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Studies on the Transition Metal Complexes of Acids and Imides with Amine Bases

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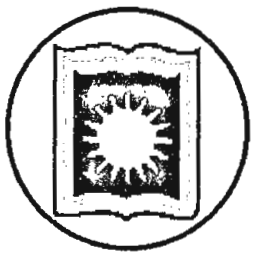
University of Rajshahi

STUDIES ON THE TRANSITION METAL COMPLEXES OF ACIDS AND IMIDES WITH AMINE BASES



M.Phil
in
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Submitted By

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DEPARTMENT OF CHEMISTRY, UNIVERSITY OF RAJSHAHI

RAJSHAHI-6205, BANGLADESH

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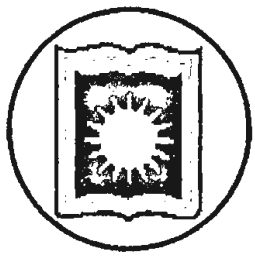


A Thesis

Submitted to the University of Rajshahi, Bangladesh in partial fulfillment of the requirements for the degree of

MASTER OF PHILOSOPHY
IN
CHEMISTRY

Submitted By

Md. Mahabubar Rahman

B.Sc (Hons) M.Sc (Raj)

INORGANIC RESEARCH LABORATORY

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF RAJSHAHI

RAJSHAHI-6205, BANGLADESH

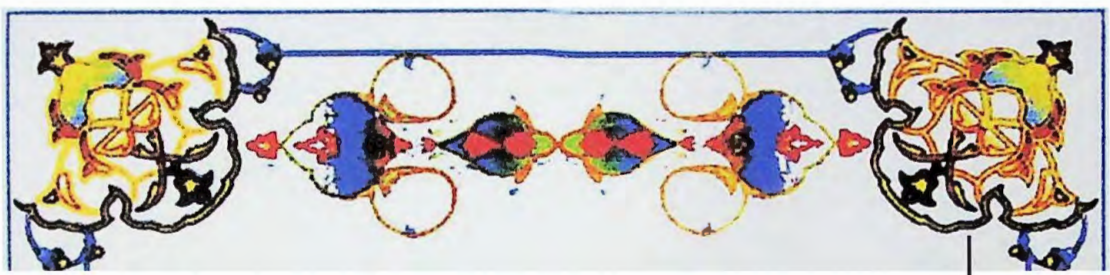
JUNE, 2010

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF RAJSHAHI
BANGLADESH

DECLARATION

I hereby declare that the research work submitted in the thesis entitled "**STUDIES ON THE TRANSITION METAL COMPLEXES OF ACIDS AND IMIDES WITH AMINE BASES**" to the Department of Chemistry, University of Rajshahi for the degree of **Master of Philosophy** is the result of my own investigation and not ever been submitted before for any degree, diploma or other similar title of any University. The work has been carried out under the supervision of Professor **Dr. M. Saidul Islam,** Department of Chemistry, University of Rajshahi, Bangladesh.

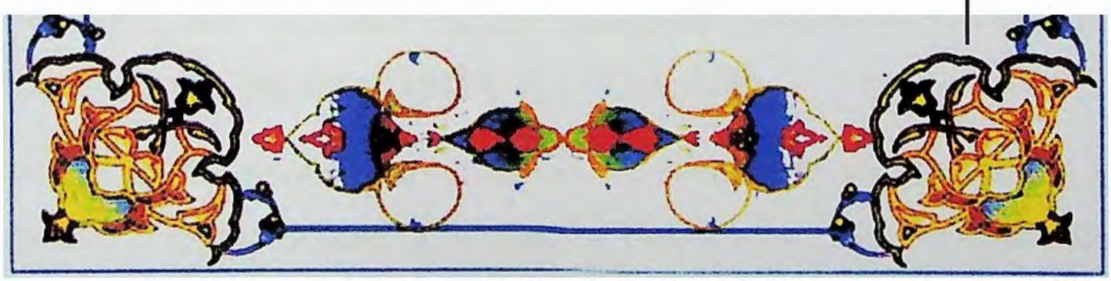
29.06.10.
(Md. Mahabubar Rahman)
B.Sc (Hons) M.Sc (Raj)
June, 2010



Dedicated

To

My Beloved Parents and Teachers



DEPARTMENT OF CHEMISTRY
UNIVERSITY OF RAJSHAHI
BANGLADESH

DECLARATION CERTIFICATE

I certify that the thesis entitled "**STUDIES ON THE TRANSITION METAL COMPLEXES OF ACIDS AND IMIDES WITH AMINE BASES**" submitted by **Md. Mahabubar Rahman** in partial fulfillment of the requirements for the degree of Master of Philosophy is the candidate's own achievement and is not a conjoint work with any one else. This is an original study of the author and no part of this thesis has been submitted to any degree, diploma or associateship of any other similar title. The author carried out his research under my supervision and Guidance in the Inorganic Chemistry Laboratory, Department of Chemistry, University of Rajshahi.

I have gone through the final draft and wholeheartedly recommended its submission for the degree of **Master of Philosophy. Mr. Mahabubar Rahman** has fulfilled the entire requirement according to the rules of the University for Submission of a dissertation for the degree of **M.Phil.**

29.6.2010

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Md. Mahabubar Rahman
The Author

ABSTRACT

This thesis is presented on the interaction of metal ions with stoichiometric amounts of organic ligands containing O and N donors of which metal complexes have been widely used in biological and catalytical point of view. The thesis is divided into ten chapters.

1. First one is an introductory chapter. The chapter is designed to provide sufficient background and usefulness of the present study.

2. The second chapter describes the experimental techniques which include the physical measurement and analytical techniques.

3. Third chapter has been devoted to the preparation and characterization of mixed ligands complexes of Zr(VI) ions with oxalic acid and heterocyclic amines. The general formula of the complexes are as follows; [Zr(IV) $(oxa)_2$ L_2]. Where oxa = oxalic acid L = Q, 2-Apy, 8-HQ, α–Pic, 2,2'–Bipy. The complexes were prepared in the solid form and characterized by elemental analysis, conductivity, magnetic measurements, infrared, and electronic spectroscopic studies. The infrared spectra of the complexes confirmed the co-ordination of metal ion with ligands. The presence of water molecule inside the co-ordination sphere was also confirmed by infrared spectra. Electronic spectra and megnetic measurement confirmed that the Zr(IV) complexes were of octahedral structure.

4. The fourth chapter describes the preparation and characterization of mixed ligand complexes of Zr(IV) ions with malic acid and heterocyclic amines. The general formula of the complexes are as follows; [Zr (IV) $(Mal)_2$ L_2] where Mal = Malic and L = 8-HQ, Q,

2,2'-Bipy, IQ, α–Pic. The complexes were prepared in the solid form and characterized by the usual methods. The infrared spectra of the complexes confirmed the coordination of metal ion with ligands. The Zr(IV) complexes are assumed to have octahedral structures based on the electronic spectra and magnetic measurement.

5. Fifth chapter allocates the preparation and characterization of mixed ligand complexes of Zr(IV) ions with organic acid and heterocyclic amines. The general formula of the complexes are as follows; [Zr(IV) $(oxa)_2$ L_2], [Zr(IV) $(Mal)_2$ L_2] and [Zr(IV)] $(MA)_2$ L_2] where oxa = oxalic acid, Mal = Malic acid, MA= Methanoic acid, L = ala, β-Ph-ala. These complexes were analyzed chemically for the metal, carbon, hydrogen and nitrogen. Their structures have been determined by carrying out spectral and magnetic studies. The infrared spectra of the complexes confirmed the coordination of metal with ligands. The presence of water molecule inside the co-ordination sphere was also confirmed by infrared spectra. Electronic spectra and magnetic measurement confirmed the octahedral structure of Zr(IV) complexes.

6. Sixth chapter has been devoted to the preparation and characterization of mixed ligand complexes of V(IV) ions with some organic acid and amine bases. [$V(IV)_2$ L_2 L'_2] where, L = oxa (1,5), MA (2), EA (3), PA (4), Mal (6), L' = ala, 2,2'-Bipy. The complexes were prepared in the solid form and characterized by previously mentioned method. The infrared spectra of the complexes confirmed the coordination of metal ion with ligands. The observed magnetic moment values of complexes indicated that these complexes are diamagnetic. This diamagnetism is

supported by the small negative values obtained from their magnetic susceptibility. Electronic spectra and magnetic measurement confirmed that the V(IV) complexes were of octahedral structure.

7. Seventh chapter describes the preparation and characterization of mixed ligand complexes of V(IV) with acids and amine bases. The general formula of the complexes are $[V(IV)L_2L'_2]$. Where L=Mal, oxa, MA, EA,PA L'=β-Ph-ala. The complexes were prepared in the solid form and characterized by usual methods. IR spectra of the complexes indicate that the co-ordination of motel Ion with amino groups. Magnetic measurement and electronic spectra of the complexes confirmed the octahedral structure.

8. Eighth Chapter deals with the preparation and characterization of mixed ligand complexes of Zr(III) with Phthalimide as primary and amino acids as secondary ligands. The general formula of these complexes are as follows; $K[Zr(IV)\ (Phtha)_2\ L_2]$ (where, Phtha = Phathalimide, L = Q,2-Apy,8-HQ,Py, α-Pic). The complexes were prepared in the solid form and characterized by usual methods. IR spectra of the complexes indicated the co-ordination of metal ion with amino group through nitrogen and carboxylic acid group through oxygen ion and imide through–NH. Electronic spectra and other measurements confirmed their octahedral structure.

9. Ninth chapter we have studied the antimicrobial activity of all the complexes of chapter-3 to chapter-7. Disc diffusion methods were employed for antimicrobial assays against ten pathogenic bacteria (five gram positive and five gram negative) and ten fungi. The

complexes containing 2-aminopyridine and 8-hydroxyquinoline, py, α-pic as secondary ligands are much more microbial active than the other complexes.

10. This chapter describes the antifungal activity of the complexes against six pathogenic fungi viz.

    i. Trichoderma species

    ii. Fusarium species

    iii. Botarydiptoden species

    iv. Aspergillus flavus

    v. Aspergillus species

    vi. Mucor species

    vii. Penicillium

    viii. Bipolaris species

    ix. Epidermophton floccosum

    x. Aspergilus niger

    xi. Candida albicans

The results revealed that the complexes are more micorobial toxic than the free metal ions or ligands. The complexes containing, 8-hydroxy-quinoline, 2,2′-bipyridyl, iso-quinoline, 2-Apy, py, alaline as secondary ligands are much microbial active than the other complexes.

Symbol and Abbreviations

Oxa	:	Oxalic acid
Mal	:	Malic acid
MA	:	Methanoic acid
EA	:	Ethanoic acid
PA	:	Propanoic acid
Q	:	Quinoline
IQ	:	Iso quinoline
8-HQ	:	8-Hydroxy quinoline
ala	:	Alanine
β-Ph-ala	:	β-Phenyl alanine
α- Pic	:	α - Picoline
2,2′-Bipy	:	2,2′- Bipyridyl
DMSO	:	Dimethylsulphoxide
DMF	:	N,N′ dimethyl formamide
IR	:	Infrared
gm	:	Gram
υ	:	Absorption maximum
%	:	Percent
ml	:	Milliliter
k	:	Kelvin
Fig	:	Figure
UV	:	Ultra Violet
No	:	Number
λ	:	Conductance
xg	:	Mass Susceptibility
μg	:	Micro gram
B.M	:	Bohr Magneton
L	:	Ligand

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CHAPTER ONE

GENERAL INTRODUCTION

CHAPTER-1
GENERAL INTRODUCTION

1.1 General Introduction:

In recent years coordination compounds deserve extreme attraction of modern researches for their ever increasing academic and commercial interest. Coordination compounds make a challenge to the inorganic chemists. In the early days of the chemistry they seemed unusual (hence the name complex ions) and seemed to defy the usual rules of valence.

Coordination chemistry at present stands as a land mark in the field of scientific advancement, embracing most diverse branches of science, engineering and technology. The coordination compounds are expanding very rapidly in the diversified field of chemistry. This expansion is due to the various factors such as improved understanding of bonding theories and reaction mechanism, physical methods of studying molecular structures and properties, precise and profound techniques of carrying out chemical reaction and the need to understand the catalytic process. The rapidly developing field of bio-inorganic chemistry is centered in the presence of coordination compounds that are found to play a vital role in living systems e.g. vitamin B_{12} co-enzyme, 5-deoxyadenosine cobalamine, hemoglobin, myoglobin, cytochromes and hemocyanin in the form of coordination compounds[1]. The complex compounds have large utility in metallurgical operations, in dying and textile industries, in analytical chemistry and in medical science.

Coordination chemistry plays an outstanding role in the biological system that cause interesting changes, i.e. change of oxidation number and coordination number of metals. This is partly due to an extensive and important involvement of such complexes in bio-inorganic chemistry.

It has now been well established that many of the chemical elements including metal ions control a vast range of biological process, thus giving new dimensions to coordination chemistry.

1.2 Metal Complex:

A complex has been defined as a species formed by the association of two or more simpler species capable of independent existence[2]. When one of the simpler species is a metal ion, the resulting entity is known as a metal complex. A characteristic feature of such a complex is that the metal atom occupies a central position in it. Thus a metal complex may be defined as a compound containing a central metal ion or atom to which are attached oppositely charged ions and/or metal molecules whose number usually exceeds the number of molecules which are attached (co-ordinated) to the central metal are called ligands.

In a narrow sense, the complex formation may be regarded as reversible association of one or more metal ions and ligands occurring in a solution. In the wider sense every Lewis acid-Lewis base reaction involving essentially the formation of a co-ordinate covalent bond can be called a complex formation reaction.

Alfred Werner in 1893 put forward his classical theory, what is now commonly referred to as Werner's co-ordination theory[3,4], on the basis of primary and secondary valence. One of the major advancements in the field of chemistry has been the development of theories of bonding

particularly related to metal complexes in order to understand their structures and properties, for wider applications three theories are currently used to describe the nature of the bonding in transition metal complex. These theories are (i) the valence bond theory[5,6] (ii) the crystal field theory and[7,8] (iii) the molecular orbital theory[9-11].

Now this time, metal complexes are the most active research field of inorganic chemistry. A survey of articles in recent uses of the journal of inorganic chemistry indicates that perhaps 70% could be considered to deal with metal complexes. Progresses in this are chemistry has received an added impetus because of its many applications to chemical industry and biology. It has been clearly understood and supported that many of the chemical elements including metal ions control a vast range of biological processes going a new dimension to co-ordination chemistry[12]. The rapidly developing field of bio-inorganic chemistry is centred on the presence of metal complexes in living systems.

1.3 Mixed Ligand Complex

Mixed ligand metal complex is the compound in which the metal ion is simultaneously bonded to one or more different kinds of ligands.[13] In aqueous solution most metal ions are present as aquo complexes. In the course of complexes formation the ligands replace the water molecules of the aquo complexes. All the water molecules will be replaced only when the complex with the maximum coordination number of the central metal atom has been formed. The mixed donor complexes are those chelate complexes whose ligands contain different kinds of donor atoms.[14] Thus mixed donor complexes may be formed by 8-hydroxy quinoline (donor atom N and O), dithiazone (donor atom N and S), etc. The mixed ligand metal complexes are likely to be important as models for

metalloenzyme—substrate complexes and also as components of the multi—metal multi-ligand systems in biological fluids and thus provide a strong impetus for increasing interest in this area[15]. Perrin *et al.*[16-18] have observed that the addition of another ligand B to a complex MB which already bears a ligand B is more difficult than adding B to a complex MA which contains a different ligand, A. A set of data of stability constants of various complexes illustrate the unusual stability of mixed ligand complexes as compared to complexes containing only one kind of ligand. Although it is not clear why this should be so, it is an observation, which continues to reappear.[19]

1.4 Ligands

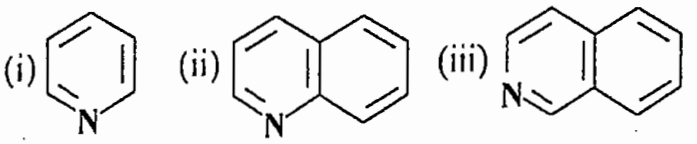
A ligand may be defined as any molecule or ion that has at least one pair of electron that can be donated. Thus ligands are Lewis bases. There are many classes of ligands.[20]

(a) ***Classical type of ligands:*** These ligands act as electron pair donors to acceptor ions or molecules and form complexes with all types of Lewis acid metal ions or molecules.

(b) ***Non–classical type of ligands:*** These are π-bonding or π-acid ligands and form complexes largely with transition metal atoms or ions (PR_3, CO etc.).

Ligands can be defined another way on the basis of the number of unpaired electrons e.g.,

Monodentate ligands: The ligands which have only one donor atom can co-ordinate to the central metal atom/ion at one site only, are called monodentate ligands. e.g., pyridine, quinoline, iso-quinoline (Fig.1.1)



Pyridine Quinoline Iso-quinoline

Fig. 1.1

Bidentate ligands: The ligands having two donor atoms that can co-ordinate to the central metal atom/ion at two site, are called bidentate ligands e.g, 2,2' Bipyridyl, 8-Hydroxy quinoline, 2-ainino pyridine, α-picoline (Fig-1.2)

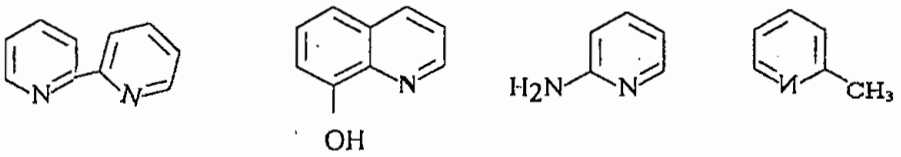


Fig. 1.2

Tridentate ligands: The ligands having three donor atoms are called tridentate ligands e.g., triaminopropane (Fig. 1.3)

$CH_2(NH_2)—CH(N^*H_2)—CH_2(N^*H_2)$

Fig. 1.3

Tetradentate ligands: The ligands having four donor atoms are called tetradentate ligands e.g, Triethylenetetramine (Fig. 1.4).

$(CH_2)_2—N^*H—(CH_2)_2—N^*H—(CH_2)_2$

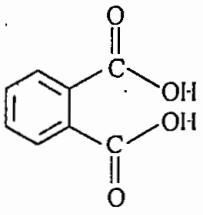
N^*H_2 N^*H_2

Fig. 1.4

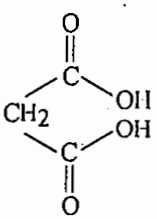
Multidentate ligands: The ligands having more than one donor atoms or ions are called multidentate. The ligands are attached to the same central atom producing a cyclic structure called chelate complex and the processes of complex formation are called chelation. The greatest tendency to form chelate complex is found in poly functional ligands whose donor atoms are separated by two or three carbon atoms. The rings produced by chelate formation will then believe to be six membered. The stability of the complexes also depends considerably on the chelate ring size.

1.5.1 Dicarboxylato Ligands

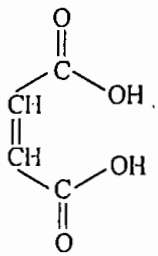
In the present work deprotonated dicarboxylic acid, named malonic acid has been used as dicarboxylato ligand. Although dicarboxylic acids have no co-ordination position but under suitable condition (slightly alkaline medium) these acids loose protons from both the carboxyl groups and act as dinegative bidentate ligands. They tend to form 6, 7, 8 and 9 membered chelate ring is their respective cases. Stable chelate rings of five and six members are numerous and well known, but rings of seven or more members are comparatively less common.



phthalic acid



malonic acid



maleic acid

In complex compounds, the co-ordination number of the central metal atom/ion is occupied according to the power of the ligands. First ligand is called primary ligand and the second ligand is called the secondary ligand respectively.

The stability of the mixed ligand complexes depends on the ligand stability factors and shape of ligands.

