ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

SYNTHESIS AND CHARACTERIZATION OF Mn (II) AND Zn (II) COMPLEXES OF MIXED LIGAND 2, 2'-BIPYRIDINE AND CITRIC ACID

BY. MELKAMU TAYE

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

SYNTHESIS AND CHARACTERIZATION OF Mn (II) AND Zn (II) COMPLEXES OF MIXED LIGAND 2, 2'-BIPYRIDINE AND CITRIC ACID

A Graduate Project

Submitted to School of Graduate Studies of

Addis Ababa University

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Chemistry

BY: MELKAMU TAYE

JULY 2020

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

SYNTHESIS AND CHARACTERIZATION OF Mn (II) AND Zn (II) COMPLEXES OF MIXED LIGAND 2, 2'-BIPYRIDINE AND CITRIC ACID

ADVISOR Dr. YONAS CHEBUDE

BY: MELKAMU TAE

JULY 2020

SYNTHESIS AND CHARACTERIZATION OF Mn (II) AND Zn (II) COMPLEXES OF MIXED LIGAND 2, 2'-BIPYRIDINE AND CITRIC ACID

By: Melkamu Taye Aga Signature: ----------

This project work has been submitted for examination with my approval as a university advisor.

Advisor: Dr.Yonas Chebude

Signature:_____

Place and date of submission: School of Graduate Studies

Addis Ababa University

July 2020

SYNTHESIS AND CHARACTERIZATION OF Mn (II) AND Zn (II) COMPLEXES OF MIXED LIGAND 2, 2'-BIPYRIDINE AND CITRIC ACID

Approved by the Examining Board:-

	Signature	Date
Dr. Yonas Chebude (Advisor)	_____	_____
Dr. Negash Getachew (Examiner)	_____	_____
Dr. Girum Ayalneh (Examiner)	_____	_____

Abstract

Solvothermal synthesis of Zn (II) ion with mixed ligand 2,2'-Bipyridine and citric acid resulted in new Zn:Hcit:$(bpy)_1$ (1) $[Zn_3(C_6H_5O_7)_2\ (C_{10}H_8N_2)_3.(H_2O)_2\ ].6H_2O.(NH_3)_3$ and Zn:Hcit:$(bpy)_2$ (2) $[Zn_3\ (C_6H_5O_7)_2\ (C_{10}H_8N_2)_6]$ (Hcit=citric acid, bpy =2,2'-Bipyridine) the first was obtained from zinc chloride, citric acid and 2,2-bipyridine in 3:2:3 molar ratio while the latter was obtained in 3:2:4 molar ratio. The coordination of the complex depends on the variations of pH value and metal to ligand ratio. The synthesis of Mn (II) complex Mn; Hcit:$(bpy)_2$, $[Mn_3(C_6H_5O_7)_2\ (C_{10}H_8N_2)_4.(H_2O)_2\ ].12H_2O$ was obtained from hydrated manganese salt, citric acid and 2,2'-bipyridine in 3:2:4 molar ratios respectively.

The complexes were characterized on the bases of elemental analysis, molar conductance, FT-IR and Uv-vis spectroscopy.

Key; Zn: Hcit: $(bpy)_1$=(Hcit= citric acid, bpy =2,2'-bipyridine)

Zn: Hcit:$(bpy)_2$

Mn: Hcit:$(bpy)_2$

Acknowledgment

First of all, I would like to give the greatest possible glory and thanks to my God, the one responsible for the accomplishment of this work.

I am deeply indebted to Dr.Yonas Chebude for his invaluable guidance, constant encouragement, unreserved support, consultation and comments throughout this work.

I am very thankful to W/rt Makida Fanos and W/rt Debora Mamo for running my samples IR and kind help me during the laboratory work.

I am very much thankful to the department of chemistry AAU, for providing me with all the needed chemicals and materials.

I also wish to acknowledge Dr. AddisalemYeneabat Dean of AAU College of Natural and Computational Sciences allowed to live in the University.

I would like to say thanks to B/G Educational Bureau and Debate Woreda for giving this chance and paying salary in the duration of the program.

I would like to give special thanks to my mother W/o Hirpe Assege, my sisters Tejitu Taye, MuluTaye, and my brothers Dereje Taye, Inspector Fikeru Taye, Petros Taye, and Tewdros Adefa for their encouragement and moral and financial support.

I have however no words to thank my wife W/o Maritu Amsalu and my first daughter Fenet Melkamu who stayed with me in time of sadness, hardship, and happiness throughout the program.

Last but not least I would like to thank physical chemistry students (M.Sc.) especially Ato Hailu Wolde for Uv-vis measurements of my samples.

Declaration

I the undersigned confirm that the results reported in this work were 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 2020. No part of this work shall be published in scientific journals or reported in the media or presented at a conference without the knowledge and consent of my Advisor, who is the chief scientist responsible for any publication. Furthermore if the work is published the institutional address given should be that of the Chemistry Department, AAU.

Table of Contents

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBERVATIONS

AAS – Atomic Absorption spectroscopy

Uv-vis – Ultraviolet-visible

IR – Infrared

mg – Milligram

Bpy – Bipyridine

Ar – Aromatic

DMSO – Dimethylsulfoxide $(CH_3)_2S=O$

KBr – Potassium bromide

TLC – Thin-layer chromatography

nm – nanometer

ppm- parts per million

mmol –millimole

(W7-J) - A. Degassed Raney nickel catalyst

HAC – Acetic acid

Cur- Curcuminate

CHAPTER ONE

1. INTRODUCTION

Coordination complexes are considered to be a significant class of compounds in chemistry due to their structural diversity and binding protocols [1]. Such complexes find interesting applications in a variety of fields like catalysis and biology. For many years biology and coordination chemistry were considered as separate fields of research. Now research has proved that coordination compounds play some important and diversified roles in biological systems like energy storage, oxygen transport, proper functioning of different enzymes, electron transfer, and selective oxidation of carbon-hydrogen bonds, nitrogen fixation and photosynthesis [2]. Studies revealed that metal complexes show greater biological activity than free organic compounds. Augmentation of biological activity is reported by implementation of transition metals into Schiff bases. In fact, lipophilicity of a drug is increased through the formation of chelates which increases the drug action due to its effective permeability into the site of action [3].

A Schiff base (or azomethine) is a class of organic compound that contains a carbon nitrogen double bond with the nitrogen atom connected to an alkyl, aryl or hetero aryl group, but not hydrogen. They have the general formula $R_1R_2C=N-R_3$, where R_3 is an alkyl, aryl or hetero aryl group that makes the Schiff base a stable imine. Hugo Schiff a German chemist reported the first Schiff base in 1864 [4].

Metal complexes of pyrimidine have been extensively studied in recent years owing to their great variety of biological activity ranging from antimalarial, antibacterial, antitumor, antiviral activities etc.[5,6] In this project works our investigation has been concentrated on some of the multidentate ligands containing N and O donors that are widely used in the synthesis of the novel metal complexes. Among these ligands I was used 2, 2'bipyridine as N-doner and citric acid as O-doner ligands. The complexes have been prepared and characterized using several physical tools, in particular elemental analysis, molar conductance, infrared; and electronic spectroscopy were used to investigate the chemical structure of the prepared complexes. Some common examples of N-donor and O-donor ligands are given in Fig 1

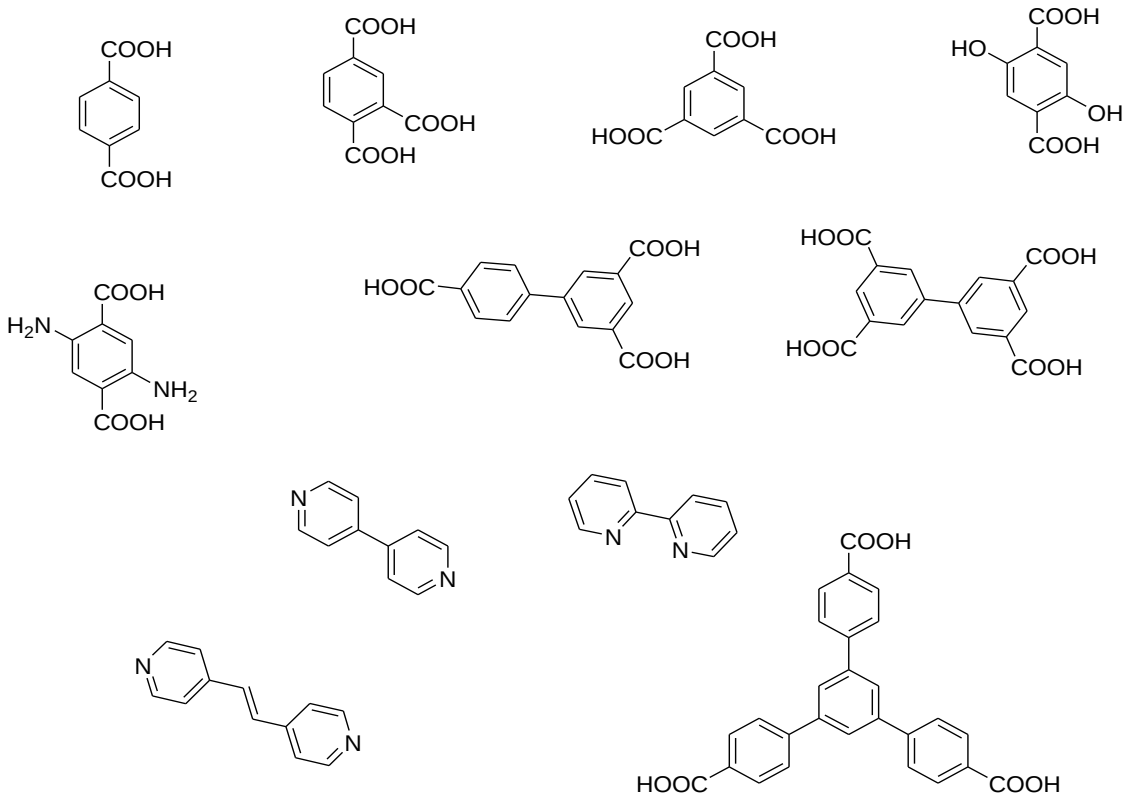


Fig 1: **some common examples of N-donor and O-doner ligands**

CHAPTER TWO

2. Literature review

2.1. Mixed-Ligand metal complexes

Mixed ligand complexes have been found to act as an active catalyst in reactions of industrial importance including hydrogenation, hydro formation, and oxidative hydrolysis of olefins and carboxylation of methanol. These complexes have also shown catalytic activity in various oxidation reactions of environmental and biological importance [7-11].

The synthesis of a variety of mixed-ligand complexes of just one metal ion is imaginable, and by considering different metal ions, a huge number of such complexes could be synthesized. This provides an excellent chance for the study of structure-function relationships. A large number of such complexes have been synthesized and studied. Among them, mixed-ligand Cu(II) complexes based on heterocyclic bidentate ligands such as 1,10-phenanthroline, 2,2-bipyridine and related derivatives are of great interest [12- 14]. Some mixed ligand complexes of Mn(II), Co(II), Cu(II), Ni(II) and Zn(II), (sheme-1) with o-vanillidene-2aminobenzothiazole and 1,10-phenanthroline were synthesized and characterized by Neelakantan et al [15].

