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MASTER'S THESIS (CHEM.750)

SYNTHESIS AND STRUCTURAL STUDIES OF MIXED LIGAND COMPLEXES DERIVED FROM DIMETHYLGLYOXIMATE AND 4, 4'-BIPYRIDINE USING Ni^{2+}, Cu^{2+} and Zn^{2+} METAL IONS

BY: DIBORAH MAMO

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By: Diborah Mamo

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Abstract

Ni (II), Cu (II) and Zn (II) complexes have been synthesized using solvo-thermal synthesis method. Divalent Ni and Cu chlorides hydrates were reacted with dimethylglyoxime and 4, 4'-bipyridine in 1:2:2 mole ratio and zinc chloride was reacted with the same ligands in 1:2:1 ratio. Methanol was used as medium in all these reactions. The products obtained under reflux conditions (NDB, CDB, ZDB) were structurally investigated on the basis of elemental (C, H, N) analysis, FTIR spectra, magnetic susceptibility measurements and XRD studies. The studies support the formation of crystalline mixed ligand complexes with metal: uni-negative dimethylglyoximate (DMG):4, 4'-bipyridine (4, 4'-bpy) mole ratio as 1:2:2 for Ni (II) and Cu (II) complexes and 1:2:1 for Zn (II) complex. In these DMG behaves as a bidentate ligand and 4, 4'-bpy is a monodentate ligand. The Ni (II) complex has subnormal magnetic moment. Octahedral geometry for Ni (II)and Cu (II) complexes and five coordinate square pyramidal geometry for Zn (II) complex were proposed.

Key words: Ni (II), Cu (II), Zn (II), mixed ligand complexes, 4, 4’ bipyridine, dimethylglyoxime

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Declaration

I declare that the results presented in this paper entitled "SYNTHESIS AND STRUCTURAL STUDIES OF MIXED LIGAND COMPLEXES DERIVED FROM DIMETHYLGLYOXIMATE AND 4, 4'-BIPYRIDINE USING Ni^{2+}, Cu^{2+} and Zn^{2+} METAL IONS" are from the studies carried out by me with the guidance of my advisors Prof.V.J.T.Raju and Dr.Yonas Chebude in the department of Chemistry, Addis Ababa University. No paper in any scientific journals or presentation in any international conference was made with the results in this paper. All materials used in this investigation have been properly recognized.

Name: Diborah Mamo

Signature _____________

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List of Abbreviations

IR--Infrared

DMG---dimethylglyoxime

NDB--Nickel Dimethylglyoxime 4, 4'-Bipyridine

CDB---Copper Dimethylglyoxime 4, 4'-Bipyridine

ZDB--- Zinc Dimethylglyoxime 4, 4'-Bipyridine

PXRD--- Powder X- Ray diffraction

T —Temperature

M –Metal

4, 4'-bpy---4, 4'-Bipyridine

List of Appendices

1. Introduction

Coordination compounds are molecular compounds formed from a central atom or ion surrounded by small molecules called ligands. The resulted compound is called a complex or, if it is charged, a complex ion. Mixed ligand complexes are usually formed when a solution of metal ion contains more than one kind of complexing ligands. The simplest example of mixed ligand complex formation is when only two different kinds of ligands are coordinated to the central metal ion (M) and these ligands are the cause for different properties of complexes. [1, 2]

In the studies of mixed ligand complexes, ligands which form quite stable (1:1) chelates with metal ions have been considered as primary ligands (A).The tendency of the primary complex (MA) to combine with a second ligand (L) has been measured by pH metric method. The method is used to measure pH because the formation of the primary complex (MA) take place at low pH and the resulted complex remains stable even up to higher pH values where there is combination with the secondary ligand. [3] In this paper other way of mixed ligand complex formation is used that simultaneously combine 4, 4’ bipyridine and dimethylglyoxime ligands with the metal ion.

2. Statement of problem

Waste water released from industries has high level of heavy metals which are toxic. Mixed ligand complexes derived from different ligands and metals have been used to absorb heavy metals. In this project, synthesis and characterization of mixed ligand complexes of Ni(II), Cu(II) and Zn(II)using dimethylglyoxime and 4, 4 bipyridine ligands are undertaken, with a view to generate some new compounds having promising applications.

3. Objective

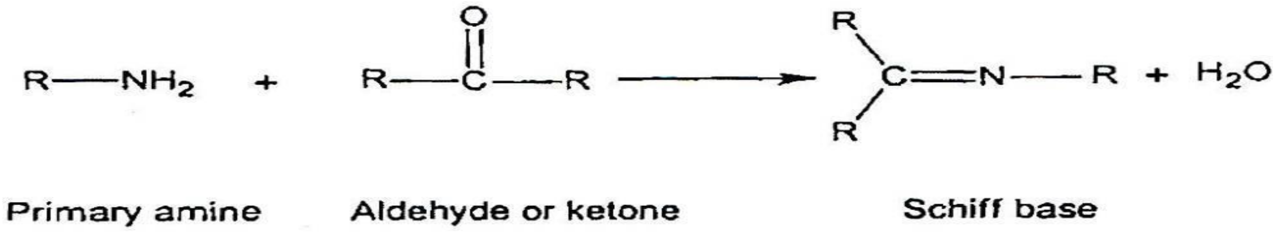
-To synthesize and structural study Ni (II), Cu (II) and Zn (II) based mixed ligand complexes using 4, 4'-bipyridine and dimethylglyoxime ligands.

- To remove heavy metals from waste water by adsorption using the Ni (II), Cu (II) and Zn (II) complexes

4. Literature review

4.1 Coordination compounds

Coordination chemistry deals with metals and ligands. Metal coordination occurs when lone pair electrons from a ligand are donated to an empty orbital in a metal ion. Ligands are Lewis bases that have lone pairs on nitrogen, oxygen, sulphur, etc and bind with transition metals which are Lewis acids. These Lewis bases (ligands) can be divided into unidentate, bidentate and multidentate types. Ligands that can bind to a metal through only one donor atom at a time are unidentate. Many ligands that can bind simultaneously through more than one donor atom are called polydentate. Of the polydentate, those that bind through two, three, four, five or six donor atoms are called bidentate, tridentate tetradentate, pentadentate and hexadentate, respectively. Ligands containing an azomethine group (-CH=N-) are known as Schiff bases. They have a general formula R1R2C=N-R3, where R3 is a phenyl or alkyl group that makes them a stable imine. [4-7].



Scheme- 1: Schiff base formation

Schiff bases have been widely used as ligands because they form highly stable coordination compounds. The reagents that form metal chelates are very useful both in qualitative and quantitative analysis. The organic chelating ligands containing oxime functional groups have been studied a lot because of their application in analytical chemistry for the detection or separation of metal ions. Tschugaeff first introduced dimethylglyoxime as a gravimetric reagent for nickel after that analytical applications have been found for a variety of bidentate chelating oximes such as dioximes, acyloinoximes and aromatic-orthohydroxyoxime. [2].

