prepared in good yield, and their physical properties were analyzed and presented in table 1. The percentage yield of the Schiff base was 75 % while that of the complexes were 64 and 67 %. The Schiff base ligand was yellow cotton-like while the Co(II) and Ni(II) complexes were brown and green respectively. It was found that the melting point of the Schiff base was 251^{O}C and the decomposition temperatures of the metal(II) complexes were 275 and 281^{O}C, this is an indication of their thermal stability.

The Molar conductance of metal(II) complexes was carried out in DMSO by dissolving 0.001g of each sample in 10cm^3 of DMSO in a test-tube, the conductivity cell was immersed into each solution, and the result was recorded after allowing the reading to stabilize. All measurements were carried out at room temperature. Molar conductance values were 14.58 and 12.65 $\Omega^{-1}cm^2mol^{-1}$ for Co(II) and Ni(II) complexes. These low values suggest their non-electrolytic nature as reported by Eman (Eman, 2015) The effective magnetic moments values of 4.67and 3.35B.M show the paramagnetic nature of the complexes.

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

Compounds	Color	% yield	M.P. (^{O}C)	D. Temp (^{O}C)	μff (B.M.)	Molar Conductance ($\Omega^{-1}cm^2 mol^{-1}$)
L (Ligand)	Yellow	75	251	-	-	-
$[CoL(H_2O)_3].H_2O$	Brown	64	-	275	4.67	14.58
$[NiL(H_2O)_3].H_2O$	Green	67	-	281	3.35	12.65

Keys: M.P = Melting Point, D. Temp. = Decomposition temperature

Solubility Test

Some common organic solvents and water were used to determine the solubility of the Schiff baseand its metal(II) complexes. From the result of solubility test presented in table 2, the Schiff base and its metal(II) complexes were found to be soluble in dimethylsulfoxide and dimethylformamide, insoluble in hexane and water and slightly soluble in methanol. while the complexes are insoluble in acetone and CCl_4.

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

Compound	Solvents					
	Acetone	n-hexane	CCl_4	DMF	DMSO	Methanol	water
L (Ligand)	SS	IS	S	S	S	SS	IS
$[CoL(H_2O)_3].H_2O$	IS	IS	IS	S	S	SS	IS
$[NiL(H_2O)_3].H_2O$	IS	IS	IS	S	S	SS	IS

Keys: S = Soluble, SS = Slightly Soluble, and IS = Insoluble

Elemental Analysis

The elemental analysis values of the Schiff base and its metal (II) complexes for C, N and H determined, indicated that the stoichiometry of the complexes are 1:1 (metal to ligand ratio) and recorded in table 3. The elemental analysis data of the Schiff base suggested the formation of $C_{17}H_{14}N_2O_3$ while that of the complexes revealed the formation of $[CoL(H_2O)_3].H_2O$ and $[NiL(H_2O)_3].H_2O$. This is in consistent with similar work done by (Abubakar, *et al*., 2017).

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

Compound	Found /(Calculated) %			
	% N	% C	% H	% M
L (Ligand)	8.90	64.39	4.18	-
$[CoL(H_2O)_3].H_2O$	6.34 (6.61)	47.99 (48.24)	3.37 (4.25)	13.92
$[NiL(H_2O)_3].H_2O$	6.58 (6.62)	48.88 (48.26)	5.40 (4.76)	13.88

FTIR Analysis

The infrared spectral analysis of the Schiff base and its metal(II) complexes were determined. The band observed at 3339cm^{-1} in the Schiff base was assigned to *v*(OH). This band disappeared in the metal(II) complexes,which indicated the involvement of phenolic oxygen atom in bonding with the respective metal(II) ions.Similar result was reported by Abdullahi and Gareth (Abdullahi and Gareth, 2013) The broad bands at 3402 and 3391cm^{-1}in the spectra of the complexes were assigned to water of hydration as reported (El-ajaily *et al*., 2006 and Siddappa and Chandrakant, 2012). The FTIR spectral data of the Schiff base determined showed a band at 1622cm^{-1} and it was assigned to *v*(C=N), a feature of azomethine group. The same band was observed to shift to lower frequencies: 1577and1599cm^{-1} in the complexes suggesting coordination of the Schiff base to the respective metal(II) ions (Mounika *et al*., 2010; Rasha, nd Farah, 2012). New bands attributable to v(M-N) appeared in the metal(II) complexes spectra (Table 4).