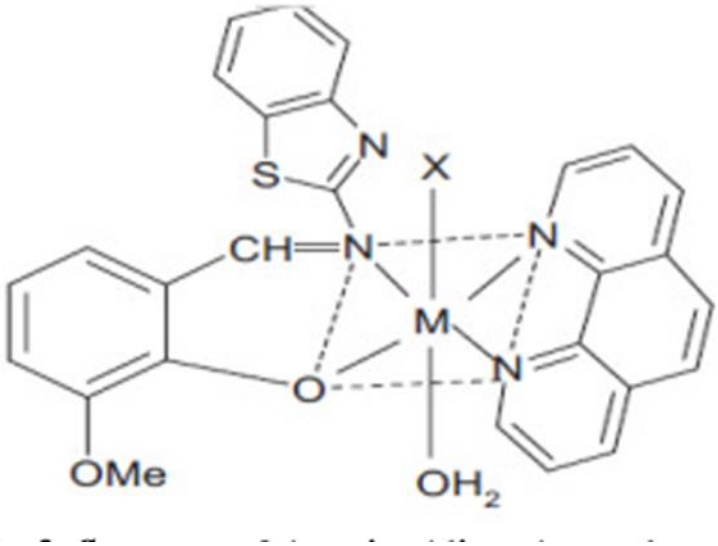


Fig 2 structure of metal complex

Mixed-ligand M (II) complexes based on heterocyclic bidentate ligands such as 1,10-phenanthroline, 2,2-bipyridine and related derivatives was also studded. Among these mixed-ligand Zn(II) complexes with curcuminate, 2,2'bipyridine, and carboxylates have been reported.(two novel Zn(II) compounds, [Zn(CH_3COO)(cur)(bpy)](1)·CH_3OH·$2H_2O$ and [Zn(PhCOO)(cur)(bpy)] (2)·CH_3OH).[16]. Combinations of Zn (II) with cur– and one of the aromatic spectator ligands (2, 2'-bipyridine, phenanthroline, terpyridine derivatives, etc.) show anti-proliferative activity in different cancer cell lines in vitro. Because of the cur– moiety, these complexes emit fluorescence light in the green part of the spectrum, which enables investigation of their interaction with DNA and proteins by optical methods [17, 18]. Furthermore, in some Zn (II) complexes with cur –, anti-diabetic activity has also been observed [19].

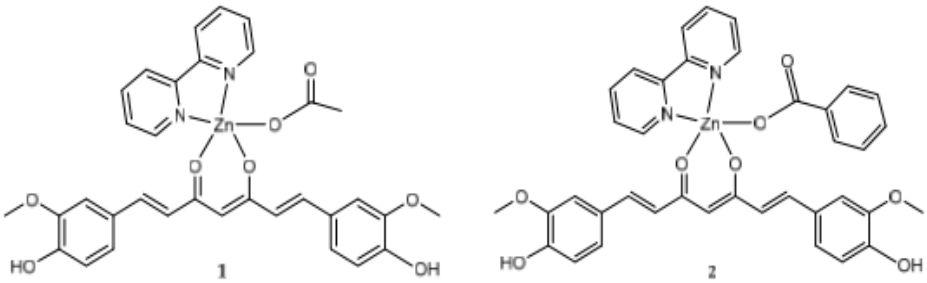


Fig 3: **Structure [Zn (CH_3COO) (cur) (bpy)](1) and [Zn(PhCOO)(cur)(bpy)](2)**

Literature review shows that many factors such as organic ligands, metal ions/metal clusters, reaction conditions, temperature, pH value play an important role in the control of the structures and functions of these hybrid materials [20]. Generally, these hybrid materials could be rationally synthesized by selecting organic ligands and metal ions [21]. A subtle change of one of the above factors such as the reaction temperature, ligand/metal ratio, and pH value may lead to a drastic change in the structure in the dimension and topology, as well as in the properties, which makes the control of the obtained structure difficult [22-24].

To understand the influences of pH, metal/ligand molar ratio, and temperature on the structures of the complexes and interaction of the zinc (II) ion with the malato ligand to give different coordination modes of certain monomeric and polymeric zinc malate complexes was reported. [25]

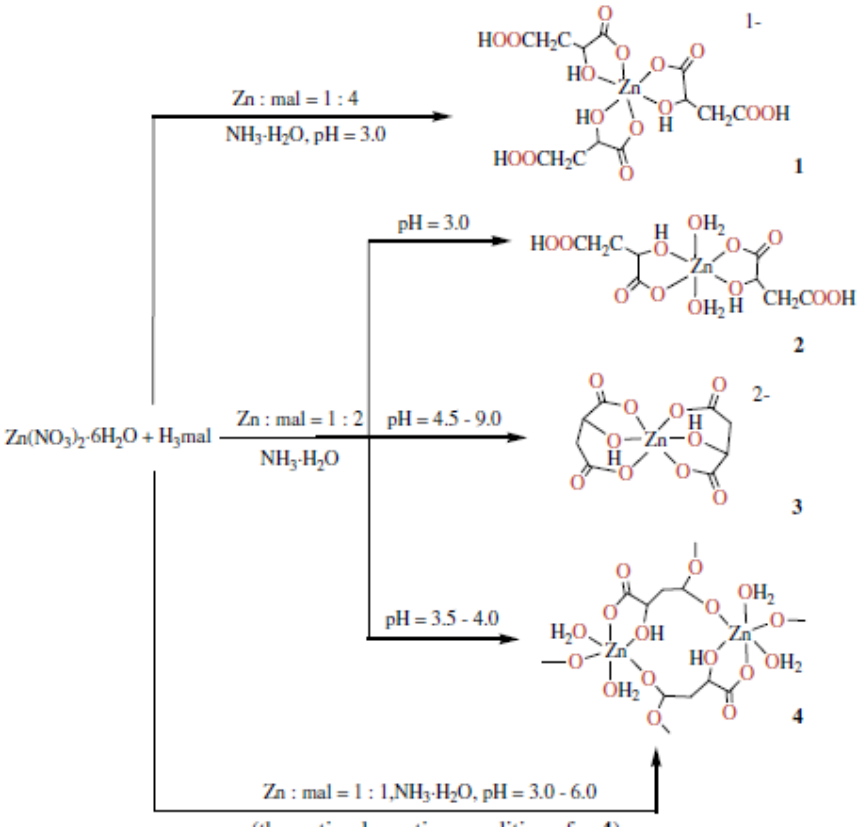


Fig 4 Synthesis of zinc (II) malato complexes at various pH values and the molar ratio

In addition to the above Zn(II) malato complexes two citrate phenanthroline mixed-ligand complexes of zinc, $[Zn(Hcit)(phen)(H_2O)][Zn_2(Hcit)(phen)_2(H_2O)_3]$ $13.5H_2O$ (1), and $[Zn_3(Hcit)_2(phen)_4]_n.14nH_2O$ (2) with different metal-to-ligand molar ratio was reported. The synthetic conditions for 1 and 2 are very similar except for the different metal-to-ligand molar ratio and pH value. The first was obtained from the reaction of zinc nitrate, citric acid and phenanthroline in a molar ratio of 3:2:3, while a slightly excess of

phenanthroline results in the formation of the product 2 in a molar ratio 3:2:4. [26]

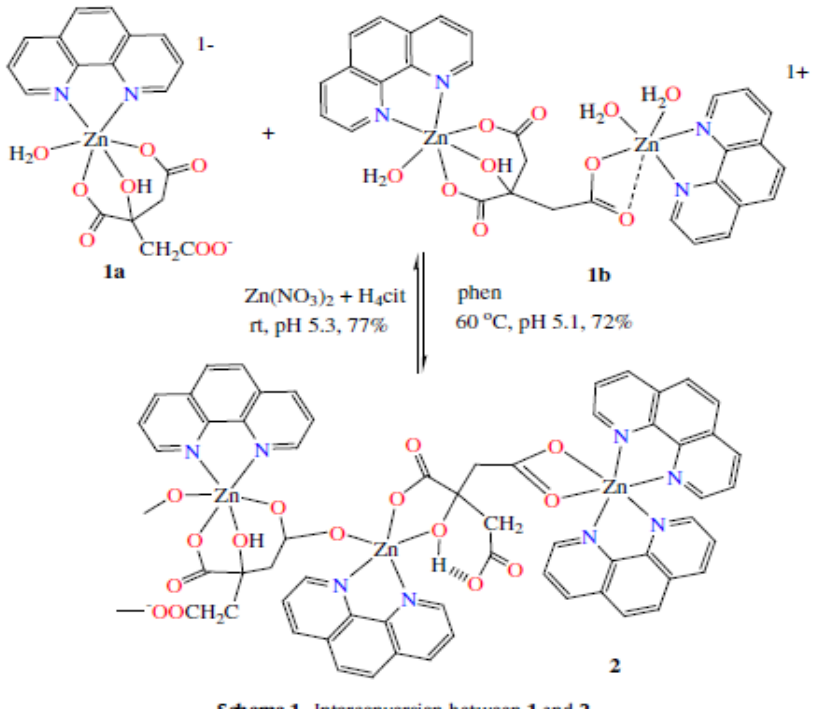


Fig 5 : **pH and molar ratio dependent structure of (1) and (2)**

2.2. Bipyridine and its chemistry

Bipyridine is an organic heterocyclic compound containing two pyridine rings linked at one carbon site on each ring, with general formula $C_{10}H_8N_2$. Each ring holds a tri-unsaturated six-membered ring of five carbon atoms and one nitrogen atom. Bipyridine is a white solid to some extent soluble in water and soluble in organic solvents. Six isomers of the simplest bipyridine exist. The rules of nomenclature would indicate the position of N atoms in the ring. The six possible region isomers of Bipyridine: (1) 2,2′-bipyridine; (:2) 2,3′-bipyridine; (3) 2,4′-bipyridine; (4) 3,3′-bipyridine; (5) 3,4′-bipyridine; (6) 4,4′-bipyridine. It is prepared by the dehydrogenation of pyridine using Raney nickel [27]

$2C_5H_5N \rightarrow (C_5H_4N)_2 + H_2$

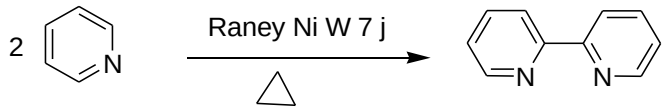


Fig 6**: synthesis of 2, 2'-bipyridine**

2.3. Metal complexes of bipyridine

2, 2'-Bipyridine (2,2'-bipy) is a chelating ligand that forms complexes with most transition metal ions that are of wide academic interest. Various of these complexes have distinctive optical properties, and some are of interest for analysis. Its complexes are used in studies of electron and energy transfer, supramolecular and materials chemistry, and catalysis. It is a bidentate chelating ligand, forming complexes with several transition metals. Ruthenium complexes and platinum complexes of bipy exhibit intense luminescence, which may have practical applications.

$Ru(bpy)_2(Cl)_2$ is a typical precursor in most syntheses of ruthenium polypyridine complexes, a family of chemicals of growing importance which has been tested as mimics of photosynthetic centers [28], phosphorescent dyes for photovoltaic cells[39] or light-emitting diodes[30], and fluorescent probes for biomolecules such as DNA[31] It is prepared by heating of a solution of ruthenium (III) chloride, 2, 2'-bipyridine and lithium chloride in N, N-dimethylformamide (DMF) and refluxing for several hours.

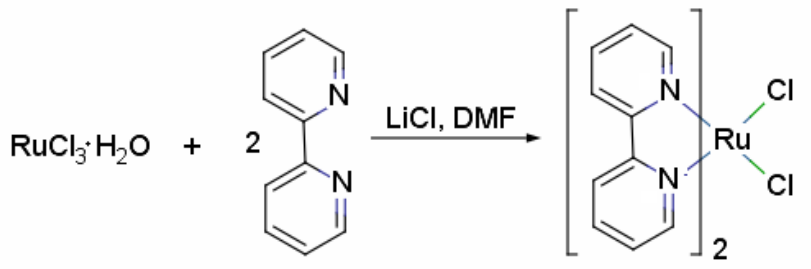


Fig 7 : **Complexation of bipyridine**

Bipyridine complexes absorb strongly in the visible part of the spectrum. The electronic transitions are characterized to metal-to-ligand charge transfer (MLCT). In the "tris(bipy) complexes" three bipyridine molecules coordinate to a metal ion, formulated as

$[M(bipy)_3]^{n+}$ (M = metal ion; Cr, Fe, Co, Ru, Rh and so on; bipy = 2,2′-bipyridine). These complexes have six-coordinated, octahedral structures and two enantiomers as the structures shown below.

