ADDIS ABABA UNIVERSITY COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES DEPARTMENT OF CHEMISTRY

SYNTHESIS AND CHARACTERIZATION OF Zn(II) AND Mn(II) MULTINUCLEAR MIXED LIGAND COMPLEXES DERIVED FROM CITRIC ACID & 2,2'-DIPYRIDYLAMINE

By

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STUDIES ON SYNTHESIS AND CHARACTERIZATION OF Zn(II) AND Mn(II) MULTINUCLEAR MIXED LIGAND COMPLEXES

A GRADUATE PROJECT SUBMITTED TO ADDIS ABABA UNIVERSITY COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY.

By

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ABSTRACT

Multinuclear complexes of Zn(II) from citric acid and 2, 2'-dipyridylamine and Mn(II) from 2, 2'-dipyridylamine were successfully synthesized by template method. All complexes were particularly colored and stable to atmospheric condition. All the synthesized complexes were characterized by elemental analysis, AAS analysis, IR and UV-vis spectroscopy, magnetic susceptibility and conductance measurement. Analytical data of the mixed ligand complexes shows zinc metal to citric acid to 2,2'-dipyridylamine ligand (zinc: citric acid: dpa) ratio of 3:2:3 for Cpd-1 and 3:2:4 for Cpd-2 and manganese metal to 2,2'-dipyridylamine ligand ratio 4:3 for Cpd-3. In the Zn(II) complexes (Cpd-1 & 2), the mixed ligand acts as an O, and N-donor and in the Mn(II) complex, (Cpd-3), 2, 2'-dipyridylamine ligand act as N-donor. Attempt to synthesized the mixed ligand complex with Mn(II), one of the ligand (citric acid) was not reacted with it, (Mn^{+2}). Based on the elemental analysis, conductance, spectral, magnetic, AAS, and UV-vis data, all Zn(II) and Mn(II) complexes were proposed to have an octahedral geometry.

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I would also thank Addis Ababa University, chemistry department for providing materials and chemicals necessary to accomplish my study.

DECLARATION

I the undersigned confirm that this is my original work obtained by research carried out by me under the supervision of my advisor in the Faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2019 - 2020. No part of this work shall be published in any scientific journals or presented at conferences without the knowledge and consent of my advisor. Finally this work has not been submitted for a degree in any other university and all sources used for the study have been duly acknowledged.

By Gezahegn kefelegn

Signature _____

Date_____

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LIST OF ABRREVIATIONS AND SYMBOLS

MOF ⇒ Metal-organic framework

PCP ⇒ Porous coordination polymer

IR ⇒ Infrared

UV-vis ⇒ Ultraviolet visible

AAS ⇒ Atomic absorption spectroscopy

nm ⇒ nanometers

DMF ⇒ Dimethylformamide

DMSO ⇒ Dimethylsulfoxide

THF ⇒ Tetrahydrofuran

ppm ⇒ parts per million

mp ⇒ melting point

Λ_M ⇒ = Molar conductance

Cal. ⇒ Calculated

Sol. ⇒ Soluble

Insol. ⇒ Insoluble

Part. ⇒ Partially

EA. ⇒ Ethylacetate

Cpd ⇒ Compound

Cpd-1 ⇒ $C_{42}H_{60}N_{11}O_{16}Zn_3$

Cpd-2 ⇒ $C_{52}H_{78}N_{12}O_{27}Zn_3$

Cpd-3 ⇒ $C_{30}H_{55}Cl_8Mn_4N_9O_{14}$

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IR spectrum of 2, 2'-dipyridylamine ligand

CHAPTER ONE

1.1. GENERAL INTRODUCTION

During recent years, transition metals' complexes of the Schiff base have received a lot of attention because of their potential applications in medicinal and pharmaceutical field.[1] As a result of their stable complex formation with transition metal ions and Schiff base linkage (C=N) taking part in the complex formation processes, these complexes are seen as a model compound and play an active role in the development of coordination chemistry.[2] The azomethine (Schiff base) nitrogen atom has lone pair electron, which has significant ability to form complexes with different metal ions, given rise to potential biochemical applications.[3] Metal complexes of nitrogen or oxygen chelating agent derived from carbonyl and amino Schiff base have certain uses in biological, clinical, analytical and pharmaceutical areas.[4] Due to the demand of new metal-based antibacterial and antifungal compounds, metal organic chemistry is becoming an emerging area of research.[5] A survey of the literature reveals that several works has been carried out on the synthesis and characterization of the mixed ligand complexes.

1.2. Schiff base ligands

Schiff bases have important role in the development of (coordination compounds) chemistry as they readily form new complexes with metals.[6] These compounds are played in the field of inorganic chemistry and various aspects of organometallic compounds.[7] Schiff base and its complexes containing azomethine group, (Figure-1).

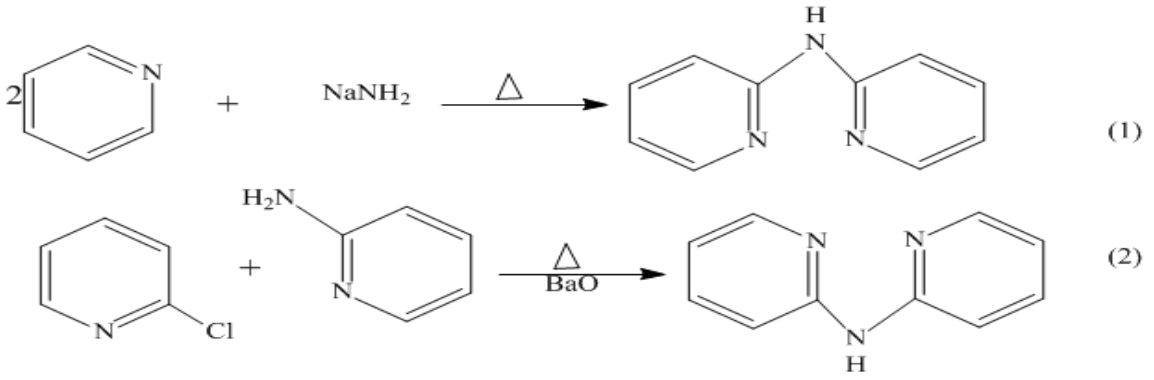

Figure-1. Synthesis of Schiff base (-N=C-NH-C=N- , diimine) with different methods

The (-HC=N-) group is particularly suited for binding to metal ions and the N atom lone pair (C=N:) and when contain one or more donor atoms in addition to (–C=N-) group they act as polydentate ligands or macro-cycles.

Transition metal complexes containing Oxygen and Nitrogen donor Schiff base ligands have been of research interest for last year's and act as active sites and thereby catalyze chemical reactions.[8]

1.3. Schiff base-metal complexes

There are many literature reviews on the synthesis and characterization of Schiff base metal complexes.[9] Schiff base metal complexes are generally synthesis by treating metal halides (MX_n) with Schiff base ligands under suitable experimental conditions.

Generally transition metal ions are used to prepare coordination complexes with different oxidation states, interesting new physicochemical properties and different coordination structures & geometries. [10,11]

1.4 Statement of the problem

A significant increase in the rate of mortality of people exposed to infection diseases is very concerning issue. The main reason of such diseases is bacteria that are extremely resistant to different antibiotics (metallic complexes). In recent years, there have been enhanced interest in the synthesis of new metallic complexes containing diimine, (N=C-NH-C=N), because of their many applications. Metallic complexes derived from heterocyclic, (N=C-NH-C=N), have acquired more attention in the field of inorganic chemistry because of their potential applications. Hence, this research definitely contributes new multinuclear mixed ligand complexes of zinc and manganese metals.

1.5. Significance of the study

Zn(II) and Mn(II) metal ion complexes possess considerable potential in many applications including biological, clinical, catalytic, antibiotics etc. These and other useful applications of Zn(II) and Mn(II) complexes derived from mixed ligand of citric acid and 2, 2'-dipyridylamine initiated actively to undertake extensive research work in this area.

1.6 Limitation of the study

In this work, multinuclear complexes of Zn(II) and Mn(II) have been synthesized from mixed ligand of citric acid and 2, 2'-dipyridylamine. In general, no more experimental journals (literatures) about diimine (-N=C-NH-C=N-), and also Zn(II) and Mn(II) multinuclear complexes.

2. OBJECTIVES AND SCOPE OF THE STUDY

2.1 General objective

General objective of the study was to synthesize and characterize the new Zn(II) and Mn(II) mixed ligand complexes from citric acid and different ratio of 2,2'dipyridylamine ligands.

2.2 Specific objectives

- Synthesis of the desired complex of Zn(II) metal and mixed ligands of citric acid and 2, 2'-dipyridylamine with 3:2:3 molar ratio of metal to ligands, respectively.
- Synthesis of complex from Zn(II) ion, citric acid and 2, 2'-dipyridylamine ligand with 3:2:4 metal to ligands molar ratio, respectively.
- Synthesis of complex from Mn(II) metal, citric acid and 2, 2'-dipyridylamine ligand with 3:2:4 metal to ligands molar ratio, respectively.

In this study, Zn(II) and Mn(II) metal chlorate salts, citric acid, 2, 2'-dipyridylamine and NH_4OH have been chosen for the synthesis of the multinuclear mixed ligand complexes.

The starting materials, the ligand as well as the metal complexes will be characterized on the base of the decomposition temperature, conductivity and magnetic measurement, AAS, IR spectra, UV-vis spectra, elemental analysis and solubility.

3. LITERATURE REVIEW

3.1. Metallic complexes

Transition metal complexes containing heterocyclic compounds have been considerable interest in terms of structural chemistry, catalysis and biological functions. The field has undergone spectacular growth due to the synthesis of multidentate ligands from heterocyclic compound and the complexes of such ligands form with metal ions.[12] There are a number of multidentate ligands that play important roles in coordination chemistry and catalyst designing.

The degree of interaction between the metal center and the neutral ligand atom can exert a profound influence on the reactivity of the resulting complexes. A large number of multidentate ligands have been synthesized and investigated for their metal binding character. Several ligands possessing, (C=N), group are known as Schiff bases.[13]
Transition metal bond with organic ligands are known to possess potential activities in the areas of biological, clinical, analytical, catalytic, microbial, insecticidal, antibiotic, food additive, tumor inhibitor, cell division etc.