1.5.2 Amine Ligands

Amine ligands are widely used in most of the present complexes. Among these the heterocyclic amines are the most important. Although heterocyclic amines contain tertiary nitrogen atoms, they co-ordinate readily with metal atoms. Most of the heterocyclic amines are used as corrosion inhibitors[21-23] and their complexes with platinum and copper have been tested as antitumor[24] and antibacterial[25] agent. 3-aminopyridine has strong anticonvulsive effects.[26-27] The chlorinated species of 8-hydroxyquinoline has been proved as antibacterial and antifungal agents[28] and the diiodo derivative is administered to overcome zinc deficiency in animals.[29] Derivatives of copper and tin of 8-hydroxyquinoline are antifouling agents[30,31] and 8-hydroxyquinoline itself protects the industrial oils form the growth of bacteria and fungi in them.[32,33] Studies on the metal complexes of heterocyclic amines have been carried out by several workers.[34-49]

1.5.3 Biologically Active Ligands

The ligands that can form compounds essential for life are called biologically active ligands.

The synthetic macrocyclic complexes, particularly with the tetradentate nitrogen donor ions, are most important from the biological viewpoint mainly due to their structural similarities to the natural macrocyclic complexes like vitamin $B_{12,}$, chlorophyll, hemoglobin, etc. Special compound such as hemoglobin forms bonds with protein through oxygen, acts as a ligand. Beside myoglobin, glycoprotein etc, (Sugar + Protein =

Glycoprotein) metal chelation is involved in many important biological processes, which play important and multifarious roles in biological systems. The intriguing mode of function of these natural systems is now well understood.[50,51] The vital functions performed by the natural systems can largely be determined by the nature of the metal ions enclosed in it. For example, the catalytic properties of vitamin B_{12} and its coenzyme are due to the ability of the cobalt ion to act as a storehouse for an electron that can be released or accepted as required. The metal ions in natural macrocyclic complexes are trapped in such a complicated structure that the fundamental properties of these metal ions are still not well understood. It is, therefore, reasonable to synthesize simple macrocyclic complexes, which can be considered as model compounds. Some of these compounds could mimic the properties of their natural counterparts and investigations with them would provide us an easier approach to the study of fundamental properties of metal ions encapsulated in the macrocyclic environment.

The rapid developing field of bioinorganic chemistry is centered on the presence of metal complexes in living systems.

1.6 Organisms

1.6.1 Bacteria

(i) Genus *Staphylococcus*

Characteristics: Gram-positive coccus; cells in clusters (reflecting ability to divide in more than one plane); individual cells approximately 1μm in diameter. Some strains produce capsules. Non-fastidious capable of aerobic and anaerobic respiration.

Diseases: Boils; skin sepsis; post-operative wound infection; scalded skin syndrome; catheter—associated infection; food—borne infection; septicemia; endocarditic; toxic shock syndrome; osteomyelitis; pneumonia.

(ii) Genus *Streptococcus*

Characteristics: Gram-positive cocci in chains ceils <1 μm diameter, non-motile, non-sporing.

Diseases: Infections of upper respiratory tract and of skin and soft tissue e.g. pharyngitis, cellulites; erysipelas, lymphadenitis. Toxic manifestations include scarlet fever. Non-suppurative sequelae (acute glomerulonephritis and rheumatic fever) important complications of both skin anti throat infections.

(iii) Genus *Bcillus*

Characteristics: Large (4-10 μm) Grain-positive, spore-forming, encapsulated rods. Spores are formed only alter the organism is shed from the body Respires aerobically.

Diseases: Anthrax is a significant disease in animals both domesticated and in the wild. It is a zoonosis and humans are usually infected by contact with infected hides or bones. Wool sorters disease i.e., respiratory or inhalation anthrax, is now rare. Intestinal anthrax is rare in humans but remains a possibility that attracts interest as an aspect of biological warfare.

(iv)Genus *Escherichia*

Characteristics: Gram-negative rod; motile; +/- capsule. Non-fastidious, facultative anaerobe; bile tolerant; capable of growth at 44°C.

Diseases: Urinary tract infection; diarrhoeal diseases; neohatal meningitis; septicaemia.

(v) Genus *Salmonella*

Characteristics: Gram-negative, motile, lion-sporing rods, all except S. typhi are non-capsulate, capable of aerobic and anaerobic respiration. **Diseases:** Vast majority cause diarrhoeal disease; very occasionally invasive (particularly *S.cholerae-suis*). Sickle cell disease predisposes to osteomyelitis. *S. typhi and S. paratyphi* cause systemic disease, typhoid and paratyphoid (enteric fevers).

(vi)Genus *Shigella*

Characteristics: Gram-negative rods. Non-motile (in contrast to salmonellae) non-capsulate and is capable of aerobic and anaerobic respiration.

Diseases: Bacillary dysentery and is very rarely invasive.

(vii) Genus *Pseudomonas*

Characteristics: Aerobic Gram-negative rod and is motile by means of polar flagella, able to utilize a very wide range of carbon and energy sources and to grow over a wide temperature range. Does not grow an aerobically (except when nitrate is provided as a terminal election acceptor).

Diseases: *P. aeruginosa* is an opportunist pathogen, which can infect almost any body site given the right predisposing conditions. It causes infections of skin and burns, it is a major lung pathogen in cystic fibrosis patients and can cause pneumonia in incubated patients. It can also cause urinary tract infections, septicaemia, osteomyelitis and endocarditis.

1.6.2 Fungi

(i) Genus *Aspergillus*

Characteristics: Filamentous fungi causing opportunistic infections in immunocompromised patients. It occurs widely in external environment. Invade lungs and blood vessels.

Diseases: Aspergillosis. Some causes mycosis of human.

(ii) Genus *Candida*

Characteristics: Dimorphic fungus, occurring as yeast on mucosal surfaces as component of normal flora, but forms hyphae when invasive. Produces opportunistic infections in stressed, suppressed and antibiotic-treated individuals. *Paracocidioides brasiliensis* in central and South America has many similarities.

Diseases: Candidiasis, thrush.

(iii) Genus *Colletotrichum*

Characterization: Mycelium of the fungus is ceptate, hylime or slightly brownish, conidia produce on phialides, canidia one celled and crescent shaped. It is an imperfutifungi, but some species of them perfect stage were discovered, it is a plant pathogenic fungus.

Diseases: Different species of this genus are performed various sever disease, such as red rot of sugarcane, anthracnose of mango, jute, bean etc.

(iv) Genus *Trichophyton*

Characterization: *Trichophyton* is a fungus of dermatophytes, Mycelium hylime, septate.

Diseases: Causal agent of some severs human and birds disease such as ringworm.

(v) Genus *Fusarium*

Characterization: *Fusarium* is a fungus of imperfutifungal. Mycelium hylime, septate, canidia hylime, conidia septate, crescent shaped and grow on phialides.

Diseases: Causal organisms of some plant diseases viz., *Fusarium* wilt, root rot, etc.

(vi) Genus *Penicellium*

Characterization: Mycelium septate and branched, conidia produced on conidiophore. It is a saprophytic fungus and grows on rotted fruit, wood, leather arid many other foods.

Diseases: Some species of the genus are formed human and plant disease, Essential antibiotic 'penicillin' reduced form that fungus.

(vii) Genus *Trichophyton*

Characterization: It is a plant pathogenic fungus. Mycelium ceptate, conidia oval shaped and produced in stroma.

Diseases: It is responsible to various types of soft rot of papaya, guava, litchi, and foot rot of coconut, dieback of lemon and black-band disease of jute.

1.7 Survey of the Previous Work

The mixed ligand complexes of Zirconium (IV) and Vanadium (IV) with carboxylic acid as primary and heterocyclic bases as secondary ligands have been prepared and characterized.[52-54] A very few survey has been done on the metal complexes of adipic or dibasic acid. Agafonova carried

out the precipitation and separation studies of some bivalent metal ions.[55,56] The complexes are insoluble in polar solvents but soluble in non-polar solvents. They also have prepared mixed ligand monomeric complexes of some metal ions with diphenic and other carboxylic acids as primary and amine bases as secondary ligands.[57-60] Prelesnik *et al.,* have prepared a dimeric copper complex with phthalic acid and 2, 2'-bipyridine.[61] As early as 1921, Duff reported a monomeric mixed ligand complex of cobalt (III) with homophthalic acid and ethylenediamine, where homophthalato ligand led to the formation of a 8-membered ring. The metal complexes of malonic and succinic acid and their various activities were found in the literature.[62-71] All of these experimental works and evidences static our faith in the formation of dibasic acid complexes with metal atoms.

Malic acid may be used as an analytical reagent[72] and also as a bidentate ligand in the formation of complexes with metal ions. Paajanea *el al.* (1999) investigated on the weather resistance of specimen treated with a mixture of tall oil and malic anhydride in a one-year exposure test and a 670- hour ageing test in a weather chamber was superior to that of untreated specimens of wood. A fairly hard hydrophobic film developed on the wood surface during the ageing process. The treatment inhibited the growth of blue stain and mould fungi.[73]

The preparation and characterization of mixed ligand complexes of Zr(IV) and V(IV) with diphenic acid as primary and some heterocyclic bases as secondary ligands have been reproted.[74] Analytical properties of diphenic acid have been studied by Agafonova and Ryazanovs,[75] Sharma,[76] Sharma and Islam[77,78] have reported some mixed ligand

complexes containing diphenate ions and amine bases. The influence on the position of the carboxylic group on complex formation of salts from biphenyl dicarboxylates has been investigated by Macarovici and Schimidt.[79] They have shown that the carboxyl groups in diphenic acids led to the fonnation of monomeric complexes. Pataskewas and Danopoulos[80] have reported the ESR studies of copper diphenate complexes with amines. Mixed ligand complexes of transition metal diphenate with amines have also been studied by Ara-Blesa.[81]

Malonate complexes are known with Zr(IV) metals and have been reviewed by Stadler and Schindler.[82] Complex formation between iron(III) with oxalate, malonate, succinate and glutarate ions have been studied by Demeux *el al.*[83] They have shown that the stability order of the chelates of iron(III) is oxalate ≅ malonate> succinate ≅ glutamate. The metal complex of malonic and succinic acids and their various, activities are found in the literature.[84-92] Saha and Mitra[93] have studied the thermal investigation and thermal decomposition reactions of metal oxalato, malonato and succinato complexes and found that the thermal stability of the complex decreased with the increase of the standard potential of the central metal ion. Costantino *et al.* [94] have prepared oxalato complex of copper containing 1, 10 phenanthroline and aquo ligands and its crystal structure have been discussed. They have shown that the complex is monomeric and co-ordination is 4+1 in a square pyramidal geometry, with a water O atom in the apical position. A similar observation with malonato complex has been reported by kwik *et al.*[95]

The metal complexes of phthalic acid have been studied both from pharmacological[96,97] and industrial[98-102] point of view as indicated by

available literatures. The literature, are also rich with reports on the mixed ligand complexes prepared by using phthalic acid as primary and heterocyclic amine bases[102-107], polyamines[108] and thiocarbamides[109] as secondary ligands.

James and co-workers reported the fungicidal properties of six triphenyl tin (IV) compound representing metal coordination number of four through six.[110] These experiments were conducted against a number of soil and plant pathogenic fungi and compared with the results obtained from triphenyl tin chloride. While all the compounds examined proved to be effective fungicides, differences at the concentration levels tested were not sufficiently pronounced to relate the degree of toxicity to the molecular structure.

Amongst the various factors affecting the activity of a drug, its ability to form stainless chelate rings has been shown quite important. Further, it has been pointed out that certain metal complexes of drugs proved more potent than the pure drugs which measured by Chakrabarti and Shinde.[70] In this study, some metal complexes of oxytetracycline, an important antibiotic drug have been synthesized and screened for their activity towards gram–positive and grain–negative bacteria. Viz Zr(IV) and V(IV).

Kuncheria and co–workers[111] have studied the biological activity of the complex of Cu(II) with N_1–isonicotinoyl–3–methyl–5–pyrazolone (IMP) and N_1–isonicotinoyl–3–methyl–4–hydroxobenzylicline–5–pyrazolone, (IMHP) having the formula $CLI(NO_3)_2$ IMP and $CuCl_2$ IMHP. In vitro cytotoxic studied using these drugs indicated that 100% cytotoxicity could be produced to Ehrilich ascites tumor cells at a concentration of 10μg/ml.

Tiwari anti co-workers synthesized the benzothiazole ligand and its metal complexes with bivalent Cu, Co, Ni, Cd, Fe, and Zn.[112] Their antibacterial and antifungal activities have been studied.

Sabastiyan and co-workers[113] synthesized the complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with sulphur donar ligand 1-(N,N-dicyclohexylamino) methylthiouiea (DCMT) $(C_6H_{11})_2$ NCH_2N $HCSNH_2$ and studied the structural characterization and antimicrobial activity.

Tominage *et al.*[114] and Burger *et al.*[115] deal simultaneously and independently with thermal decomposition of Iron (II) pyridine chloride and Iron (II) pyridine thiocyanate mixed ligand complexes. The products of this decomposition were isolated and their Mossbauer spectra were also recorded.[116]

Sharma *et al.*[117,118] have reported a number of mixed ligand complexes of Titanium (III) and Vanadium (IV) with imides and heterocyclic amines for example, quinoline, isoquinoline, α–picoline or pyridine, 2, 2′–bipyridyl, 2-aminopyridine and 8–hydroxy quinoline. The complexes were characterized by elemental analysis, conductivity and magnetic measurements and infrared and electronic spectroscopy.

Sharma *et.al.*[119] also reported a number of mixed ligand complexes of Zr(IV) and V(V) with dibasic acid as primary and heterocyclic bases as secondary ligands. The secondary ligands were quinoline, isoquinoline, pyridine, 2– aminopyridine and 8–hydroxy quinoline. All these complexes were characterized by usual methods.

Islam *et. a.l*[120] reported a number of mixed ligand complexes of Zr(IV) and V(IV) with dibasic acid and amine bases for example, quinoline, isoquinoline. Pyridine, α-picoline, 2–amino pyridine, 2-2′–bipyridyl.

8–Hydroxy quinoline. The complexes were characterized usual methods. It has been suggested that the complexes of Zr(IV) and V(IV) have octahedral structures respectively.

1.8 Reason to choose the Project

The creation of powerful new materials for innovative applications is one of the big scientific and technical challenges of our days. This challenge can only be met by a multidisciplinary approach, in which, however, preparative Chemistry plays a fundamental role. It provides the compounds, which eventually will be shaped into new devices by materials material scientists. The design of the macroscopic properties of a material by the deliberate selection and tailoring of nanoscopic building blocks is a new approach in inorganic chemistry. One of the modern methods for preparing inorganic materials from molecular precursors is the sol-gel process. Not only has it allowed the preparation of known materials in a new way, but also materials with novel composition and properties. The aspects of designing inorganic materials, is becoming a realistic possibility.[121]

Metal alkoxides serve as precursors for the formation of oxide networks via inorganic polymerization reactions. Oxide material of composition, are now accessible as ceramic powders and fibers, glasses, thin films, dyeing fabrics or coatings. Many oxides materials were prepared by sol-gel processing, starting from mixtures of hydrolysable compounds (alkoxides, carboxylates, *etc.*). The sol-gel materials developed by this approach, those composed of both organic and inorganic components (organic-inorganic hybrid materials) are particularly useful.

Organic molecules are embedded in an inorganic matrix. These materials are synthesized by carrying out the hydroxolysis and condensation of the inorganic compound. The advantage of hybrid materials is that no extensive modification of the starting compounds required. Various organic–inorganic hybrid polymers with interpenetrating organic and inorganic networks have been prepared, and organic molecules entrapped in the inorganic matrix without losing their chemical properties.[122]

The organic compounds containing carboxylic or dicarboxylic groups have both salt forming and coordinating properties. The resulting complexes are generally insoluble in polar solvents and soluble in non–polar solvents and hence are very important form analytical, industrial and pharmaceutical point of view. The derivatives of complexes hence proved to be important medicinal agents and have been suggested for the use in the treatment of arthritis, tuberculosis, convulsion and epilepsy. Dibasic acid and its esters have antiauxin activity.[123] Dezelic and Nikolin have prepared nicoline–phthalate–$CuCl_2$ which has industrial properties.[124] Metal salts of phthalic acid and its chlorinated derivatives containing long chain aliphatic amines give fungicidal protection of canvas duck[77]. Metal ions co-ordinate with carboxylic acid groups also have antiseptic properties of films, fibers and fabrics. In the present investigation heterocyclic amines have been used in most of the cases as secondary ligands. It has great importance in biological and industrial fields. The human body contain as many as 81 out of 92 naturally occurring elements.[125] Most of these elements in trace levels which have also of great importance for human physiology indeed some of them are essential for life itself.[126] Such as complex compounds occur in nature, in blood (hemoglobin) which is an iron complex and functions as oxygen carrier of the blood stream. Similarly the green colors of the leaves are

due to a complex of magnesium with chlorophyll. Some elements also be toxic even in any concentration is above a certain level. From the nutritional point of view those essential elements, almost found in trace concentration levels pay an important role in biochemical processes. In addition to all benefits due to modern technology, the increasing industrial activity is introducing contaminants in food, water and air.

The use of chemical products in agriculture and change in the diets of animals, have produced large change in food compositions. Some complexes are used as insecticides.

1.9 Aim of the present work

In view of the great importance of the metal complexes, as pointed out above, a program was undertaken to achieve following objectives:

(a) Preparation and characterization of mixed ligand complexes of Zr(IV) and V(IV) metal ions with malic acid and some heterocyclic amines.

(b) Synthesis and characterization of metal complexes of Zr(IV) with imides with amine bases.

(c) Studies on the antibacterial activities of the prepared complexes.

(d) Studies on the anti fungal activities of the prepared complexes.

(e) Determination of Minimum Inhibition Concentration (MIC) of some of the biologically active compounds.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES

CHAPTER-2
EXPERIMENTAL TECHNIQUES

2.1 Introduction

In this chapter, experimental techniques other then the methods of preparation of specific compounds will be discussed. The chapter thus includes:

(i) The chemicals.

(ii) Analytical techniques.

(iii) Physical measurement.

2.2 The chemicals.

2.2.1 Chemicals / Reagents used and their specifications:

No.	Neme of the chemicals / Reagents	Molecular formula	Formula weight	Suppliers	Purity
1.	Zirconyl (IV) Chloride	$ZrOCl_2$	322.25	BDH (England)	97%
2.	Vanadyl Sulphate	$VOSO_4.2H_2O$	253	BDH (England)	97%
3.	Oxalic acid	$H_2C_2O_4$	126.07	BDH (England)	97%
4.	Malic acid	$C_4H_6O_5$	134.09	BDH (England)	99%
5.	Methanoic acid	H_2CO_2	46	BDH (England)	98%
6.	Ethanoic acid	$H_4C_2O_2$	60.05	BDH (England)	98%
7.	Propanoic acid	$H_6C_3O_2$	74.08	BDH (England)	97%
8.	Quinoline	C_9H_7N	129.16	BDH (England)	Pure
9.	ISO-Quinoline	C_9H_7N	12.916	BDH (England)	Pure

10.	8-Hydroxy quinoline	C_9H_7NO	145.15	Baker (India)	Pure
11.	Pyridine	C_5H_5N	79.10	Tomas Baker (India)	99%
12.	2-Amino pyridine	$C_5H_6N_2$	94.12	BDH (England)	98%
13.	Alanine	$C_3H_7NO_2$	89.10	E. Merck (Germany)	99%
14.	β -Phenylalanine	$C_4H_{11}NO_2$	16.5	E. Merck (Germany)	99%
15.	α- Picoline	C_6H_7N	93.13	BDH (England)	98%
16.	2.2' Bipyridyl	$C_{10}H_8N_2$	156.19	BDH (England)	98%
17.	Potassium hydroxide pillets	KOH	56.09	E. Merck (Germany)	99%
18.	Triethylamine	$(C_2H_8)_3N$	101.19	BDH (Eng land)	99%

2.2.2 Chemicals used as organic solvents:

No.	Organic solvents	Formula	Suppliers	Purity
1.	Absolute ethanol	C_2H_5OH	Carew and Co. (Bangladesh)	99%
2.	DMSO	$(CH_3)_2$ SO	Merck, (Germany)	99%
3.	Acetone.	$CH_3CO–CH_3$	BDH (England)	99%
4.	DMF	$(CH_3)_2$ CONH	BDH (England)	99%
5.	Methanol	CH_3OH	Tomas Baker (India)	99.5%

2.3. Analytical techniques

2.3.1 Analysis for carbon, hydrogen and nitrogen

Analysis for the complexes of carbon, hydrogen and nitrogen were carried out Microanalytical Services at the University of St. Andrews, Scotland and by Regional Sophisticated instrumentation center, Central Drug Research Institute, Lucknow, India.