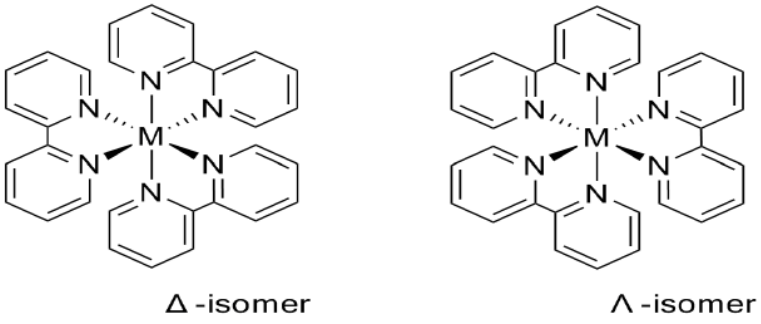


Fig 8: metal coordination mode of bipyridine

Important and classical coordination compounds 2, 2'-Bipyridine are

•Mo $(CO)_4$ (bipy), derived from $Mo(CO)_6$.

• [Ru $(bipy)_3$] Cl_2, a well-known luminophore.

• $[Fe(bipy)_3]^{2+}$ is used for the colorimetric analysis of iron io

2.4. The chemistry of citric acid

Citric acid is a carboxylic acid commonly found in the metabolism of plants, animals, and microorganisms [32] . Because it is one of the most important organic acids, it is widely used in the food, beverage, chemical and metallurgical industries. Due to the wide application of citric acid, its microbial production continues to be of interest for extensive study [33]. Moreover, the large demand of citric acid indicates the need to find alternatives for its efficient production either using low-cost substrates or by improving the potency of the microorganisms.[34] . Citric acid belongs to the strongest fruit acid and is commonly found in human organisms and plays a crucial role in the Krebs cycle also called the citric acid cycle. Salts of citric acid occur in bones where they are responsible for the regulation of the size of apatite crystals. Citric acid and its compounds

are used in medicine as supplements and drugs as well as in cosmetics as an antioxidant and acidity regulator

2.5. Metal complex of citric acid

Citric acid shows a significant tendency towards the formation of all kinds of complexes with metal ions, from relatively weak ones with alkali metal ions and alkaline earth metal ions to very strong ones with heavy metal ions or lanthanides. Citric acid, a hydroxycarboxylic acid, has been an attractive candidate as a linking agent in the design of potentially useful coordination compound for its availability and naturally occurring chelating ability. [35-36] Significant properties of the complex formation of citric acid are associated with the character of their functional carboxyl and hydroxyl groups. The relatively low protonation value of the carboxyl groups makes them a potential coordination site of metal ions in the low pH values. Moreover; chelate complexes of citric acid increase the bioavailability and assimilability of metal ions in biological systems. [37-38]. Citric acid molecule comprises one α-position hydroxyl group, one α-position carboxyl group, and two β-position carboxyl groups, and contains at least seven potential donor sites capable of coordinating metal ions. This type of structure permits the formation of coordination complexes of novel structure types [39–43]. Citric acid with the seven potentially O–donor atoms are an asymmetric ligand which can be assembled around metal ions in diverse arrangements as a chelating and bridging spacer. Citric acid is a very attractive agent in the design of potentially useful compounds as monomeric, binuclear and polymeric complexes with both d- and f-electron metal ions Citrate ligand is an asymmetric spacer, and can be assembled around metal centers in diverse arrangements, consequently resulting in multidimensional coordination polymers. The potential modes of metal coordination to citric acid are shown in scheme 5. [44]

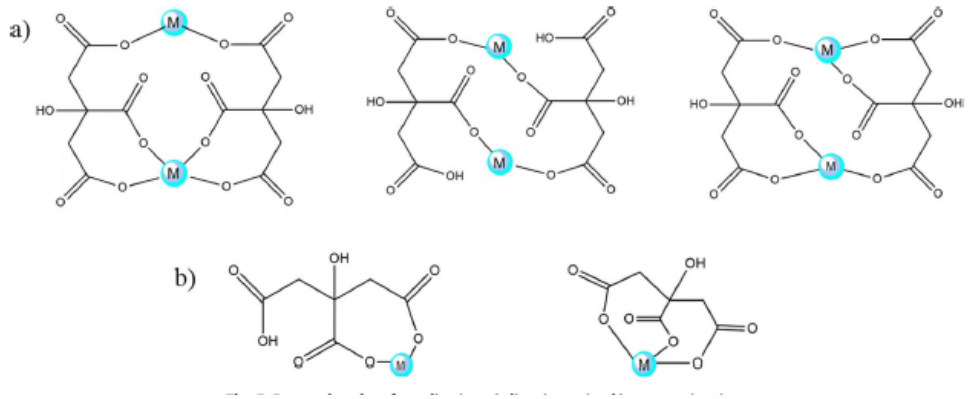


Fig 9 : coordination mode of citric acid

Numerous metal complexes of this potentially multidentate ligand have been studied. The reactions of citric acid ($C_6H_8O_7$) with various divalent transition metals (Cd, Zn, Cu, and Co) in acidic solution or under hydrothermal conditions (pH) = (1-4) have resulted in the isolation of five new coordination compound with versatile multidimensional structure. The five metal citrate complexes, namely, $[Cd_3(Hcit)_2(H_2O)_5,H_2O]_n$ (1), $[Cd_3(Hcit)_2(H_2O)_2]_n$ (2), $[Zn_3(Hcit)_2(H_2O)_2]_n$ (3) $[Cu_2(Hcit)(H_2O)_2]_n$ (4), and $[Co(H_2cit)(H_2O)]_n$ (5) [45] . The formation of metal citrate complexes is frequently influenced by pH, mole ratio, temperature, and concentration of the reactants. By control of the reaction conditions, it is possible to prepare complexes with specific structures [46]

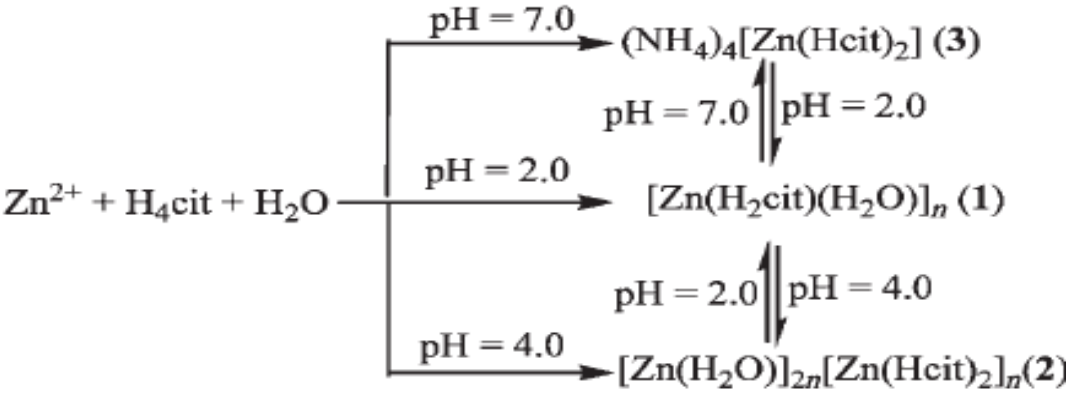


Fig 10 : Synthesis and inter conversion of Zn(II) citrate complex

2.6. The chemistry of divalent manganese, d^5

Manganese is a silvery-gray metal that resembles iron. It is hard and very brittle, difficult to fuse, but easy to oxidize [47]. Manganese metal and its common ions are paramagnetic [48]. The most common oxidation states of manganese are +2, +3, +4, +6, and +7, though all oxidation states from −3 to +7 have been seen. Manganese (II) most commonly exists with high spin, S = 5/2 ground state because of the high pairing energy for manganese (II). The ion forms many complexes in which the metal is octahedrally coordinated and most of them are high spin implying the absence of ligand field. There are no spin-allowed d–d transitions in Mn (II). Four spin forbidden bands are observed in the visible region, which corresponds to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, $^6A_{1g} \rightarrow {}^4E_g$ and $^6A_{1g} \rightarrow {}^4A_{1g}$ transitions [49]. For the Mn (II) complexes, there is only one configuration for five unpaired electrons, which corresponds to the half-filled d-shell and is spherically symmetric. The ground state term is ^6S and belongs to the $^6A_{1g}$ group. The d-d transitions for the high-spin manganese (II) complexes are spin-forbidden. The intensity of the electronic transition from ground state (^6S) to the states of fourfold multiplicity are very weak and since Mn(II) ion has a d^5 configuration the same type of energy level diagram is applied whether the metal ion is in octahedral or in tetrahedral environments [50].

2.7. The chemistry of divalent zinc, d^{10}

Zinc is attractive metal as a central metal ion in coordination chemistry. It is the only metal that is present in all enzyme classes and is the second most abundant trace metal in humans after iron. In a variety of biological processes zinc performs different physiological functions, e.g., as a structural component (zinc fingers), as a catalytic factor (enzyme cofactors in six main enzyme classes), or as a signaling mediator. [51, 52] Combinations of Zn (II) with curcuminate (cur–) and one of the aromatic spectator ligands (2 2’-bipyridine, phenanthroline, terpyridine derivatives, etc.) show anti-proliferative activity in different cancer cell lines in vitro. [53] Furthermore, in some Zn(II) complexes with curcuminate, anti- diabetic activity has also been observed [54]. The divalent zinc ion is exceptionally stable concerning oxidation and reduction and so it does not participate in redox reactions, in contrast to Mn, Fe, and Cu. The d^{10} configuration of Zn^{2+} indicates that zinc complexes are not subject to ligand field

stabilization effects and so coordination number and geometry are only dictated by ligand size and charge. Zinc is an element of borderline hardness so that nitrogen, oxygen and sulfur ligands can all be accommodated, in contrast to magnesium and calcium, which favor binding to oxygen. Therefore, zinc binds strongly to many proteins [55] . This metal ion is diamagnetic and does not possess any d-d transition due to a d^{10} configuration [56].

2.8. STATEMENT OF THE PROBLEM

Design and synthesis of organic chelating agents containing nitrogen and oxygen as donor atoms and their metal complexes is an interesting field of research for their different types of activities. In this case, bi-dentate N,N chelating agent such as 2,2'-bipyridyl has played a vital role in building many mixed-ligand complexes for their desired predictable co-ordination behavior and their electrochemical and photo physical properties .but the PH dependent nature of Zn citrate with bipyridine was not much studied. In this regard this paper presents effectiveness of the carboxyl groups of citric acid and 2,2'-bipyridine in coordination and characterized the different structure at different PH value.

2.9. Significance of the study

Metal complexes of pyrimidine have been extensively studied in recent years owing to their great variety of biological activity ranging from antimalarial, antibacterial, antitumor, antiviral activities. Therefore

i. The study is used as supportive for further studies of metal complexes of pyrimidine and

ii. The synthesized materials contribute to the fields of coordination chemistry. Moreover, the worth of work is demonstrated by the investigation of the properties that may be exhibited by the synthesized compounds on the basis of their structural features.

2.10. Limitation

1. Absence of conductivity measurement in our laboratory.
2. It takes time to get the laboratory technician for running the sample (AAS).

2.11. Objective of the work

A new class of hybrid materials, coordination compounds has attracted tremendous interests from scientists not only owing to their diverse topological frameworks but also owing to their promising applications in luminescence, catalysis, magnetism, and gas storage. Under this background, much effort has been devoted to this field with the aim of rational design and construction of coordination compounds, and simultaneously, many effective synthetic strategies also have been successfully established and developed by chemists. Among these strategies to construct coordination compounds, the mixed-ligand self-assembly strategy is one of the most effective and the most commonly used methods to synthesize new functional Compounds. Based on the above considerations, in this work, I was selected O-donor ligand citric acid and N-donor ligand (2,2-bpy) as the mixed-ligand targeted to the synthesis and characterization of Mn(II) and Zn(II) metal complexes in 3:2:3 and 3:2:4 metal -to -ligand ratio at different pH values.