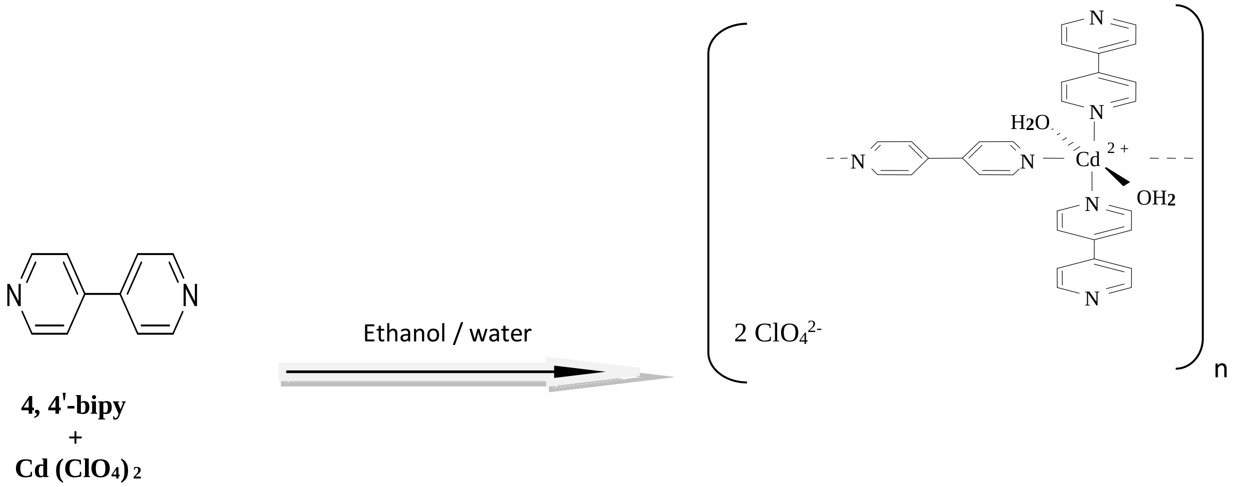
In complexes the metal atom itself has a number of roles, based on its coordination geometry, oxidation state and magnetic electronic and photochemical behaviors [8].

4.2 Nitrogen Donor Ligands

The ligands used in this thesis are nitrogen donor ligands that donate electron through nitrogen.

i. 4, 4'-Bipyridine ($C_{10}H_8N_2$)

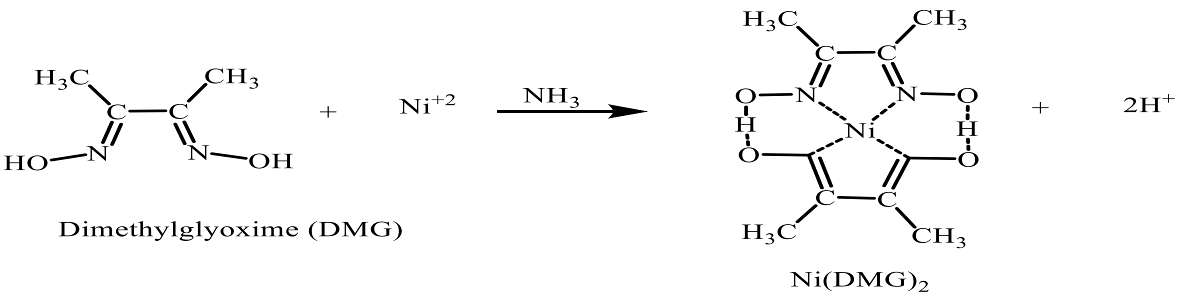
4, 4'-Bipyridine is derivative of two pyridine **(C_5H_5N)** which are linked by a bond between position C-4 and C-4'**.** It is bridging ligand and mainly used to form a large number of polynuclear structures.



Scheme- 2: Formation of coordination polymer from cadmium perchlorate and 4, 4'-bipy [9]

ii. Dimethylglyoxime($C_4H_6(NOH)_2$)

Dimethylglyoxime is an organic dioxime compound derivate from diketone butane-2, 3-Dione. It is a bindentate ligand that has nitrogen atoms as two pairs of electrons donor and mainly used in the preparation of nickel dimethylglyoxime complex. [10]



Scheme-3: Formation of Ni(DMG)$_2$[10]

4.3 The chemistry of Divalent metal ion complexes

4.3.1 The chemistry of Ni (II) complexes

Ni (II) forms a large number of complexes: the main structural types are square-planar, tetrahedral, and octahedral.[11]

i.Square planar complexes:

Square planar is the preferred geometry for majority of four coordinated Ni (II) complexes. The square planar ligand set causes one of the d-orbital's ($d_{x^2-y^2}$) to be uniquely high in energy and leave it vacant but the other four d-orbital's are filled by the eight electrons. Square planar Ni (II) complexes are diamagnetic.

ii. Tetrahedral complexes:

For regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties. The tetrahedral Ni (II) complexes with $^3T_1$(F) ground state generally exhibit two spin allowed transitions $^3T_1 \rightarrow {}^3A_2$and $^3T_1$ (F) → $^3T_1$ (P).The transition from the ground$^3T_1$ (F) state to the $^3T_1$ (P) state occurs in the visible region (15,000 cm^{-1}) and is relatively strong ($\varepsilon \approx 102$) compared to the corresponding $^3A_{2g} \rightarrow {}^3T_{1g}$transition in octahedral complexes.

The magnetic moments of truly tetrahedral Ni (II) complexes should be about 4.2 B.M at room temperature because the ground state$^3T_1$(F) has much inherent orbital angular momentum. This value decrease with slight distortions like fairly regular tetrahedral complexes have magnetic moments of 3.5 - 4.0 B.M and the more distorted ones have magnetic moment values ranging from 3.0- 3.5B.M.

iii. Octahedral complexes:

Octahedral Ni (II) complexes having $^3A_{2g}$ground state are expected to have three spin-allowed transitions. These are $A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions in the ranges of 7000 - 13000, 11000 - 20000 and 19000 – 30,000 cm^{-1}, respectively. Thus complexes have two unpaired electrons and magnetic moments ranging from 2.9-3.4 B.M.

4.3.2 The chemistry of Cu (II) complexes

Cu (II) state is the most stable and important for copper. The cupric ion Cu^{+2} has electronic configuration d^9 and one an unpaired electron. Its compounds therefore are colored and paramagnetic. Distorted octahedral arrangement is common in copper compounds with two long bonds and four short ones. The distortion occurs because the d_{z^2}orbital is doubly occupied while the $d_{x^2-y^2}$ orbital is only singly occupied and this prevents the ligands approaching along the +z and –z directions from coming close to the copper as those approaching along +x,-x +y and –y direction. The Octahedral complexes without any distortion are expected to have only one d-d absorption band corresponding to $^2E_g \rightarrow {}^2T_{2g}$ transition. Cu (II) complexes are blue or green due to the absorption band in the region of spectrum 600-900 nm.

Magnetic momentsvalues are range from 1.75- 2.20 BM for those that do not have Cu-Cu interaction. [11]

4.3.3 The chemistry of Zn (II) complexes

The divalent zinc ion is exceptionally stable in contrast to the first row transition series. The d^{10}configuration of Zn^{+2}indicates that zinc complexes are not subject to ligand field stabilization effects because all the d orbital's are filled by electrons so coordination number and geometry are only determined by ligand size and charge. Zinc complexes have coordination number 4, 5 and 6. They are mostly known by tetrahedral and octahedral structure.