2.3.2 Determination of Vanadium

A definite amount of sample (0.2-0.3g) was decomposed with concentrated HNO_3 and the residue was dissolved in water. Ammonium hydroxide was added to this solution to precipitate the hydrous oxide of the metal which was filtered off, washed and ignited to constant weight and then weighed as V_2O_5[127]

2.3.3 Determination of Zirconium

A known weight of the complex (0.2-0.3g) was ignited in air until a constant weight was attained and then weighed as metal oxide.[128,129]

2.4 Physical Measurements

2.4.1 Weighing

The weighing operation was performed on a METTLER PM200 electronic balance.

2.4.2. Conductivity

Conductivities were measured at room temperature in suitable solvents using a WPA CM35 conductivity meter on a SCHOOTT CG857

electronic conductometer and a dip-type cell (WPA) with platinized electrodes. Normally 5×10^{-4}M solutions of the complexes were used for this purpose. The cell was calibrated with 0. 1 N and 0.001N aqueous potassium chloride solutions and it had a cell constant of 0.986 cm^{-1}.

2.4.3 Infrared spectra

Infrared spectra were recorded on a Genesis series FTIRTM 9423-240-08061 infrared spectrophotometer as KBr pellets in the region 4000-400 cm^{-1} and as Nujol mulls sandwiched between CsI plates in the reign 400–200 cm^{-1} polystyrene standards were used to calibrate the spectra.

2.4.4 Electronic spectra

Electronic absorption spectra were run on a LKB Ultrospec K-4053 spectrophotometer. The spectra of cobalt (II) and nickel (II) complexes were obtained with a Shimadzu UV–visible recording spectrophotometer (Model–160). Solution spectra at room temperature were obtained in 1 cm cell. Solid state spectra were recorded as Nujol mulls on filter paper.[130]

The compounds were ground in the mulling agent until a fine particle size was obtained. The mulls were then taken on the filter paper strips and placed in the cells to obtain the spectra.

The visible and UV spectroscopy is a simple but powerful tool which gives information on the geometric of the complexes. In a typical transition by metal complexes, the observed spectrum in general consists of a series of d-d bands which are in the visible region and depends on the donor atom of the ligand and on the metal ion.

2.4.5 Magnetic measurement:

From the measurements of magnetic moment, one can find the number of unpaired electrons present in the possible configuration. If a substance is placed in field of intensity H gauss than B, the magnetic induction of the field within the substance is given by

$$B = H + 4\pi I$$

Where, I = Intensity of magnetization induced by the field. I/H is called the volume susceptibility of the substance and is given the symbol χ_v. In the most cases, a more useful quantity is the magnetic susceptibility per unit mass or mass susceptibility, χ_g, equal to χ_v/d, where d is the density of the substance in gm/cm^3. It is convenient to regard χ_v as dimensionless and χ_g as having the dimensions of reciprocal density. The molar susceptibility, χ_M is $\chi_g \times$ the molecular formula weight of the substance.

For the compounds containing paramagnetic ions, diamagnetic corrections are made to get χ_M (corr). For paramagnetic metal ions, it is customary to obtain effective magnetic, moments, $\mu_{eff,}$ in Bohr magneton (B.M) calculated from

$$\mu_{eff,} = 2.8 \sqrt{(\chi_{M(Corr)} \times T)}$$

Table-1

No of unpaired electron	Total angular moments (s)	Magnetic moments μ_s (B.M)
1	$\frac{1}{2}$	1.73
2	1	2.83
3	$1\frac{1}{2}$	3.87
4.	2	4.9
5.	$2\frac{1}{2}$	5.92

The idea on magnetic measurements can he applied to understand the stereochemistry of metal complexes.

2.4.6 Measurement of the magnetic susceptibilities

Working principle of the balance:

The Sherwood scientific magnetic susceptibility Balance (M.S.B) was used for the present measurements. The balance uses the same principle as that of the Gouy method. Introduction of the Sample between the poles of one pair of magnets produces as deflection of the beam which is registered by means of phototransistors.

The following general expression for mass susceptibility χ_g in C.G.S units in the same manner as for traditional Gouy method.

$\chi_g = C_{BAL.} l(R-R_O)/ 10^9 m$.....1

Where, C= Constant of the Balance

R= Reading obtained for tubes plus sample

R_O= The empty tube reading (normally, —vc)

1= Sample length (cm) and m= Sample mass (gm)

Calibration of the balance

The magnetic susceptibility balance (M.S.H) must be calibrated before the use of the balance.

The balance is to be used mainly for solid sample, than **a solid calibrant** [preferable I $\{HgCo(SCN)_4\}$] was used.[131] The constancy of the calibration as checked using a sealed-off sample of $MnCl_2$ solution.

Procedure:

1. The zero knob of magnetic susceptibility balance was turned until numerical display showed zero and calibration sample. HgCo(SCN) was inserted into sample holder, It was then allowed to settle to give the numerical display.

2. Reading was recorded and calibration constant was calculated from the formulae:

$C_{Bal} = C_{tube}/ (R-R_O)$

$= (1766.842) / [830-(- 1 7)]$

$= 2.086$.....(ii)

From (i) (ii) we get

$\chi_g = 2.086 \times 1 \times (R-R_O)/ 10^9 \times m$.....(iii)

Operation of the balance:

1. The range knob was turned to the XI scale and was allowed to warm for 10 minutes before use.
2. The zero knob was adjusted until the display reads 000. The zero was adjusted on each side.
3. An empty sample tube of known weight was placed into the tube guide and was taken the reading. R_O.
4. Te sample was packed and noted the sample mass m in grams and the sample length, 1in cm.
5. The packed sample tube was placed into the tube guide and as taken the reading, R.

The mass susceptibility, χ_g was calculated using.

$$\chi_g = 2.086 \times 1 \times (R-R_O)/ 10^9 \times m$$

The temperature was recorded from a thermometer situated in the balance Diamagnetic corrections were made using pscal's constraints.

Table-2

Pascal's constraints for elements ($X10^{-6}$)[132]

H	-2.93
C	-6.00
N (open chain),	-5.55
S	-15.0
P	-140.0
O	-4.6
CNS	36.0
CN	18

2.4.7. Melting point

An electro thermal Melting point Apparatus was used for the determination of melting or decomposition point.

2.4.8. Molecular weight

The molecular weight of some of the complexes were determined in nitrobenzene (K_f = **8.** 1) by the cryoscopy method using a Beckmann Apparatus.

2.4.9. Thin layer chromatography (TLC)

Thin layer chromatography provides a means of separation, purification and identification of a mixture of compounds. This technique involves an absorbent (usually silica gel) as a stationary phase and a solvent or solvent mixture as the mobile phase. Due to the differences in mobility of the components, they are separated from each other by the solvent.

TLC Plates

The cleaned grease free glass plates (20 cm × 5 cm) are washed with water followed by acetone and dried in an electrical oven. The plates were then placed on a frame (Quick -fit, England) and the spreader was placed in position. A suspension of silica gel (25g in 55cm^3 distilled water) was transferred to the spreader, set with appropriate thickness and the spreader was drawn across the plates. A uniform layer of absorbent was obtained. The glass plates thus coated with silica gel (E. Merck, TLC grade) were allowed to stay in position at room temperature until the surface became completely dried. These plates were then kept for 2 hours in an oven at 60°C for activation and then these were ready for use.

Procedure

The solutions of the components under investigation were spotted with glass capillaries to the TLC plates about 2 cm from the bottom. The plates were then placed downwards in a chromatographic tank so that the spotted marks remained above the solvent surface. The tank contained the developing solvent or solvent mixture. The plates were removed when the solvent front reached 1 .5 cm below the upper edge. The plates were than dried and the chromatograms were developed by putting them in an iodine chamber.

CHAPTER THREE

SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF ZIRCONIUM (IV) WITH OXALIC ACID AND AMINE BASES

CHAPTER-3

SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF ZIRCONIUM (IV) WITH OXALIC ACID AND AMINE BASES

3.1 Introduction

A very few references are available on the mixed ligand complexes of zirconium (IV) metal ions. Mixed ligand complexes using dibasic acids as primary and amines as secondary ligands have been prepared and characterized. Islam *et al.*[133-135] have prepared mixed ligand complexes of Zr (IV) with dibasic acid with heterocyclic amines. Studies on the metal complexes of dibasic acid and heterocyclic amines have been carried out by several groups of workers but nothing is reported on the mixed ligand complexes of Zr (IV) with oxalic acid and simple amines.

Here we will mention the preparation and characterization of some new mixed ligand complexes of Zr (IV) and V (IV) with oxalic acid and amine bases, e.g, Quinoline , 8-Hydroxy Quinoline, Pyridine, 2-Amino-Pyridine, α-Picolin, 2,2′-Bipyridyl.

The transition metal complexes play an important role in microbiological activity. These type of complexes have also shown microbiological activities which have been published other than my asking complexes. So we are also interested to work in this area.

3.2 Experimental

3.2.1 Chemicals and reagent:

As stated in Chapter-2 Page No-22

3.2.2 Physical measurement:

As described earlier in Chapter-2 Page No-24

3.2.3 Preparation:

General preparation of Zr (IV) Complexes:

General method for preparation of $[Zr(IV)(oxa)_2L_2]$ where oxa = oxalicacid, L= Quinoline, 8-Hydroxy Quinoline, Pyridine, 2- Amino pyridine, α –Picoline. 2,2′ – Bipyridyl respectively.

An ethanolic solution of Zirconyl chloride (0.001 mole) and oxalic acid (0.002 mol) were mixed in the calculated ratio with constant stirring but no precipite was observed. Then 25 ml of ethanolic solution of L (0.002 mole) was added to the resulting mixture and heat on a magnetic regulator hot plate with constant stirring. Then 30ml of an aqueous solution of the KOH was added dropwise to the mixture of Complex $[Zr (IV)(oxa)_2(Q)_2]$, $[Zr(IV)(oxa)_2 (2\text{-}Apy)_2]$, $2K^+[Zr(IV)(oxa)_2(8\text{-}HQ)]2\text{-}$, $[Zr(IV) (oxa)_2(py)_2]$, $[Zr(IV)(oxa)_2 (\alpha\text{-}Pic)_2]$, $K^+[Zr (IV) (oxa)_2 (2,2'\text{-}Bipy)]^-$ with stirring. The volume of the solution was reduced by heating to half an hour and allowed to cool. The precipitate formed was filtered, washed several times with ethanol and dried in a desiccators over anhydrous calcium chloride ($CaCl_2$).

3.3 Results and Discussion:

The Zirconium Complexes were obtained according to the following reactions:

$ZrOCl_2.\ 8H_2O+2(oxa)+2L+\ 4KOH \rightarrow K[Zr\ (oxa)_2L_2]+KCl+H_2O$

Where oxa=oxalic acid, L=Quinoline, 8-Hydroxy quinoline, pyridine, 2-Amino pyridine. α-Picoline, 2,2′-Bipyridyl.

3.3.1 Elemental analysis and conductivity measurement:

Elemental analysis along with other data and their physical properties are presented in tables 3.1 and 3.2. The molar conductance were measured in N,N'-dimethyl formamide. The conductance value (Table 3.1) indicated that the complexes (1-6) were non-electrolytic in nature.

3.3.2 Magnetic measurements:

The observed values of effective magnetic moment (μ_{eff}) at room temperature are given in table 3.1. The magnetic moment values of Zirconium (IV) Complexes are -0.239 to -0.421 B.M indicated that these complexes were diamagnetic in nature.

3.3.3 Electronic spectra:

The electronic spectral data (table 3.3) of the complexes 1-6 showed bands between 335-380 nm regions due to the charge transfer band only.[136] The UV-visible spectra of the complexes (2-4) are shown in Fig. (3.6-3.7).

3.3.4 IR Spectra:

The Complexes display υ(C=O) band at 1440-1480cm^{-1} and υ(C-O) band at 1300-1357 cm^{-1}, significantly lower than the value of free oxalic acid (1700-1440 cm^{-1}), which indicate that the co-ordination of oxalic acid through their carboxylate anions. Further the presence of M-O and M-N bonding is evident from the appearance of υ(M-O) modes at 470-520 and υ(M-N) modes at 400-415 cm^{-1} in the spectra of the complexes. In the complex-2 a broad band appears at 3230-3340 cm^{-1} in which υ(NH_2) band of the complex is probably hidden.

The characteristic ring vibration of the heterocyclic amines in the range 1400-1600 cm^{-1} generally show significant changes on Complexsation[171] but in our present complexes these band could not be distinguished because of overlapping with υ(C=O) and υ (C-O) stretching bands. The in plane and out-of-plane ring deformation modes of the heterocyclic amines observed at 520 and 720 cm^{-1} respectively.

Major IR spectral data for the complexes are given in table 3.4.

Table-3.1: Physical properties of the complexes

Complex No	Complexes	Colour	Melting point or d temperature (± 5^{0}C)	Molar conductance (ohm^{-1} Cm^2 mol^{-1})	Magnetic moment (μ_{eff}) B.M.
1	[Zr(IV) $(oxa)_2$ Q_2]	Cream	250^{0}C	0.234	Dia
2	K^+[Zr(IV) $(oxa)_2$ (2-Apy)]$^-$	White	258^{0}C	0.106	-0.239
3	$2K^+$[Zr(IV) $(oxa)_2$ $(8\text{-HQ})_2$]$^{2-}$	Cream	266^{0}C (d)	20.617	Dia
4	[Zr(IV) $(oxa)_2$ $(Py)_2$]	White	280^{0}C (d)	0.447	-0.321
5	[Zr(IV) $(oxa)_2$ $(\alpha - Pic)_2$]	Cream	240^{0}C	1.735	Dia
6	K^+[Zr(IV) $(oxa)_2$ (2,2′-Bipy)]$^-$	off white	260^{0}C (d)	0.766	-0.421

Where :

d	=	Decomposition
Dia	=	Diamagnetic
oxa	=	Oxalic acid
Py	=	Pyridine
Q	=	Quinoline
2Apy	=	2-Amino-pyridine
8HQ	=	8-Hydroxy quinoline
α -Pic	=	α -Picoline
2, 2'Bipy	=	2, 2'-Bipyridyl

Table-3.2: Data of the elemental analysis of the complexes

Complex No	Complexes	Molecular weight		Metal %		Carbon%		Nitrogen%		Hydrogen%	
		Cal	Found	Cal	Found	Cal	Found	Cal	Found	Cal	Found
1	$[Zr(IV)\ (oxa)_2\ Q_2]$	525.22	525.32	17.36	17.46	50.26	50.30	5.33	5.38	2.66	2.75
2	$K^+[Zr(IV)\ (oxa)_2\ (2\text{-}Apy)]^-$	455.22	455.29	21.45	21.49	39.50	39.58	13.16	13.26	2.82	2.88
3	$2K^+[Zr(IV)\ (oxa)_2\ (8\text{-}HQ)_2]^{2-}$	473.22	473.33	19.22	19.27	50.71	50.79	5.91	5.97	3.80	3.87
4	$[Zr(IV)\ (oxa)_2\ (Py)_2]$	425.22	425.28	21.45	21.48	39.50	39.57	6.58	6.66	2.35	3.38
5	$[Zr(IV)\ (oxa)_2\ (\alpha - Pic)_2]$	453.22	453.27	20.12	20.22	42.36	42.41	6.17	6.25	3.09	3.15
6	$K^+[Zr(IV)\ (oxa)_2\ (2,2'\text{-}Bipy)]^-$	473.22	473.31	15.74	15.81	49.72	49.82	9.66	9.75	2.76	2.85

Where:

oxa = Oxalic acid
Py = Pyridine
Q = Quinoline
2Apy = 2-Amino-pyridine
8HQ = 8-Hydroxy quinoline
α-Pic = α-Picoline
2, 2'Bipy = 2, 2'-Bipyridyl

Table-3.3: Electronic spectral data of the complexes

Complex No.	Complexes	λ max (nm)
1	$[Zr(IV)\ (oxa)_2\ Q_2]$	345
2	$K^+[Zr(IV)\ (oxa)_2\ (2\text{-}Apy)]^-$	380
3	$2K^+[Zr(IV)\ (oxa)_2\ (8\text{-}HQ)_2]^{2-}$	335
4	$[Zr(IV)\ (oxa)_2\ (Py)_2]$	355
5	$[Zr(IV)\ (oxa)_2\ (\alpha - Pic)_2]$	345
6	$K^+[Zr(IV)\ (oxa)_2\ (2,2'\text{-}Bipy)]^-$	340

Where :

oxa	=	Oxalic acid
Py	=	Pyridine
Q	=	Quinoline
2Apy	=	2-Amino-pyridine
8HQ	=	8-Hydroxy quinoline
α -Pic	=	α -Picoline
2, 2'Bipy	=	2, 2'-Bipyridyl

Table-3.4: IR data of the complexes (Band Maxima in Cm^{-1})

Complex No	Complexes	υ(N – H)	$\upsilon(C=N)$	υ(C = O)	υ(C – O)	υ(M – O)	υ(M – N)
1	$[Zr(IV)\ (oxa)_2\ Q_2]$	-	1650	1440	1350	470	410
2	$K^+[Zr(IV)\ (oxa)_2\ (2\text{-}Apy)]^-$	3330, 3240	1630	1460	1340	500	411
3	$2K^+[Zr(IV)\ (oxa)_2\ (8\text{-}HQ)_2]^{2-}$	-	1629	1467	1320	500	400
4	$[Zr(IV)\ (oxa)_2\ (Py)_2]$	-	1670	1490	1300	510	401
5	$[Zr(IV)\ (oxa)_2\ (\alpha - Pic)_2]$	-	1655	1480	1357	520	415

Where:

oxa	=	Oxalic acid
Py	=	Pyridine
Q	=	Quinoline
2Apy	=	2-Amino-pyridine
8HQ	=	8-Hydroxy quinoline
α -Pic	=	α -Picoline
2, 2'Bipy	=	2, 2′-Bipyridyl