CHAPTER THREE

3.1. Chemicals and Equipment

Chemicals; Zinc chloride ($ZnCl_2$), manganese chloride tetra hydrate ($MnCl_2.4H_2O$) 2, 2-bipyridine ($C_{10}H_8N_2$) and mono hydrated citric acid ($C_6H_8O_7.H_2O$) were used. All starting chemicals were reagent grade, purchased from Alfa-Aesar and used without further purification. Other reagents and solvents used in this investigation are ammonium hydroxide. nitric acid, perchloric acid, distilled water; DMSO, acetonitrile hexane, HAC, and chloroform were also used.

3.2. Physical and analytical measurements

Zee nit 700 P (analytikjena) Flame-AAS was used to measure the amount of metal in ppm (μg/ml) in their prepared $3x10^{-3}$ M solution. Elemental analysis of C, H, and N was determined using FLASHEA 1112 elemental analyzers. The IR spectra of the products were taken using KBr pellets (Spectrum 65 PerkinElmer) in the range of 4000 -400 cm^{-1}. The electronic (Uv-Vis) absorption spectra were measured on SPECTRONI GENESYTM 2PC Uv-Vis spectrophotometer in the range of 200 – 800 nm region in distilled water and DMSO. The melting point was determined using start SMP3, Digital Melting point apparatus. Molar conductance of the complex in distilled water was recorded at room temperature with JANEWAY 4330 conductometry.

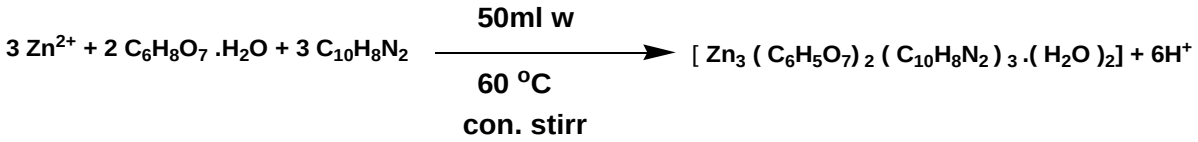
3.3, Synthesis of the complexes

3.3.1 Synthesis of Zn:Hcit:$(bpy)_1$ complex (3:2:3 ratio)

Procedure-1

- $ZnCl_2$ (0.41 g, 3.0 mmol) was dissolved in 50 ml distilled water in 250 ml volumetric flask.
- Citric acid (0.42 g, 2.0 mmol) and 2.2-Bipyridin (0.468 g, 3.0 mmol) were added to a stirred solution of $ZnCl_2$ solution.
- The pH of the solution was adjusted to 5.1 with ammonium hydroxide and magnetic stirrer was added.

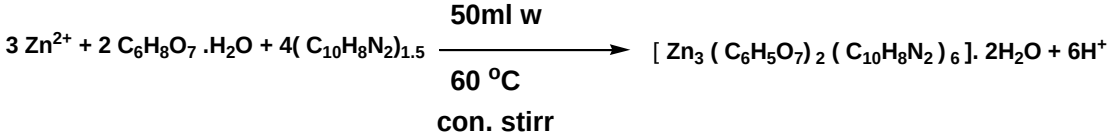
- The mixture was heated in a water bath at 60 ℃ for about 96 hours.
- The mixture was allowed to stand and cooled to room temperature and put in the refrigerator for two days to give a solid crystalline product.
- The product was isolated by filtration and dried in air (Yield; 200.4 mg, 15 %).



3.3.2 Synthesis of Zn:Hcit:$(bpy)_2$ complex (3:2:4 ratio)

Procedure-2

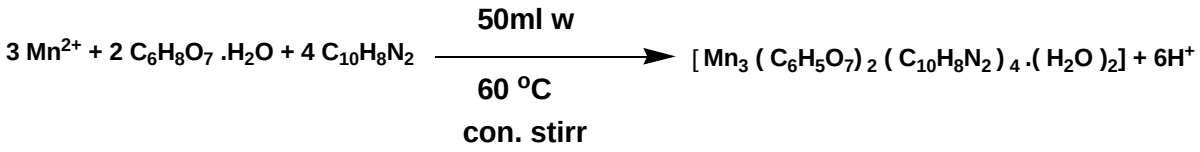
- $ZnCl_2$(0.41 g, 3.0 mmol) was dissolved in 50 ml distilled water in 250 ml volumetric flask.
- Citric acid (0.42 g, 2.0 mmol) and 2.2-Bipyridine (0.624 g, 4.0 mmol) were added to stirred solution of $ZnCl_2$.
- The pH of the solution was adjusted to 5.5 with ammonium hydroxide.
- A magnetic stirrer was added.
- The mixture was heated in a water bath at 60 ℃ for about 96 hours.
- The light pink color is observed.
- The mixture was down from the stand and cooled to room temperature and then put in the refrigerator for two days to give a solid crystalline product.
- The product was isolated by filtration and dried in air (Yield; 294.1 mg, 20%).



3.3.3 Synthesis of Mn:Hcit:$(bpy)_2$ complex (3:2:4 ratio)

Procedure-3

- $MnCl_2.4H_20$ (0.41 g, 3.0 mmol) was dissolved in 50 ml distilled water in 250 ml volumetric flask
- Citric acid (0.42 g, 2.0 mmol) and 2.2-Bipyridine (0.624 g, 4.0 mmol) were added to stirred solution of $MnCl_2.4H_2O$
- The pH of the solution was adjusted to 5.5 with dilute ammonium hydroxide.
- The mixture was heated in a water bath at 60 ℃ for about 96 hours.
- The black color is observed.
- The mixture was allowed to cool to room temperature to give a solid crystalline product.
- The product was isolated by filtration and dried in air (Yield; 260.8 mg, 18%).



CHAPTER FOUR

4. Results and discussions

4.1. Physical properties

The prepared metal complexes were stable at room temperature having various colors with a melting point / decomposition temperature of greater than 300 ℃ .Zinc (II) complexes is soluble in water, DMSO, and acetic acid but insoluble in hexane and chloroform. Mn (II) complex is partially soluble in water, DMSO and acetic acid but insoluble in chloroform and hexane. The purity of the complexes was tested by TLC. A single spot for each of the complexes was observed which confirms the purity of the complex.

Table 1: Physical characteristics of the complexes

Compound	Color	Appearance	M.pt /Decomposition Temperature ℃	Yield
Zn:Hcit $(bpy)_1$	Grey	Powder	362	15.45%
Zn:Hcit:$(bpy)_2$	Pinc	Powder	370	20.24%
Mn:Hcit:$(bpy)_2$	Black	Powder	325	18.35%

4.2. Elemental analysis

For Zn:Hcit:$(bpy)_1$ complex the elemental analysis result showed that the calculated percentage values of C, H, and N were closed to the experimental measured values of C, H, and N. This correlation of calculated values and the experimental measured values of C, H and N, indicating the formation Zn:Hcit: $(bpy)_1$ complex with the formula $\mathbf{[Zn_3(C_6H_5O_7)_2(C_{10}H_8N_2)_3.2H_2O].6H_2O.(NH_3)_3}$ which its total number of each atoms are (empirical formula) $\mathbf{C_{42}H_{59}N_9O_{22}Zn_3}$

In, Zn; Hcit: $(bpy)_2$ complex the calculated percentage values of C, H and N was closed to the experimental measured values of C, H, and N, respectively. This calculated values and the experimental measured values of C, H and N, indicating the formation of Zn:Hcit:$(bpy)_2$ complex with the formula **$[Zn_3 (C_6H_5O_7)_2(C_{10}H_8N_2)_6].2(H_2O)$** which its total number of each atoms are (empirical formula) **$C_{72}H_{62}N_{12}O_{16}Zn_3$**;

In Mn: Hcit: $(bpy)_2$ complexes the calculated percentage values of C, H and N was closed to the experimental measured values of C, H, and N, respectively. This calculated values and the experimental measured values of C, H and N indicating the formation of Mn:Hcit:$(bpy)_2$ complex with the formula (**$[Mn_3(C_6H_5O_7)_2 (C_{10}H_8N_2)_4.(H_2O)_2]\cdot 12H_2O$)**

The elemental analyses of the metal complexes are summarized in table 3.

Table 2: Elemental analysis of the metal complex

Compound	**C %** **Cal (found)**	**H %** **Cal (found)**	**N %** **Cal (found)**
Zn:Hcit:$(bpy)_1$ $C_{42}H_{59}N_9O_{22}Zn_3$	40.74 (41.07)	4.8 (5.66)	10.18 (10.14)
Zn:Hcit:$(bpy)_2$ $C_{72}H_{62}N_{12}O_{16}Zn_3$	56.87 (58.33)	4.08 (5.7)	10.97 (11.75)
Mn:Hcit:$(bpy)_2$ $C_{52}H_{70}Mn_3N_8O_{28}$	43.98 (44.42)	4.97 (4.40)	7.89 (7.15)

4.3. Molar Conductance

The complexes were dissolved in distilled water and the molar conductivities of 10^{-3} M of their solutions at 25 ℃ were measured. The Specific conductance (k) of 10^{-3} M solution of the complexes at 25 ℃ is 0.01 mS/cm for Mn: Hcit: $(bpy)_2$, 1 mS/cm for Zn: Hcit: $(bpy)_1$ and 0.53 mS/cm for, Zn: Hcit: $(bpy)_2$. The relation ΛM=1000k/M is used to calculate the molar conductance (ΛM) of the complex where M is the molar concentration of the complex, k is the specific conductance. When these values are converted by using the above relation the molar conductance, Λm, of the complex tabulated in table 4.

Table 3 Molar Conductivity of the metal complexes in distilled water

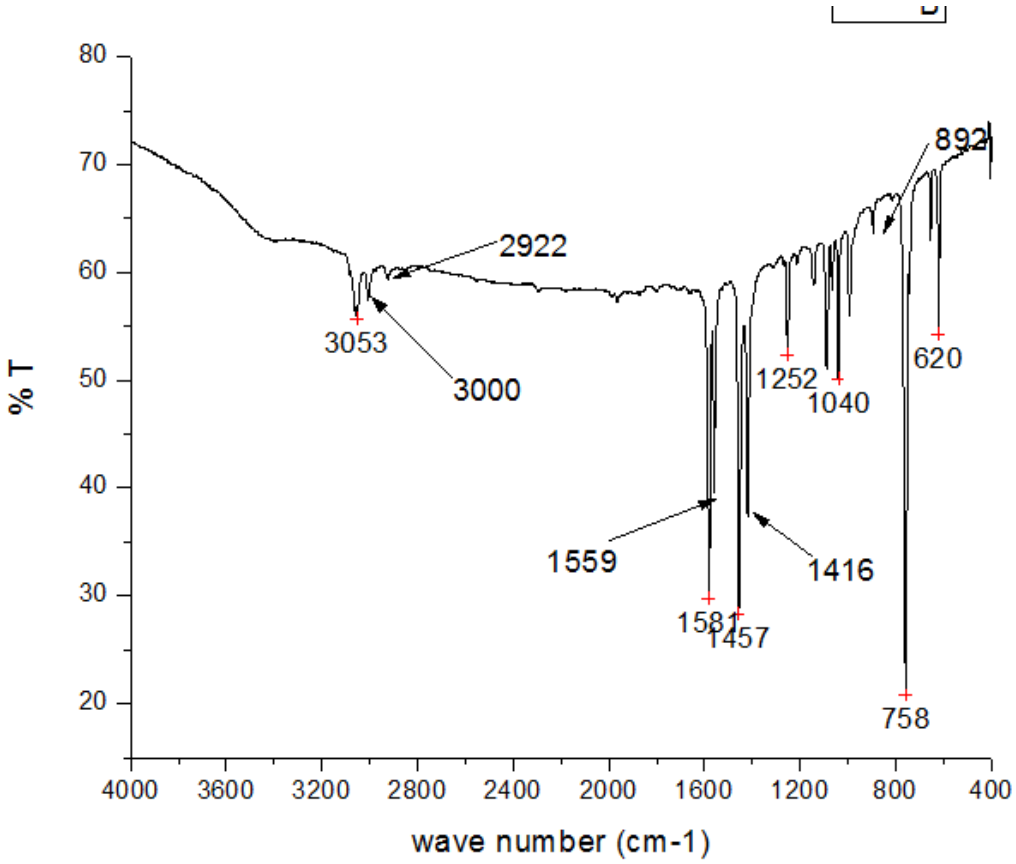
Metal Complex	Solvent	Λm in S / cm^2. mol	Type of Electrolyte
Zn:Hcit:$(bpy)_1$	Distilled Water	1000	Electrolyte
Zn:Hcit:$(bpy)_2$	Distilled Water	530	Electrolyte
Mn:Hcit:$(bpy)_2$	Distilled Water	10	Non electrolyte

4.4. IR spectrum of the complex

When the IR spectra of the Zn:Hcit:$(bpy)_1$, Zn:Hcit:$(bpy)_2$ and Mn:Hcit:$(bpy)_2$ metal complexes were compared with that of the IR spectra of free 2, 2-bipyridine (ligand) certain shifts and new bands were found. Free citric acids contain two functional groups carboxyl group and alcohol therefore it shows a very strong and broadband covering the wide range between 2500 cm^{-1} to 3500 cm^{-1} for the O-H stretching.