Zinc is one of the most biologically used metals. Most enzymes in biochemistry have zinc atom in the reactive center. [11]

4.4 Properties of mixed ligand complexes

Properties of mixed ligand complexes determinetheir uses in analyticalchemistry. The main properties are: [12]

- Chemical individuality of similar elements

The coordination number of the central atom displays chemical individuality of the complex relating it with other complex that has the same element.

- Stability

Mixed ligand complexes have ability to stabilize the oxidation state of a central atom which is unstable under certain condition.

4.5 Application of mixed ligand complexes

Mixed-ligand complexes are generallymore biologically active than the ligand itself and have application such as:

- Catalysis

Some metal ligand complexes are used to catalyze reactions such as oxidation, oxidative cleavage and hydroformylation.

Ni (II) mixed ligand complexes derived from deprotonated 8-hydroxyquinoline and amino acid have been used as homogeneous catalysts for ester hydrolysis. [13]

- Antimicrobial activities

Mixed ligand metal complexes have strong antibacterial and antifungal activity [14]

Ni (II), Co (II) and Cu (II) mixed-ligand complexes of dimethylglyoxime and 2-aminophenol are used as antimicrobial against *Escherichia coli*, *staphylococcus aureus*, *Aspergillusniger*and *Aspergillusflavus*. [15]

- Anti oxidant activity

Mixed ligand complexes derived from copper (II), dimethylglyoxime, adenine and ortho-phenylenediaminehave antioxidant activity [16]

4.6 Ways of formation of mixed ligand complexes

In mixed ligand complex formation five ways of reaction can occur [3]

1. Both the ligands can combine simultaneously with the metal ion to form a mixed ligand complex in a single step.

   $$M + A + L \longleftrightarrow MAL$$

2. Due to slight differences in the affinities of the ligands for the metal ion, a mixed ligand complex can result by two overlapping steps.

   $$M + A + L \longleftrightarrow MA + L \longleftrightarrow MAL$$

3. Due to wide differences in the affinities of the ligands for the metal ion, the mixed ligand complex formation can take place in distinct separate steps.

   $$M + A + L \longleftrightarrow MA + L \longleftrightarrow MAL$$

4. A mixture of two simple chelate compounds may be formed instead of a mixed ligand complex. The chelates will be containing different ligands bound to the same metal ion.

   $$2M + nA + nL \longleftrightarrow MA_n + ML_n$$

5. Instead of forming a mixed ligand complex, a simple complex is formed between one ligand and the metal ion, while the other ligand remains unbound in the solution.

   $$M + A + L \longleftrightarrow MA + L$$

5. Experimental

5.1 Chemicals

Chemicals used in this experiment were dimethylglyoxime ($C_4H_6(NOH)_2$), nickel chloride hexahydrate ($NiCl_2•6H_2O$), zinc chloride ($ZnCl_2$), copper chloride dihydrate($CuCl_2•2H_2O$), 4,4'-bipyridine hydrate ($C_{10}H_8N_2.H_2O$) and distilled water. Methanol was used as a solvent for synthesis and purification. The reagents are from Sigma- Aldrich.

5.2 Synthesis Method

Solvo-thermal synthesis method: In this method reactants are mixed in the presence of solvent as a medium by heating to a certain temperature. This synthesis method is used because it is simple and easily controlled.

5.3 Instruments

- ✓ **FT-IR spectrometer**

FT-IR spectrometer is a useful instrument that is used for structure analysis and functional group identification of materials. The basic principle of the instrument is vibrations of molecules occur by absorbing infrared radiations with specific wavelengths. Infrared spectroscopy is used for qualitative analysis because every material possesses unique infrared spectrum depending on its structures and symmetry. [18]

In this thesis the infrared spectra were recorded from 400 to 4000 cm-1 on a Perkin Elmer Spectrum 65FTIR spectrometer using KBr pellets.

Fig- 2 Perkin Elmer Spectrum 65 FT-IR spectrometer

- ✓ **Elemental analyzer**

CHNS elemental analyzer is used for determination of carbon, hydrogen, nitrogen and sulphur percent in a sample. Catalytic redox reaction is taken to convert C, H, N and S to a variety of detectable gases. Carbon converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/ oxides of nitrogen and sulphur to sulphur dioxide. If other elements like chlorine are present, they will be converted to combustion products like hydrogen chloride. [18]

In this thesis EA1112 Flash CHNS/O analyzer is used for determination of carbon, hydrogen and nitrogen percent in the samples.

Fig- 3 EA1112 Flash CHNS/O analyzer

- ✓ Magnetic susceptibility balance

Magnetic susceptibility balance is used to determine magnetic properties of compounds. AUTO magnetic susceptibility balance works by moving magnets on the stationary sample. The magnetic property of a sample is determined by the nature of electrons in it. Paired electrons neutralize magnetic forces but free unpaired electrons which are attracted to a strong magnetic field give rise to magnetic forces. [19]

In this thesis MSB-AUTO Magnetic Balance (Sherwood Scientific) is used to determine the magnetic property and number of unpaired electron in the sample.

Fig- 4 MSB-AUTO Magnetic Balance (Sherwood Scientific)

- ✓ **X-ray Diffractometer**

X-ray diffractometer determine crystalline properties of synthesized products using X-ray radiation. Powder X-ray diffraction is used to test whether the synthesized sample have the same crystal structure with the single crystal. [18]

In this thesis Rigaku Miniflex 600 X-ray Diffractometer with Cu-Kα radiation is used to determine if the synthesized samples are crystals or not.

Fig- 5 Rigaku Miniflex 600 X-ray Diffractometer

5.4 Synthesis

The products were named as NDB, CDB and ZDB respectively, where in the first letter indicates metal, the second letter denotes dimethyl glyoximate and the third letter stands for 4, 4’-bipyridine. The mole ratios of metal chloride: dimethyl glyoxime: 4, 4’-Bipyridine were taken as 1:2:2 and 1:2:1.

5.4.1 NDB synthesis

A mixture of 0.948 gm (4 mmol) of nickel chloride hexahydrate, 0.928 gm (8mmol) of dimethylglyoxime and 1.392 gm (8 mmol) of 4, 4'-bipyridine hydrate were taken in a clean 250 ml flask. 100 ml aqueous methanol was added and the contents were refluxed for 8 hours with continuous stirring at 65°C. The deep red color of the solution faded and faint red colored precipitate was formed. The product was filtered under suction and repeatedly washed with methanol. On open drying 1.476gm of the product was obtained with 45 % percentage yield.

5.4.2 CDB synthesis

A mixture of 0.170 gm (1mmol) of copper chloride dihyhdrate, 0.232gm (2 mmol) of dimethylglyoxime and 0.348gm (2 mmol) of 4, 4'-bipyridine hydrate were taken in a clean 250 ml flask. 100 ml aqueous methanol was added and the contents were refluxed for about 10 hours with continuous stirring at 65°C. The color of the solution was changed from gray to green. The product was filtered under suction and repeatedly washed with methanol. On open drying 0.458 gm of the product was obtained with 61% percentage yield.

5.3.3 ZDB synthesis

$ZnCl_2$ salt has a property to absorb moisture. This property makes it difficult to weight zinc chloride on the beam balance because the salt is soluble in water. To get the dehydrated salt some amount of zinc chloride was added on white dish then the dish was put on hot plate.