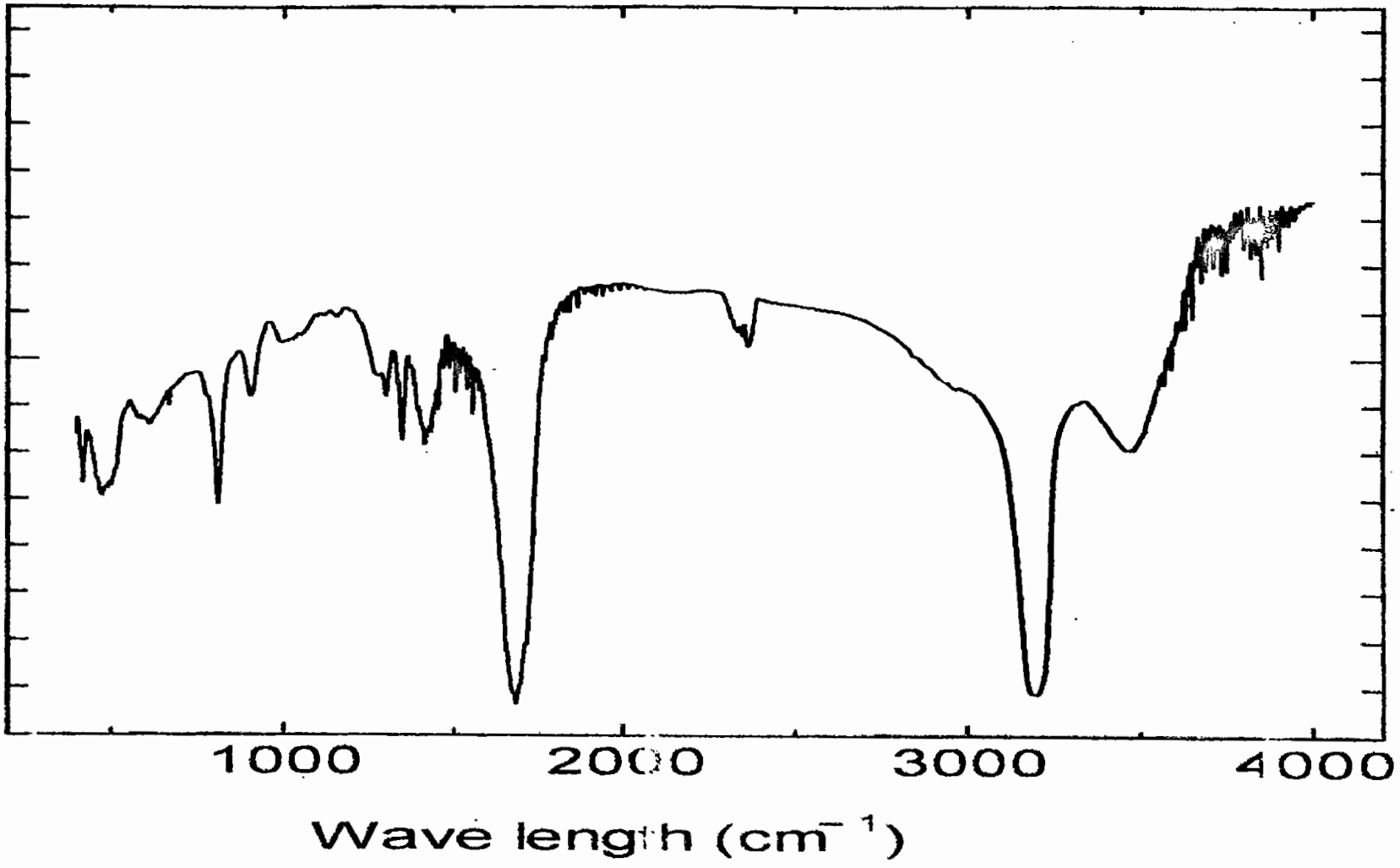


Fig. 3.1: IR spectrum of $[Zr(IV)(oxa)_2Q_2]$

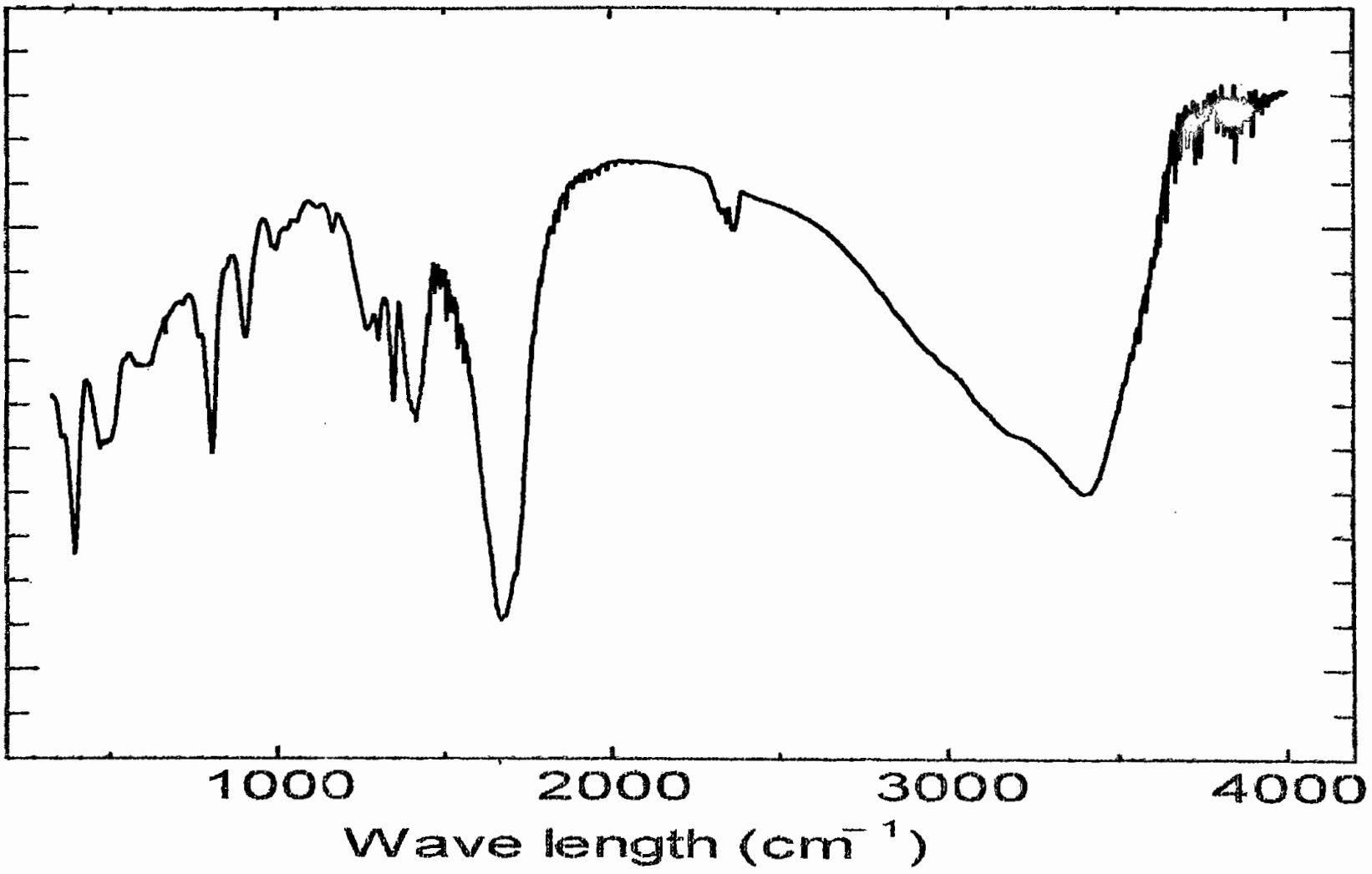


Fig. 3.2: IR spectrum of $[Zr(IV)(oxa)_2(2\text{-}Apy)_2]$

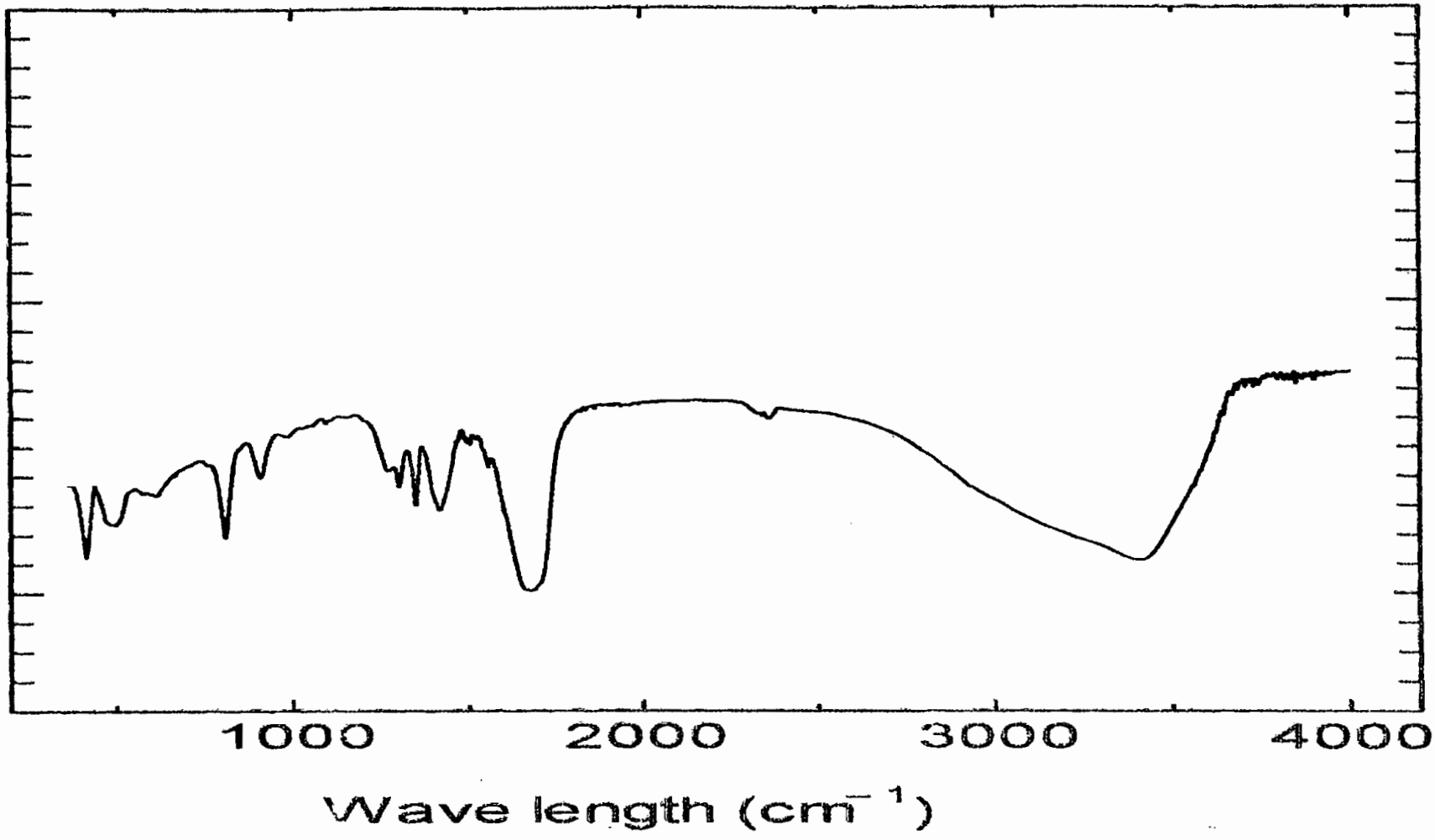


Fig. 3.3: IR spectrum of $2k^{+}$ $[Zr(IV)(oxa)_2(8\text{-}HQ)_2]^{2-}$

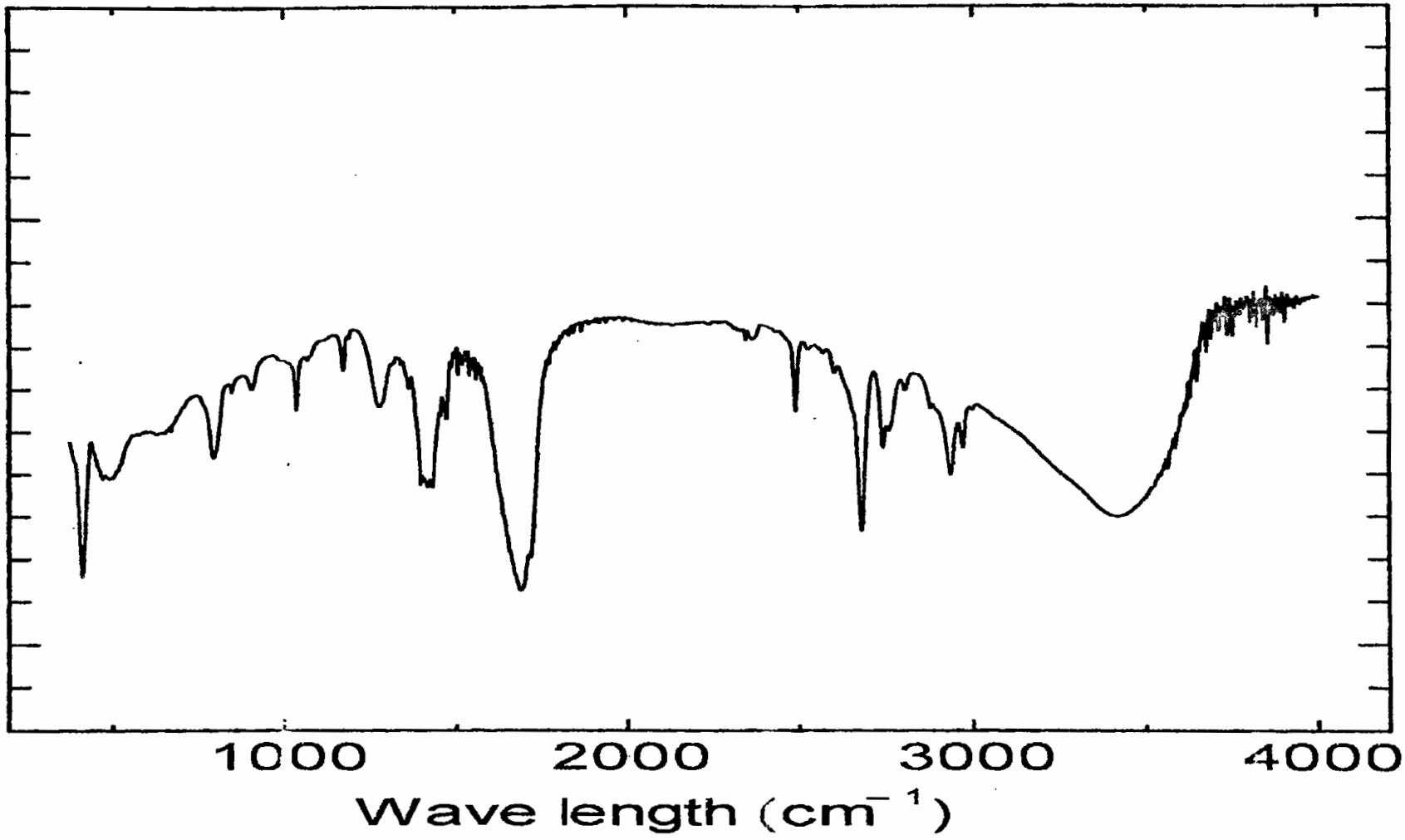


Fig. 3.4: IR spectrum of $[Zr(IV)(oxa)_2(Py)_2]$

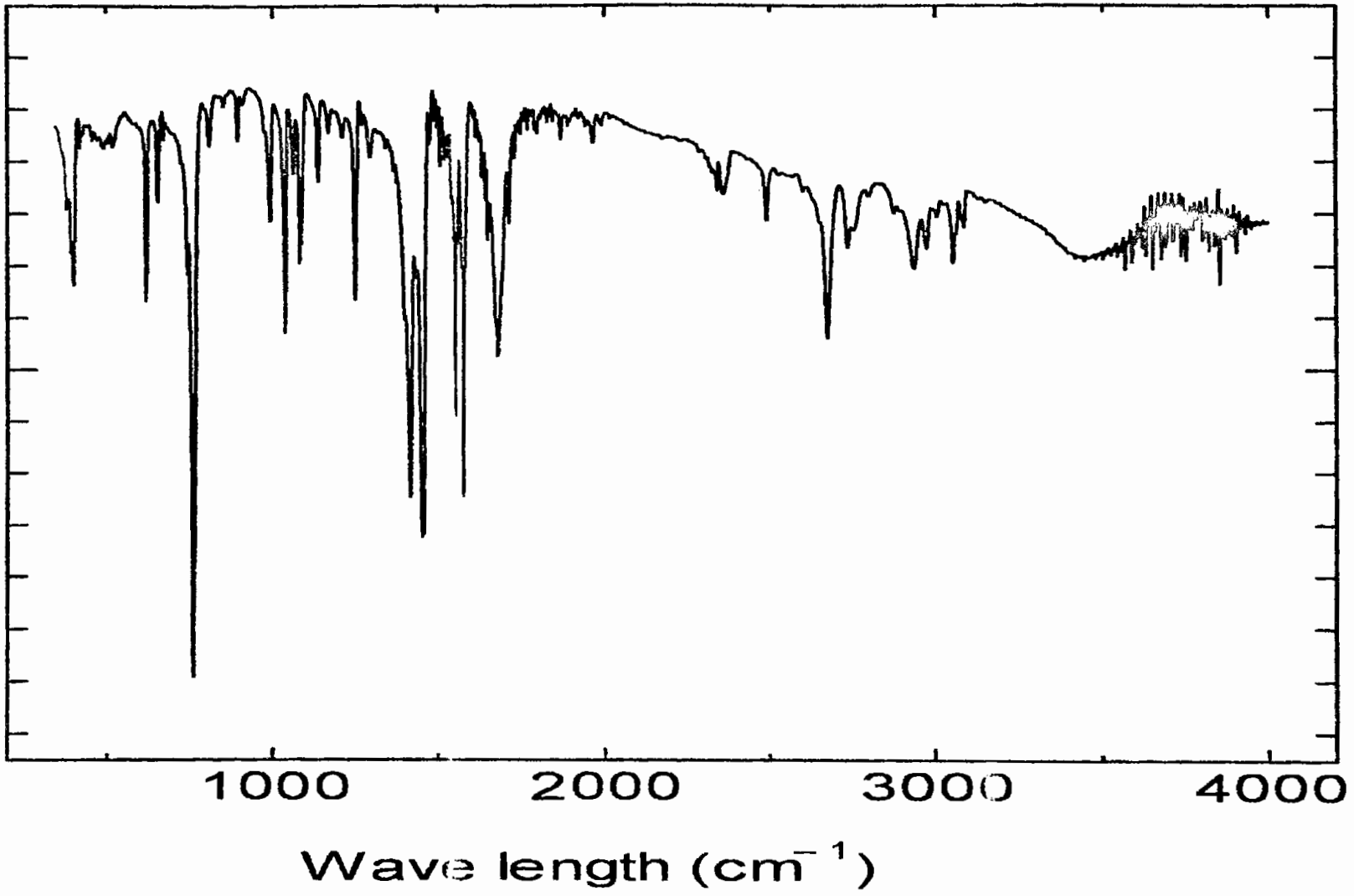


Fig. 3.5: IR spectrum of $[Zr(IV)(oxa)_2(2,2'\text{-Bipy})_2]$

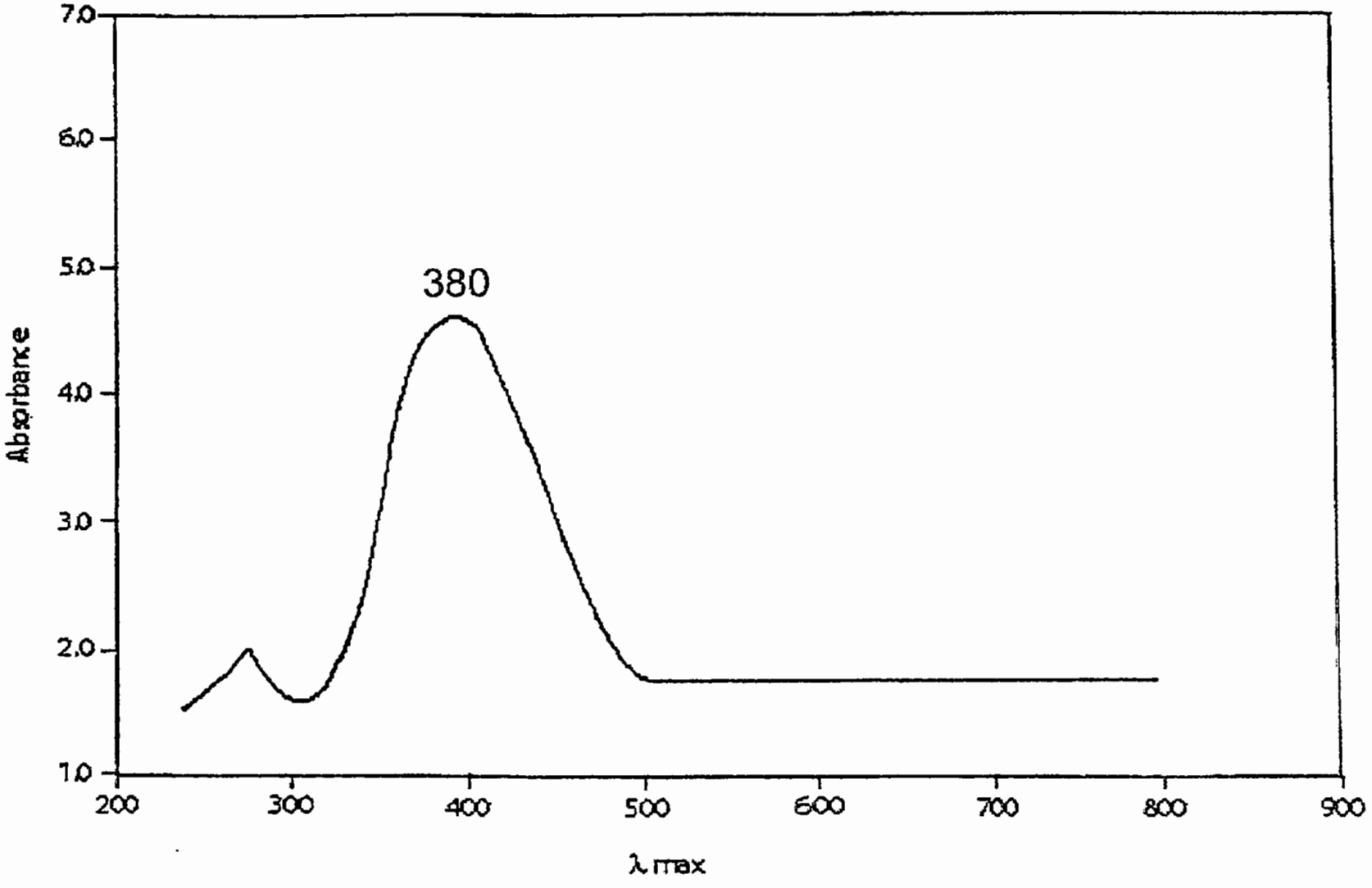


Fig.-3.6: UV-Visible spectrum of [Zr(IV) $(oxa)_2$ $(2\text{-}Apy)_2$] Complex-2

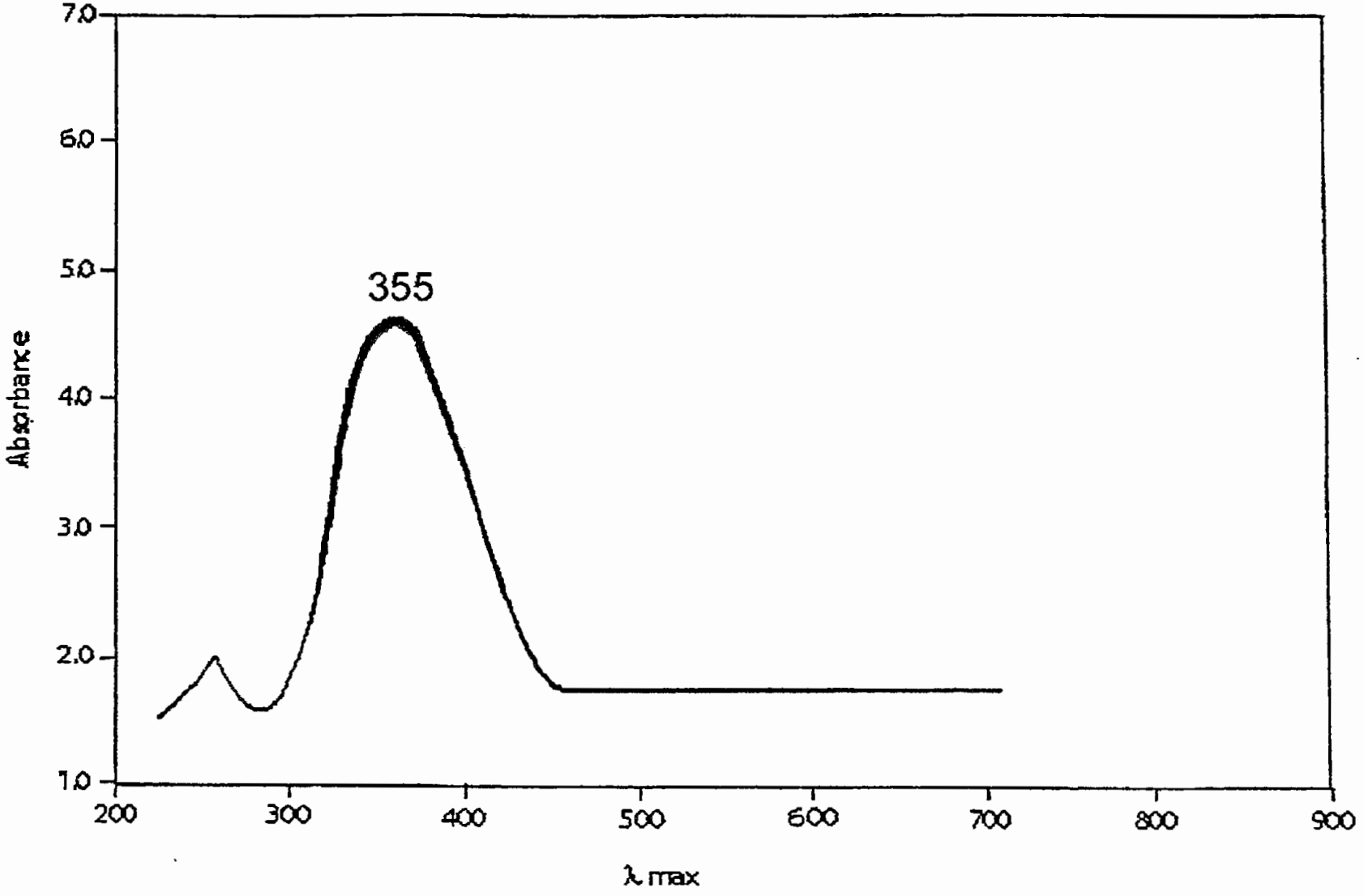


Fig.-3.7: UV-Visible spectrum of [Zr(IV) $(oxa)_2$ $(Py)_2$] Complex-4

3.3.5 Conclusion:

From the above discussion the structure of zirconium (IV) Complexes are assignable to octahedral stereochemistry. On the basis of the above discussion the possible structure of the complex (2) are given in the figure (3.6). Similarly the structure of other complexes may also be given.

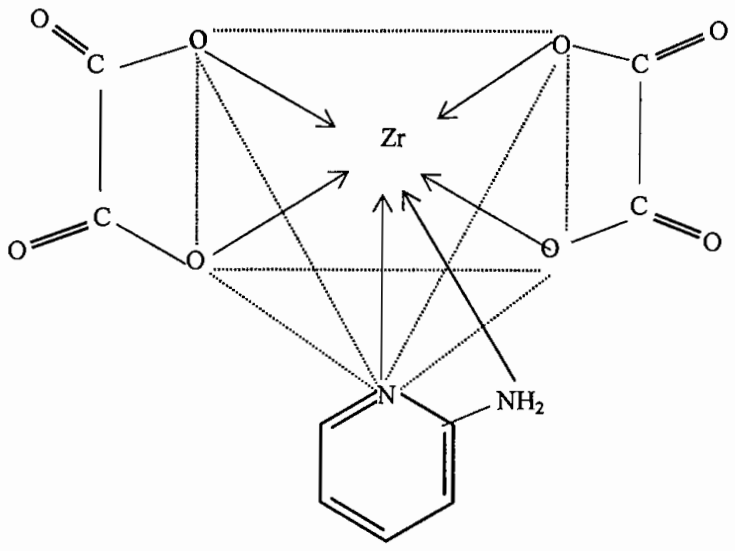


Fig-3.6: Possible structure of the Complex (2) [Zr(IV) $(oxa)_2$ (2-Apy)]

CHAPTER FOUR

PREPARATION AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF ZIRCONIUM(IV) WITH MALIC ACID AND AMINE BASES

CHAPTER – 4

PREPARATION AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF ZIRCONIUM (VI) WITH MALIC ACID AND AMINE BASES

4.1 Introduction:

Some new mixed ligand complexes of Zirconium (IV) with organic dibasic acids and heterocyclic amines have been prepared and characterized by Islam[137-141]. Agafonova and Ryazanov carried out the precipitation studies of some common bivalent metal ions. Malic acid has been used as a selective reagent for the amperometric determination of Zirconium (IV). Sharma *et. al.*[142-146] determined the stability of mixed ligand complexes of V (IV), Th(IV) with malic acid. They have also studied the thermodynamic function of Mn(II), Cu(II) and Pb(II) complexes with malic acid. Mixed ligand complexes of Zr(IV) with malic acid and heterocyclic amines have been prepared by Sharma and Islam.[147-149]

With this additional information over the topic in continuation of the work we prepared some new mixed ligand complexes of Zr(IV) with malic acid and amine bases, e.g. Quinoline, 8-Hydroxy quinoline, iso-Quinoline, α-Picoline, 2,2'-Bipyridyl.

4.2 Experimental

4.2.1 Chemicals and reagents:

As stated in Chapter-2, Page No.-22

4.2.2 Physical measurements:

As stated in Chapter-2, Page No.-24

4.2.3 Preparation:

General method of preparation of [Zr(IV) $(Mal)_2L_2$] where Mal=Malic acid L= 8-Hydroxy quinoline, quinoline, 2,2′-Bipyridyl Iso-quinoline, α-Picoline etc.

Stated as earlier Page No-34

4.3 Results and Discussion:

The Zirconium Complexes were obtained according to the following reactions:

$$ZrOCl_2.8H_2O + 2(Mal) + 2\,L + 4KOH \rightarrow K\,[Zr(Mal)_2\,L_2\,] + KCl + H_2O$$

Where:

Mal = Malic acid

L = 8-Hydroxy quinoline, Quinoline, 2,2′- Bipyridyl, Iso- quinoline,

α-Picoline.

4.3.1 Elemental Analysis and Conductivity measurements:

The analytical data and other physical, properties of the complexes are given in table 4.1. Zirconium Complexes were soluble in DMF and DMSO. The analytical data are in good agreement with the proposed, empirical formulae of the present complexes. Their structures have been confirmed by conductivity magnetic measurements and electronic spectral data. (Table-4.1)

The molar conductance of 10^{-3}M solutions of the complexes in DMSO were measured at 28°C. The molar conductance values indicate that all the complexes are non-electrolytic in nature.

4.3.2 Magnetic measurements:

The observed values of the effective magnetic moments of the complexes at room temperature are given in table 4.1. Zirconium(IV) complexes are 1.71-1.78 B.M indicated that these complexes were diamagnetic in nature.

4.3.3 Electronic Spectra:

All the complexes of Zirconium were diamagnetic in nature which indicated no change in the oxidation state of the metal ions on complex formation. The spectra of the solution Zirconium (IV) complexes (1-5) Showed bands (330-360) nm region due to the charge transfer band only. The UV-visible spectra of the complexes (4-1) are shown in Fig. (6.4-6.5).

4.3.4 IR Spectra:

The complexes display υ(C=O) band at 1440-1460cm^{-1} and υ(C=N) band at 1630-1670 cm^{-1}. υ(C-O) band at 1330-1350 cm^{-1}, significantly lower than the value of free oxalic acid 1700-1440 cm^{-1}, which indicate the co-ordination of oxalic acid through their carboxylate anions. Further the presence of M-O bonding and M-N bonding is evident from the appearance of υ(M-O) modes at 500-520 and υ(M-N) modes at 400 – 420 cm^{-1} in the spectra of the complexes[180]. In the complex-1 a broad band appears at 3370 cm^{-1} in which υ(OH) band of the complex are probably hidden.

The infrared spectrum of 8-Hydroxy quinoline shows υ(OH) modes at~ 3600 cm^{-1}. The band is shifted to lower frequencies in the complex (1) at 3370 cm^{-1}, which indicate the coordination with hydroxy oxygen. The characteristic ring vibration of the 8-Hydroxy quinoline in the range 1400-1600 cm^{-1} was observed.

The characteristic ring vibration of the heterocyclic amines in the range (1400-1600) cm^{-1} generally show significant changes on Complexation but in our present complexes these bands could not be distinguished because of overlapping with υ(C=O) and υ (C-O) stretching bands. The in plane and out-of-plane ring deformation modes of the heterocyclic amines observed at 520 ~ 720 cm^{-1} respectively.

Major IR spectral data for the complexes are given in table 4.4.

Table-4.1: Physical properties of complexes

Complex No	Complexes	Colour	Melting point or d temperature (± 5°C)	Molar conductance (ohm^{-1} Cm^2 mol^{-1})	Magnetic moment (μ_{eff}) B.M.
1	$2K^+[Zr(IV)\ (Mal)_2\ (8\text{-}HQ)_2]^{2-}$	yellow	230°C	25.139	Dia
2	$[Zr(IV)\ (Mal)_2\ (Q)_2]$	white	255°C	0.319	Dia
3	$K^+[Zr(IV)\ (Mal)_2\ (2,2'\text{-}Bipy)]^-$	light orange	300°C	24.0159	1.71
4	$[Zr(IV)\ (Mal)_2\ (IQ)_2]$	cream	215°C	1.299	1.78
5	$[Zr(IV)\ (Mal)_2\ (\alpha - Pic)_2]$	cream	235°	0.777	Dia

Where :

d = Decomposition
Dia = Diamagnetic
Mal = Malic acid
Q = Quinoline
8-HQ = 8-Hydroxy quinoline
α-Pic = α-Picoline
2, 2'Bipy = 2,2'-Bipyridyl

Table-4.2: Data of the elemental analysis of the complexes

Complex No	Complexes	Molecular weight		Metal %		Carbon%		Nitrogen%		Hydrogen%	
		Cal	Found	Cal	Found	Cal	Found	Cal	Found	Cal	Found
1	$2K^{+}[Zr(IV)\ (Mal)_2\ (8\text{-}HQ)_2]^{2-}$	647.22	447.12	14.09	14.02	48.20	48.10	4.32	4.22	3.70	3.65
2	$[Zr(IV)\ (Mal)_2\ (Q)_2]$	613.22	613.10	14.87	14.77	50.87	50.70	4.56	4.44	3.85	3.70
3	$K^{+}[Zr(IV)\ (Mal)_2\ (2,2'\text{-}Bipy)]^{-}$	667.22	667.03	13.67	13.56	50.35	50.24	8.39	8.33	3.59	3.48
4	$[Zr(IV)\ (Mal)_2\ (IQ)_2]$	613.22	613.08	14.87	14.71	50.87	50.77	4.56	4.50	3.85	3.80
5	$[Zr(IV)\ (Mal)_2\ (\alpha - Pic)_2]$	541.22	541.11	16.85	16.80	44.34	44.30	5.17	5.11	4.06	4.00

Where :

Mal = Malic acid
Q = Quinoline
8-HQ = 8-Hydroxy quinoline
α-Pic = α-Picoline
2, 2'Bipy = 2,2'-Bipyridyl

Table-4.3: Electronic spectral data of the complexes

Complex No.	Complexes	λ max (nm)
1	$2K^{+}[Zr(IV)\ (Mal)_2\ (8\text{-}HQ)_2]^{2-}$	350
2	$[Zr(IV)\ (Mal)_2\ (Q)_2]$	345
3	$K^{+}[Zr(IV)\ (Mal)_2\ (2,2'\text{-}Bipy)]^{-}$	340
4	$[Zr(IV)\ (Mal)_2\ (IQ)_2]$	360
5	$[Zr(IV)\ (Mal)_2\ (\alpha - Pic)_2]$	330

Where :

Mal = Malic acid
Q = Quinoline
8-HQ = 8-Hydroxy quinoline
α-Pic = α-Picoline
2,2′ Bipy = 2,2'-Bipyridyl

Table-4.4: IR Data of the complexes (Band Maxima in Cm^{-1})

Complex No	Complexes	$\upsilon(O-H)$	υ(N–H)	υ(C = N)	$\upsilon(C=O)$	υ(C – O)	υ(M – O)	$\upsilon(M-N)$
1	$2K^+[Zr(IV)\ (Mal)_2\ (8\text{-}HQ)_2]^{2-}$	3370	-	1650	1460	1340	507	403
2	$[Zr(IV)\ (Mal)_2\ (Q)_2]$	-	-	1670	1440	1330	515	410
3	$K^+[Zr(IV)\ (Mal)_2\ (2,2'\text{-}Bipy)]^-$	-	-	1660	1450	1350	500	400
4	$[Zr(IV)\ (Mal)_2\ (IQ)_2]$	-	-	1630	1445	1340	520	402
5	$[Zr(IV)\ (Mal)_2\ (\alpha - Pic)_2]$	-	-	1660	1455	1360	510	420

Where :

Mal = Malic acid
Q = Quinoline
8-HQ = 8-Hydroxy quinoline
α-Pic = α-Picoline
2,2′ Bipy = 2,2'-Bipyridyl