This is due to either the unused coordination sites present on the metal and ligand systems, or due to the selective oxidation state of the complexes metal ions in the coordination scope.[14]
The effectiveness of metal chelates in various branches of theoretical and applied chemistry is now generally accepted. These components which form metal chelates are used broadly in both qualitative and quantitative analysis. 2, 2'-dipyridylamine was extensively investigated as a neutral N, N chelating ligand and also as an analytical reagent.
Substituted 2, 2'-dipyridylamine can be synthesized to enhance the chelating capacity. It can be introduced on the heterocyclic as well as the non-heterocyclic regions through suitable reaction paths, while appropriately judging the electronic, steric and chelating factors. The choice of substitution and derivatization can have profound influence on the chelating abilities. The rigidity and neutrality of 2, 2'-dipyridylamine make it an

interesting ambidentate chelating ligand due to N, N (N-donor) sequences available for metal binding. However, the chelating sequence may differ due to electronic factors and hard or soft behaviors. But the molecule is still a rigid system, which can provide coordination in one plane. The system can be made flexible to provide three dimensional coordination through derivative of a variety of secondary amines.[15]

3.2. Organic ligands (O or N-donor)

The organic ligands, which are used for complexes, generally contain coordinating functional group such as carboxylate, amine, or pyridine. The formations of complexes are highly influenced by the Schiff base. Thus, selecting a suitable organic ligand with versatile binding modes to coordinate to a metal ion is very important in the reaction of complexes systems with desired structure and properties. Some typical chelating ligands are given in, (Figure-2).

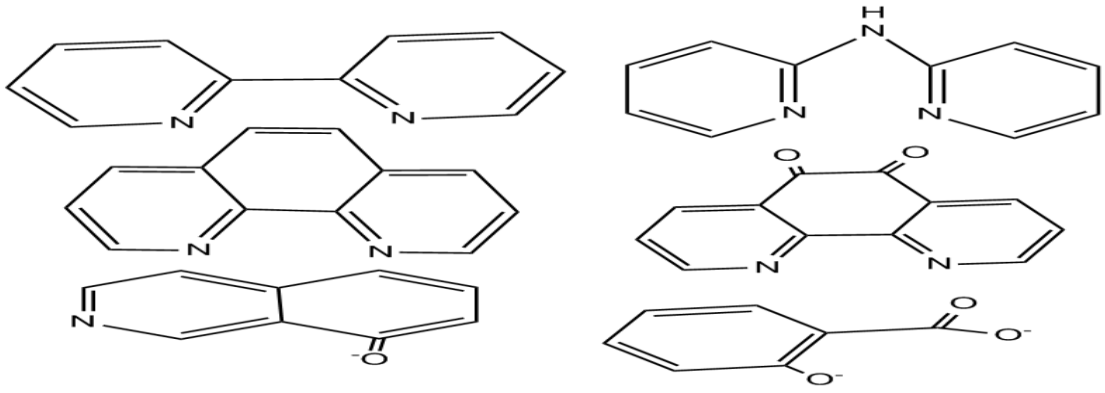

Figure-2. Some examples of chelating ligands

Multifunctional ligands with more than one coordination site are often used to prepare complexes. Among these polycarboxylate ligands play an important role because their versatile coordination modes, from terminal to various bridging modes, can generate interesting complexes structures with desired properties. Even in similar ratio of metal ion and carboxylate anion, polycarboxylate (O-donor) ligands can yield a variety of complexes depending on the different bonding modes and various possible conformations (Ghoshal *et al.,* 2004; Ghosh *et al.,* 2007).

3.2.1 Nitrogen donor ligands (N-donor)

Nitrogen donor ligands have been widely employed as linkers in complexes synthesis. Schiff based ligands show better donor ability towards the metal centers in comparison to primary amines, producing more stable complexes.

The metal nitrogen coordination bond is relatively labile in comparison to a metal carboxylate bond, and this allows easy rearrangements during the reaction and producing a range of new structural designs. Most pyridyl ligands are neutral, and once reacted with a cationic metal center the network produced will retain a charge that must be balanced by counter ions, which have to be incorporated into the mixed ligand complexes.

3.2.2. 2, 2'-dipyridylamine ligands

Acyclic ligands containing one or more pyridyl units are attractive candidates because of their role in a variety of catalytic processes including oxidation and hydrolysis. [16, 17]

The ligand of 2, 2'-dipyridylamine has been one of a useful ligand for synthesis different types of complexes. [18] It consists of two pyridyl rings bridged by a secondary amine, (Figure-3).

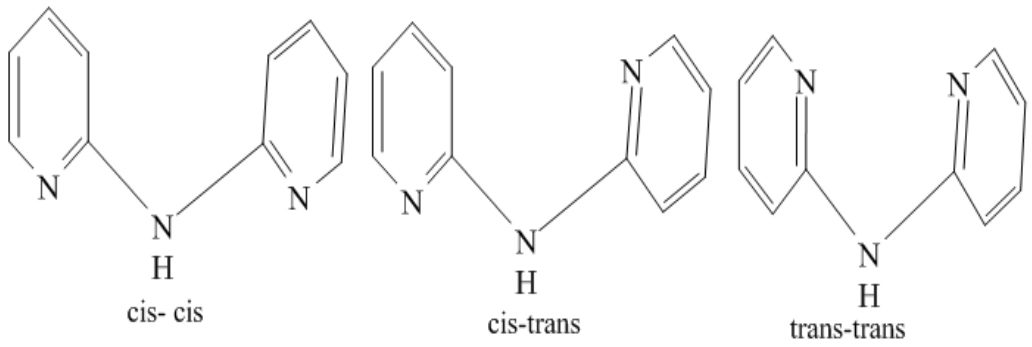

Figure-3. Conformations of 2, 2'-dipyridylamine ligand

In the neutral ligand the central N-atom (2^{O} amine, -NH) is not strongly basic, but imparts a degree of flexibility to the ligand. It has been reported to possess a number of possible coordination modes towards metal centers, in both the neutral and ion forms, as shown in, (Figure-5) below. [19]

An additional dimension to this ligand is the incorporation of an amino group, which is the site of deprotonation, providing another coordination site.

Deprotonation of 2, 2'-dipyridylamine by a base, the negative charge on the $[dpa]^-$ anion can be delocalized around both aromatic rings, (Figure-4).

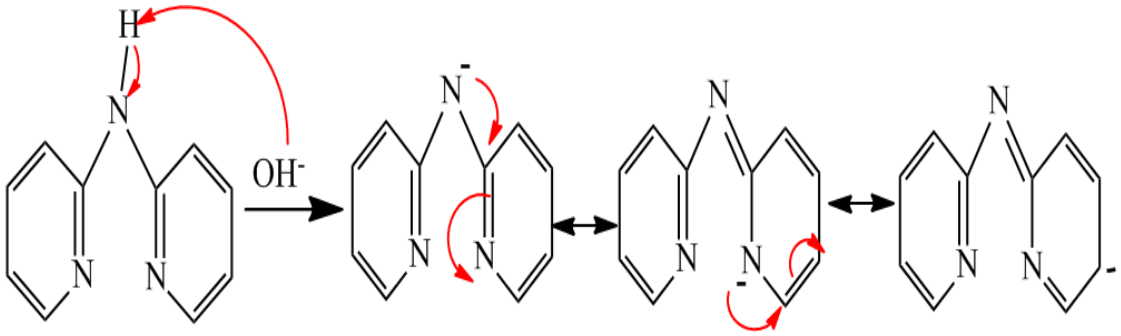

Figure-4. Resonance stabilization of the $[dpa]^-$ anion

When N,N -chelation is the preferred mode of coordination, deprotonated 2, 2'-dipyridylamine often acts as a rigid organic donor, forcing the metal center to extended conjugated aromatic ligand system.[20]

Free rotation around the two single bonds surrounding the (-NH) group can result in an alternate orientation of the pyridyl nitrogen's relative to the amino nitrogen. Thus, a variety of coordination modes for dpa has been observed, (Figure-5).[21,22]

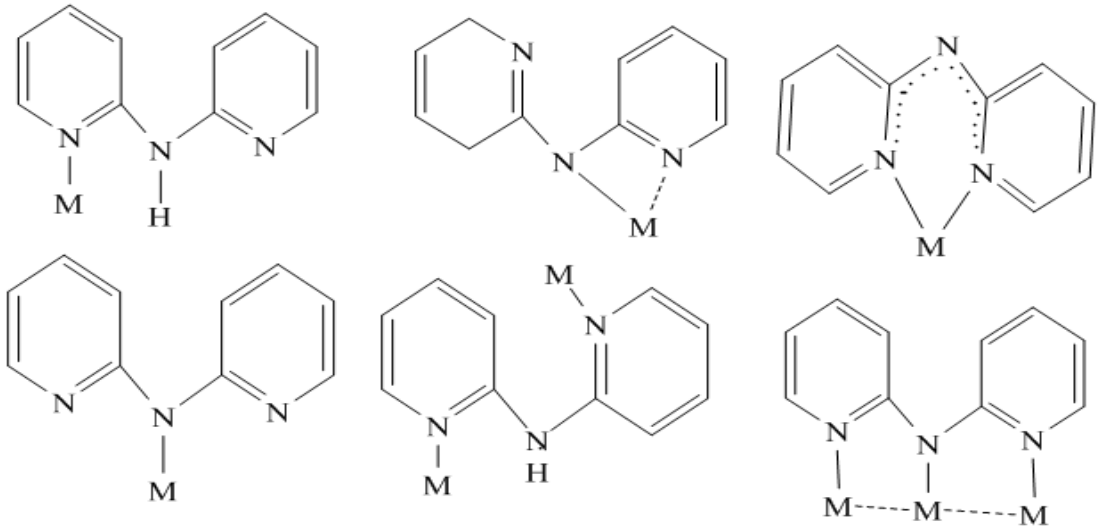

Figure-5. Different coordination modes of dpa and the $[dpa]^-$ anion

3.2.3 Carboxylate ligands (O-donor)

Carboxylate-metal complexes have been investigated over the last few years due to their interesting coordination chemistry, unusual structural features, remarkable physical and chemical properties, and potential applications as dyes, extractants, drugs, pesticides, catalysts.[23]

The rational design and synthesis of novel metal carboxylates with structural diversity are still a great challenge. Several factors such as the coordination nature of metal ions, counter anions, solvents, metal to ligand ratio, pH value and reaction temperature have been found to influence the structures of complexes.[24]

Hydroxypolycarboxylic acids can act not only as hydrogen-bond acceptors, but also as hydrogen-bond donors to form extended structures by means of additional hydrogen-bond interactions.[25] The diverse coordination modes of citrate contribute largely to the formation of various structural types for transition metal citrates, such as mononuclear, dinuclear and polynuclear structural units.