A mixture of 0.544gm (4 mmol) of the zinc chloride dehydrated, 0.928gm (8mmol) of dimethylglyoxime and 0.696gm (4 mmol) of 4, 4'-bipyridine hydrate were taken in a clean 250 ml flask. 100 ml aqueous methanol was added and the contents were refluxed for 9 hours with continuous stirring at 65°C. White color of solution was formed. The product was filtered under suction and repeatedly washed with methanol. On open drying 1.815 gm of the product was obtained with 84% percentage yield.

6. Results and discussion

6.1 Physical properties

The compounds are stable at RT. They do not melt, but decompose. They are insoluble in common organic solvents.

Table -1: Physical properties of NDB, CDB and ZDB complexes

Complex code	Color	Percentage yield	Decomposition temperature
NDB	Red	45%	316 °C
CDB	Green	61%	340 °C
ZDB	White	84%	330 °C

6.2 IR Spectral studies

The IR spectra of NDB, CDB, and ZDB are presented in figure 6-8 and the results are summarized in Table-2.

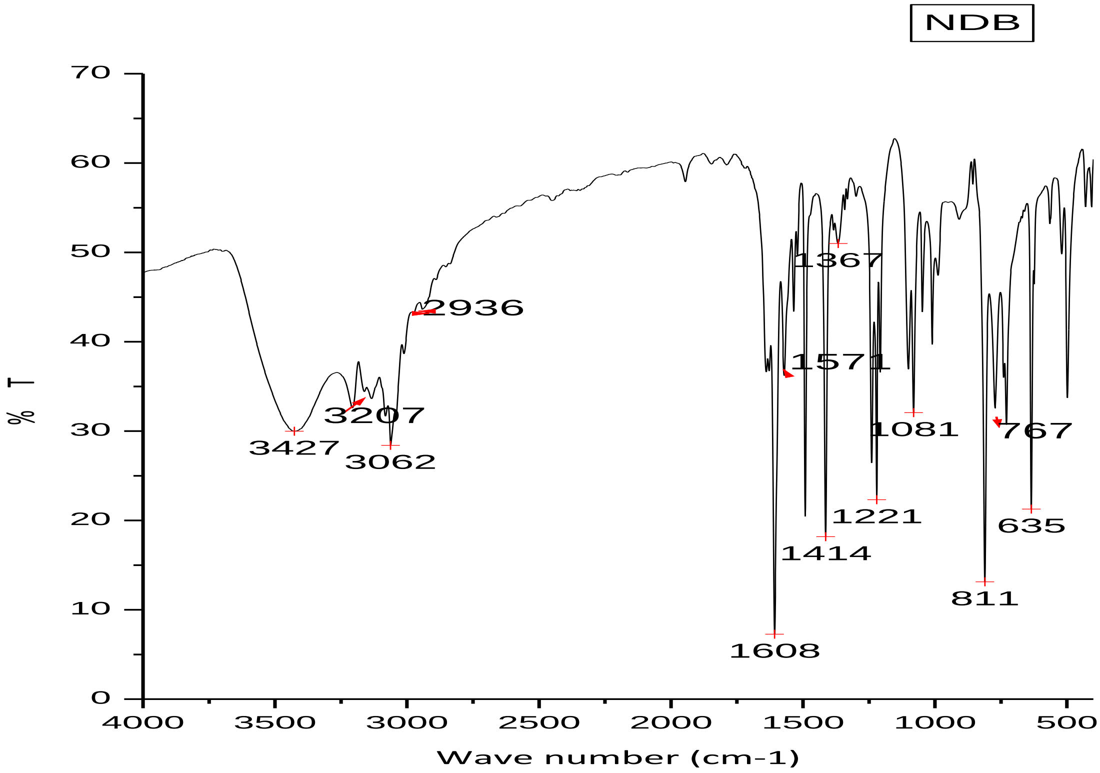


Fig-6: IR spectrum of NDB

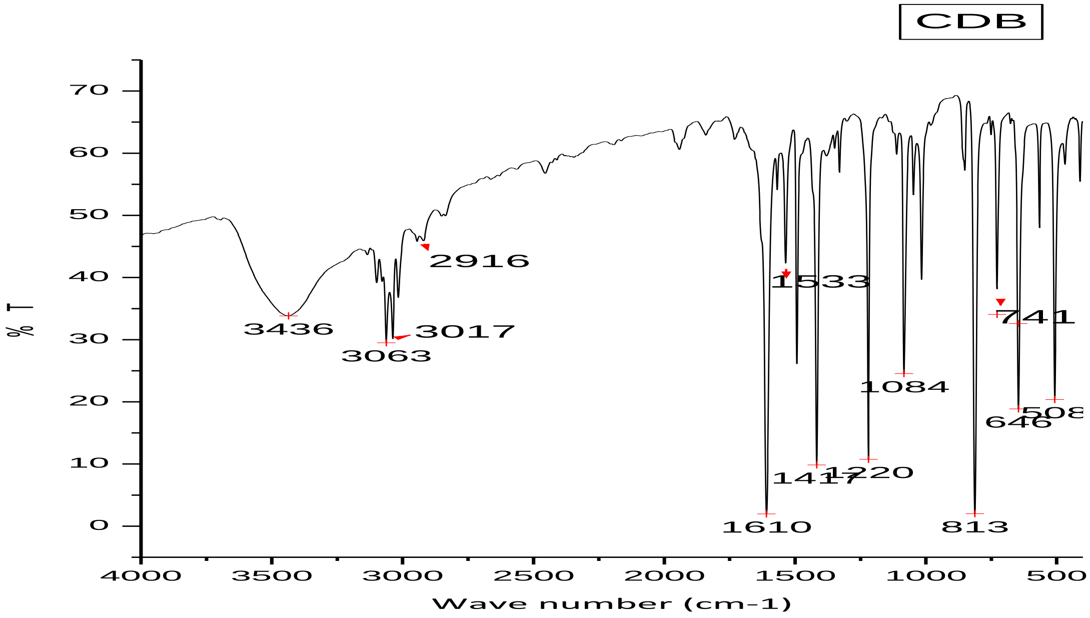


Fig-7: IR spectrum of CDB

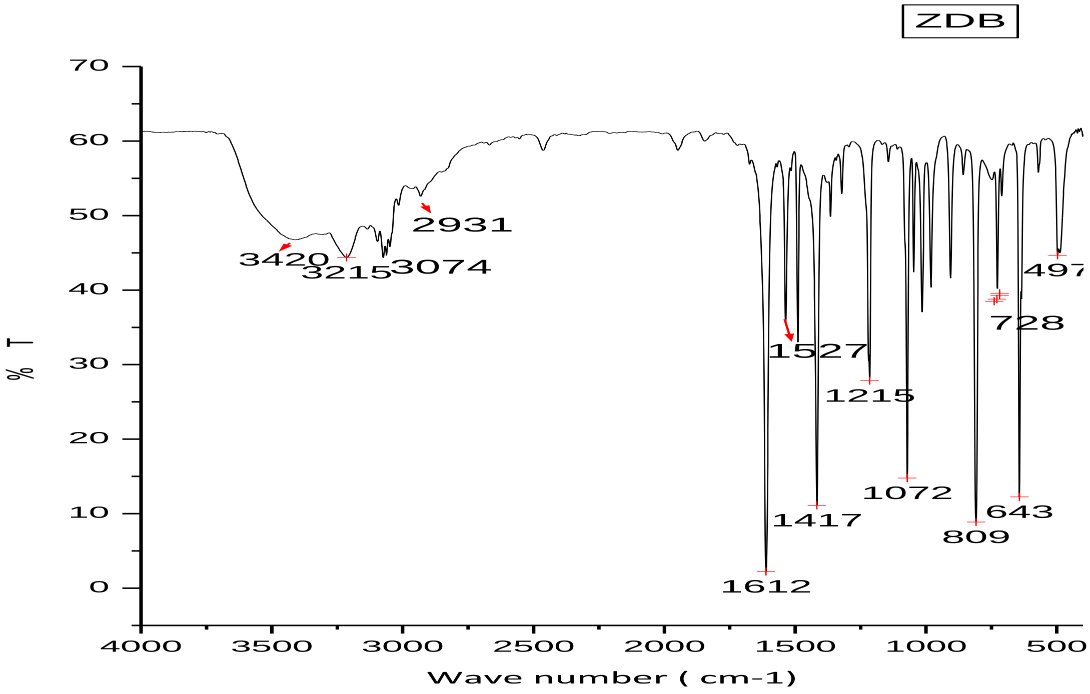


Fig-8: IR spectrum of ZDB

Table-2: Summarized IR Spectra results of NDB, CDB and ZDB complexes

IR band Assignments	NDB (cm^{-1})	CDB (cm^{-1})	ZDB (cm^{-1})	4, 4'-bpy hydrate (cm^{-1})	DMG (cm^{-1})
υ(-OH)	3500-3300	3500-3300	3500-3300	3500-3100	3500-3100
υ (C-H)sp^2asym	3207	3063	3215	-----	-----
υ (C-H) sp^2sym	3062	3017	3074	3029	-----
υ (C-H) sp^3	2936	2916	2931	2898	2930
υ(overtone)	2000-1600	2000-1600	2000-1600	2000-1600	-----
υ(C=C)	1608	1610	1612	1657	-----
υ (C=N)	1571, 1525	1533, 1500	1527, 1510	1598	1523
υ (N-O) asym	1414	1417	1417	------	1438
υ (N-O) sym	1221	1220	1215	-------	1364
υ (C-C)	1011	1084	1072	1075	1144
υ(C=N-O)	767	741	728	-----	746
υ(M-L)	500,495	525,500	530,497	----	----

In all the complexes the broad band's between 3500-3300 cm^{-1} correspond to the OH stretching from DMG, H_2O and CH_3OH. (C-H) sp^2 symmetric and asymmetric stretching bands in the range 3062- 3215cm^{-1}, overtones between 2000-1600 cm^{-1} and C=C bands around 1600 cm^{-1} are due to the aromatic functions of 4, 4'-bipyridine. (C-H) sp^3 stretching bands around 2900 cm^{-1} are from the methyl groups of the DMG. Bands in between 1500 cm^{-1} and 1571 cm^{-1} indicate the presence of C=N bonds which come from 4, 4'-bipyridine and DMG. (N-O) asymmetric and (N-O) symmetric stretching bands are located in the range 1414 cm^{-1} - 1215 cm^{-1}, which are due to the DMG. Bands around 1000 cm^{-1} indicate C-C bond stretching. Bands in the range 728-767 cm^{-1} indicate presence oxime group of the DMG. Non- ligand bands in between 530 cm^{-1} and 495 cm^{-1} confirm metal-ligand bonding.

Modification of band frequencies, band widths, band shifts and band intensities particularly with respect to coordinating functions such as C=N and the appearance of non-ligand bands show the presence of dimethylglyoximate and 4, 4'-bipyridine in the coordination sphere