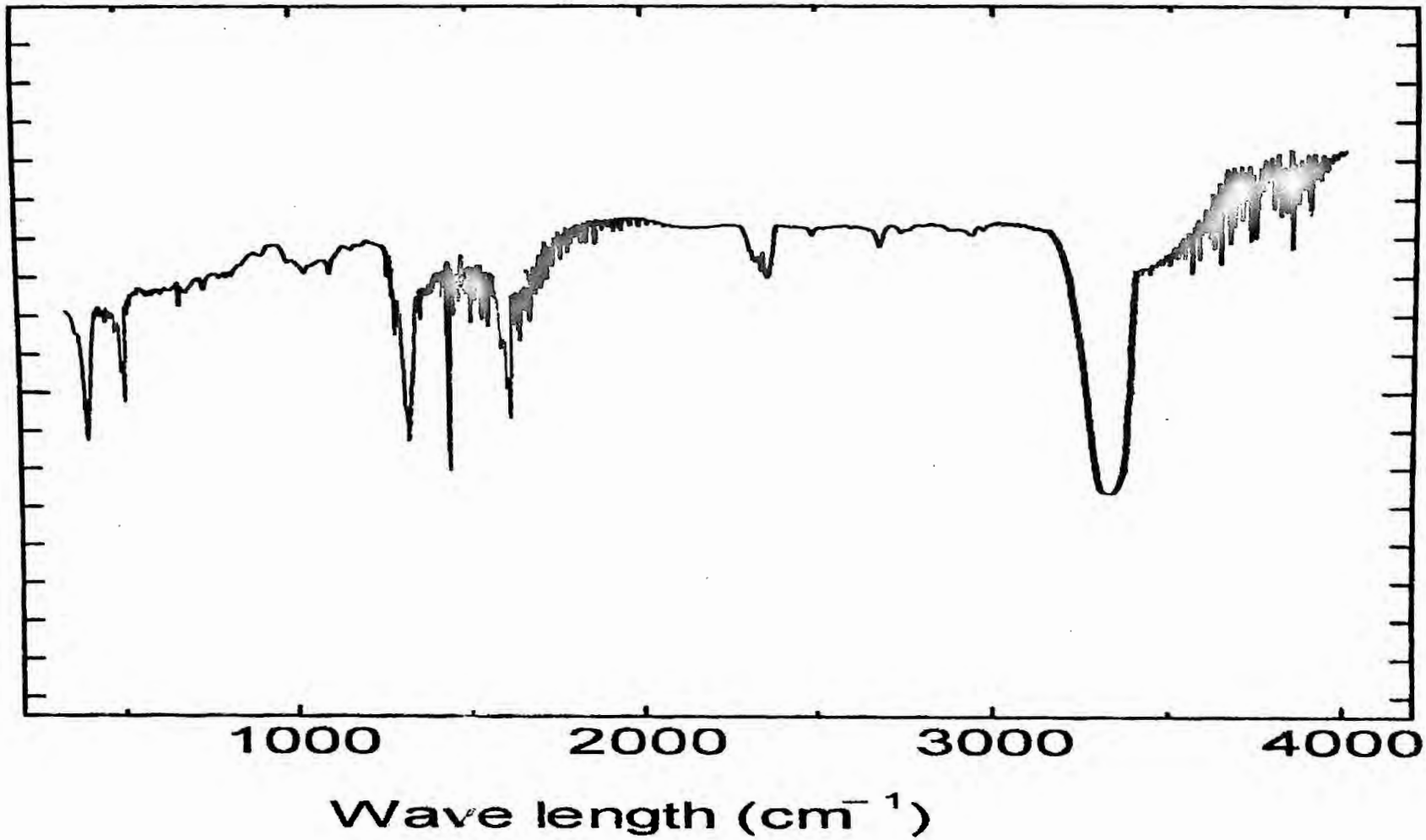


Fig. 4.1: IR spectrum of $2k^{+}[Zr(IV)\ (Mal)_2\ (8\text{-}HQ)_2]^{2-}$

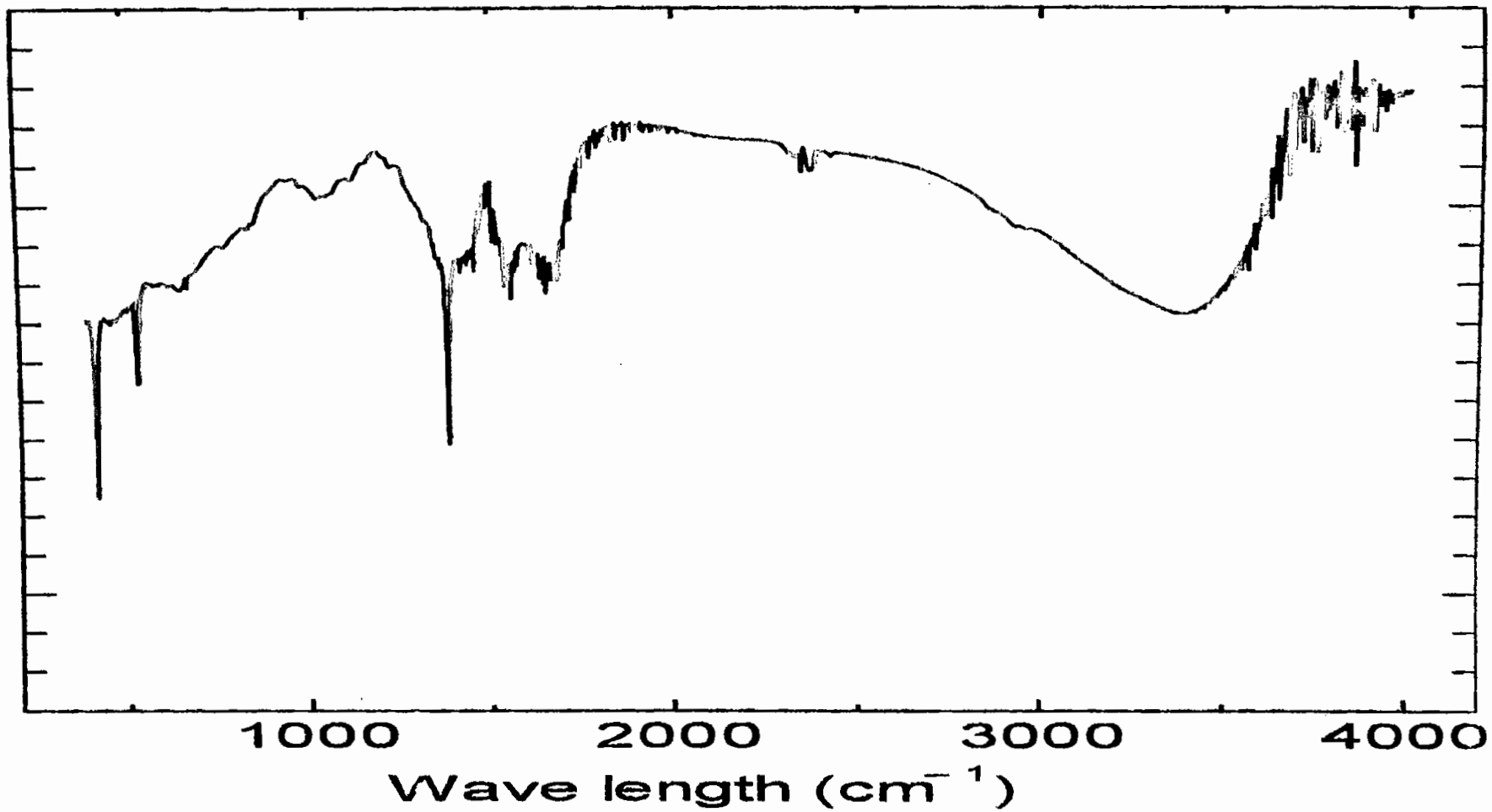


Fig. 4.2: IR spectrum of $K^{+}[Zr(IV)(Mal)_2(2,2'Bipy)]^{-}$

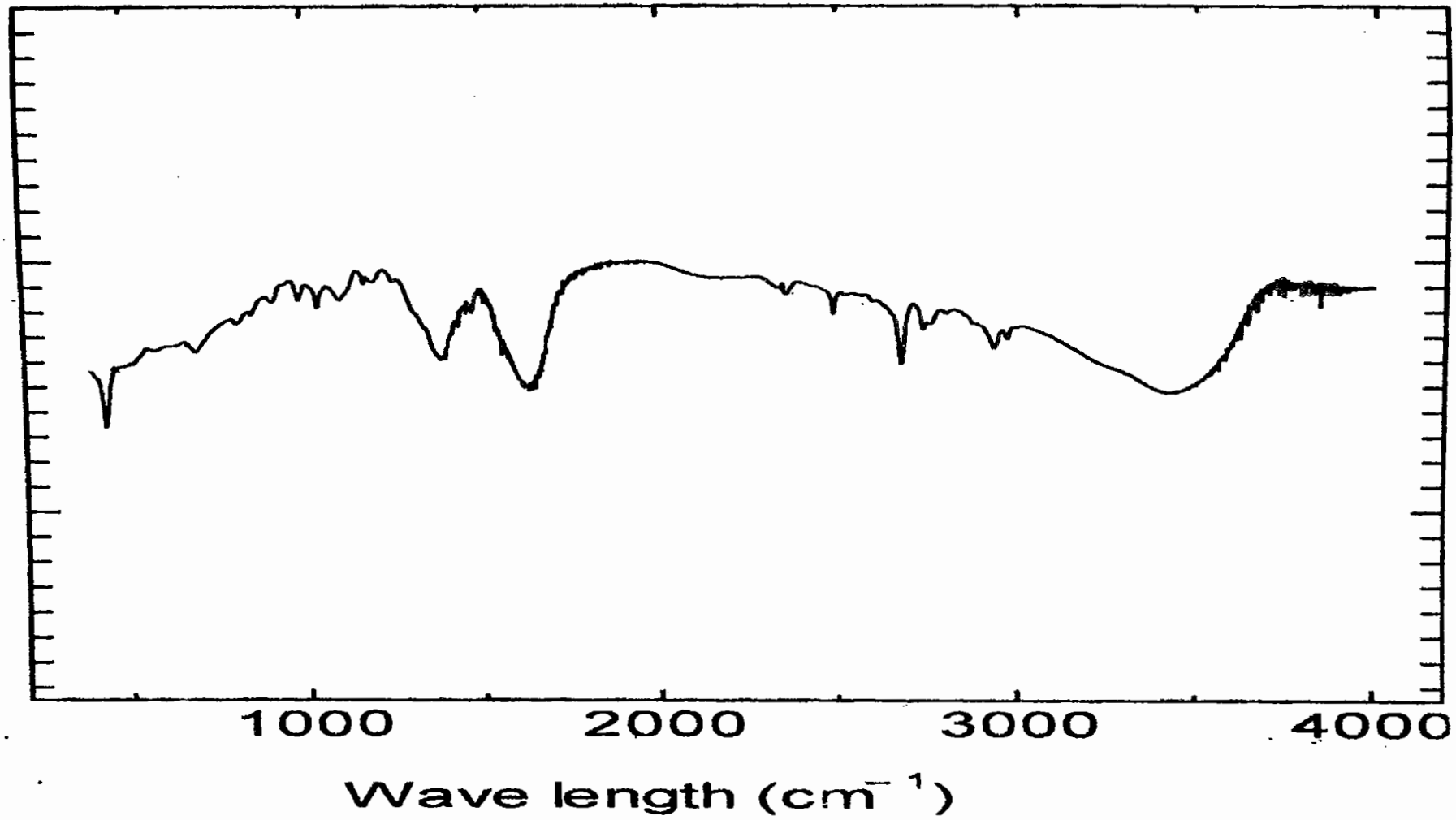


Fig. 4.3: IR spectrum of $[Zr(IV)(Mal)_2(\alpha\text{-}Pic)_2]$

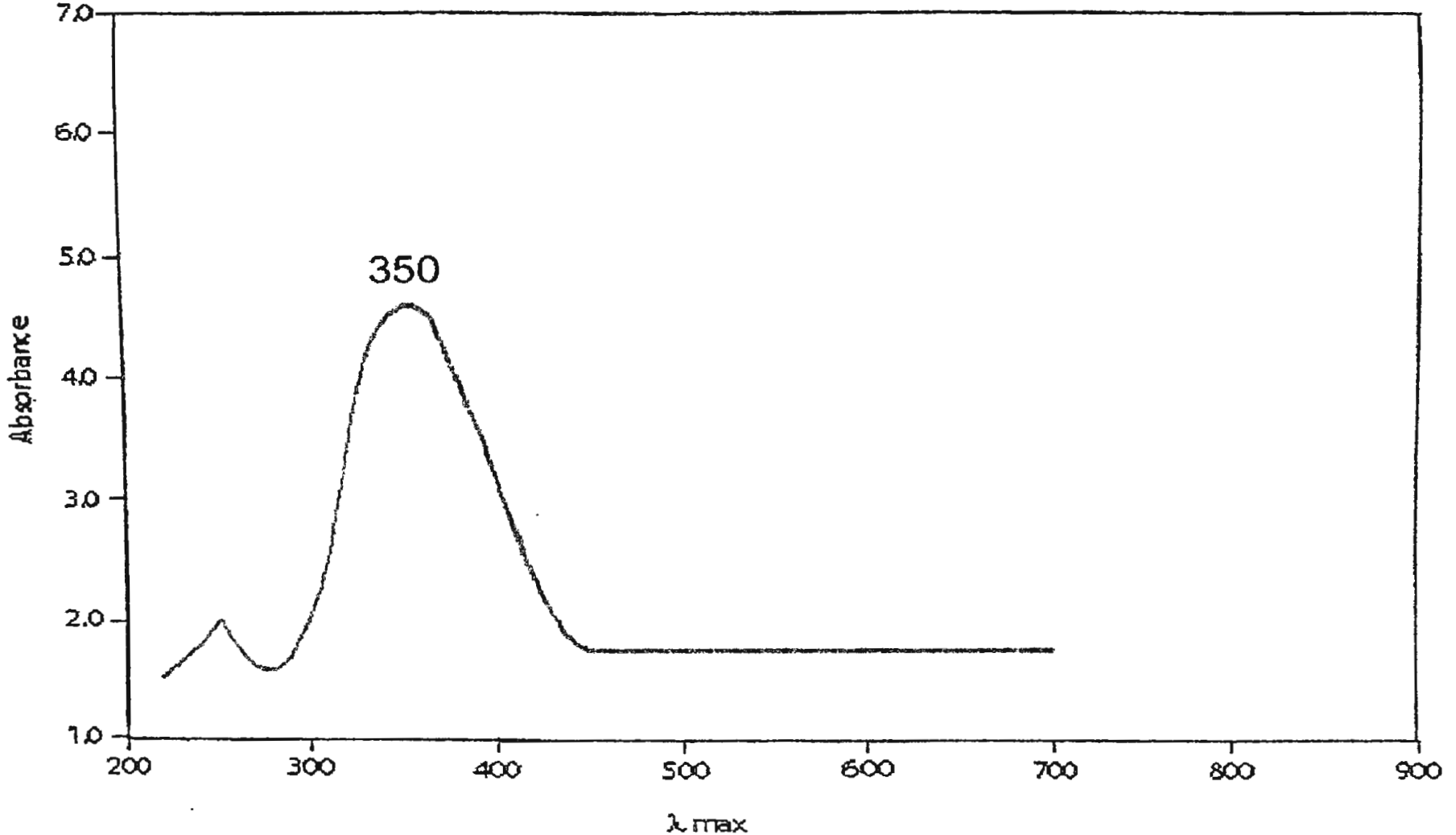


Fig.-4.4: UV-Visible spectrum of $2K^{+}[Zr(IV)\ (Mal)_2\ (8\text{-}HQ)_2]^{2-}$ Complex-1

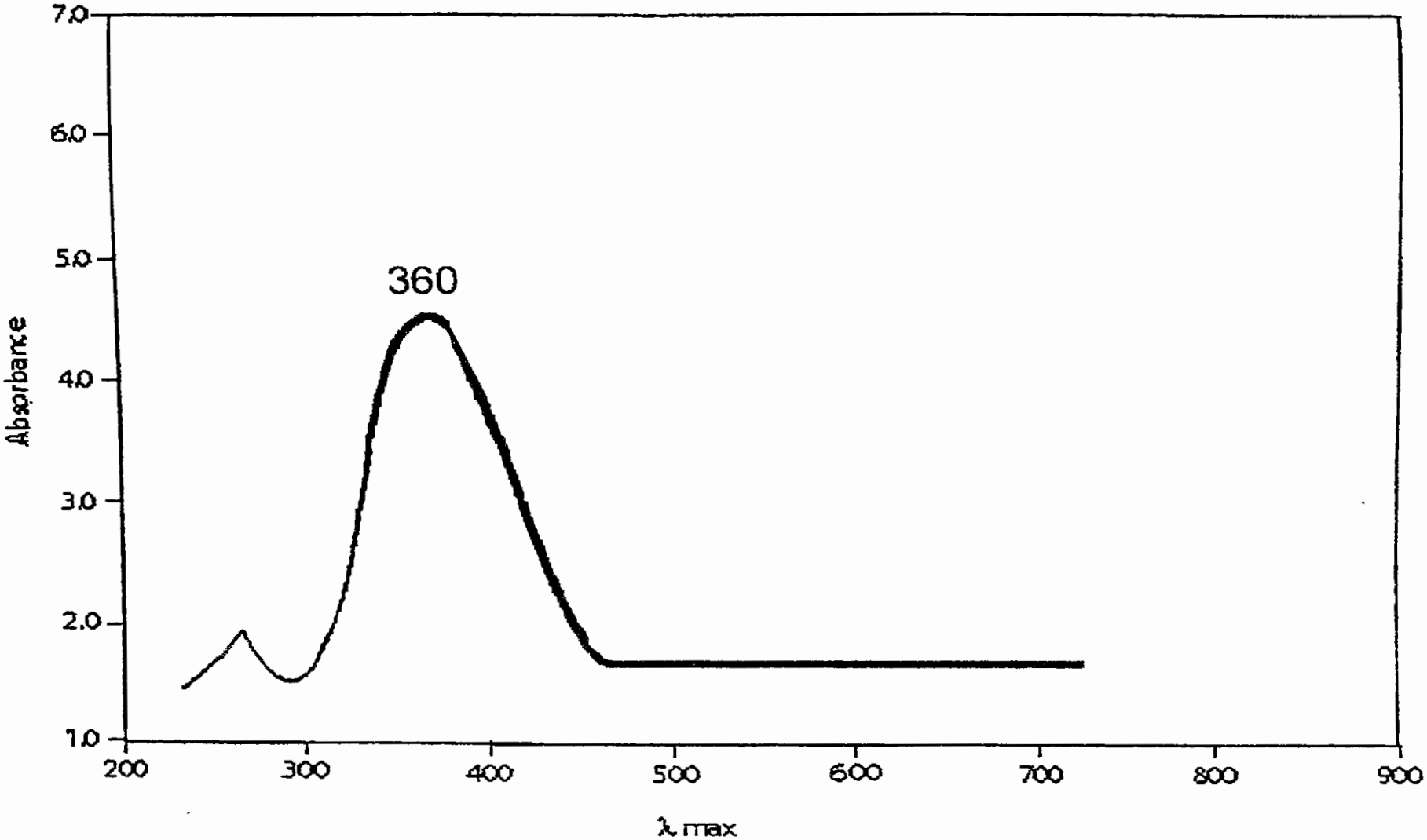


Fig.-4.5: UV-Visible spectrum of [Zr(IV) $(Mal)_2$ (IQ_2)] Complex-4

4.4 Conclusion:

From the above discussion the structure of zirconium (IV) Complexes are assignable to octahedral stereochemistry. On the basis of the above discussion the possible structure of the complex (2) are given in the figure (4.5). Similarly the structure of other complexes may also be given.

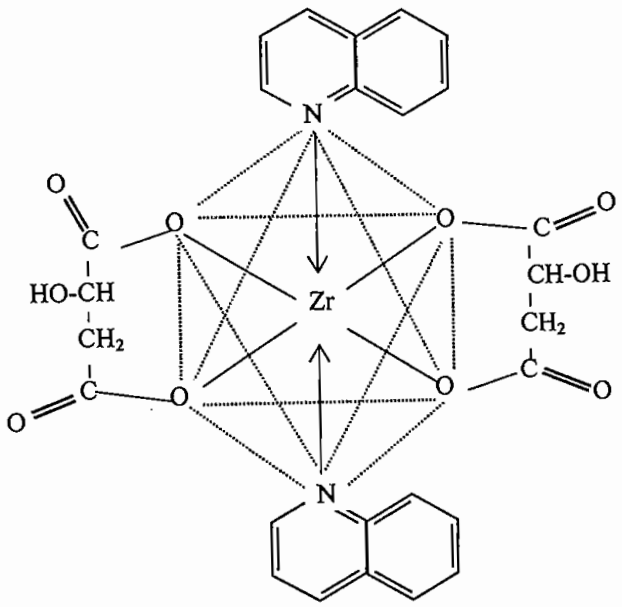


Fig. 4.5: Possible structure of the Complex-2 [Zr (IV) $(Mal)_2$ Q_2]

CHAPTER FIVE

STUDIES ON THE TRANSITION METAL COMPLEXES OF ZIRCONIUM (IV) WITH ORGANIC ACIDS AND AMINE BASES

CHAPTER-5

STUDIES ON THE TRANSITION METAL COMPLEXES OF ZIRCONIUM (IV) WITH ORGANIC ACIDS AND AMINE BASES

5.1 Introduction:

An exhaustive survey of the existing literature reveals that a very little has been done on the Zirconium (IV) Complexes with organic acids. Mixed ligand complexes of Zr(IV) ion containing some monodentate and multidentate organic ligands have been studied by Tarafder and co-workers.[150] Further more Tarafder *et.al.*[151] reported the existence of some mixed ligand complexes of Zr(IV). Amino acids have a great importance in biological and industrial field. Most of them are used as corrosion inhibitors and furthermore as an anti-bacterial, anti convulsive, anti fungal and anti-fouling agents. Islam *et.al.*[152] have studied anti-microbial activities of some mixed ligand complexes with organic acid and the study showed that the synthesized complexes were biologically active, although, some of them showed relatively lower activity.

Persuaded by these concepts and present needs, we here in report the preparation, characterization and antimicrobial study of Zr(IV) complexes with organic acids and amino acids (alanine and β-phenyl alanine) as secondary ligands.

5.2 Experimental:

5.2.1 Chemicals and reagents:

As stated in Chapter-2 Page No.-22

5.2.2 Physical measurements:

As described earlier in Chapter-2 Page No.-24

5.2.3 Preparation:

General method for preparation of [Zr(IV) $L_2L'_2$] where L= Oxalic acid, Malic acid, Methanoic acid and L' = Alanine, β-phenyl alanine.

As described earlier in Chapter-2 Page No.-34

5.3 Results and Discussion:

The Zirconium Complexes were obtained according to the following reactions:

$ZrOCl_2.\ 8H_2O + 2L+2L' + 4KOH \rightarrow K\ [Zr(IV)\ L_2L'_2] + KCl + H_2O$

Where L = oxalic acid, Malic acid, methanoic acid.

Acid L' = Alanine, β- phenyl alanine.

5.3.1 Elemental analysis and conductivity measurements:

Elemental analysis along with other data and their physical properties are presented in tables 5.1 and 5.2, The molar conductance were measured in N, N′-dimethyl formamide. The conductance value (Table 5.1) indicated that the complexes (1-6) were non-electrolytes in nature.

5.3.2 Magnetite measurements:

The observed values of effective magnetic moment (μ_{eff}) at room temperature are given in table 5.1. The magnetic moment values of Zirconium (IV) Complexes indicated that these complexes were diamagnetic in nature.

5.3.3 Electronic spectra:

The electronic spectral data are given in table 5.3. Among the complexes 1-6 showed bands between 330-370 nm regions due to the charge transfer band only. The UV-visible spectra of the complexes (1, 5) are shown in Fig. (5.7, 5.8).

5.3.4 IR Spectra:

As earlier described in Page No.-53

Major IR spectral data for the complexes are given in table 5.4.