The extended properties of organic ligands that coordinate metal ions in different fashion can give rise to an infinite combination of both organic and inorganic parts leading to the formation of complexes.

The carboxylate functionality allows chelation of metal ions to yield rigid and geometrically determined clusters. However, the major challenge is finding the appropriate conditions that permit the formation of metal clusters.

3.3. Metal ions

Transition metal ions are often used as versatile connectors in the construction of complexes. The first row transition metal ions, such as Zn^{2+}, Co^{2+}, Fe^{3+}, Cu^{2+},Ni^{2+} and Mn^{2+} are commonly used. Some alkali metal ions, alkaline earth metal ions and rear earth metal ions have also been employed as metal nodes for constructing complexes structures.[26] The important characteristics of metal ions are the number and orientation of their binding sites (coordination numbers and coordination geometries),(Figure-6)

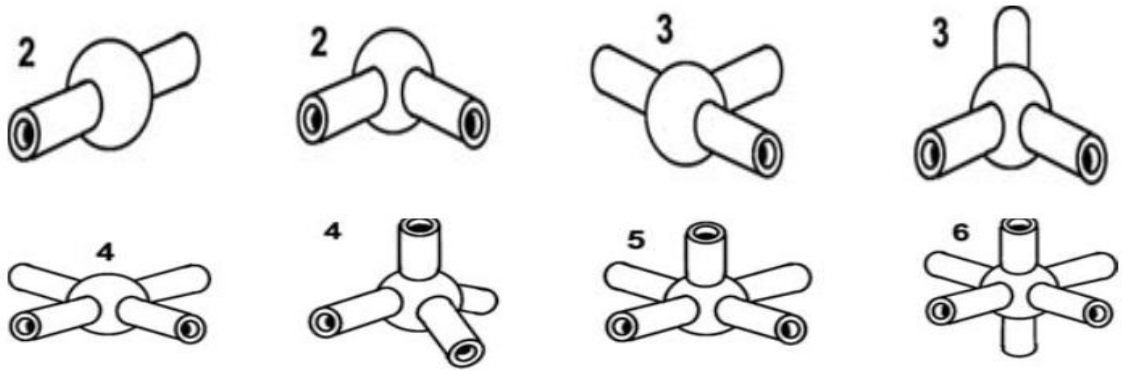

Figure-6**.** Examples of coordination numbers and geometries of metal ions

Depending on the metal and its oxidation state, coordination numbers can range from 2 to 6, giving rise to various geometries, such as linear, square planar, tetrahedral, square pyramidal, octahedral etc., which play an important role in directing the complexes structures.

3.3.1 Chemistry of Zn(II)

Zinc is the heaviest member of the first row transition series of elements and belongs to group 12 of the periodic table, along with Cd and Hg. The element has one main oxidation state (+2).

In general zinc has a specific role in complexes formation because of the unique properties of the coordination compounds of the zinc ions.

Zn(II) ion electron configuration, (d^{10}), indicated that, zinc complexes are not subject to ligand field stabilization effects and so coordination number and geometry is only dictated by ligand size and charge. Thus, Zn(II) forms very important coordinated octahedral complexes.

Zinc (II) is an ion of border line hardness and displays high affinity for nitrogen and oxygen donor atoms.[27-29] This metal ion is diamagnetic and does not have any d-d transition state because of full filled of 3d orbital.[30]

3.3.2 Chemistry of Mn(II)

Manganese containing coordination complexes are great interest due to their unique magnetic properties as well as their variety of functions in chemistry.[31] A very large number of nitrogen bridging compounds have been synthesized. Among the transition metal ions, manganese-based coordination compounds have received considerable interest in biochemistry and versatile catalytic activities.[32,33]

In continuation, we aim to investigate the binding of this tailored diimine, (N=C-NH-C=N), to paramagnetic Mn(II). dpa may behave us a versatile ligand ranging from monodentite, chelating didentate to bridging tridentate [34,35]. However. Harnessing hydrogen bonded networks through its active amine (-NH-) hydrogen as a proton donor that may lead to supramolecular structure is very scarce.

Manganese is widespread in biology because of its availability in different oxidation states controlling the active site of structures, physicochemical properties and functions of enzymes. Weak interactions of non-covalent forces are found in several metallo-enzymes and metalloproteinase affecting a number of biologically important complexes.[36]

3.4 Complex synthesis methods

Generally, the synthesis of complexes is achieved using soluble salts as source of metal such as metal nitrates, sulfates, chlorates or acetates. Nitrogen or oxygen (N-or O-donor ligands) containing ligands (Schiff base) are commonly used as coordination donor. [46]

Polar organic solvents, typically amine (triethylamine), amide (diethylformamide, dimethylformamide) or water is normally required. After combination of these metal salts and organic components, (Schiff bases), complexes are formed with different method of reaction. There are two important methods for the synthesis of complexes. They are direct interaction and template methods of complex formation.

4. EXPERIMENTAL

4. Materials and Methods

4.1. Apparatus and Instruments

For different purposes of this study, various ordinary laboratory glass wares, gloves have been used. IR spectrum was recorded using Spectrum 65 Perkin-Elmer FT-IR spectrometer in the range of 4000 - 400 cm^{-1}. Magnetic susceptibility of Mn(II) compound was measured using Sherwood magnetic balance. Elemental analysis of C, H & N were done by using EA 1112 Flash CHNS/O Elemental analyzer. Molar conductivity of the products was recorded at room temperature using conductivity meter. Metal analysis was done with Zeenit 700 p (Analytikjena) Flame-AAS. Electronic spectra of the synthesized complexes were recorded in the UV-vise region (200-600 nm) by SPECTRONIC GENESYTM 2PC UV-vis spectrophotometer. Melting or decomposition points were determined with digital melting point apparatus.

4.2. Chemicals and Reagents

The chemicals used for the synthesis of complexes were an Analytical grade. Anhydrous citric acid, $ZnCl_2$, $MnCl_2 \bullet 4H_2O$, 2, 2'-dipyridylamine, concentrated, HNO_3, aqueous ammonia solution, solvents such as ethanol, chloroform, dimetylsulfoxide (DMSO), dimetylformamide (DMF), acetonitrile, acetone, dichloromethane, tetrahydrofuran (THF) and water. All the chemicals utilized in these work were analytical grade.

4.3. Experimental methods

Synthesis of the desired products of compound-1, 2 and 3 were undertaken by direct interaction methods. In addition, the analytical works such as IR spectrum, UV-vis spectrum, and measurement of melting point or decomposition temperature, solubility, conductivity, magnetic property, and Elemental analysis of CHN etc. were conducted at Addis Ababa University, Department of Chemistry.

4.4. Synthesis of Zn(II) complex (Cpd-1)

Hydrated citric acid (0.42 g or 2.0 mmole) and 2, 2'-dipyridylamine (0.514 g or 3.0 mmole) were added to a stirred solution of $ZnCl_2$ (0.4086 g or 3.0 mmole) in water (50 ml) with 3:2:3 molar ratio of inorganic metal, citric acid and organic ligand, respectively.

The pH of the solution was adjusted to 5.1 with dilute NH_4OH. The mixture was heated in a water bath at 60^0C for 108 hours. After heating for four days, the mixture was cooled to room temperature and kept for one week to give white (precipitate) metallic complex as shown in, (Figure-7).

Figure-7. Compound-1 before and after filtration

The product (white precipitate) was filtered and washed with distilled water to remove impurities and dried in air. Yield, 734.1g, (64%).

Scheme-1:- The chemical reaction of complex-1.

$$ZnCl_2 + H_2cit{\bullet}H_2O \rightarrow [ZnH_2cit{\bullet}H_2O] \text{ (cluster of inorganic metal ion)} + 2HCl$$

$$[Zn(H_2cit)H_2O] + C_{10}H_9N_3 \rightarrow [Zn(H_2cit)(C_{10}H_9N_3)H_2O] \text{ .....….....(a)}$$

$$2ZnCl_2 + H_2cit{\bullet}H_2O + 2C_{10}H_9N_3 \rightarrow [Zn_2(H_2cit)(C_{10}H_9N_3)_2(H_2O)] + 4HCl \text{ .....(b)}$$

$$[Zn(H_2cit)(C_{10}H_9N_3)H_2O] \text{ (a)} + [Zn_2(H_2cit)(C_{10}H_9N_3)_2(H_2O)] \text{ (b)}$$