6.3 Elemental analysis

Table -3: Elemental analysis results

Complex	M.wt (gm/mol)	Found (Cal)		
Ni $(C_4H_7N_2O_2)_2\,(C_{10}H_8N_2)_2$ $+13H_2O$	835.313	%C	%H	%N
		40.13 (40.22)	5.34 (6.70)	14.24 (13.40)
$Cu(C_4H_7N_2O_2)_2\,(C_{10}H_8N_2)_2$ $+12H_2O+4CH_3OH$	950.166	40.32 (40.41)	6.60 (7.36)	12.14 (11.78)
$Zn(C_4H_7N_2O_2)_2\,(C_{10}H_8N_2)$ $+5H_2O$	541.81	39.21 (39.86)	4.79 (5.90)	15.23 (15.50)

The Elemental analysis results show C, H and N found percentages are consistent with the composition of the calculated values for NDB, CDB and ZDB complexes.

The elemental analysis data shows the formation of products with metal: dimethyl glyoximate: bipyridine as 1:2:2 for Ni (II) and Cu (II) complexes and as 1:2:1 for Zn (II) complex. DMG behaves as mono basic bidentate ligand, while 4, 4’-bipyridine behaves as a neutral monodentate ligand in all the complexes. They do not include chloride ions in the composition. The absence of white precipitate with silver nitrate reagent confirms this. The complexes incorporate a number of water in case of Ni (II) and Zn (II) complexes, and water and solvent methanol in Cu (II) complex. The elemental analysis data suggest the formulation of mixed ligand complexes with water and methanol molecules on the crystal sites. The data also suggest octahedral geometry for NDB and CDB complexes, and five coordinate square pyramidal geometry for Zn (II) complex.

6.4 Magnetic susceptibility of Ni (II) complex

$Xg = 2.645 \times 10^{-6}$ (Xg = gram susceptibility was measured at 294.15 K)

$\chi_M = \chi_g * \mathrm{M.wt}$ (X_M= Molar Magnetic susceptibility and M.wt = Molar weight of the sample)

$= 2.64 \times 10^{-6} \times 835.313$

$= 0.002205$

To get number of unpaired electrons we can use the following equation;

$$\chi_M.\mathrm{T} = \frac{1}{8}n(n+2)$$

$0.002205 \times 294.15 \times 8 = n^2 + 2n$

$n^2 + 2n - 5.18 = 0$

$n = 1.485$

Table-4: Magnetic Susceptibility measurement result at T= 294.15 k

Sample Code	M.wt(gm/ mol)	χ_g	χ_M	n	Nature of the sample
NDB	835.313	2.645×10^{-6}	0.002211	1.485	Paramagnetic

Octahedral geometry is suggested for NDB based on the elemental analysis data and Ni^{+2} in such geometry have two unpaired electrons but the magnetic data indicates average electro density per metal is 1.485 electrons, which is subnormal. It is proposed that there may be some stacking interaction between the mixed ligand complex molecules. The complex contains Ni $(DMG)_2$in the equatorial plane and two bipyridine molecules in the perpendicular/axial plane, can promote stacking and consequently nickel –nickel interaction. This interaction may be responsible for the subnormal magnetic moment value.

6.5 X- ray diffraction analysis

The XRD spectra of NDB, CDB and ZDB complexes are presented figure 9, 10 and 11.