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

Compound	*v*OH (cm^{-1})	*v*H_2O (cm^{-1})	*v*C=N (cm^{-1})	*v*C-O (cm^{-1})	*v*M-N (cm^{-1})	*v*M-O (cm^{-1})
L (Ligand)	3339	-	1622	1383	-	-
$[CoL(H_2O)_3].H_2O$	-	3402	1577	1235	557	687
$[NiL(H_2O)_3].H_2O$	-	3391	1599	1231	598	762

Antimicrobial and antifungal Activity

The antimicrobial actvity results of the screened ligand and its metal(II) complexes are given in the table 5. The Schiff base and its complexes were screened for their antibacterial activities against the selected bacteria isolates of *Eschirichia coli,Salmonella typhi*and *Staphylococcus aureus,*by disc diffusion method. This may be due to the interaction of the metal(II) complexes with lipoproteins of the cell. It was discovered that the metal(II) complexes possess more effect in inhibiting the microbial growth. This is possibly because of the interaction of the metal(II) complexes with lipoproteins of the cell. Therefore the metal(II)complexes can restrict the usual functioning of the microbial cell. Similar result was reported by Yahyazadeh and Azimi (Yahyazadeh, 2013). Furthermore, higher stability of the complexes at higher temperature can also allow them to be used as a potential antimicrobial agent. Similar result was also recorded in table 6 for antifungal activity shown by selected fungi isolates of *Aspergillus flarus, Asphergillus niger and Mucor iudicus* respectively

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

Compound	Concentration (μgcm^{-3})	Bacterial inhibition zones in mm		
		Staphylococcus aureus	Eschirichia coli	Salmonella typhi
L (Ligand)	1000	07	09	08
	2000	06	08	10
	3000	09	07	09
$[CoL(H_2O)_3].H_2O$	1000	11	12	09
	2000	13	16	13
	3000	16	17	16
$[NiL(H_2O)_3].H_2O$	1000	09	10	12
	2000	12	15	14
	3000	14	20	17

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

Compound	Concentration (μgcm^{-3})	Fungal inhibition zones (mm)		
		Aspergillus flarus	Mucor iudicus	Asphergillus niger
L (Ligand)	1000	06	03	04
	2000	08	05	06
	3000	09	07	07
$[CoL(H_2O)_3].H_2O$	1000	09	10	10
	2000	12	13	12
	3000	15	21	15
$[NiL(H_2O)_3].H_2O$	1000	12	08	09
	2000	14	15	10
	3000	17	18	18

CONCLUSION

Schiff base with its metal(II) complexeswere synthesized and characterized. The molar conductance values of the metal(II) complexes obtained were low, indicating the non electrolytic behavior of the metal(II) complexes. The elemental analysis data suggested 1:1 (metal to ligand ratio). The infrared data indicated that the ligand was coordinated to the central metal(II) ion in a tridentate manner via the azomethine nitrogen and phenolic oxygen atoms after deprotonation. The result of the solubility tests showed that the ligand and its metal(II) complexes were soluble in dimethylsulphoxide (DMSO) and dimethylformamide (DMF), slightly soluble in acetone and ethanol and insoluble in water and n-hexane. The metal(II) complexes were found to be more active than the ligand but less than the reference drugs *Amoxicillin* and *Ketoconazole* used.

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APPENDICES

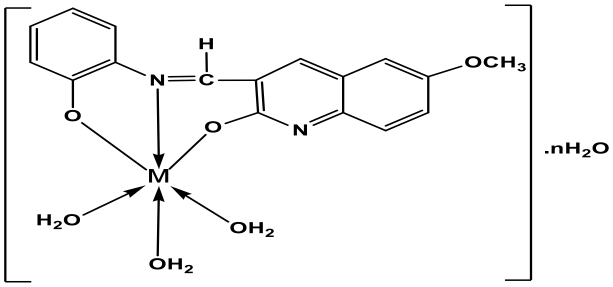

Fig 1. Proposed general molecular structure of metal(II) complexes.
Where M is Co(II) and Ni(II).