$$\downarrow 2NH_4OH,\ 60^OC$$

$$Zn_3(H_2cit)_2(C_{10}H_8N_3)_3(H_2O)_3$$

Scheme-2. Mechanism of compound-1

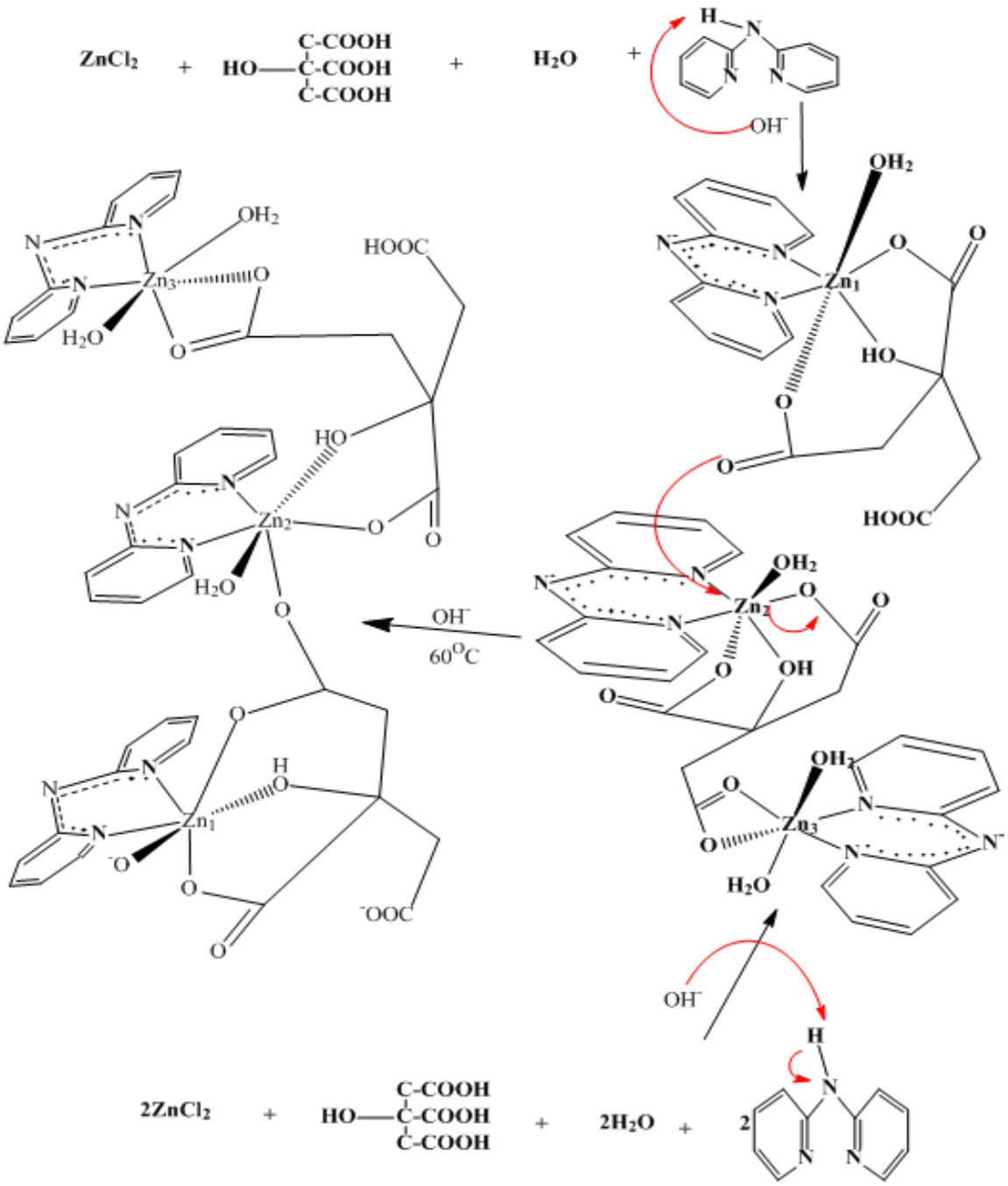

Figure-8. Mechanism of chemical reaction (Cpd-1)

The citrate ligand exhibits an interesting connection mode with zinc ions. One citrate group acts as a tridentate - monodentate ligand, bridging two zinc ions, while the other acts as a bidentate - bidentate ligand, bridging two zinc ions (Figure-8).

The 2, 2’-dipyridylamine is deprotonated with base and the negative charge on the $[dpa]^-$ anion can be delocalized inside the new formed ring, (Figure-9).[30,31]

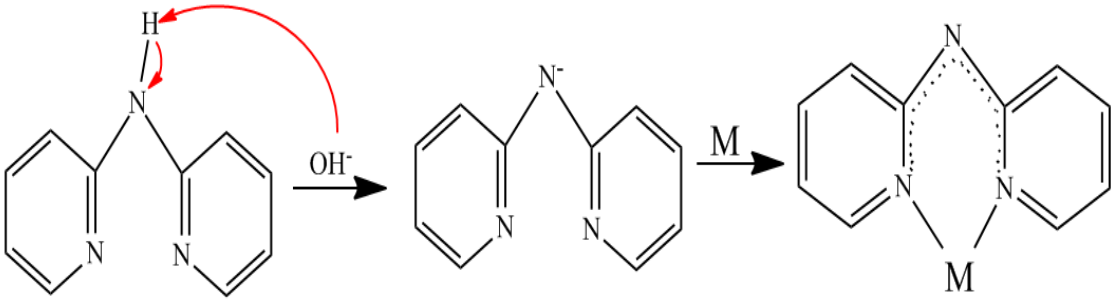

Figure-9. Coordinated 2, 2’-dipyridylamine anion resonance

In compound-1, there are three zinc atoms, two citrate ligands, and three 2, 2’-dipyridylamine ligands, (Figure-10).

The Zn1 atom is six-coordinated by four oxygen atoms and two nitrogen atoms in octahedral coordination geometry. Among the above mentioned oxygen atoms, three are from α-hydroxy, α-carboxy and β-carboxy groups of one citrate anion, and one is from water. The two nitrogen atoms are from one 2, 2’-dipyridylamine ligand.

The Zn2 center is six coordinated by one oxygen atom from water, two nitrogen atoms from one 2, 2’-dipyridylamine ligand, two oxygen atoms from α-hydroxy and α-carboxy groups of one citrate ligand and one oxygen atom from the bridging β-carboxy group of the other citrate ligand in a octahedral coordination geometry.

The Zn3 center is six-coordinated by two nitrogen atoms from 2, 2’-dipyridylamine, two water molecules, and the two oxygen atoms from one β-carboxy group of citrate, containing a weak coordinated Zn_3-O bond. Especially, two oxygen atoms of one β-carboxy group coordinate to Zn(II) ion forming a four-member ring with a O-Zn3-O-C.

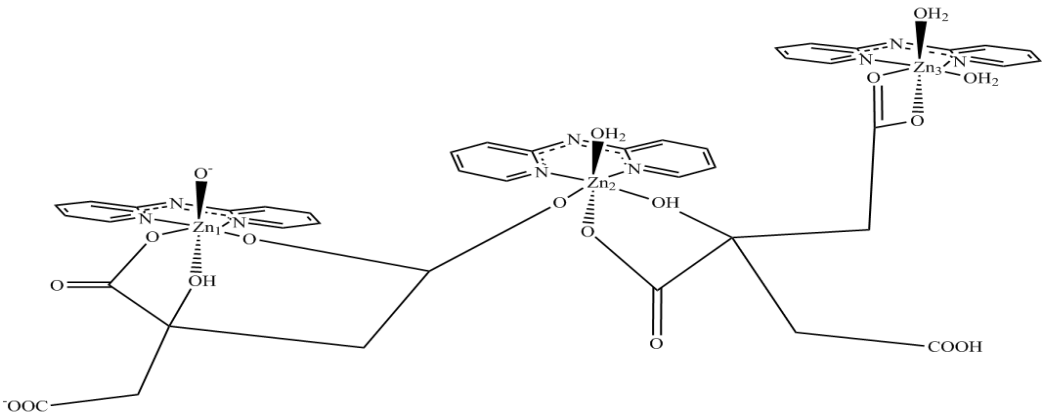

Figure-10. Compound-1 chemical structure, $Zn_3((H_2cit)_2(C_{10}H_8N_3)_3(H_2O)_3$

4.5. Synthesis of Zn(II) complex (Cpd-2)

Citric acid (0.42 g, 2.0 mmole) and 2.2'-dipyridylamine (0.685g, 4.0 mmole) were added to a stirred solution of $ZnCl_2$ (0.4086 g, 3.0 mmole) in water (50 ml) with the ratio of 3:2:4 of $ZnCl_2$, $C_6H_8O_7H_2O$ and $C_{10}H_9N_3$, respectively.

The pH of the solution was adjusted to 5.5 with dilute NH_4OH. The mixture was heated in a water bath at 60^0C for four days (108 hours). After four days, the mixture was cooled at room temperature and left standing for one day to give white (precipitate) crystalline product, (Figure-11).

Figure-11. Compound-2 before filtration

The product (white precipitate) was filtered and washed with distilled water to remove impurities and dried in air. Yield, 842.7gm, (63.3%). The chemical reaction is as follows.

$3ZnCl_2 + 2H_2cit{\bullet}H_2O \rightarrow Zn_3(H_2cit)_2(H_2O)_2$ (cluster of inorganic metal ions) $+ 6HCl$

$Zn_3(H_2cit)_2(H_2O)_2 + 4C_{10}H_9N_3 + 4NH_4OH \rightarrow [Zn_3(H_2cit)_2(C_{10}H_8N_3)_4(H_2O)_2]{\bullet}9H_2O$

In compound-2, there are three zinc atoms, two citrate ligands, and four 2, 2'-dipyridyl amine ligands. The Zn1 atom is six-coordinated by four oxygen atoms and two nitrogen atoms in octahedral coordination geometry. Among the above mentioned oxygen atoms, three are from α-hydroxy, α-carboxy and β-carboxy groups of one citrate anion, and one is from water. The two nitrogen atoms are from one 2, 2'-dipyridylamine ligand.

The Zn2 center is six coordinated by one oxygen atom from water, two nitrogen atoms from one 2, 2'-dipyridylamine ligand, two oxygen atoms from α-hydroxy and α-carboxy groups of one citrate ligand and one oxygen atom from the bridging β-carboxy group of the other citrate ligand in a octahedral coordination geometry.

Interestingly, there exists a strong intra-molecular hydrogen bond between the coordinated hydroxy oxygen atom O4 and oxygen atom O5, (Figure-12), of uncoordinated β-carboxy group in the citrate ligand. The Zn3 center is six-coordinated by four nitrogen atoms from two chelate 2, 2'-dipyridylamine and two oxygen atoms from the β-carboxy group of one citrate ligand in octahedron geometry, (Figure-12). The trinuclear units are further expanded to form a 2D network with coordination bond and intr-molecular hydrogen bond.

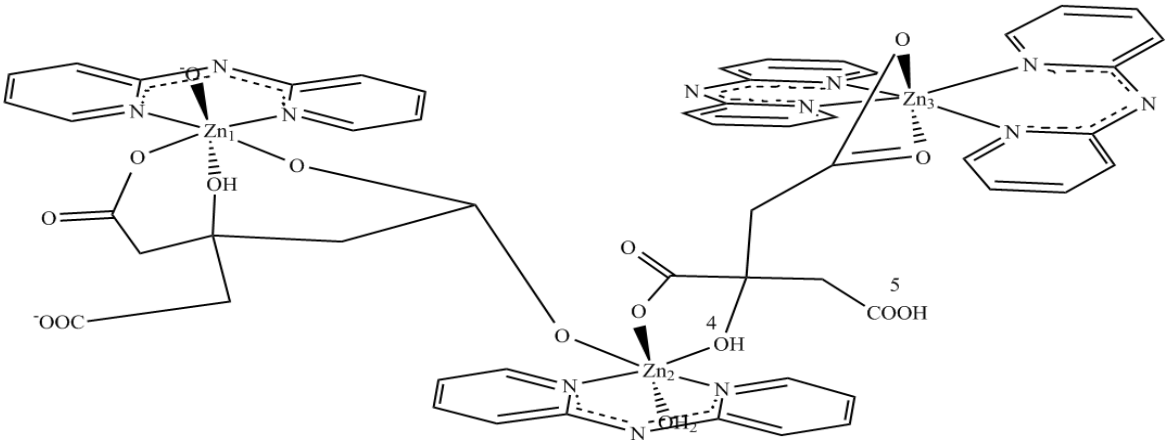

Figure-12.Compound-2 chemical structure, $Zn_3((H_2cit)_2(C_{10}H_8N_3)_4(H_2O)_2$

In summary, two zinc (II) compounds have been synthesized from the reactions of zinc chloride with citrate and 2, 2'-dipyridylamine in aqueous solution at $60^{O}C$, in weak acidic solution. The elemental analysis displays that slightly changing the metal-to-ligand molar ratio leads to the different structures but similar AAS, conductivity, physical property.