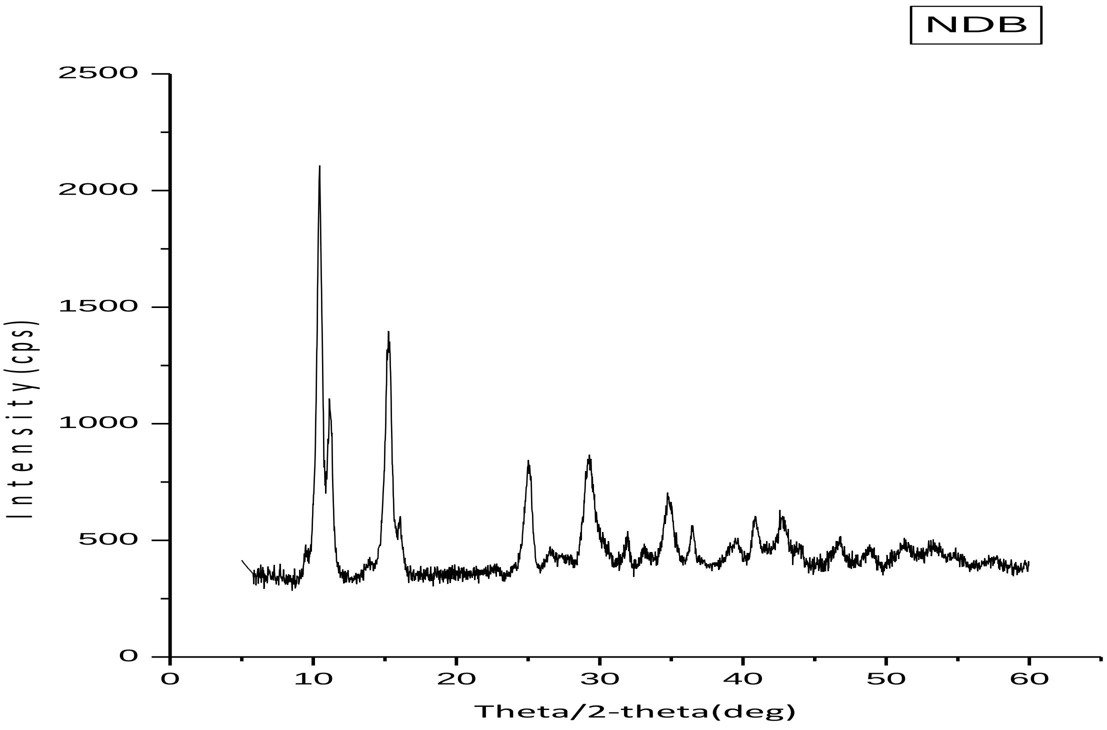


Fig- 9.XRD Spectrum of NDB

NDB shows sharp peaks at 2θ =10.42°, 15.32°, 24.77° and 29.37°. The width of 2θ =10.42° is useful peak since it has high intensity which is used to determine crystals size.

$$D=\frac{0.9*\lambda}{(\beta)\cos\theta}$$

From the above equation, *D* is the crystallite size in (nm), λ is the radiation wavelength used (λ = 0.15406 nm), θ is the Bragg angle and β is the full width at half-height of the diffraction peak in radian (β=0.00762). Thus, the crystal size (D) of NDB complex is 38.12nm

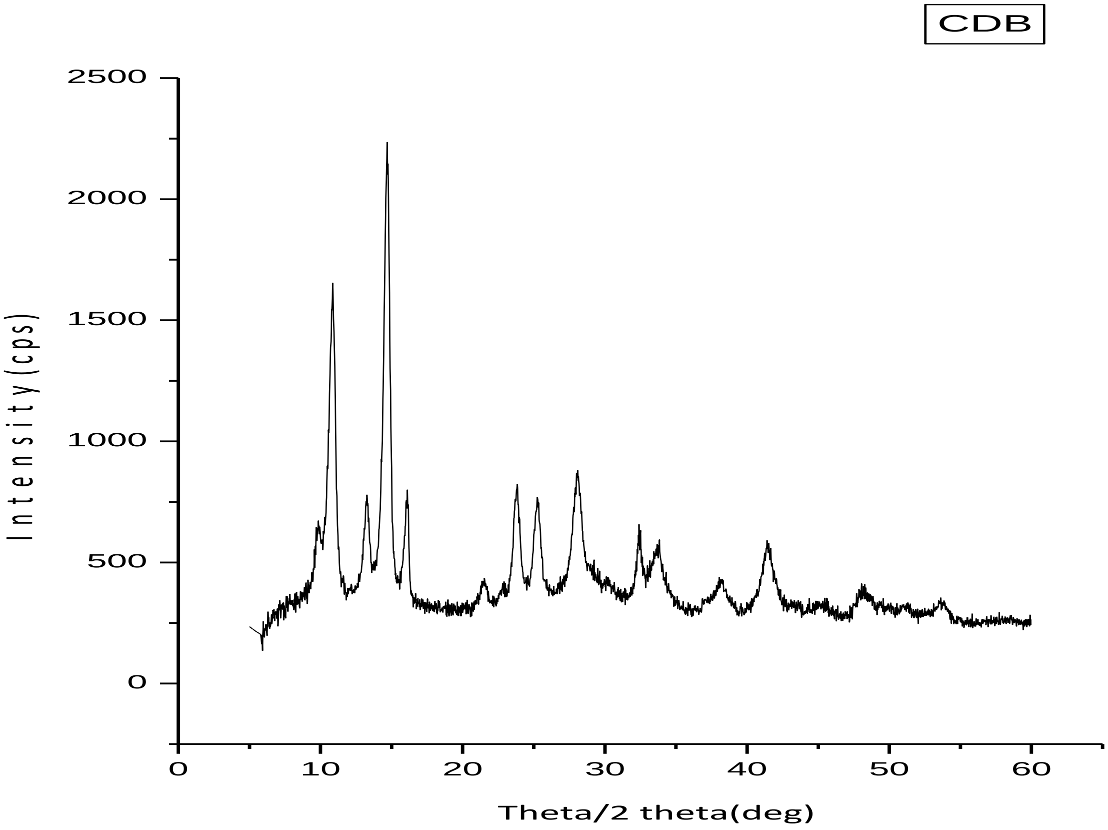


Fig- 10.XRD Spectrum of CDB

CDB shows sharp peaks at 2θ =10.81°, 14.96°, 23.96° and 25.56°. The width of 2θ =14.96° is useful peak since it has high intensity which is used to determine crystals size.

$$D=\frac{0.9*\lambda}{(\beta)\cos\theta}$$

From the above equation, *D* is the crystallite size in (nm), λ is the radiation wavelength used (λ = 0.15406 nm), θ is the Bragg angle and β is the full width at half-height of the diffraction peak in radian (β=0.00797).). Thus, the crystal size (D) of CDB complex is 47.62nm