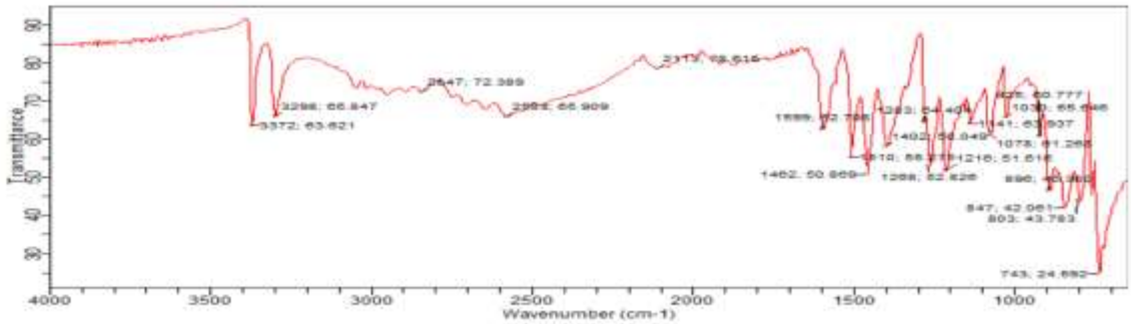

Fig 3.FTIR of the Schiff base ligand

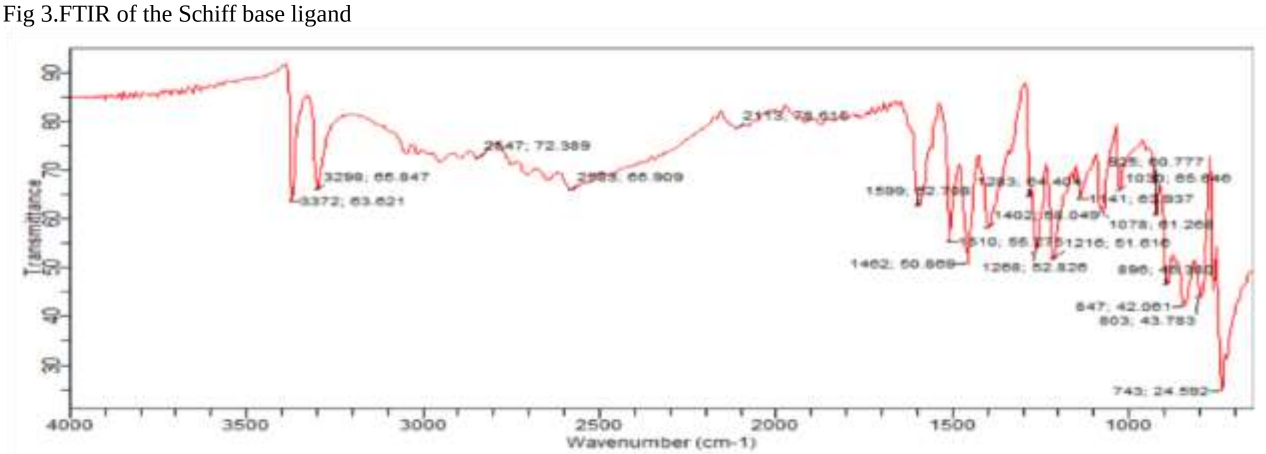

Fig 3.FTIR of 2-Aminophenol

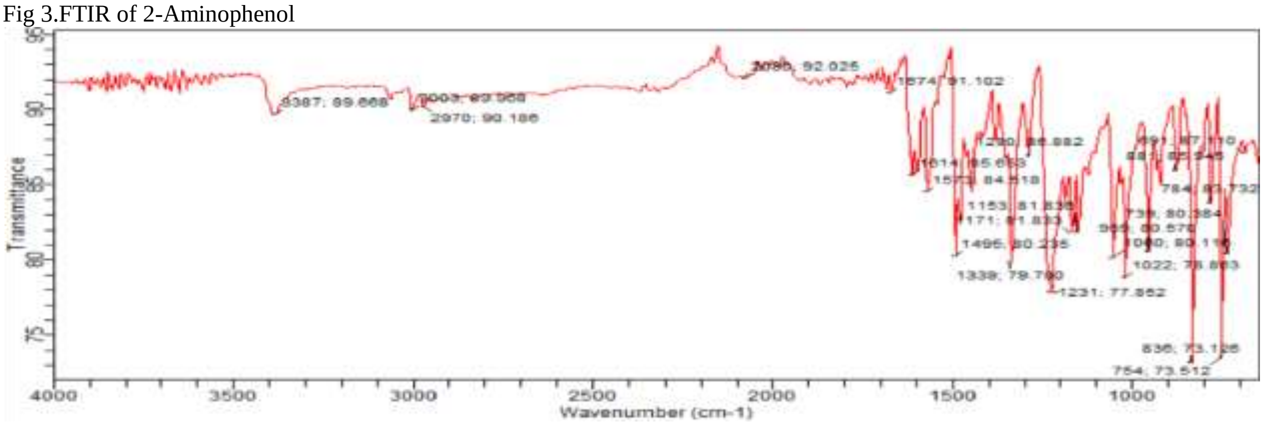