In the free 2,2-bipyridine, a weak band observed from 3100-2900 cm^{-1} due to C-H (Ar) stretching. A strong band observed at 1581 cm^{-1} and 1559 cm^{-1} is due to C=C (Ar) stretching. Two bands at 1457 and 1416 cm^{-1} correspond to C=N stretching. The band observed between 900 – 650 cm^{-1}due to C-H (Ar) out of plane bending.

IR Spectrum of free (bpy)



Comparison of the free citric acid and 2,2-bipyridine spectra with that of the Zn:Hcit:$(bpy)_1$, Zn:Hcit:$(bpy)_2$ and Mn:Hcit:$(bpy)_2$ complexes, the following are the main features.

The notable features of the IR spectrum of Zn:Hcit:$(bpy)_1$ complex.

(i), The new strong broadband formed at 3428 cm^{-1} in the Zn: Hcit: $(bpy)_1$ complex indicates the presence of vO-H stretching of water.

(ii), The (C-H) stretching vibration frequency in the free 2.2-Bpy ligand at 3053 cm^{-1},3000 cm^{-1}, and 2922 cm^{-1} was shifted to 3104 cm^{-1}, 3062 cm^{-1}, and 3030 cm^{-1} in Zn: Hcit:$(bpy)_1$ is an indication of the involvement of the ligand to the complex.

(iii), There are two regions of the infrared spectra of aromatics that distinguish aromatics from organic compounds that do not have an aromatic ring. This is;

•2000 cm^{-1} - 1665 cm^{-1} (weak bands known as "overtones")

•900 cm^{-1} - 675 cm^{-1} ν C-H bend (out-of-plane or "oop" bands)

The weak overtone bands observed in the range of 2020 cm^{-1} – 1860 cm^{-1} in the complex has confirmed the involvement of aromatics (2,2-bipyridine) in the complex.

(iv). νC=C at 1581 cm^{-1} and 1559 cm^{-1} in the free 2,2-bipyridine shifted to 1599 cm^{-1} and 1566 cm^{-1} in the complex respectively indicates the formation of Zn:Hcit:$(bpy)_1$ complex

(v). The bands at 1457 cm^{-1} and at 1416 cm^{-1} in the free 2,2-bipyridine shifted to strong sharp multiple bands at 1495 cm^{-1} - 1444 cm^{-1}(characteristic of ν C=N),. This may be taken as evidence for the fact that the condensation (involvement) of the ligand was successful

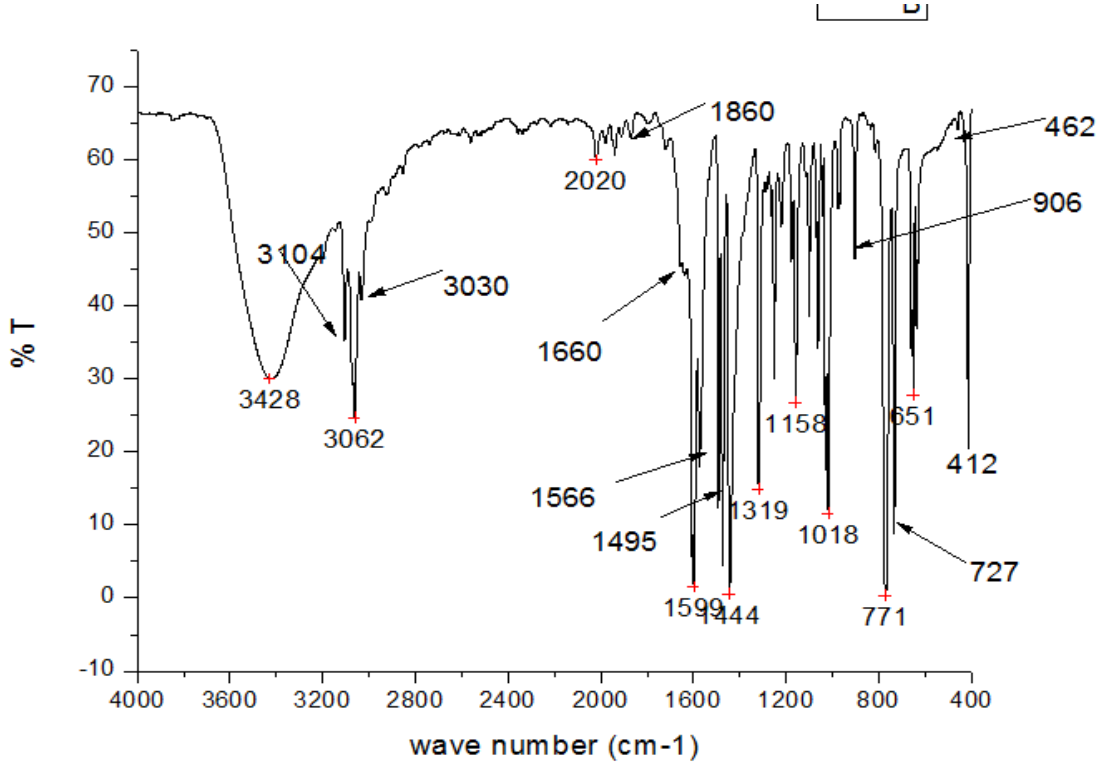
(vi), another sharp band observed at 1252 cm^{-1} was assigned for C-N vibrations of 2,2-bipyridine, these vibrations were shifted to 1319 cm^{-1} in the FTIR spectra of metal complexes. This observation suggested that the nitrogen atom on 2, 2'- pyridine ring formed a coordinate bond during the complexation.

(vii). The band at 1040 cm^{-1} and 892 cm^{-1} in the free bipyridine shifted to the sharp peaks at 1158 cm^{-1}, 1018 cm^{-1} and 906 cm^{-1} is characteristic of C-H (Ar) in-plane bending confirms the involvement of aromatics in the complex .

(viii). The disappearance of a sharp strong peak at 758 cm^{-1} in the free 2,2'- bipyridine and the appearance of two peaks in this region at 727 cm^{-1} and 771 cm^{-1} in the complex is an assignment to the C-H (Ar) out-of-plane bending of the spectrum.

(ix). The appearance of medium intensity band in the region 462 cm^{-1} and 412 cm^{-1} is assignable to Zn-N and Zn-O stretching. These assignments are based on the fact that oxygen is more electronegative than nitrogen, the M-O bond tends to be more ionic than the M-N bond and, therefore, M-O vibrations were expected to appear at lower frequencies than the M-N vibration.

IR Spectrum of Zn: Hcit: $(bpy)_1$



The notable features of the IR spectrum of in Zn: Hcit: $(bpy)_2$

In the comparison of the complex to the free ligand, the IR spectrum of Zn (ll) in both ratios is similar except a little shift of the band.

(i), The new strong broad band formed at 3400 cm^{-1} in the complex indicates the presence of vO-H stretching.

(ii), The (C-H) stretching vibration frequency in the free 2.2-Bpy ligand at 3053 cm^{-1},3000 cm^{-1}, and 2922 cm^{-1} was shifted to 3101 cm^{-1}, 3056 cm^{-1}, and 3030 cm^{-1} in Zn: Hcit:$(bpy)_2$ is an indication of the involvement of the ligand to the complex.

(iii), The over-tones, finger-like weak bands between 2020 cm^{-1} - 1860 cm^{-1} confirm the existence of aromatic ring in the complex.

(iv), vC=C at 1581 cm^{-1} and 1559 cm^{-1} in the free 2,2'-bipyridine shifted to 1596 cm^{-1} and 1552 cm^{-1} in the complex respectively indicates the formation of Zn:Hcit:$(bpy)_2$ complex

(v), The appearance of strong sharp multiple bands in the region 1495 cm^{-1} - 1442 cm^{-1}characteristic of ν C=N

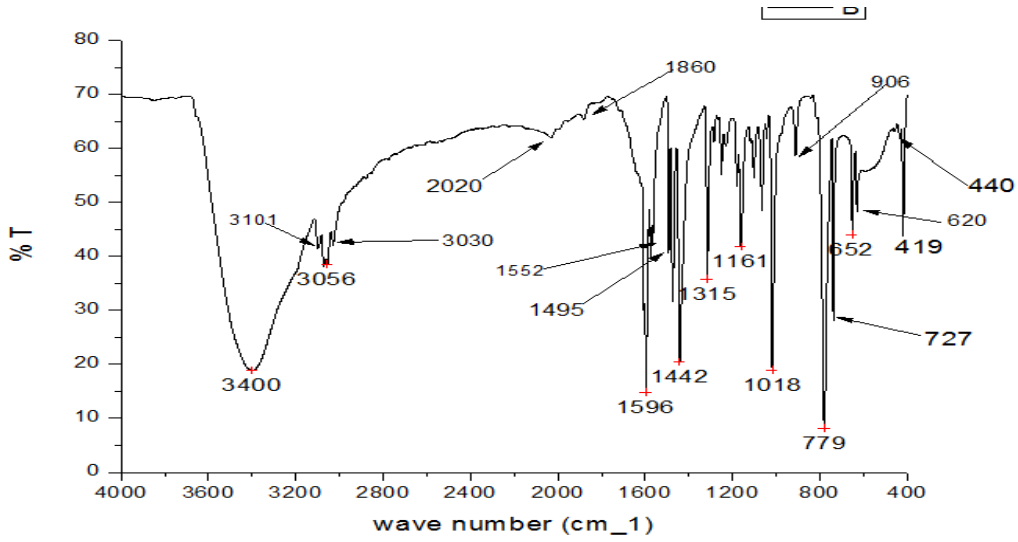
(vi), Another sharp band observed at 1252 cm^{-1} was assigned for C-N vibrations of 2, 2'-bipyridine, these vibrations were shifted to the lower frequency of 1315 cm^{-1} in the FTIR spectra of metal complexes. This observation suggested that the nitrogen atom on a 2, 2'-pyridine ring formed a coordinate bond during the complexation.

(vii), The band at 1040 cm^{-1} and 892 cm^{-1} in the free bipyridine shifted to a strong sharp peaks at 1161 cm-^{1}, 1018 cm^{-1} and 906 cm-^{1} is the characteristics of C-H (Ar) in-plane bending confirms the involvement of aromatics in the complex.

(viii), The disappearance of a strong peak at 758 cm^{-1} and the appearance of two peaks at 779 cm^{-1} and 727 cm^{-1} is the characteristics of aromatic C –H bend out of the plane.

(ix), The appearance of medium intensity bands in the region 440 cm^{-1} and 419 cm^{-1} are assignable to Zn-N and Zn-O stretching.