Both zinc metal complexes, (Cpd-1 and 2), exhibit a one-dimensional coordination polymer chain structure with trinuclear subunits, linked by the monodentate β-carboxy groups of citrate ligands and the second-dimension is linked by strong intr-molecular hydrogen bond with β-carboxy groups.

4.6. Synthesis of Mn(II) complex (Cpd-3)

Citric acid (0.42 g, 2.0 mmole) and 2.2'-dipyridylamine (0.685g, 4.0 mmole) were added to a stirred solution of $MnCl_2 \bullet 4H_2O$ (0.5937 g, 3.0 mmole) in water (50 ml) with the ratio of 3:2:4 $MnCl_2 \bullet 4H_2O$, $C_6H_8O_7H_2O$ and $C_{10}H_9N_3$, respectively.

The pH of the solution was adjusted to 5.5 with dilute NH_4OH. The mixture was heated in a water bath at $60^{0}C$ for four days, and the golden like crystals appeared from the warm solution. The mixture was cooled at room temperature and left standing for one day to give golden brown (precipitate) solid product.

The product (the golden precipitate) was isolated by filtration and washing with distilled water and dried in air. The reaction of $MnCl_2 \bullet 4H_2O$, $Hcit \bullet H_2O$ and $C_{10}H_9N_3$ results in the formation of $[Mn_4Cl_8(C_{10}H_9N_3)_3(H_2O)_{10}] \bullet 4H_2O$. Yield, 565gm, (47.4%). The chemical reaction is as follows.

$4MnCl_2 \bullet 4H_2O + 2C_6H_8O_7 \bullet H_2O \rightarrow$ No reaction at all in weak acid, pH = 5.5, at $60^{O}C$.

$4MnCl_2 \bullet 4H_2O + 3C_{10}H_9N_3 + 4NH_4OH \rightarrow [Mn_4Cl_8(C_{10}H_9N_3)_3(H_2O)_{10}] \bullet 4H_2O$

There are four manganese atoms, eight chlorine atoms, ten water molecules and three 2, 2'-dipyridylamine ligands. The Mn1 and Mn4 centers are similar with six coordinated by three oxygen atom from water, one nitrogen atom from 2, 2'-dipyridylamine and two chlorine atoms in octahedral coordination geometry, respectively.

The Mn2 and Mn3 centers are similar with six coordinated by two oxygen atom from water, two nitrogen atoms from two different 2, 2'-dipyridylamine ligands, and two chlorine atoms in a octahedral coordination geometry, respectively, (Figure-13).

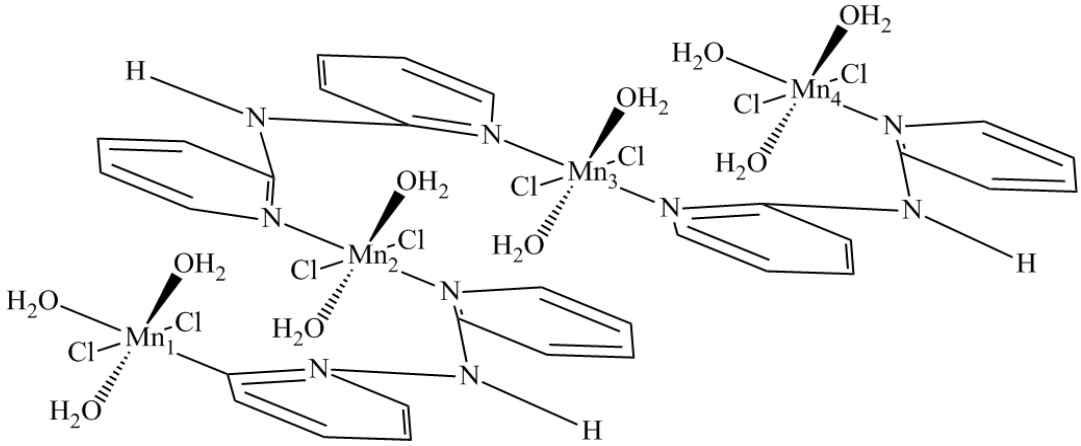

Figure-13. Compound-3 chemical structure, $[Mn_4Cl_8(C_{10}H_9N_3)_3(H_2O)_{10}]\bullet 4H_2O$

In this work, describe the synthesis and characterization of new Mn(II) complex from 2, 2'-dipyridylamine ligand. $MnCl_2$ directly react with 2, 2'-dipyridylamine ligand and formed, $C_{30}H_{55}Cl_8Mn_4N_9O_{14}$, complex.

4.7. AAS of Zn(II) and Mn(II) complexes

Procedure:- From the synthesized Zn (II) and Mn(II) complexes, 5.85 gm of Cpd-1, 6.25 gm of Cpd-2 and 5.96 gm of Cpd-3 were placed in to three clean and dry beakers, to which 10 ml of concentrated HNO_3 were added and the contents were heated gently in a hood until a few drops remained in the flasks (about 2:30 hours). Then all residues were dissolved and diluted using deionized water in each 50 ml flasks. All solutions (Cpd-1, 2 & 3) were subjected to AAS studies after appropriate dilutions.

5. RESULTS AND DISCUSSION

5.1. General

Physical properties, solubility, elemental analysis, molar conductance, electronic and IR spectrum, magnetic susceptibility, AAS of the complexes will be discussed. The complexes that have been synthesized in the laboratory are both distinctly colored and are stable to atmospheric conditions at room temperature.

The synthesized compound-1, 2 and 3 are insoluble in acetone, chloroform, diethyl ether, and n-hexane organic solvents except acetic acid and only partially soluble in solvents like methanol, water etc. The complexes of Zn(II) decomposed at higher temperature around $343^{O}C$ and $348^{O}C$, and the complex of Mn(II) decomposed at a lower temperature around $103^{O}C$.

The properties of complexes judged from the analytical and spectral data which will be presented and discussed in the following sections.

5.2. Physical characteristics of the synthesized complexes

The synthesized Zn(II) and Mn(II) complexes are colored. They are solids, stable in air at room temperature and have specific decomposition point ranges. The general physical characteristic of the synthesized complexes are given in, (Table-1) below.

Table-1**.** Physical properties of the synthesized complexes

Cpds	empirical formula of Cpds	color	appearance	product (gm)	mpt.(^{O}C)
1	$C_{42}H_{55}N_{11}O_{16}Zn_3$	White	Powder	734.1	343
2	$C_{52}H_{60}N_{12}O_{18}Zn_3$	White	Powder	842.7	348
3	$C_{30}H_{48}Cl_8Mn_4N_9O_{10}$	Golden brown	Powder	564.9	103

The decomposition point of Zn(II) complexes ($343^{O}C$ and $348^{O}C$) much higher than that of Mn(II) complex ($103^{O}C$) because of the presence of citrate. Hydroxypolycarboxylic acids can act not only as hydrogen bond acceptors, but also as hydrogen bond donors to

form strong interaction force (either intra- or inter-molecular force of attraction) and extended structures. In Mn(II) complex, there is no citrate, 2, 2'-dipyridylamine is used as a bridging ligand to connect two Mn(II) metals, in which the interaction force of attraction is weak because of that, its melting point is low.

5.3. Solubility of the synthesized complexes

Solubility test was done to identify the best suitable solvent for the following analytical and spectroscopic measurement. The synthesized complexes are soluble in acetic acid, partially soluble in water, dimethylsulphoxide, acetonitrile, ethanol, ethyl acetate, and insoluble in acetone, chloroform, diethyl ether, and n-hexane. The experimentally observed solubility of the complexes are summarized in, (Table-2).

Table-2. Solubility of the synthesized complexes

Cpd	Solvent									
	Acetic acid	Water	DMSO	Aceto-nitrile	Ethanol	EA	Aceton	Chlorofom	Diethyl ether	n-hexane
1	Sol.	Partial sol.	Partial sol.	Partial sol.	Insol.	Insol	Insol.	Insol.	Insol.	Insol.
2	Sol.	Partial sol.	partial sol.	Partial sol.	Insol.	Insol	Insol.	Insol.	Insol.	Insol.
3	Sol.	Part. Sol.	Partial sol.	Partial sol.	Insol.	Insol	Insol.	Insol.	Insol.	Insol.

5.4. AAS of metals in the synthesized complexes

The metal content in the complexes were determined spectroscopically using atomic absorption spectroscopy (AAS). Metal percentage along with C, H, N, & O percentages was used to arrive at the metal-ligand ratio in the complexes.

5.4.1 AAS of Zn(II) in compound-1

Based on the absorbance data, the concentration of Zn (II) complex was calculated.

$$\text{Zn(II) in Cpd-1:- Zn\%} = \frac{\text{Absorbance (A, ppm)} \times \textit{volume diluted}\ (50ml) \times 100}{\text{Mass of sample taken} \times 1000}$$

$$= \frac{19.9326\text{mg/L} \times 0.05\text{L} \times 100}{5.85\text{mg}}$$

$$= 17.04\%$$

5.4.2 AAS of Zn(II) in compound-2

Based on the absorbance data, the concentration of Zn (II) complex was calculated as follow.

$$\text{Zn(II) in Cpd-2 :- Zn\%} = \frac{\text{Absorbance (A, ppm)} \times \textit{volume diluted}(50ml) \times 100}{\text{Mass of sample taken} \times 1000}$$

$$= \frac{16.334\text{mg/L} \times 0.05\text{L} \times 100}{6.25\text{mg}}$$

$$= 13.07\%$$

5.4.3. AAS of Mn(II) in compound-3

Based on the absorbance data, the concentration of Mn(II) complex was calculated as follow.

$$\text{Mn(II) in Cpd-3:- Mn\%} = \frac{\text{Absorbance (A, ppm)} \times \textit{volume diluted}\ (50ml) \times 100}{\text{Mass of sample taken} \times 1000}$$

$$= \frac{20.8642\text{mg/L} \times 0.05\text{L} \times 100}{5.96\text{mg}}$$

$$= 17.5\%$$

The metal percentages obtained from this calculation were used to arrive at the metal to ligand ratio in the complexes as shown in the, (Table-3).