Table-5.1: Physical properties of complexes

Complex No	Complexes	Colour	Melting point or d temperature ($\pm 5^0$C)	Molar conductance (ohm^{-1} Cm^2 mol^{-1})	Magnetic moment (μ_{eff}) B.M.
1	K^+ [Zr(IV) $(oxa)_2$ (ala)]$^-$	off white	180^0C	30.135	Dia
2	K^+[Zr(IV) $(oxa)_2$ (β – *phala*)]$^-$	cream	220^0C	32.206	Dia
3	K [Zr(IV) $(Mal)_2$ (ala)]$^-$	white	230^0C(d)	0.345	Dia
4	K [Zr(IV) $(Mal)_2$ (β – *phala*)]$^-$	cream	260^0C(d)	0.301	Dia
5	[Zr(IV) $(MA)_2$ $(ala)_2$]	cream	238^0C	1.732	Dia
6	[Zr(IV) $(MA)_2$ (β – $phala_2$)]	white	210^0C	0.650	Dia

Where :

d = Decomposition
Dia = Diamagnetic
oxa = Oxalic acid
Mal = Malic Acid
MA = Methanoic Acid
ala = Alaline
β – *phala* = β – Phenyl alanine

Table-5.2: Data of the elemental analysis of the complexes

Complex No	Complexes	Molecular weight		Metal %		Carbon%		Nitrogen%		Hydrogen%	
		Cal	Found	Cal	Found	Cal	Found	Cal	Found	Cal	Found
1	K^+ [Zr(IV) $(oxa)_2$ (ala)]$^-$	445.22	445.12	20.48	20.45	26.95	26.90	6.28	6.20	3.14	3.04
2	K^+[Zr(IV) $(oxa)_2$ ($\beta - phala$)]$^-$	597.22	597.13	15.27	15.20	46.21	46.15	4.69	4.62	3.68	3.60
3	K [Zr(IV) $(Mal)_2$ (ala)]$^-$	533.22	533.09	17.10	17.07	31.50	43.45	5.25	5.21	4.12	4.04
4	K [Zr(IV) $(Mal)_2$ ($\beta - phala$)]$^-$	685.22	685.20	13.31	13.21	45.53	45.45	4.08	4.00	4.38	4.29
5	[Zr(IV) $(MA)_2$ $(ala)_2$]	357.22	357.15	25.53	25.44	26.87	26.77	7.83	7.72	4.47	4.37
6	[Zr(IV) $(MA)_2$ ($\beta - phala_2$)]	509.22	509.10	17.91	17.80	47.13	47.03	5.49	5.40	4.71	4.62

Where :

oxa = Oxalic acid
Mal = Malic Acid
MA = Methanoic Acid
ala =Alaline
$\beta - phala$ = β – Phenyl alanine

Table-5.3: Electronic spectral data of the complexes

Complex No.	Complexes	λ max (nm)
1	K^+ [Zr(IV) $(oxa)_2$ (ala)]$^-$	370
2	K^+[Zr(IV) $(oxa)_2$ ($\beta - phala$)]$^-$	350
3	K [Zr(IV) $(Mal)_2$ (ala)]$^-$	340
4	K [Zr(IV) $(Mal)_2$ ($\beta - phala$)]$^-$	330
5	[Zr(IV) $(MA)_2$ $(ala)_2$]	390
6	[Zr(IV) $(MA)_2$ ($\beta - phala_2$)]	355

Where :

oxa = Oxalic acid
Mal = Malic Acid
MA = Methanoic Acid
ala = Alaline
$\beta - phala$ = β – Phenyl alanine

Table-5.4: IR data of the complexes (Band Maxima in Cm^{-1})

Complex No	Complexes	υ(N – H)	υ(C = O)	υ(C = N)	υ(C – O)	υ(M – O)	υ(M – N)
1	K^+ [Zr(IV) $(oxa)_2$ (ala)]$^-$	-	1640	1490	1340	510	420
2	K^+[Zr(IV) $(oxa)_2$ (β – *phala*)]$^-$	-	1620	1440	1350	520	412
3	K [Zr(IV) $(Mal)_2$ (ala)]$^-$	-	1650	1435	1320	515	430
4	K [Zr(IV) $(Mal)_2$ (β – *phala*)]$^-$	-	1660	1450	1355	500	415
5	[Zr(IV) $(MA)_2$ $(ala)_2$]	3130	1630	1460	1335	530	425
	[Zr(IV) $(MA)_2$ (β – $phala_2$)]	-	1670	1470	1300	525	410

Where :

oxa = Oxalic acid
Mal = Malic Acid
MA = Methanoic Acid
ala = Alaline
β – *phala* = β –Phenyl alanine