IR Spectrum of Zn: Hcit: $(bpy)_2$



The notable features of the IR spectrum of Mn: Hcit: $(bpy)_2$

i, The new strong broadband formed at 3378 cm^{-1} in the complex indicates the presence of vO-H stretching of water.

ii, The (C-H) stretching vibration frequency in the free 2.2-Bpy ligand at 3053 cm-$^{-1}$,3000 cm$^{-1,}$ and 2922 cm^{-1} was shifted to 2843 cm^{-1}, 2489 cm^{-1}, 2142 cm^{-1} respectively are asymmetric and symmetric CH_2 stretching.

iii, The bands at 1457 cm^{-1} and at 1416 cm^{-1} in the free 2,2-bipyridine are disappeared and the appearance of a strong broad band at the region of 1451 cm^{-1} is the characteristics of C=N of the ligand which confirms the involvement of 2,2'-bipyridine in the complex.

V, The band at 1040 cm^{-1} and 892 cm^{-1} in the free bipyridine shifted to the medium band at 1072 cm^{-1} and 942 cm^{-1} are aromatic vC-H in-plane bending which indicate the involvement of 2, 2'-bipyridine.

Vi, The disappearance of strong band at 758 cm^{-1} in the free bipyridine and appearance of strong band at 861 cm^{-1} and a weak band at 771 cm^{-1} and 725 cm^{-1} are aromatic vC-H out plane bending.

Vii, The appearance of medium intensity band in the region 608 cm^{-1} and 505 cm^{-1} is assignable to Mn-N and Mn-O bonding respectively.

IR Spectrum of Mn: Hcit: $(bpy)_2$

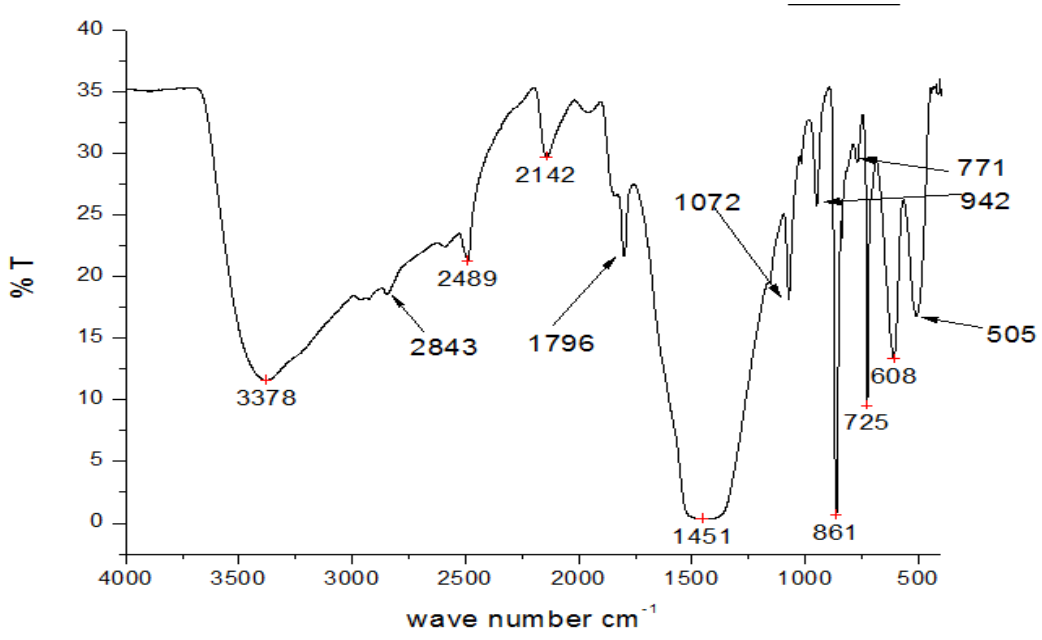


Table 4: Summary of the IR spectral data

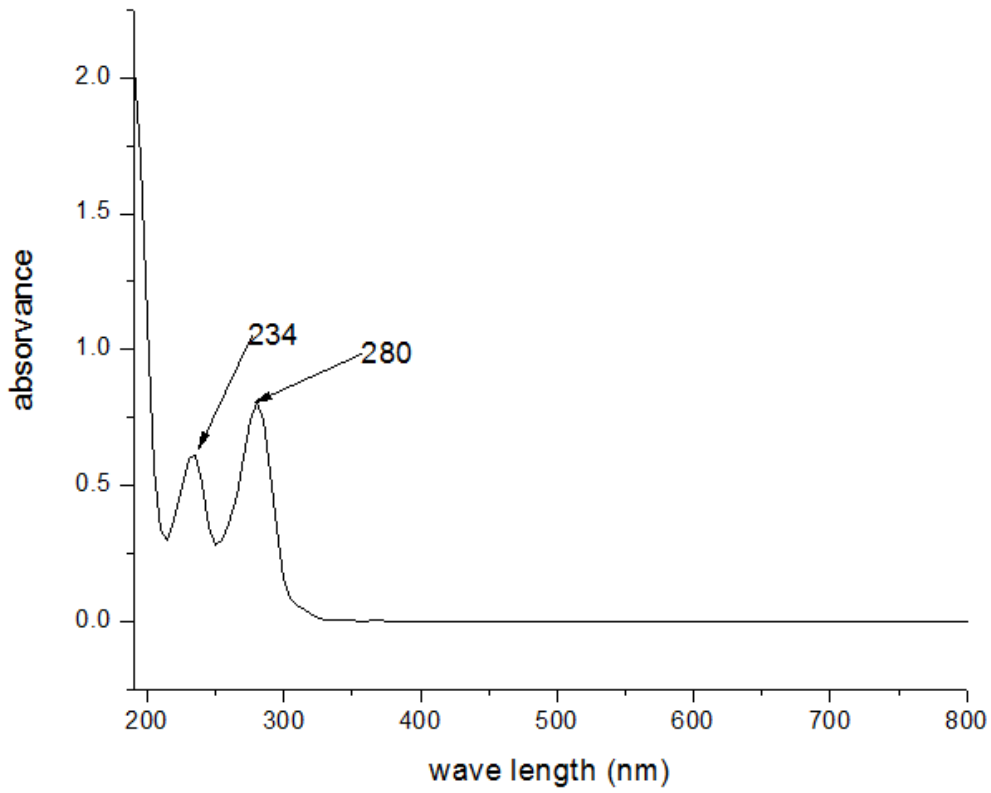
Chemical compound	2.2-bip (ligand)	Zn:Hcit:$(bpy)_1$	Zn:Hcit:$(bpy)_2$	Mn:Hcit:$(bpy)_2$
O-H stretching	_	3428	3400	3378
C-H stretching (Ar)	3053 3000 2922	3104 3062 3030	3101 3056 3030	2843 2489 2142 ,1796
C-H (Ar) bending weak overtone	2000-1665	2020 -1860	2020 -1860	
C=C stretching	1581 1559	1599 1566	1596 1552	
C=N	1457, 1416	1495, 1444	1495, 1442	1451
C-N	1252	1319	1315	-
C-H bending in plane	1040, 892	1158 1018,906	1161, 1018,906	1072&942
C-H bending out plane	758	771 727	779 727	861 , 771&725
M-N M-O	-	462 412	440 419	608 505

4.5. Electronic spectra

Electronic spectra measurements are very useful for assigning the stereochemistry of the complex based on the position and number of d-d transitions. The electronic absorption spectra of the Mn (II) and Zn (II) complexes were recorded at room temperature using DMSO and distilled water respectively.

UV- VIS Spectrum of the free 2,2-bipyridine

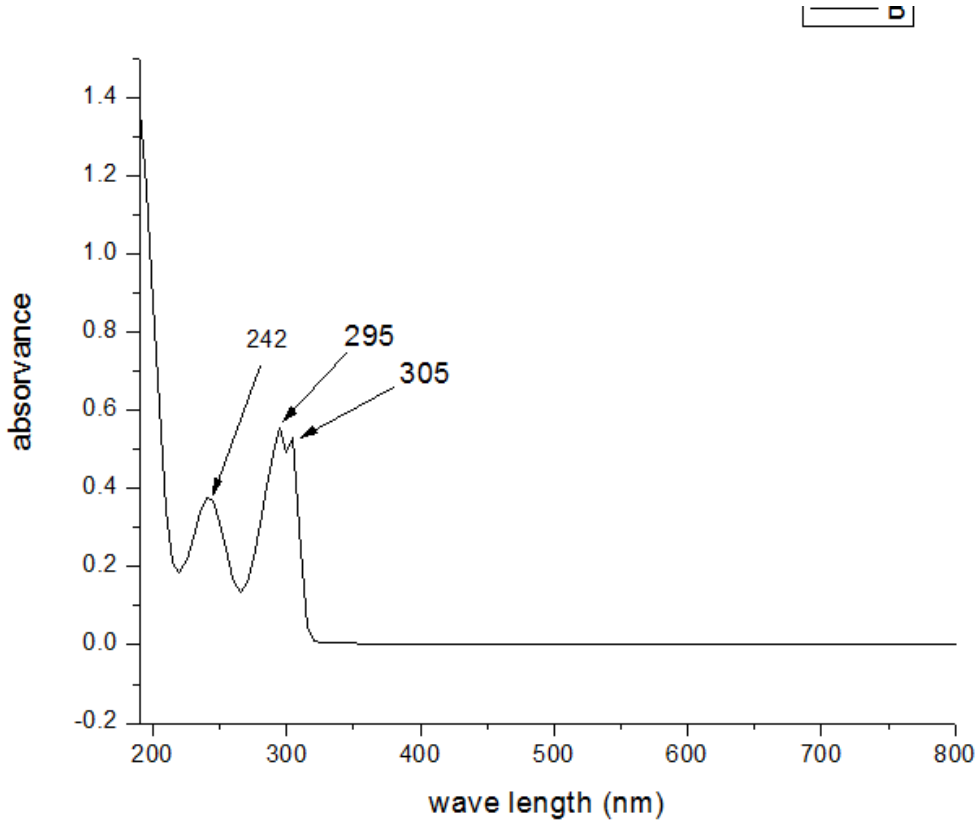
The ligand 2,2-bipyridine has two bands at 234 nm and 280 nm due to π→π* transition of the aromatic systems, while the other bands could be due to (C=N) chromophore respectively.