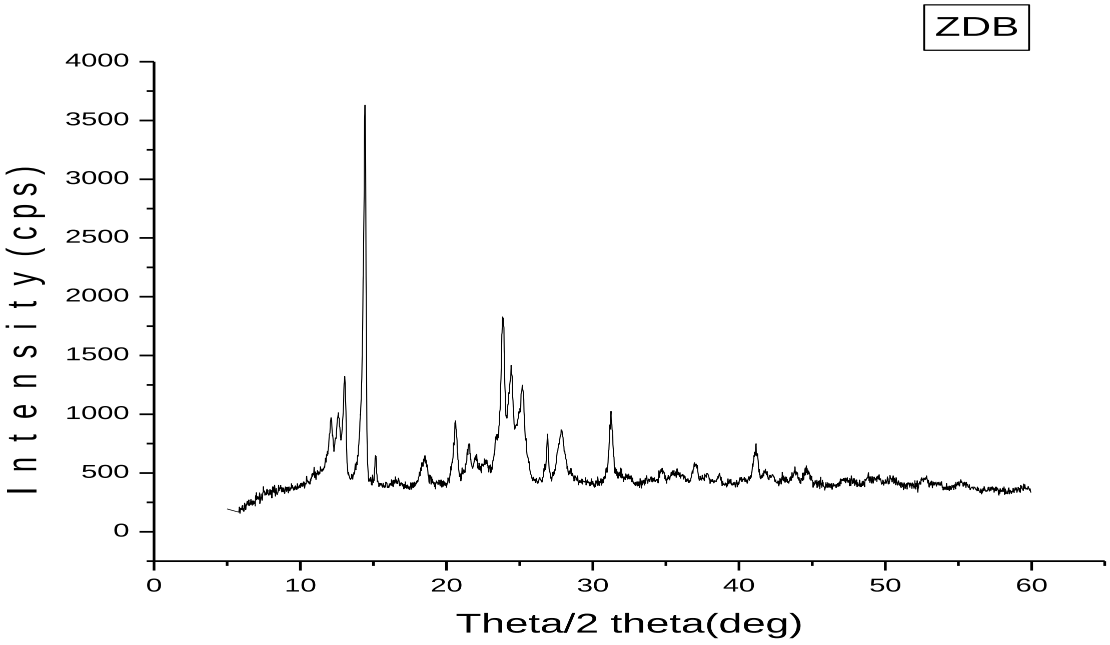


Fig- 11.XRD Spectrum of ZDB

ZDB shows sharp peaks at 2θ =12.53°, 14.46°, 23.92° and 30.79°. The width of 2θ =14.46° is useful peak since it has high intensity which is used to determine crystals size.

$$D=\frac{0.9*\lambda}{(\beta)\cos\theta}$$

From the above equation, *D* is the crystallite size in (nm), λ is the radiation wavelength used (λ = 0.15406 nm), θ is the Bragg angle and β is the full width at half-height of the diffraction peak in radian (β=0.00354).). Thus, the crystal size (D) of ZDB complex is 67.30nm

The sharp peaks of NDB, CDB and ZDB complexes and the crystalline sizes prove that the complexes are crystals.

7. Conclusion

In view of the importance of mixed ligand complexes, it was proposed to experimentally derive three mixed ligand complexes by reacting electron rich divalent period 3 metal ions (Ni^{2+}, Cu^{2+}, Zn^{2+}), dimethyl glyoxime and 4, 4'-bipyridine in selected mole ratios. Solvo-thermal synthesis method was used and the obtained products were structurally studied on the basis of analytical, FTIR spectral, magnetic, XRD data. The conclusions drawn, suggest that the formation of mixed ligand complexes. The proposed structures are presented in the following figures

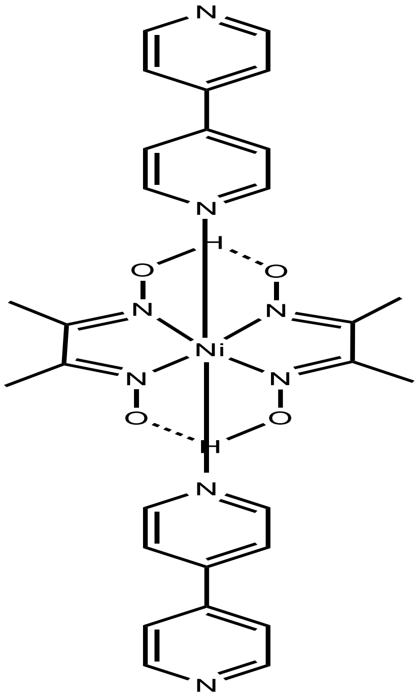


Figure- 12: The structure of NDB complex

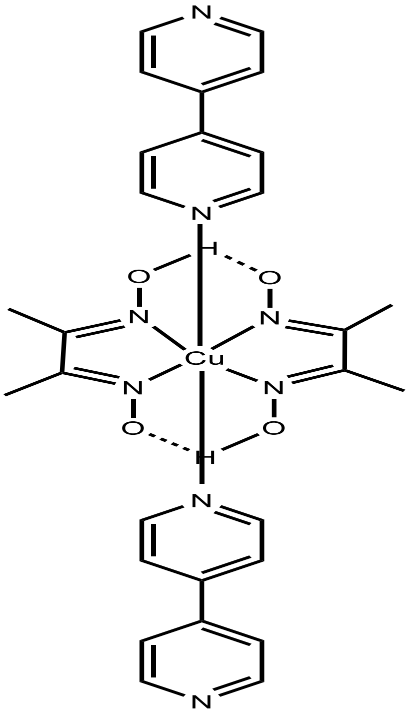


Figure- 13: The structure of CDB complex

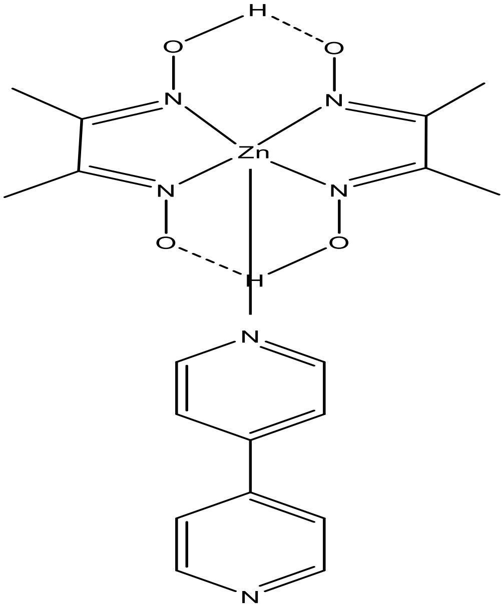


Figure- 14: The structure of ZDB complex

8. Limitations

One of the objectives of this thesis was to apply the synthesized Ni (II), Cu (II) and Zn (II) complexes in the detoxification of waste water from heavy metals by adsorption. This requires more extended studies using heavy metal ions such as Pb (II), Hg (II), Cd (II), Cr (in different oxidation states) and implementation of specific bio- and physico- chemical procedures. These studies could not be attempted due to limitations in time frame and available equipment for such studies.

9. Recommendations

Mixed ligand complexes play a crucial role in biological and other systems; therefore, the synthesis, characterization and study of their properties have great importance. In the thesis mixed complexes are derived from dimethyl glyoxime and 4, 4 bipyridine that are nitrogen donor ligands and known by their application like catalysis, water treatment, antifungal and antibacterial activities. It is recommended to continue the study and gain the application from mixed ligand complexes.