Fig 4.FTIR of Schiff base

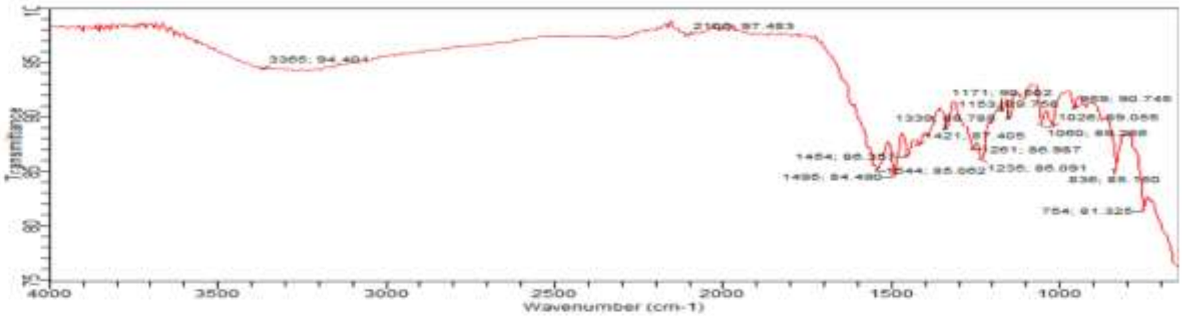

Fig 5. FTIR of Co(II) complex

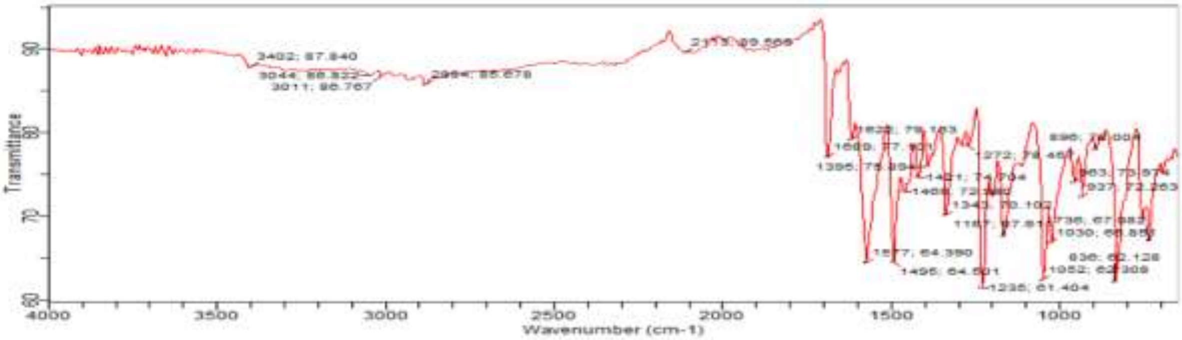

Fig 6.FTIR of Ni(II) complex