UV- VIS Spectrum of the complex Zn:Hcit:$(bpy)_1$

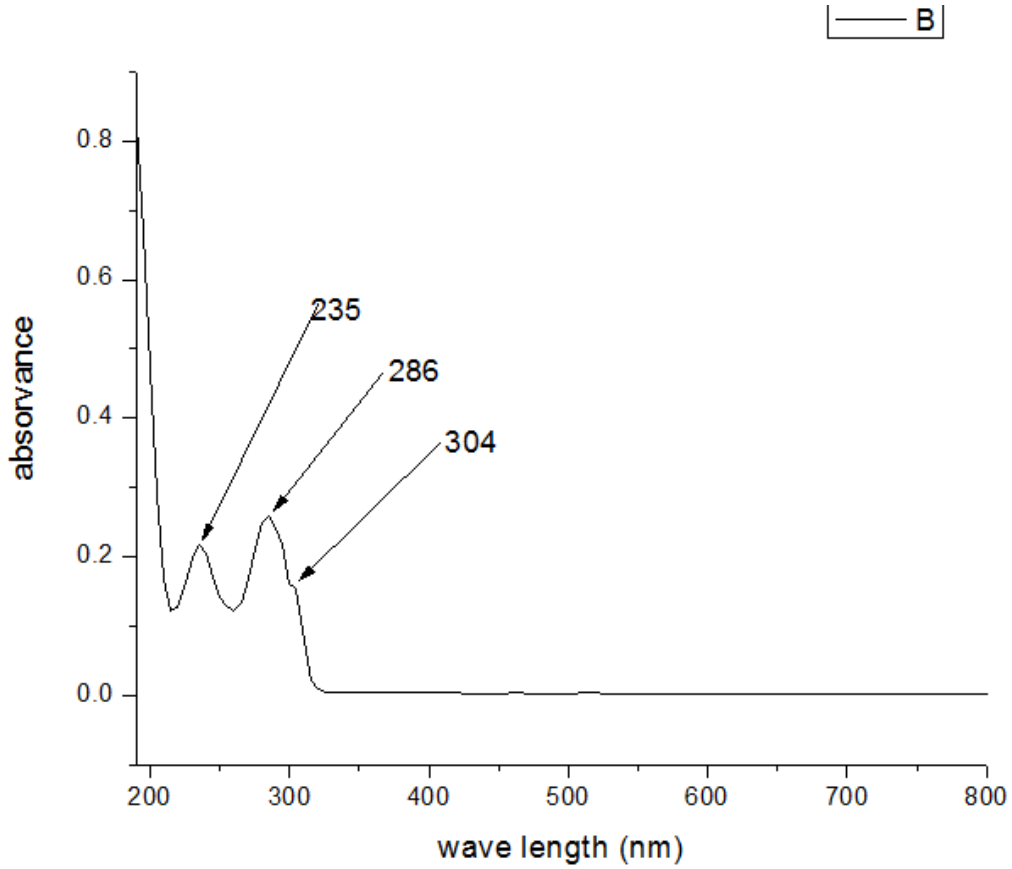
Three bands are observed at 242 nm, 295 nm, and 305 nm. The band at 242 nm is attributed to π→π* transition of the aromatic region of the 2,2-bipyridine. The band around 295 nm is due to the n →π* transition of the (C=N) group. The band at 305 nm is attributed to n →π* transition of the carboxyl (C=O) group. The electronic spectrum of the Zn:Hcit:$(bpy)_1$. complex provides evidence for the involvement of the ligand in the complex as evidenced by a bathochromic shift of the ligand from 234 nm to 242 nm and

280 nm to 295 nm. The new band observed at 305 nm corresponding to the C=O function of the carboxyl group providing evidence for the involvement of the citric acid in coordination. As Zn^{2+} is a d^{10} system no d-d transitions are possible.



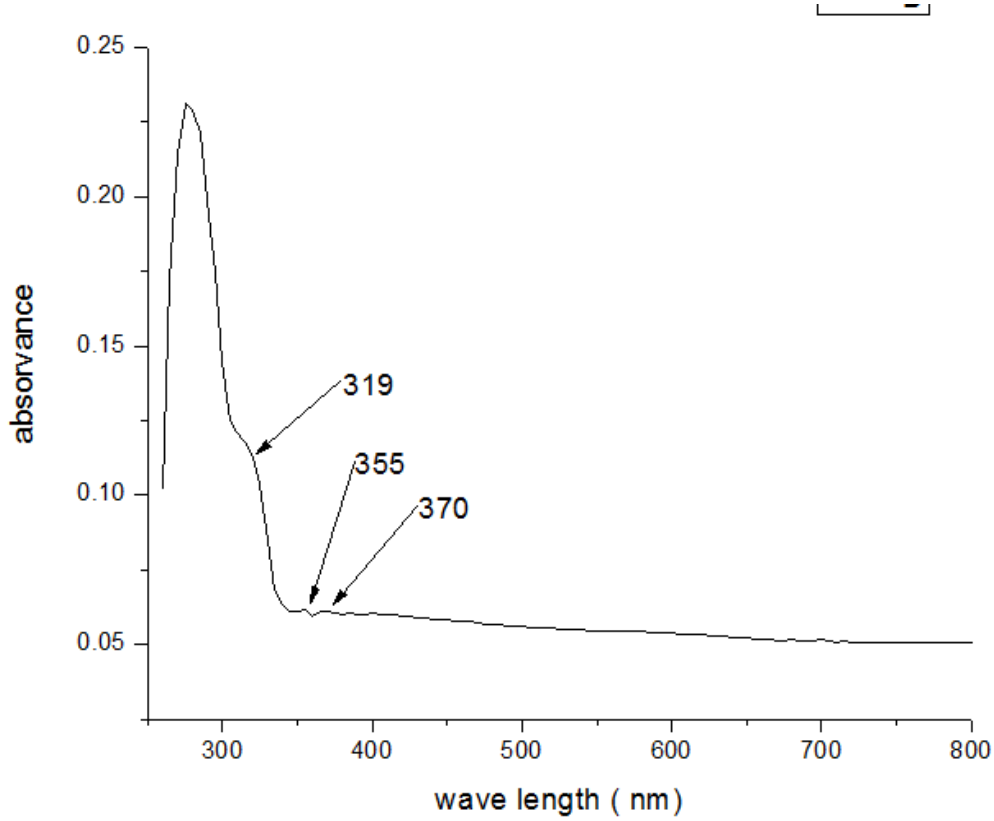
UV- VIS Spectrum of the complex Zn:Hcit:$(bpy)_2$

Similar to Zn: Hcit: $(bpy)_1$ the above Zn: Hcit: $(bpy)_2$ has three bands are observed at 235 nm, 286 nm, and 304 nm. The band at 235 nm is attributed to $\pi \rightarrow \pi^*$ transition of the aromatic region of the 2,2-bipyridine. The band around 286 nm is due to the $n \rightarrow \pi^*$ transition of C=N. The new band at 304 nm is assigned to $n \rightarrow \pi^*$ transition of the carboxyl (C=O) group of the citric acid which confirms the involvement of 2,2'-bipyridine and the carboxylate groups of the citric acid in the complex respectively.



Uv-Vis spectrum of the complex Mn:Hcit:$(bpy)_2$

The Mn (II) complex shows three bands at 319 nm, 355 nm 370 nm. The band at 319 nm is attributed to π→π* transition of the aromatic group. The band around 355 nm is due to the n →π* transition of the C=O group and 370 nm is n →π* of C=N.



4.6. Conclusion

In summary, two zinc (II), (Zn: Hcit: $(bpy)_1$ & Zn: Hcit: $(bpy)_2$ and one Manganese (II) (Mn: Hcit: $(bpy)_2$ compounds have been synthesized from the reactions of zinc chloride with citrate and 2.2'-biyridine aqueous solution. The structural analysis shows that slightly changing the metal-to-ligand molar ratio and PH value leads to the different structures. The synthesized coordination complexes are trinuclear subunits, linked by the carboxyl groups of citrate ligands.

Based on elemental analysis, Uv-vis, IR, and conductivity measurements the proposed structure of Zn:Hcit:$(bpy)_1$, Zn:Hcit:$(bpy)_2$ and Mn:Hcit:$(bpy)_2$ complexes are distorted octahedral. The proposed structures are shown below.

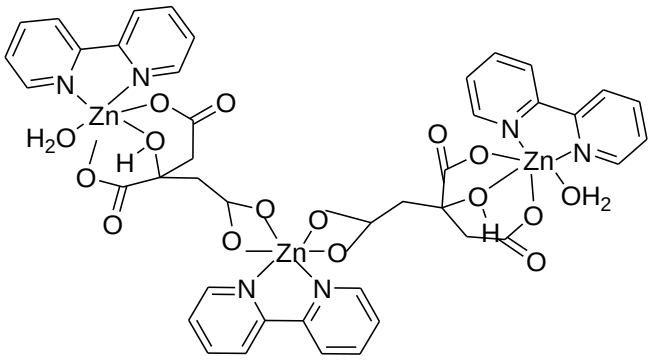


Fig 11: Proposed structure of Zn: Hcit: $(bpy)_1$

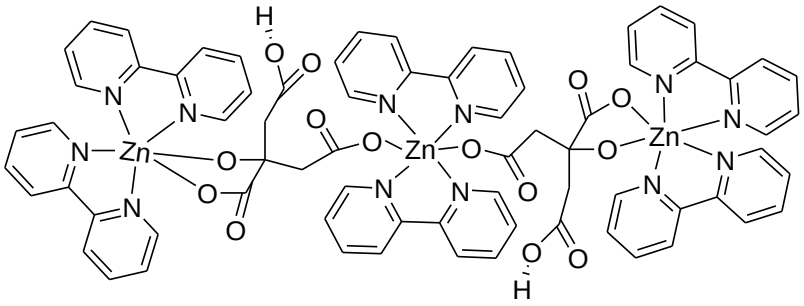


Fig 12: Proposed structure of Zn: Hcit: $(bpy)_2$

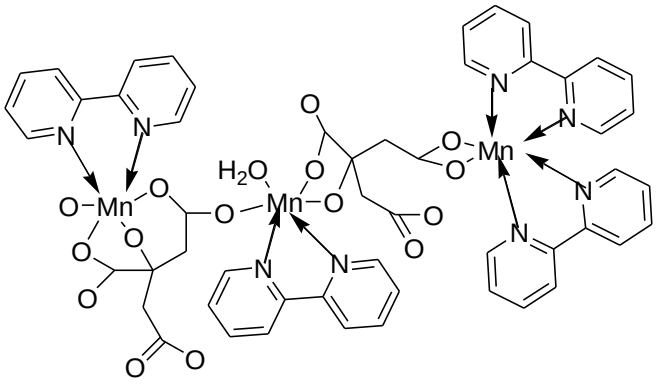


Fig 13**: Proposed structure of Mn: Hcit: $(bpy)_2$**

4.7. Recommendations

Coordination compounds play a great role in biological and other systems; therefore, the synthesis, characterization and study of their properties are very important in luminescence, catalysts and magnetism. In this project Zn(II) and Mn(II) mixed ligand complexes which are derived from 2,2- bipyridine and citric acid (N, and O doner ligands) are synthesized and characterized. Therefore, it is recommended to continue the project and gains the application from the mixed ligand complex.

5. Reference

1. Keypour, H., Rezaeivala, M., Valencia, L., Pérez-Lourido, P., & Khavasi, H. R. (2009). Synthesis and characterization of some new Co (II) and Cd (II) macro acyclic Schiff-base complexes containing piperazine moiety. Polyhedron, 28(17), 3755-3758.
2. Malik, S., Ghosh, S., & Mitu, L. (2011). Complexes of some 3d-metals with a Schiff base derived from 5-acetamido-1, 3, 4-thiadiazole-2-sulphonamide and their biological activity. Journal of the Serbian Chemical Society, 76(10), 1387-1394.
3. Hariprasath, K., Deepthi, B., Babu, I. S., Venkatesh, P., Sharfudeen, S., & Soumya, V. (2010). Metal complexes in drug research-a review. J. Chem. Pharm. Res, 2(4), 496-499.
4. Bell, S. C., Conklin, G. L., & Childress, S. J. (1963). The separation of ketimine isomers. Journal of the American Chemical Society, 85(18), 2868-2869
5. Refat, M. S., El-Korashy, S. A., & Ahmed, A. S. (2008). A convenient method for the preparation of barbituric and thiobarbituric acid transition metal complexes. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 71(3), 1084-1094.
6. Casas, J. S., Castellano, E. E., Couce, M. D., Ellena, J., Sánchez, A., Sordo, J., & Taboada, C. (2006). A gold (I) complex with a vitamin K3 derivative: characterization and antitumoral activity. Journal of inorganic biochemistry, 100(11), 1858-1860.
7. Patil, A. R., Donde, K. J., Raut, S. S., Patil, V. R., & Lokhande, R. S. (2012). Synthesis, characterization and biological activity of mixed ligand Co (II) complexes of schiff base 2-amino-4-nitrophenol-n-salicylidene with some amino acids. Journal of Chemical and Pharmaceutical Research, 4(2), 1413-1425.
8. ASHOKAN, R., Satishkumar, S., Akila, E. K. A. M. P. A. R. A. M., & Rajavel, R. A. N. G. A. P. P. A. N. (2017). Synthesis, characterization and biological

activity of Schiff base metal complexes derived from 2, 4-dihydroxyacetophenone. Chemical Science Transactions, 6(2), 277-287.