Table-3. Data of AAS of the complexes

compounds	Percentage of perspective metal		metal, citric acid and dpa ligand ratio, respectively	molar mass (gm/mol)
	calculated	found(AAS)		
1	16.7	17.04	3:2:3	1161
2	13.08	13.07	3:2:4	1332
3	17.3	17.5	3:2:4	1192

5.5. Electronic spectrum of Mn(II) and Zn(II) complexes

Electronic spectrum measurements are very useful for assigning the stereochemistry of the complexes based on the position and types of transitions. The electronic absorption spectrum of Zn(II) and Mn(II) compounds were recorded at room temperature by using the solvent of distilled water.

Zn(II) complexes (Cpd 1 & 2) have the same bands. The band at 250 nm is assigned to $\pi \rightarrow \pi^*$ transition of 2, 2'-dipyridyl ring. The band at 315 nm is assigned to $n \rightarrow \pi^*$ transition of 2, 2'-dipyridylamine (C-N-C) or carboxy groups (COOH), (Table-4).

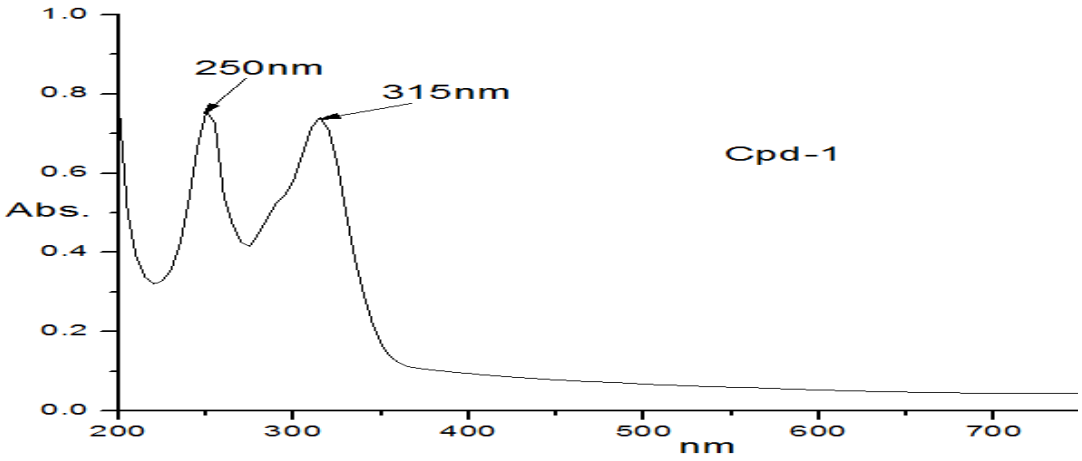

Figure-14. UV-vis spectrum of compound-1

The Mn(II) compound, (Cpd-3), shows two major bands at 260 nm and 310 nm. The band at 260 nm is attributed to π →π* transition of the 2, 2'-dipyridyl region. The band around 310 nm is due to the n →π* transition of the 2^{O} amine (-NH) group.

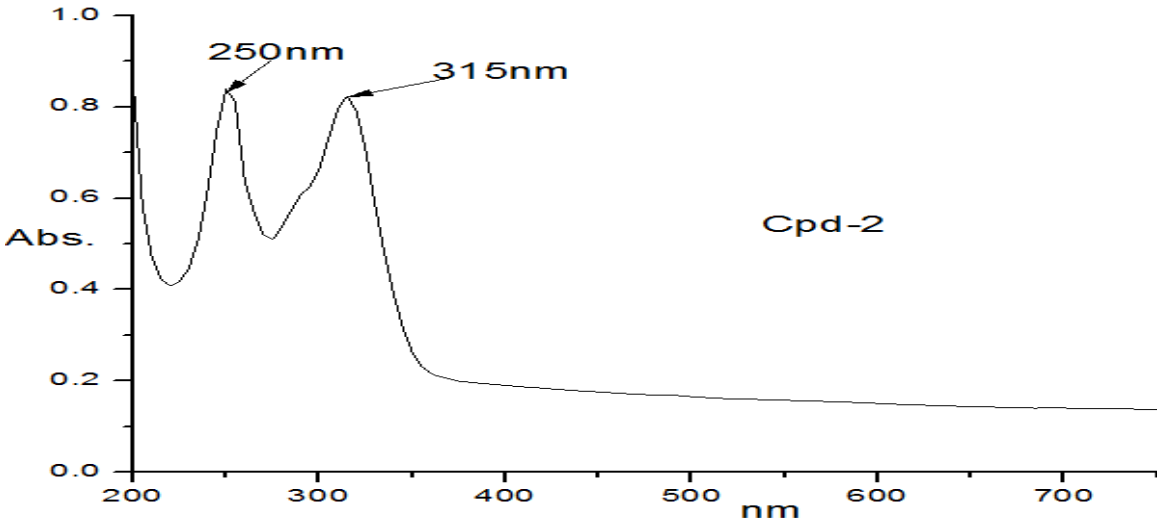

Figure-15. UV-vis spectrum of compound-2

Table-4. The electronic spectrum of Mn(II) and Zn(II) complexes

Cpds	Wavelength (nm)	Band assignment
1	250	π →π*
	315	n →π*
2	250	π →π*
	315	n →π*
3	260	π →π*
	310	n →π*

5.6. Molar conductance measurements

The specific conductance of compounds, (Cpd-1, 2 and 3), were measured in distilled water at room temperature and found to be 0.05*m*S, 0.05*m*S and 0.01*m*S, respectively. The molar conductance of each complex was calculated from the following equation.

$$\Lambda_M = \frac{1000k}{C}$$

Where: - Λ_M = Molar conductance

C = concentration of the sample (10^{-3})

K = specific conductivity of the complex

The molar conductance values which summarized in, (Table-5), indicate that all complexes, (Cpd-1, 2 and 3), are non-electrolytes. Zinc(II) complexes, (Cpd-1 & 2), have the same molar conductance. This indicated that, they have the same chemical properties.

Table-5. Molar conductance of Zn(II) and Mn(II) in water solvent

Cpds	Molar conductance ($S\ cm^2\ mole^{-1}$)	types of electrolyte
1	50	non-electrolyte
2	50	non-electrolyte
3	10	non-electrolyte

5.7 Magnetic susceptibility measurement

In the compounds, Zn^{2+} (d^{10}) have all electrons paired. Hence it is a diamagnetic complex. Octahedral geometry is possible for Mn(II) metal (d^5) with π-acceptor ligands. The experimental gram magnetic susceptibility of Mn(II) complex was $2.18x10^{-5}$gs units at 21^{O}C. This result indicates that the complex is paramagnetic, (Table-6).The molecular weight of the complex is 1148g/mol. The following calculations were made to arrive at the magnetic moment and susceptibility of Mn(II) complex.

Magnetic moment (μ_{eff}) = $2.84\ (\chi_m\ .T\ (K))^{\frac{1}{2}}$

Molar magnetic susceptibility (χ_m) = χ_g. Molecular wt. of the compound

$$\chi_m = \chi_g.MM$$

$$8(\chi_m.\ T) = n\ (n+2)$$

Where: n - is number of unpaired electron

χ_g - is the measured gram susceptibility

χ_m - is molar susceptibility

T (K) - is temperature in Kelvin

Table-6. Magnetic susceptibility of Mn(II) complex

Cpd 3	Magnetic moment ($\mu_{eff.}$)	unpaired electron (n)
Mn(II)	1.7	1

5.8. Elemental analysis of the synthesized complexes

Elemental analysis result showed that there is a direct correlation between the calculated and the experimentally found values, indicating the formation of complexes. The elemental analysis data of the metal complexes are given in, (Table-7). The deviation in nitrogen, (Cpd-3), analysis appears to be attributed to experimental limitations. The metals, carbon and hydrogen analysis are in good match with the proposed compositions.

Table-7. Elemental analysis data for the synthesized complexes

Cpds	% of C		% of H		% of N	
	cal.	found	cal.	found	cal.	found
1	43.07	43.02	5.20	5.60	13.2	13.40
2	41.7	41.77	5.24	7.01	11.21	11.21
3	28.4	28.3	4.4	4.67	9.9	7.6

5.9. IR spectra of the synthesized complexes

FT-IR spectra of complexes 1-3 are shown in the characteristic peaks and tabulated in, (Table-8). The broad bands at 3421 cm^{-1}, 3320 cm^{-1} and 3411 cm^{-1}, 3328 cm^{-1} in the IR spectra were attributed to the (O-H) stretching of the 3^o alcohol molecule(s) and carboxylic acid in complexes 1 and 2, respectively (Hsieh et al., 2006; Maurya et al., 2011).

The peaks correspond to the ring stretching frequencies ν(C=N) and ν(C=C)) of the synthesized complexes were observed at 1538 and 1435 cm^{-1}, 1540 and 1433 cm^{-1}, 1590 and 1528 cm^{-1} for complexes 1-3, respectively.

By comparing the IR spectrum of free 2,2'-dipyridylamine ligand, (**Appendix-1**), with complexes 1-3, it was found that ν(C=N) peaks of the 2,2'-dipyridylamine 1598 cm^{-1} observed was slightly shifted to lower frequencies upon coordination to the metal center with 1538 cm^{-1} , 1540 cm^{-1} and 1590 cm^{-1}, respectively. Therefore, these indicating that the coordination of the (C=N) to metals of Zn(II) and Mn(II).

In Mn(II) complex, there is no bands or peaks of 3^o alcohol or carboxylic acid oxygen, it indicated that citric acid didn't react with manganese in weak acid, pH = 5.5, at 60^OC.

5.9.1 IR spectrum of 2, 2'-dipyridylamine ligand

The IR spectrum of the 2,2'-dipyridylamine ligand shows five characteristic bands at 3405 cm^{-1}, 3258 - 3019 cm^{-1},1614 - 1580 cm^{-1}, 1531 cm^{-1} and 1231 cm^{-1} are the region for stretching vibration of υ(N-H), υ(C-H), υ(C=N), υ(C=C)and υ(C-N-C), respectively.

The bands at 3258 cm^{-1}, 3178 cm^{-1}, 3100 cm^{-1} and 3019 cm^{-1} are the characteristics region of υ(C-H) stretching vibration in the 2, 2'-dipyridylamine. The bands at 991 cm^{-1} and 767 cm^{-1} are the characteristics region in plane vibration of υ(N-H) and υ(C-H) in 2, 2'-dipyridylamine ligand.

5.9.2 Infrared spectrum of compound-1

The IR spectrum of complexes can provide valuable information as to whether or not reaction has occurred. In order to study the bonding of the ligand to the metal ion in compound-1, the IR spectrum of the free ligand must be compared with the spectrum of the complexes.