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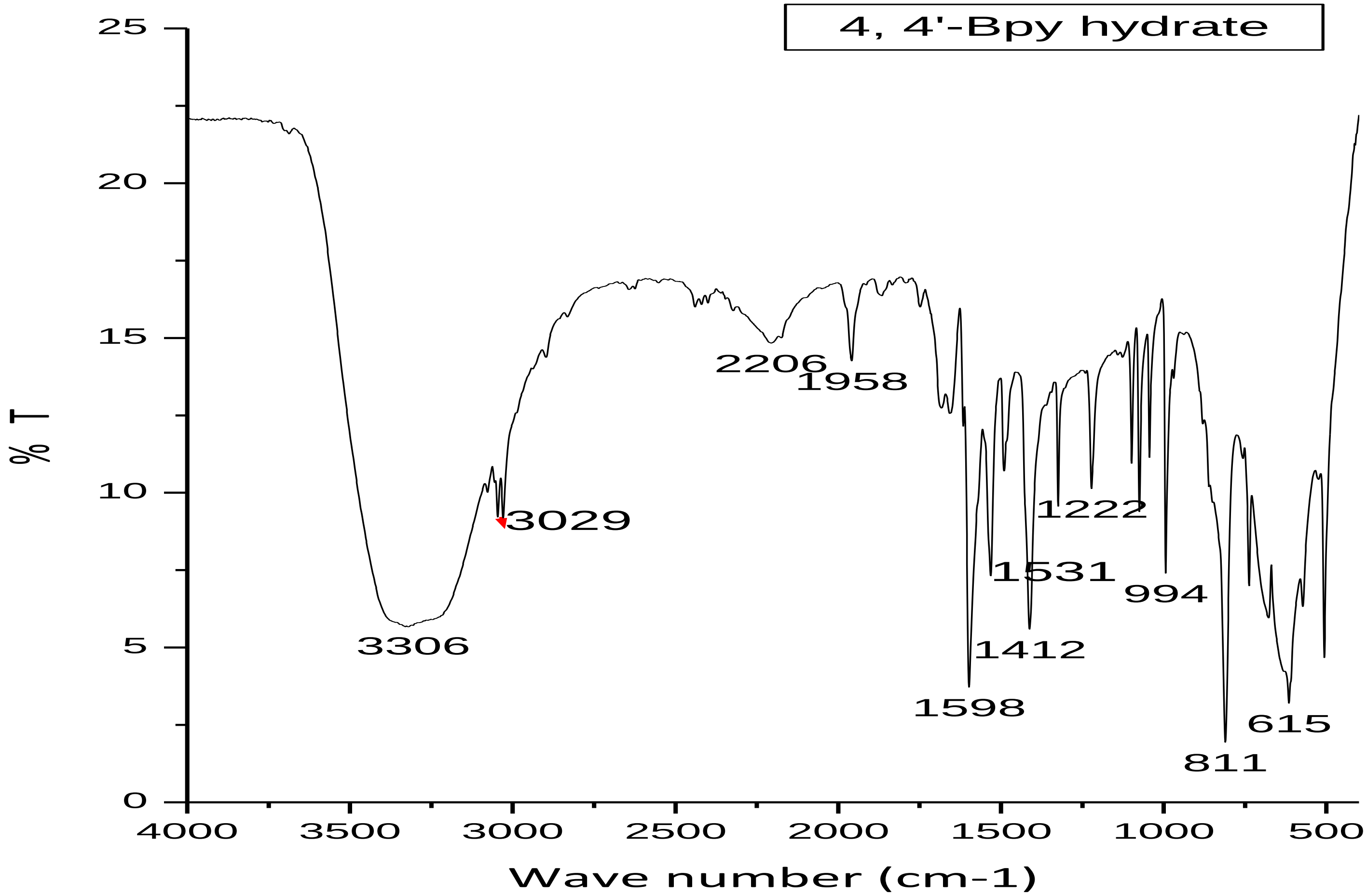
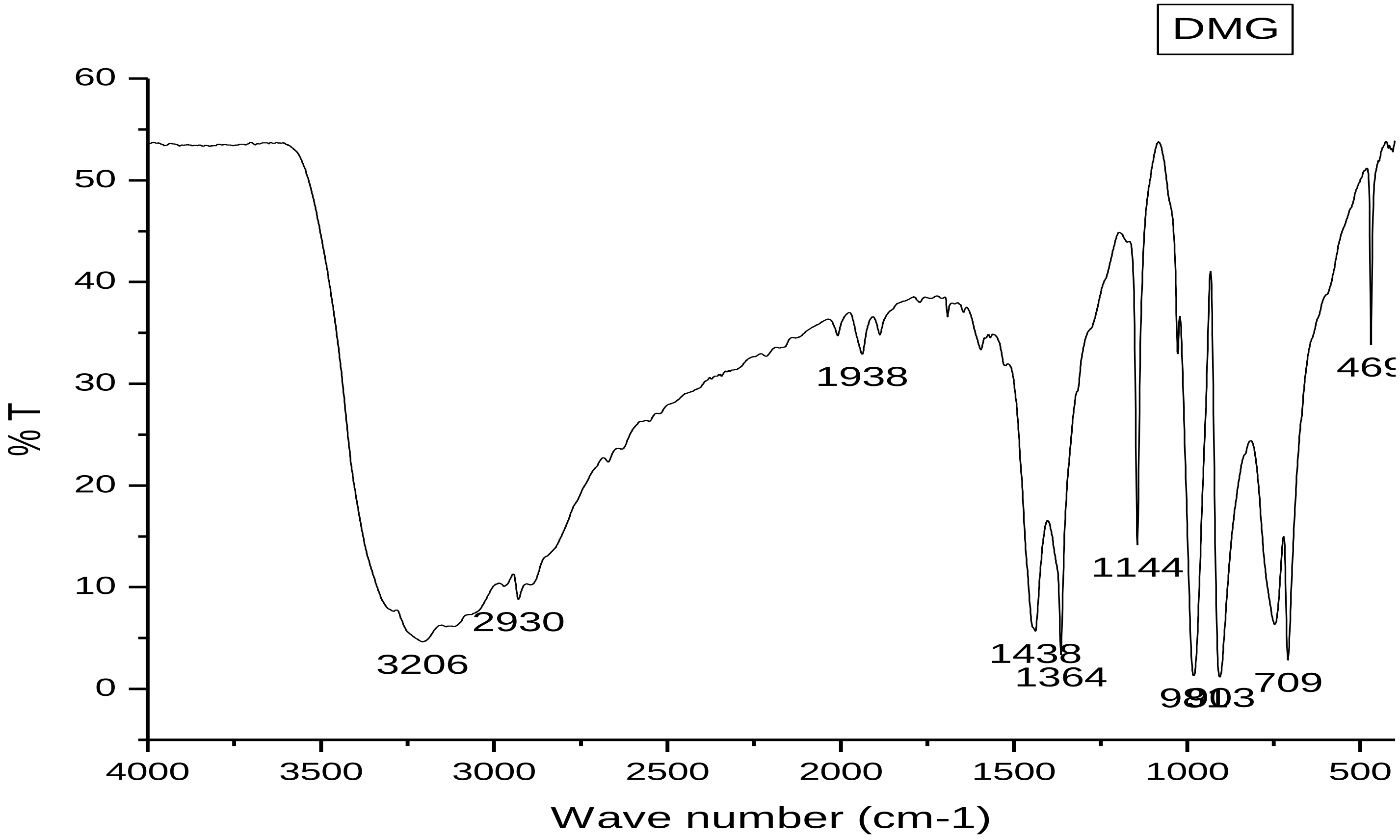
11. Appendices



Appendix-1.IR Spectrum of 4, 4'-Bpy hydrate



Appendix-2.IR Spectrum of DMG