9. Patil, A. R., Donde, K. J., Raut, S. S., Patil, V. R., & Lokhande, R. S. (2012). Synthesis, characterization and biological activity of mixed ligand Co (II) complexes of Schiff base 2-amino-4-nitrophenol-n-salicylidene with some amino acids. Journal of Chemical and Pharmaceutical Research, 4(2), 1413-1425.
10. Raman, N., Raja, Y. P., & Kulandaisamy, A. (2001). Synthesis and characterization of Cu (II), Ni (II), Mn (II), Zn (II) and VO (II) Schiff base complexes derived fromo-phenylenediamine and acetoacetanilide. Journal of Chemical Sciences, 113(3), 183-189.
11. Mishra, A. P., & Jain, R. K. (2010). Microwave synthesis, spectroscopic, thermal and biological significance of some transition metal complexes containing heterocyclic ligands. J. Chem. Pharm. Res, 2(6), 51-61.
12. Yu, L. G., Sun, Y. G., & Wang, Z. L. (2019). Mixed-ligand strategy affording two new metal-organic frameworks: Photocatalytic, luminescent and anti-lung cancer properties. Journal of Molecular Structure, 1180, 209-214..
13. Batool, S. S., Harrison, W. T., Syed, Q., & Haider, M. S. (2018). Syntheses and crystal structures of mixed-ligand copper (II)–imidazole–carboxylate complexes. Journal of Coordination Chemistry, 71(9), 1380-1391.
14. Omar, M. M., Abd El-Halim, H. F., & Khalil, E. A. (2017). Synthesis, characterization, and biological and anticancer studies of mixed ligand complexes with Schiff base and 2, 2′-bipyridine. Applied Organometallic Chemistry, 31(10), 3724.
15. Neelakantan, M. A., Esakkiammal, M., Mariappan, S. S., Dharma raja, J., & Jeyakumar, T. (2010). Synthesis, characterization and biocidal activities of some Schiff base metal complexes. Indian Journal of Pharmaceutical Sciences, 72(2), 216.
16. (Grabner, S., & Modec, B. (2019). Zn (II) Curcuminate Complexes with 2, 2′-bipyridine and Carboxylates. Molecules, 24(14), 2540..

17. Pucci, D., Bellini, T., Crispini, A., D'Agnano, I., Liguori, P. F., Garcia-Orduna, P. & Zanchetta, G. (2012). DNA binding and cytotoxicity of fluorescent curcumin-based Zn (II) complexes. MedChemComm, 3(4), 462-468.

18. Ricciardi, L., Pucci, D., Pirillo, S., & La Deda, M. (2014). Emission solvatochromic behavior of a pent coordinated Zn (II) complex: A viable tool for studying the metallodrug–protein interaction. Journal of Luminescence, 151, 138-142.

19. Al-Ali, K., Fatah, H. S. A., & El-Badry, Y. A. M. (2016). Dual effect of curcumin–zinc complex in controlling diabetes mellitus in experimentally induced diabetic rats. Biological and Pharmaceutical Bulletin, 39(11), 1774-1780.

20. Batten, S. R., Chen, B., & Vittal, J. J. (2016). Coordination Polymers/MOFs: Structures, Properties and Applications. ChemPlusChem, 81(8), 669.

21. Du, M., Li, C. P., Liu, C. S., & Fang, S. M. (2013). Design and construction of coordination polymers with mixed-ligand synthetic strategy. Coordination Chemistry Reviews, 257(7-8), 1282-1305.

22. Du, L.Y., Shi, W.J., Hou, L., Wang, Y.Y., Shi, Q.Z. and Zhu, Z., 2013. Solvent or temperature induced diverse coordination polymers of silver (I) sulfate and bipyrazole systems: syntheses, crystal structures, luminescence, and sorption properties. Inorganic chemistry, 52(24), pp.14018-14027

23. Liu, G. X., Xu, H., Zhou, H., Nishihara, S., & Ren, X. M. (2012). Temperature-induced assembly of MOF polymorphs: Syntheses, structures and physical properties. CrystEngComm, 14(5), 1856-1864.

24. Dong, Y. B., Jiang, Y. Y., Li, J., Ma, J. P., Liu, F. L., Tang, B., ... & Batten, S. R. (2007). Temperature-dependent synthesis of metal-organic frameworks based on a flexible tetra dentate ligand with bidirectional coordination donors. Journal of the American Chemical Society, 129(15), 4520-4521.

25. Zhang, R. H., Hong, Q. M., Yang, J. M., Zhang, H. L., Blackburnb, G. M., & Zhou, Z. H. (2009). Syntheses, spectroscopies and structures of zinc complexes with malate. Inorganica Chimica Acta, 362(8), 2643-2649.

26. Zhang, R. H., Xia, W. S., Wang, H., & Zhou, Z. H. (2009). Metal-organic frameworks constructed from monomeric, dimeric and trimeric phenanthroline citrate zinc building units. Inorganic chemistry communications, 12(6), 583-587.

27. Loren, J. C. (2004). Synthesis of topological isomers from manisyl-substituted polypyridine ligands (Doctoral dissertation, University of California, San Diego).

28. Viala, C., & Coudret, C. (2006). An expeditious route to cis-Ru (bpy) 2C12 (bpy= 2, 2′-bipyridine) using carbohydrates as reducers. Inorganica chimica acta, 359(3), 984-989.

29. Klein, C., Nazeeruddin, M. K., Liska, P., Di Censo, D., Hirata, N., Palomares, E. & Grätzel, M. (2005). Engineering of a novel ruthenium sensitizer and its application in dye-sensitized solar cells for conversion of sunlight into electricity. Inorganic Chemistry, 44(2), 178-180.

30. Welter, S., Brunner, K., Hofstraat, J. W., & De Cola, L. (2003). Electroluminescent device with reversible switching between red and green emission. Nature, 421(6918), 54-57.

31. Rüba, E., Hart, J. R., & Barton, J. K. (2004). [Ru (bpy) 2 (L)] Cl_2: luminescent metal complexes that bind DNA base mismatches. Inorganic chemistry, 43(15), 4570-4578.

32. Dhillon, G. S., Brar, S. K., Verma, M., & Tyagi, R. D. (2011). Apple pomace ultrafiltration sludge–A novel substrate for fungal bioproduction of citric acid: Optimization studies. Food Chemistry, 128(4), 864-871.

33. Angumeenal, A. R., & Venkappayya, D. (2013). An overview of citric acid production. LWT-Food Science and Technology, 50(2), 367-370.

34. Shukla, R., Chauhan, N., Rajak, C., & Flora, S. J. S. (2019). Flavors and Fragrances. Flavor Development for Functional Foods and Nutraceuticals, 141.

35. Dakanali, M., Kefalas, E. T., Raptopoulou, C. P., Terzis, A., Mavromoustakos, T., & Salifoglou, A. (2003). Synthesis and Spectroscopic and Structural Studies of a New Cadmium (II)− Citrate Aqueous Complex. Potential Relevance to Cadmium

(II)− Citrate Speciation and Links to Cadmium Toxicity. Inorganic chemistry, 42(8), 2531-2537.

36. Kefalas, E. T., Dakanali, M., Panagiotidis, P., Raptopoulou, C. P., Terzis, A., Mavromoustakos, T. & Salifoglou, A. (2005). PH-Specific Aqueous Synthetic Chemistry in the Binary Cadmium (II)− Citrate System. Gaining Insight into Cadmium (II)− Citrate Speciation with Relevance to Cadmium Toxicity. Inorganic chemistry, 44(13), 4818-4828.

37. Königsberger, L. C., Königsberger, E., May, P. M., & Hefter, G. T. (2000). Complexation of iron (III) and iron (II) by citrate. Implications for iron speciation in blood plasma. Journal of inorganic biochemistry, 78(3), 175-184.

38. Silva, A. M., Kong, X., Parkin, M. C., Cammack, R., & Hider, R. C. (2009). Iron (III) citrate speciation in aqueous solution. Dalton Transactions, (40), 8616-8625.

39. D. Wyrzykowski, D., Czupryniak, J., Ossowski, T., & Chmurzyński, L. (2010). Thermodynamic interactions of the alkaline earth metal ions with citric acid. Journal of thermal analysis and calorimetry, 102(1), 149-154.

40. Kotsakis, N., Raptopoulou, C. P., Tangoulis, V., Terzis, A., Giapintzakis, J., Jakusch, T. & Salifoglou, A. (2003). Correlations of Synthetic, Spectroscopic, Structural, and Speciation Studies in the Biologically Relevant Cobalt (II)− Citrate System: The Tale of the First Aqueous Dinuclear Cobalt (II)− Citrate Complex. Inorganic chemistry, 42(1), 22-31.

41. Wall, N. A., Karunathilake, N., & Dong, W. (2013). Interactions of Tc (IV) with citrate in NaCl media. Radiochimica Acta International journal for chemical aspects of nuclear science and technology, 101(2), 111-116.

42. Bíró, L., Hüse, D., Bényei, A. C., & Buglyó, P. (2012). Interaction of [Ru (η6-p-cym)(H_2O) $_3$] $^{2+}$ with citrate and tricarballate ions in aqueous solution; X-ray crystal structure of novel half-sandwich Ru (II)-citrato complexes. Journal of Inorganic Biochemistry, 116, 116-125.

43. Zhou, R. S., Song, J. F., Yang, Q. F., Xu, X. Y., Xu, J. Q., & Wang, T. G. (2008). Syntheses, structures and magnetic properties of a series of 2D and 3D lanthanide

complexes constructed by citric ligand. Journal of Molecular Structure, 877(1-3), 115-122.

44. Zabiszak, M., Nowak, M., Taras-Goslinska, K., Kaczmarek, M. T., Hnatejko, Z., & Jastrzab, R. (2018). Carboxyl groups of citric acid in the process of complex formation with bivalent and trivalent metal ions in biological systems. Journal of inorganic biochemistry, 182, 37-47.

45. Zhang, G., Yang, G., & Ma, J. S. (2006). Versatile framework solids constructed from divalent transition metals and citric acid: syntheses, crystal structures, and thermal behaviors. Crystal growth & design, 6(2), 375-381.

46. Deng, Y. F., & Zhou, Z. H. (2009). Synthesis and crystal structure of a zinc citrate complex [Zn (H_2cit)(H_2O)] n. Journal of Coordination Chemistry, 62(9), 1484-1491.

47. Holleman, A. F. (2019). Lehrbuch der anorganischen Chemie. Walter de Gruyter GmbH & Co KG

48. Lide, D. R. (Ed.). (2004). CRC handbook of chemistry and physics (Vol. 85). CRC press.

49. Ballhausen, C. J. (1962). Introduction to ligand field theory (No. 541.2). McGraw-Hill,.

50. acid was a Fluka, D. (1987). Metal Chelates of aNew Physiologically Active 0: N: Strident ate Schiff Base. Indian Journal of Chemistry, 26, 887-890.

51. Kambe, T., Tsuji, T., Hashimoto, A., & Itsumura, N. (2015). The physiological, biochemical, and molecular roles of zinc transporters in zinc homeostasis and metabolism. Physiological reviews, 95(3), 749-784.

52. Kaur, K., Gupta, R., Saraf, S. A., & Saraf, S. K. (2014). Zinc: the metal of life. Comprehensive Reviews in Food Science and Food Safety, 13(4), 358-376.

53. Pucci, D., Crispini, A., Mendiguchía, B. S., Pirillo, S., Ghedini, M., Morelli, S., & De Bartolo, L. (2013). Improving the bioactivity of Zn (II)-curcumin based complexes. Dalton Transactions, 42(26), 9679-9687.

54. Al-Ali, K., Fatah, H. S. A., & El-Badry, Y. A. M. (2016). Dual effect of curcumin–zinc complex in controlling diabetes mellitus in experimentally induced diabetic rats. Biological and Pharmaceutical Bulletin, 39(11), 1774-1780.

55. Parkin, G. (2000). The bioinorganic chemistry of zinc: synthetic analogues of zinc enzymes that feature tripodal ligands. Chemical Communications, (20), 1971-1985.

56. Rayner-Canham, G. W., Rayner-Canham, G., & Overton, T. (2003). Descriptive inorganic chemistry. Macmillan.