The four characteristic bands at 3256 cm^{-1}, 3208 cm^{-1}, 3148 cm^{-1} and 3040 cm^{-1} are the characteristic region for stretching vibration of υ(C-H) in the synthesized complexes. The (O-H) of 3^o alcohol, carboxylic acid and water molecules vibrations are generally measured between 3600 -2700 cm^{-1}, therefore, the bands observed at 3421 cm^{-1} and 3320

cm^{-1} are the characteristic region for stretching vibrations of υ(O-H) on 3^{o} alcohol molecules and carboxylic acid, respectively.

The peaks correspond to the ring stretching frequencies ν(C=N) and ν(C=C)) of the synthesized complex was observed at 1538 cm^{-1} and 1436 cm^{-1}, respectively.

The band observed 1653 cm^{-1}, 1600 cm^{-1}, 1587 cm^{-1} and 1488 cm^{-1} are the characteristic region for stretching vibration corresponding to asymmetric and symmetric of the coordinated carboxy groups ν(COO^{-}), respectively.

The bands at 3320 and 1653 cm^{-1}, attributed to non-deprotonated carboxylic acid group (COOH), of citric acid in the synthesized zinc complex, as revealed at the chemical structural, (Figure-10).

The band at 1598 cm^{-1}, υ(C=N), of 2, 2'-dipyridylamine ligand is decreased to 1538 cm^{-1}, υ(C=N), which indicate that the 2, 2'-dipyridylamine ligand donated a pair of electron to the metal Zn(II).

The stretching and bending vibration corresponding to υ(N-H) of the 2, 2'-dipyridylamine at 3405 cm^{-1}, 1665 cm^{-1}, 1342 cm^{-1} and 1313 cm^{-1} and also 991 cm^{-1} were not observed in the IR spectrum of compound-1, these confirming that its deprotonating hydrogen ion and form anion,(Figure-16).

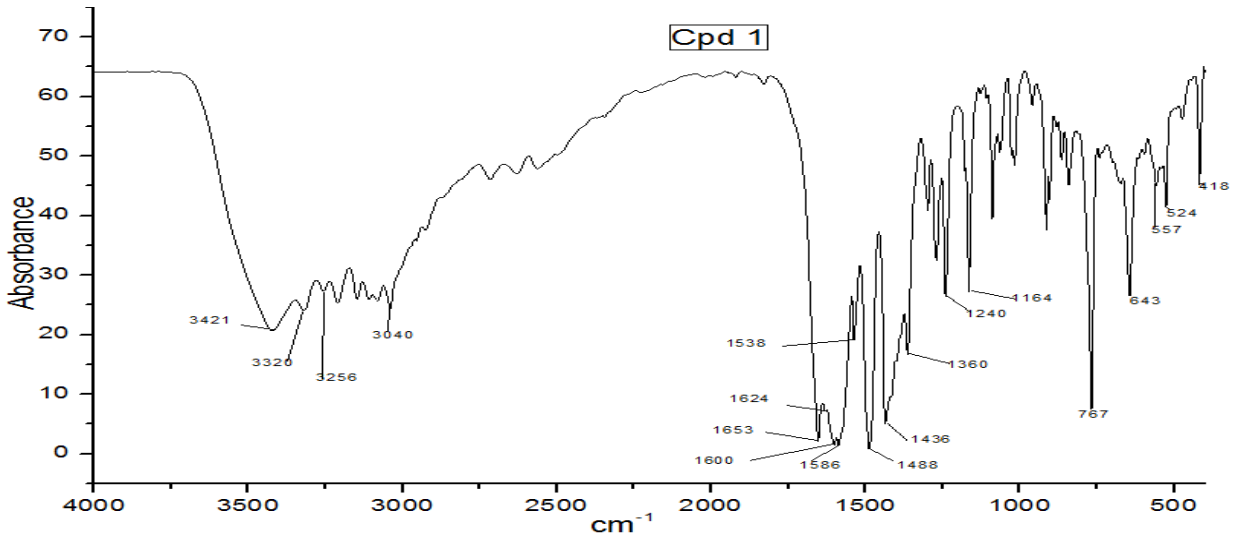

Figure-16. IR spectrum of compound-1

On the other hand, the bands observed at 1342 cm^{-1} ,1313 cm^{-1} and 1231 cm^{-1} are the characteristic regions for stretching vibrational of υ(N-H) and υ(C-N-C) 2,2'-dipyridylamine, the two bands of 1342 cm^{-1} and 1313 cm^{-1} disappear but the band of 1231 cm^{-1} is shifted to 1238 cm^{-1}, indicating that the formation of nitrogen anion with donating proton or hydrogen ion (H^+).

The binding of the ligand was further substantiated by the presence of a number of bands in the range 557 cm^{-1}, 525 cm^{-1} and 418 cm^{-1}, assignable to the M-O and M-N bonds. This is one indication for the coordination reaction that occurred between the 2, 2'-dipyridyl (C=N) ring nitrogen and the given metals.

5.9.3 Infrared spectrum of compound-2

The four characteristic bands at 3258 cm^{-1}, 3208 cm^{-1}, 3148 cm^{-1} and 3038 cm^{-1} are the characteristics region for stretching vibration of ν(C-H) in the synthesized complex. The (O-H) of 3^o alcohol, carboxylic acid and water molecules stretching vibrations are generally measured between 3600 - 2700 cm^{-1}, therefore, the relatively broad (due to hydrogen bond) bands observed at 3411 cm^{-1} and 3328 cm^{-1} are the characteristic region for stretching vibration of ν(O-H) on 3^o alcohol molecules and carboxylic acid, in the presence of hydrogen bond, (Figure-17).

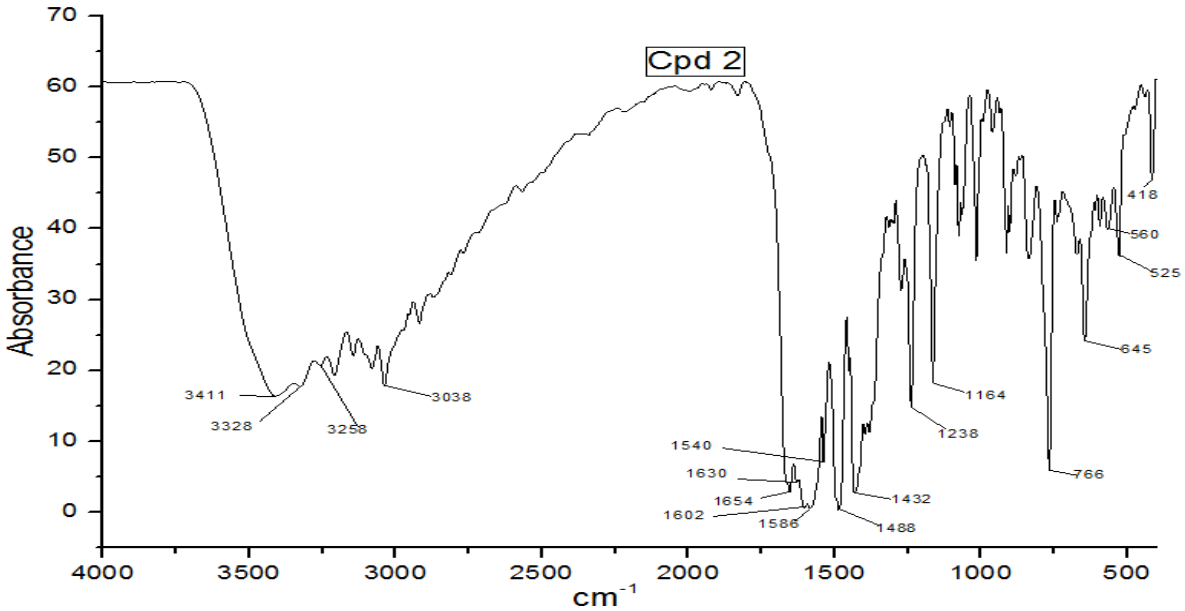

Figure-17. IR spectrum of compound-2

The peaks correspond to the ring stretching frequencies ν(C=N) and ν(C=C) of the synthesized complex was observed at 1540 cm^{-1} and 1433 cm^{-1}, respectively.

The band observed at 1654 cm^{-1}, 1602 cm^{-1}, 1586 cm^{-1}, and, 1486 cm^{-1} are the characteristic region for stretching vibration corresponding to asymmetric and symmetric of the coordinated carboxy groups ν(COO^{-}), respectively. In the compound-2 the band at 1598 cm^{-1}, (C=N), of 2, 2'-dipyridylamine decreased to 1540 cm^{-1}, υ(C=N), which indicates the 2, 2'-dipyridylamine donated a pair of electrons to the metal Zn(II).

The stretching and bending vibration corresponding to υ(N-H) of the 2,2'-dipyridylamine at 3405 cm^{-1}, 1665 cm^{-1},1342 cm^{-1}, 1313 cm^{-1} and 991 cm^{-1} were not observed in the IR spectrum of compounds-2, this confirming that the 2^{O} amine (N-H) deprotonated in the weak acidic media at pH value 5.5. On the other hand, the bands observed at 1342 cm^{-1} ,1313 cm^{-1} and 1231 cm^{-1} are the characteristic regions for stretching vibrational of υ(NH) and υ(C-N-C) 2, 2'-dipyridylamine, the two bands of 1342 cm^{-1} and 1313 cm^{-1} disappears but the band of 1231 cm^{-1} is shifted to 1238 cm^{-1}, indicating that the formation of nitrogen anion with donating hydrogen ion (H^{+}) or deprotonated the secondary amine in the weak acidic media, (Figure-12).

The binding of the ligand was further substantiated by the presence of a number of bands in the range 557 cm^{-1}, 525 cm^{-1} and 416 cm^{-1}, assignable to the M-O and M-N bonds. This is one indication for the coordination reaction that occurred between the pyridyl υ(C=N) ring nitrogen.

5.9.4 Infrared spectrum of compound-3

The IR spectrum of compound-3 shows four characteristic bands at 3430 cm^{-1}, 1595 cm^{-1}, 1528 cm^{-1} and 1227 cm^{-1} are the region for stretching vibration of υ(N-H), υ(C=N), υ(C=C) and υ_{as}(C-N-C), respectively. The band at 3259 cm^{-1}, 3182 cm^{-1} 3101 cm^{-1} and 3021 cm^{-1} are the characteristics region of υ(C-H) stretching vibration of compound-3.

The band observed at 1342 cm^{-1}, 1313 cm^{-1} and 1147 cm^{-1} are the same in compound-3 and 2, 2'-dipyridylamine which are characteristic region for stretching vibration of

υ(NH) and υ(C-N-C) in compound-3, this indicating that, the presence of secondary amine hydrogen, (Figure-13).

The band at 992 cm^{-1} and 767 cm^{-1} are the characteristics region of in plane bending vibration of (N-H) and (C-H), respectively in the synthesized complex that of similar to 2,2'-dipyridylamine ligand.

The complex of Mn(II) show a new, strong and broad peak in the region of 1595 cm^{-1}, which indicates the presence of a coordinated bond between Mn(II) metal and 2, 2'-dipyridylamine nitrogen in (C=N) group, (Figure-18).

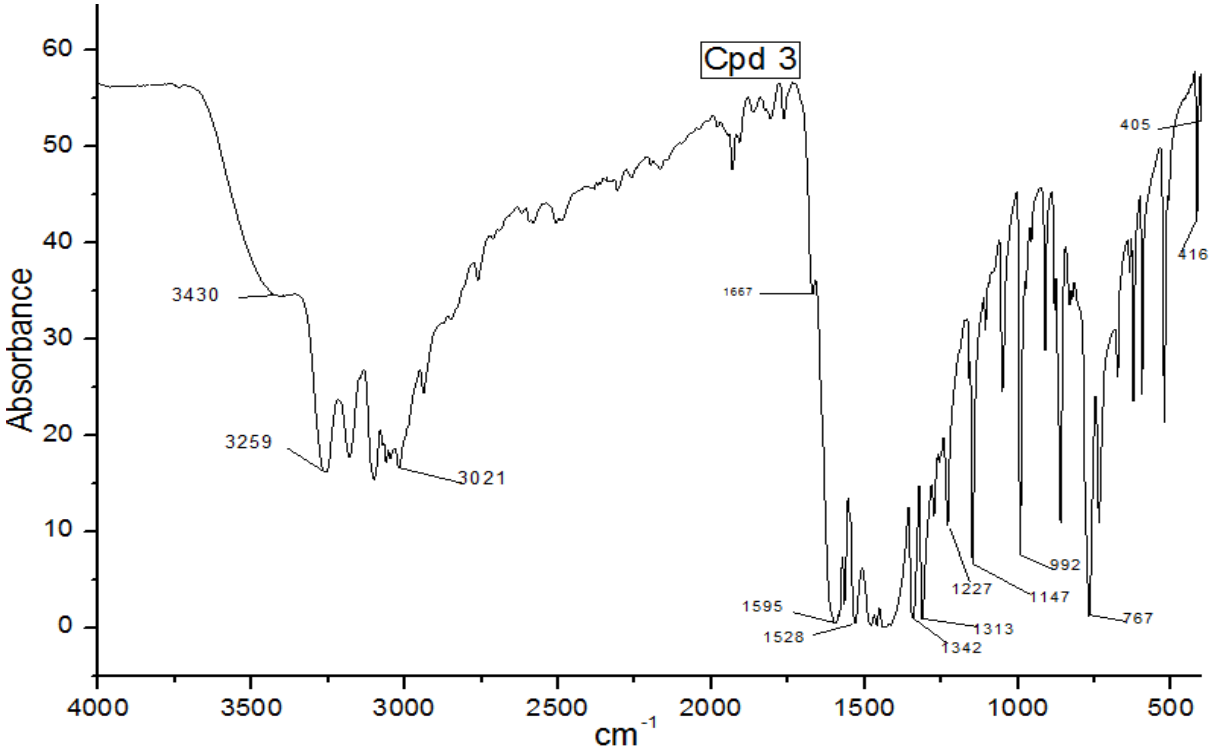

Figure-18. IR spectrum of compound-3

There is no 3^{o} alcohol and carboxylic acid oxygen peaks or bands in Mn(II) complex all over the region, this indicate that citric acid was not reacted with Mn(II) in weak acidic media, pH= 5.5, at $60^{O}C$.

Table-8**.** IR spectra of synthesized complexes and 2, 2'-dipyridylamine ligand

bond	dpa (cm^{-1})	Cpd-1 (cm^{-1})	Cpd-2 (cm^{-1})	Cpd-3 (cm^{-1})
ν(N-H)	3405 (w),1665(w) 1342&1313 (s,Ip) 991 (s,oop)	-	-	3430 (w),1667 1342 &1313, 992 (m, oop)
ν(C-H)	3258 -3019 (w)	3256 - 3040 (w)	3258 - 3038 (w)	3259 -3021 (w)
ν(O-H) 3^{O} alcohol	-	3421 (m),1627 (s), 1360,643 (m.oop)	3411 (mb),1630 (s), 645 (m, oop)	-
ν(COOH)	-	3320(m),1653(s),1600 (s) 1587 (s), 1488 (s),	3328 (mb),1654 (s), 1602(s)1586(s),1488(s)	-
ν(C=N)	1614 - 1580 (sb)	1538 (m.)	1540 (m)	1600 -1590 (sb)
ν(C=C)	1531 (s)	1436 (s) str.	1433(s) str.	1528 (s)
ν_{asy}(C-N-C)	1230 (m)	1240 (m)	1238 (m)	1227 (m)
ν_{sy}(C-N-C)	1147 (s)	1164 (m)	1164 (m)	1147 (m)
ν(M-O)	-	557, 524 (w)	560, 525 (w)	-
ν(M-N)	-	418 (W)	418 (W)	416 (w)
ν(M-Cl)	-	-	-	405 (w)

Where: -v - stands for frequency

mb - medium & broad

sb - strong & broad

w - weak

X - N, O or Cl

oop - out of plane vibration

Ip - in plane vibration

6. CONCLUSION

Mixed ligand complexes of Zn(II) and Mn(II) have been synthesized using template method by the hydrothermal processes in a mixed ligands derived from citric acid and 2, 2'-dipyridylamine in basic media in the presence of NH_4OH solution. Two different Zn(II) complexes have been synthesized from the reactions of zinc chloride and citric acid with different molar ratio of 2, 2'-dipyridylamine in aqueous solution. The elemental analysis displays that slightly changing the metal-to-ligand molar ratio leads to the different chemical structures of the two Zn(II) complexes. $MnCl_2$ was not reacted with citric acid at 60^OC in weak acidic media (pH = 5.5) but it react with 2, 2'-dipyridylamine only in the mixed ligand of the two, and obtained new multinuclear complex. Based on the elemental and metal ion analyses, IR and electronic spectrum data, magnetic and conductance data, an octahedral geometry is suggested for Zn (II) and Mn(II) multinuclear complexes.

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APPENDIX

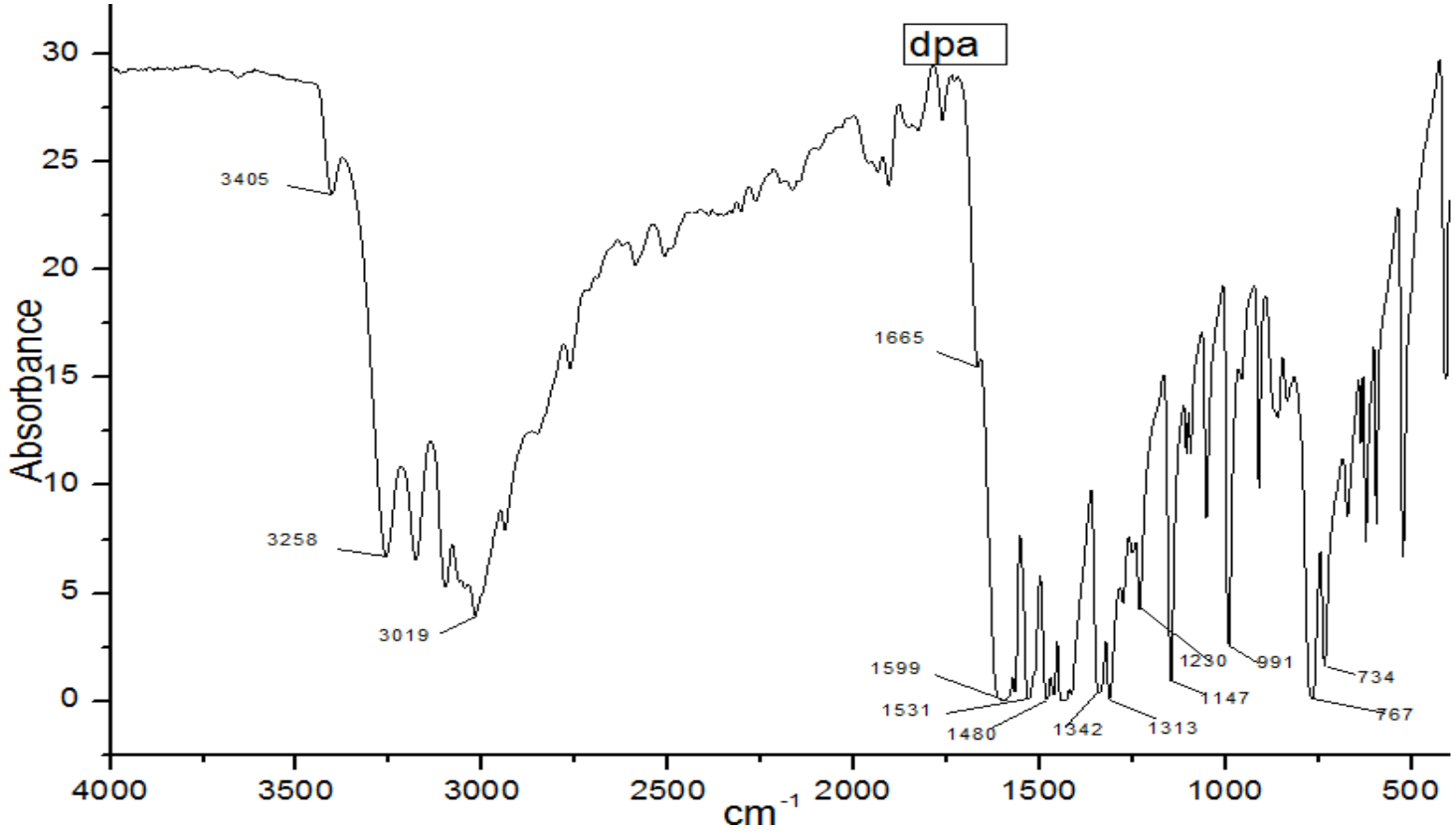

Figure-19. IR spectrum of 2, 2'-dipyridylamine ligand