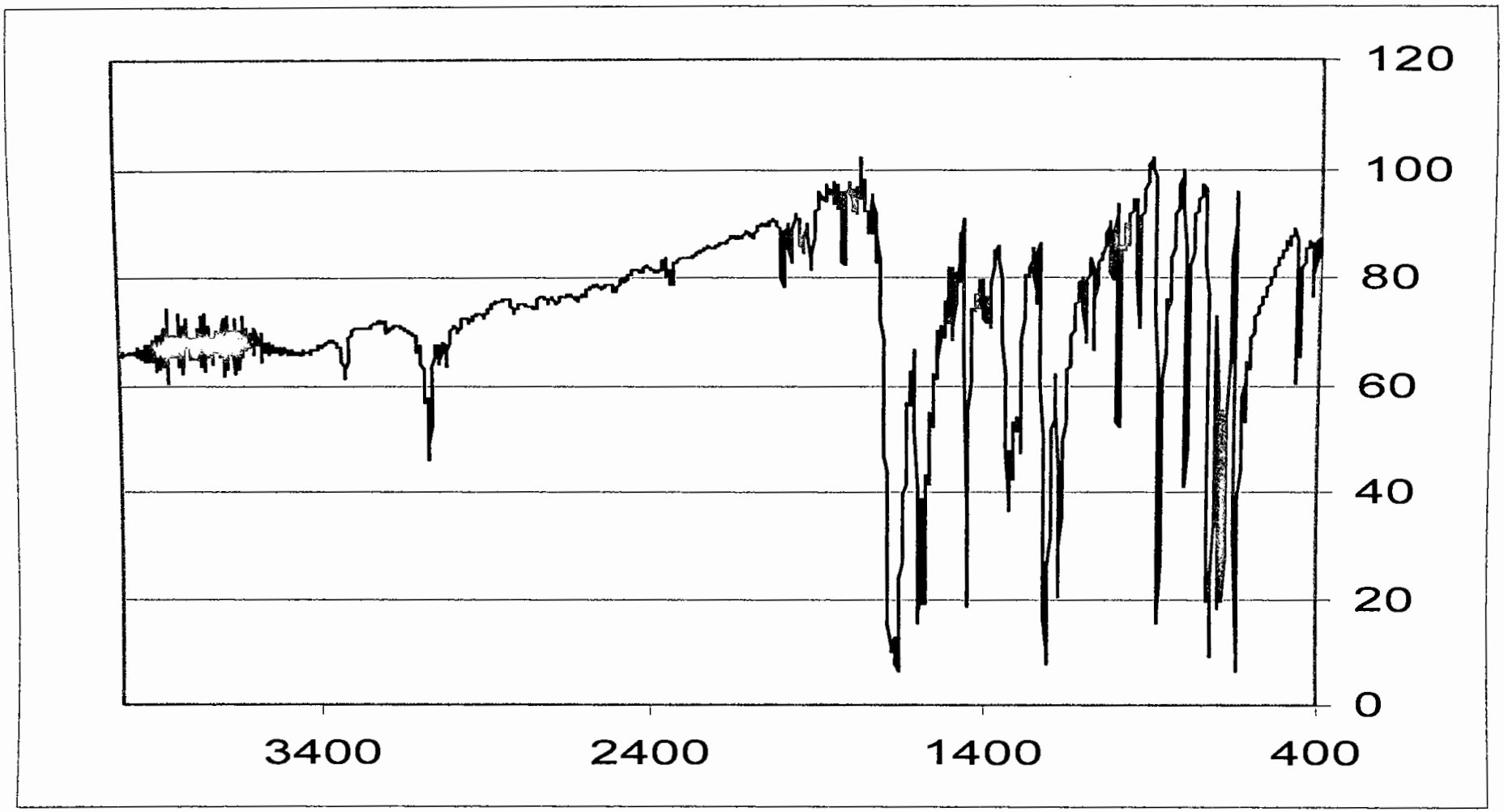


Fig. 5.1: IR spectrum of $K^+[Zr(IV)(oxa)_2(ala)]^1$

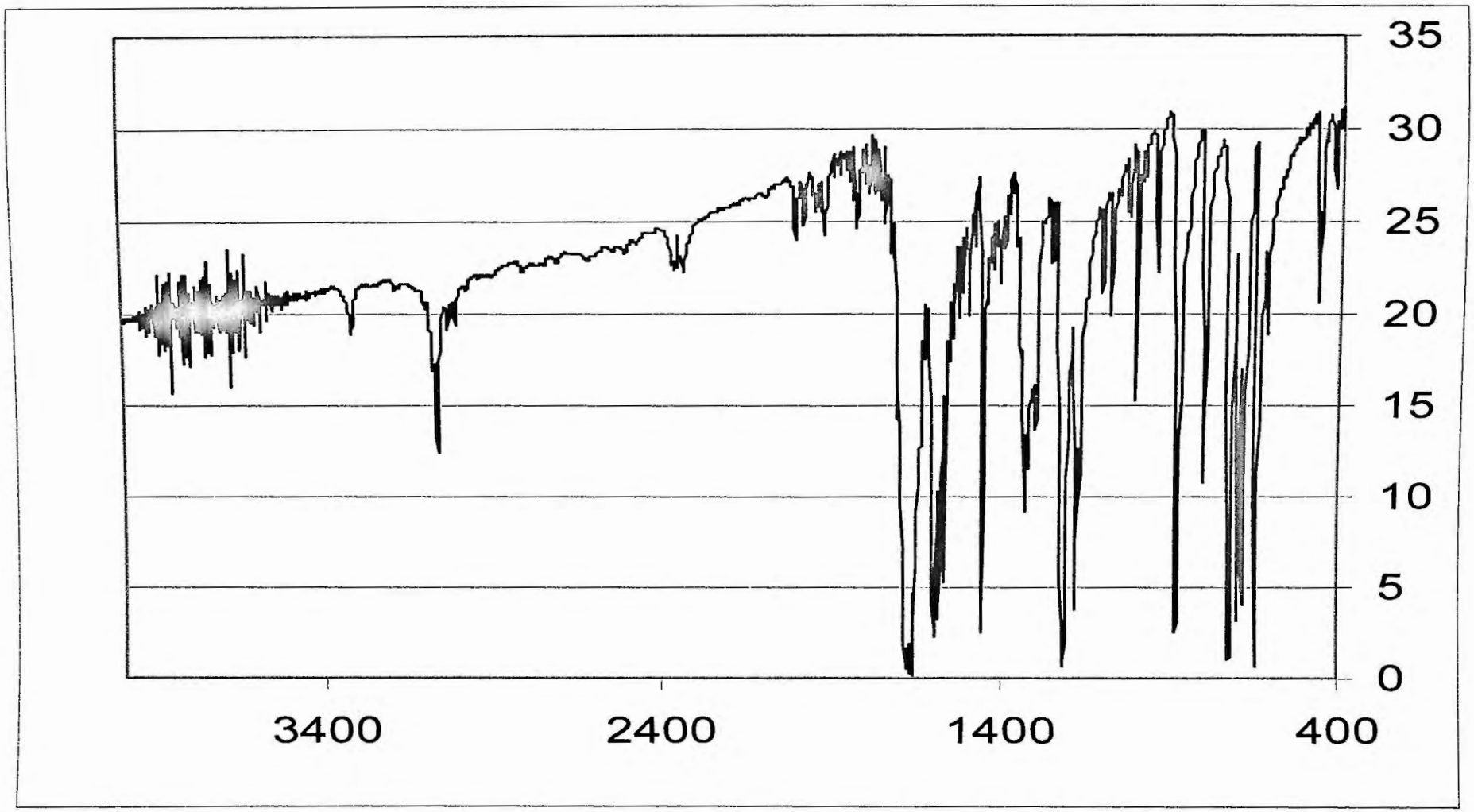


Fig. 5.1: IR spectrum of $K^+[Zr(IV)(oxa)_2(\beta\text{-ph-ala})]^-$

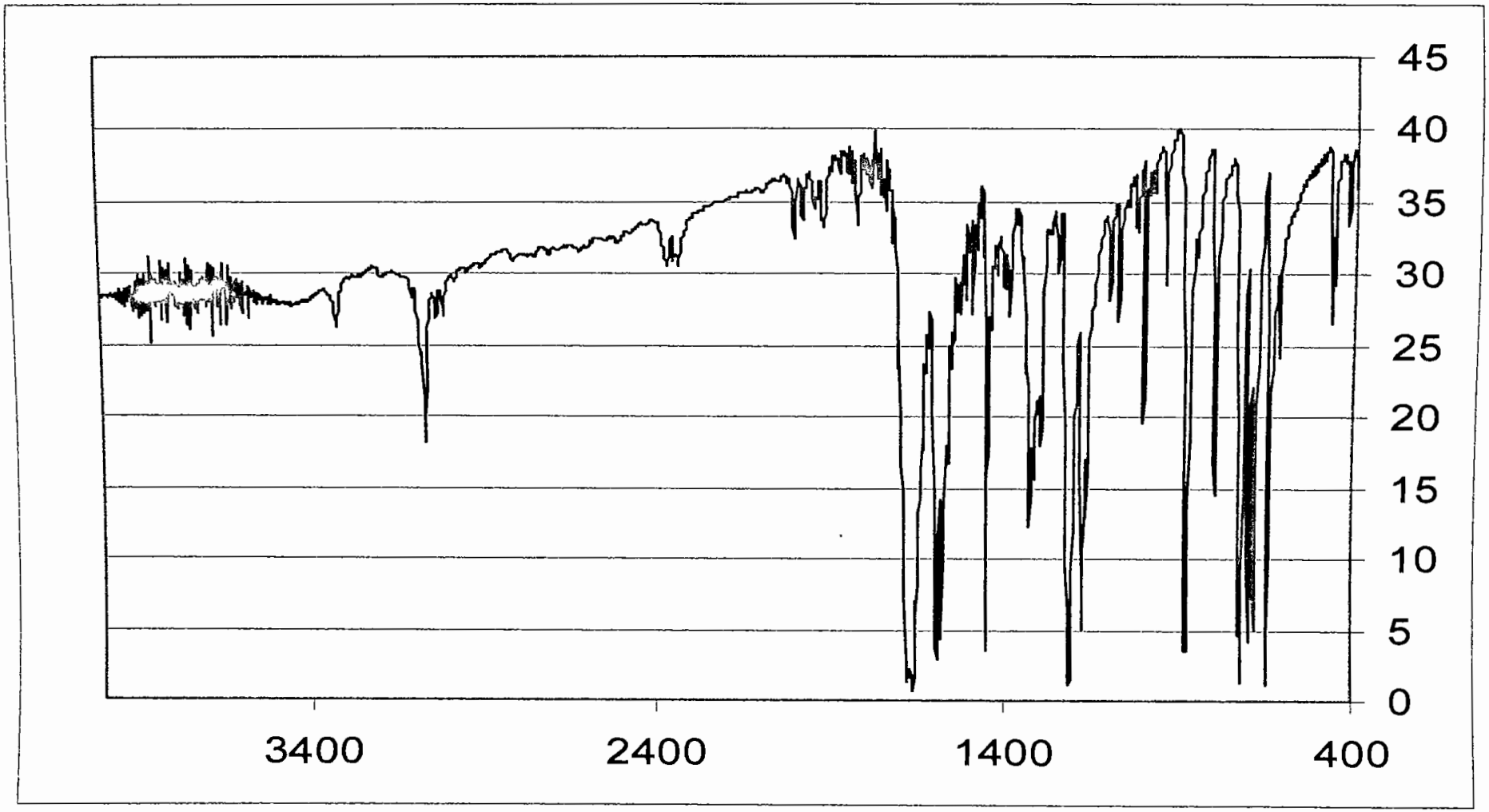


Fig. 5.3: IR spectrum of $K[Zr(IV)(Mal)_2(ala)]^-$

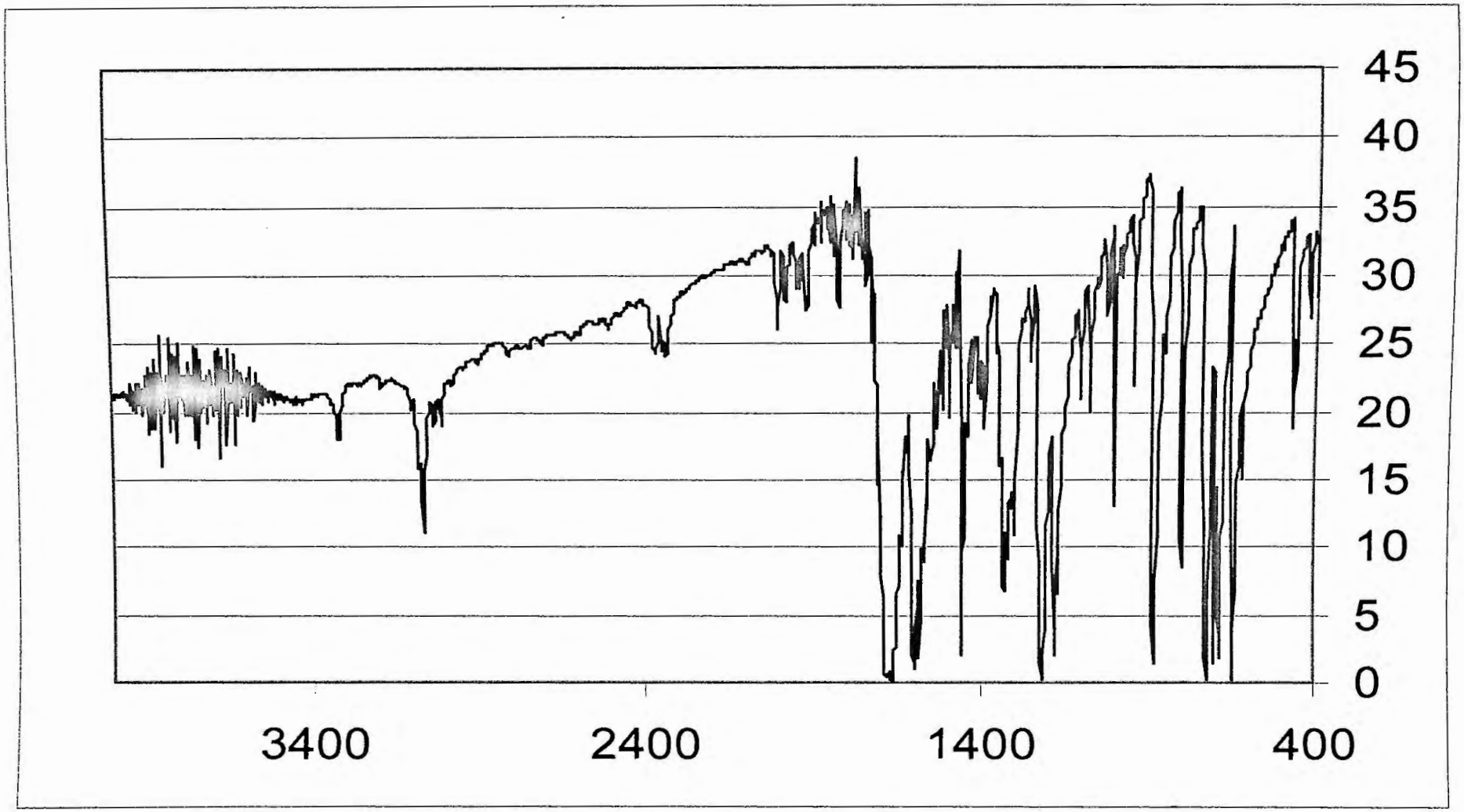


Fig. 5.4: IR spectrum of $K[Zr(IV)(Mal)_2(\beta\text{-ph-ala})]^-$

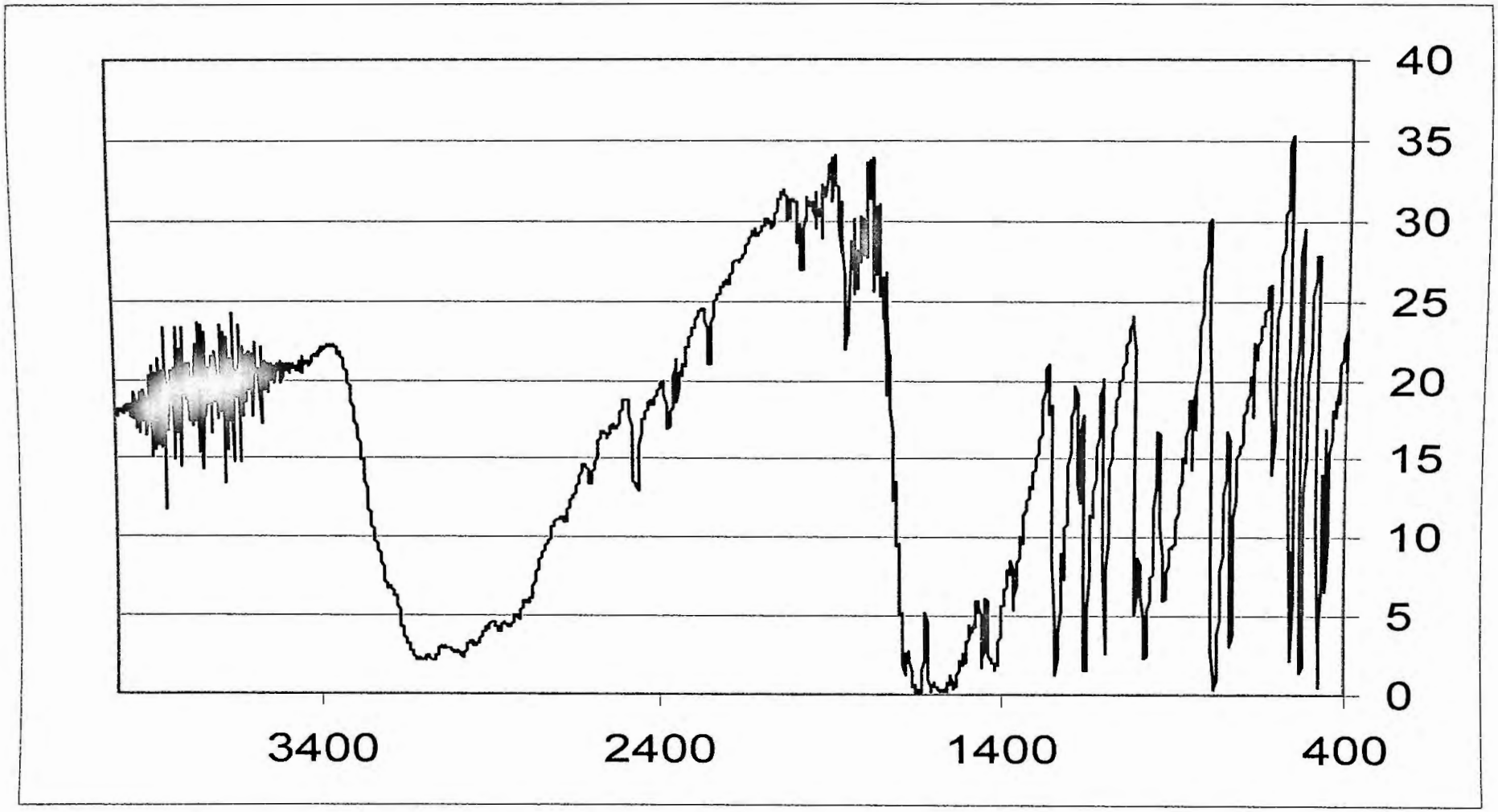


Fig. 5.5: IR spectrum of $[Zr(IV)(MA)_2(ala)_2]$

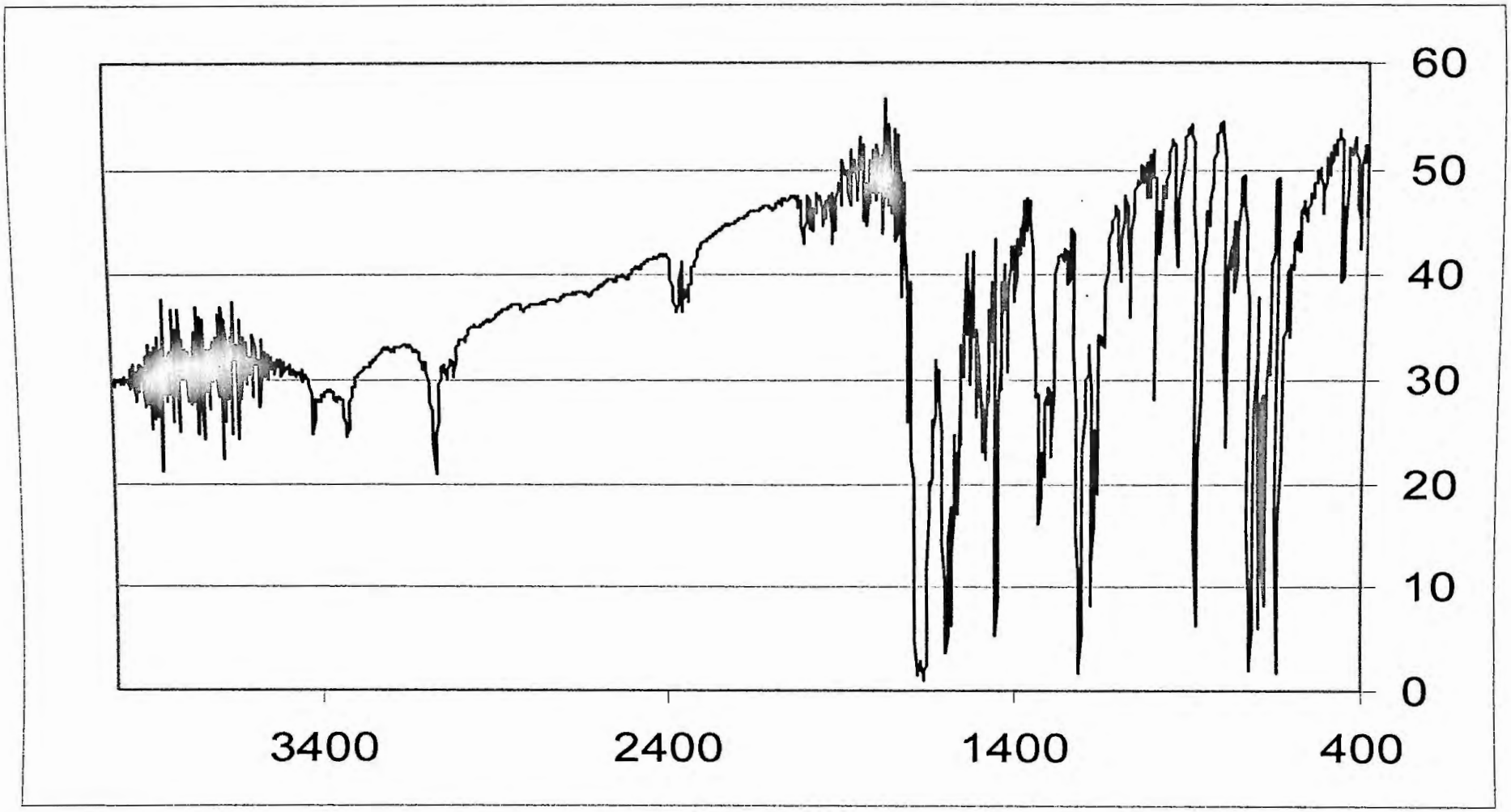


Fig. 5.6: IR spectrum of [Zr(IV)(MA)$_2$(β-ph-ala)$_2$]

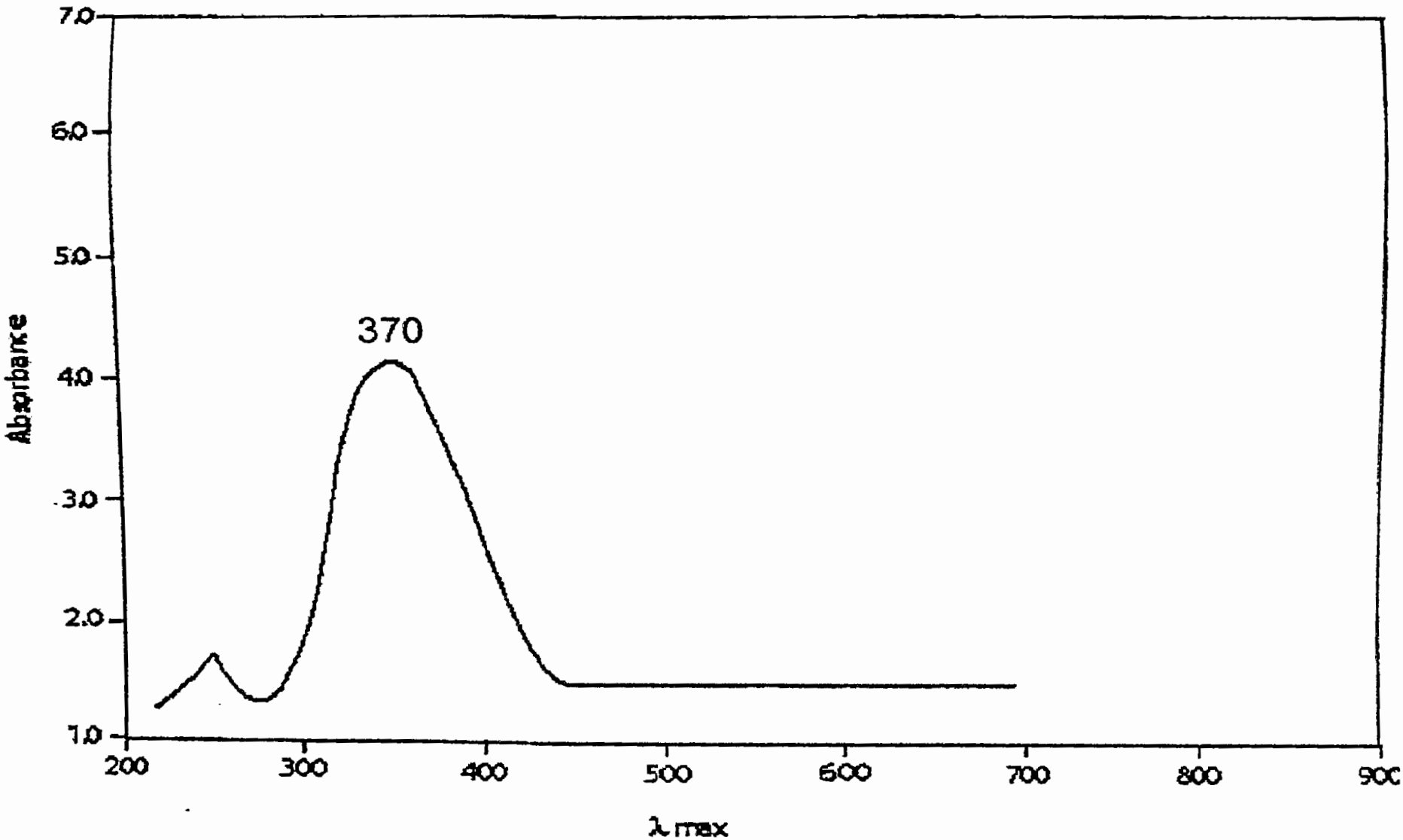


Fig.-5.7: UV-Visible spectrum of $K^+[Zr(IV)\ (oxa)_2\ (ala)]^-$ Complex-1

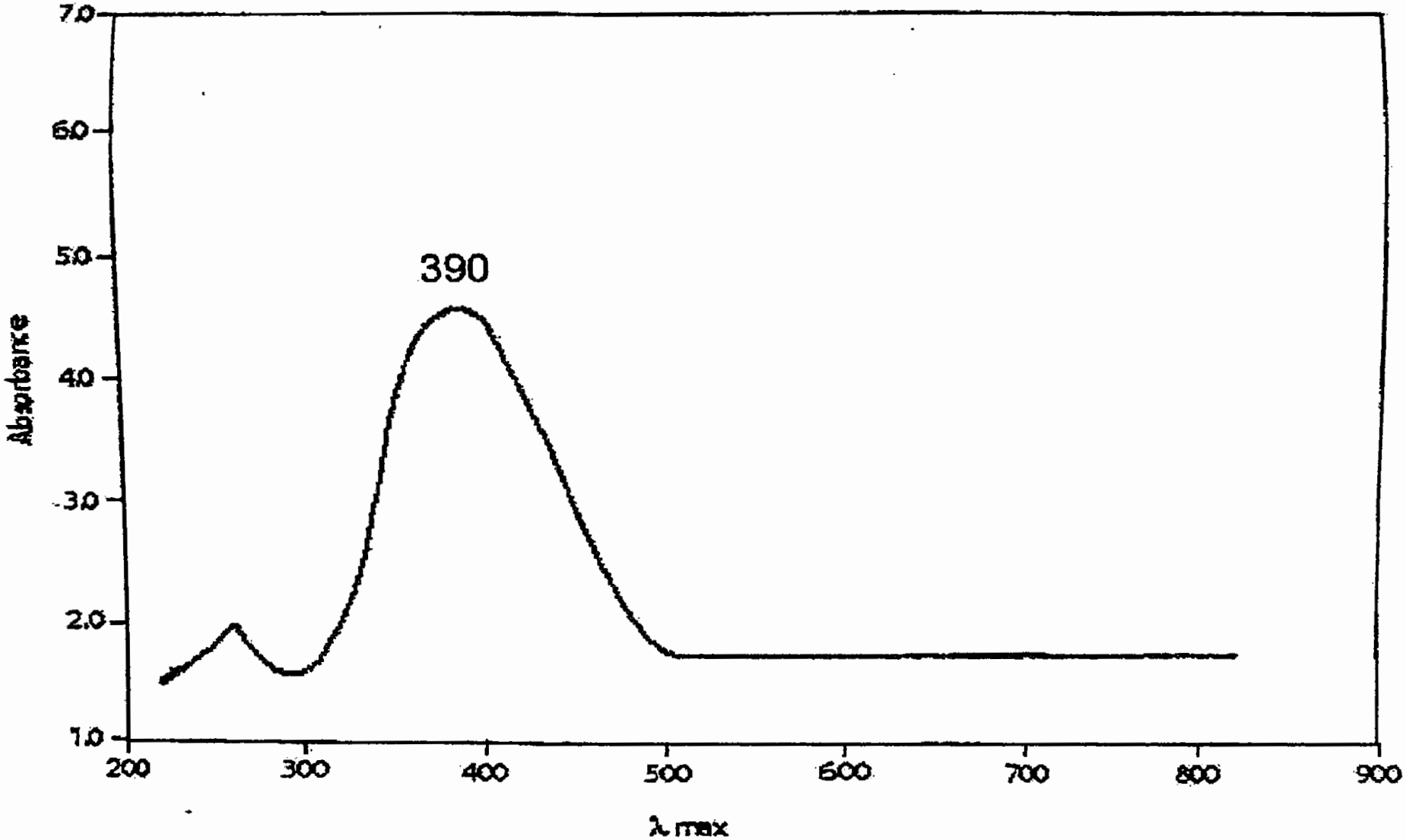


Fig.-5.8: UV-Visible spectrum of [Zr(IV) $(MA)_2$ $(ala)_2$] Complex-5

5.3.5 Conclusion:

From the above discussion octahedral structure is assignable to the prepared Zirconium (IV) Complexes.

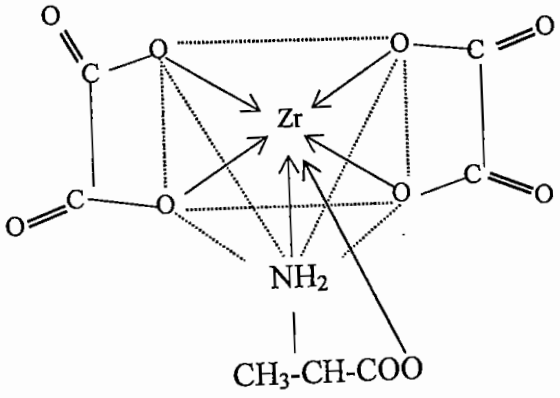


Fig. 5.7: Possible structure of the Complex (1) $K^{+}[Zr\ (IV)\ (oxa)_2\ (ala)]^{-}$

CHAPTER SIX

CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF VANADIUM (IV) WITH ORGANIC ACIDS AND ALANINE

CHAPTER – 6

CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF VANADIUM (IV) WITH ORGANIC ACIDS AND ALANINE

6.1 Introduction:

The interactions of vanadium (IV) with some organic acids have been studied by Kariya and co-workers[153]. Potentiometric[154] studies of vanadyl (IV) complexes of oxalic acids have also been reported. Equilibrium studies of ternary complexes of vanadyl ion with some organic acid[155-157] have been carried out in solution. The most extensive studies have been carried out on vanadium (IV) complexes with amine bases.[158-161] A very few references are also available on the mixed ligand complexes of vanadium (IV).[162,163]

Secondly, the amine bases have biological and industrial importance. The studies on the metal complexes of amine bases have been carried out by several group of workers, but nothing is reported on the mixed ligand complexes of vanadium (IV) acids with amines.

Keeping these facts in view, we prepared some new mixed ligand complexes of vanadium (IV) with acids i.e., Methanoic acid, Ethanoic acid, propanoic acid, oxalic acid, malic acid and amines i.e., alanine and 2,2′-bipyridyl (Bipy) as secondary ligands and characterized on the basis of usual methods as stated earlier.

6.2 Experimental :

6.2.1 Chemicals and reagents:

As described in Chapter-2, Page No.-22

6.2.2 Physical measurements

As stated in Chapter-2, Page No.-24

6.2.3 Preparation:

General method for preparation of [V(IV) L_2L_2'] where L = Oxa, MA, EA, PA, Mal and L′ = ala, 2,2′- Bipy Respectively.

As earlier described in Page No.-34

6.3 Results and Discussion:

The vanadium complexes were obtained by to the following reactions:

$VOSO_4+2L+2L'+4KOH \rightarrow K[V(IV)L_2L_2']+KCl+H_2O$

Where:

L = Organic Acids i.e; oxalic acids, Malic acids, Methanoic acids, Ethanoic acids, Propanoic acid. L′ = Alanine, 2,2'-Bipyridyl

6.3.1 Elemental analysis and conductivity measurements:

Elemental analysis along with other data and their physical properties are presented in table 6.1 and 6.2 the molar conductance were measured in N,N'-dimethyl formamide. The conductance value (Table 6.1) indicated that the complex were non-electrolytic in nature.

6.3.2 Magnetic moments:

The observed values of effective magnetic moment (μ_{eff}) at room temperature are given in table 6.1. The magnetic moment values of Vanadium (IV) Complexes are 0.731 to 0.319 B.M indicated that these complexes were diamagnetic in nature.

6.3.3 Electronic spectra:

The electronic spectral data are presented in table-6.3. The complexes 1-6 showed bands between 340-430 nm regions due to the charge transfer band only. The UV-visible spectra of the complexes (1,2) are shown in Fig. (6.4-6.5).

6.3.4 IR Spectra:

As earlier described in Page No.-53

Major IR spectral data for the complexes are given in table 6.4

Table-6.1: Physical properties of complexes

Complex No	Complexes	Colour	Melting point or d temperature ($\pm 5^0$C)	Molar conductance ($ohm^{-1} Cm^2 mol^{-1}$)	Magnetic moment (μ_{eff}) B.M.
1	$K^+[V(IV)(oxa)_2(ala)]^-$	Grey	150^0C	35.321	Dia
2	$[V(IV)(MA)_2(ala)_2]$	Deep Grey	155^0C	1.319	0.731
3	$[V(IV)(EA)_2(ala)_2]$	Deep Grey	180^0C	0.045	0.821
4	$[V(IV)(PA)_2(ala)_2]$	Grey	250^0C	0.871	Dia
5	$K^+[V(IV)(oxa)_2(2,2'-Bipy)]^-$	Light green	210^0C	32.412	0.713
6	$K^+[V(IV)(Mal)_2(ala)]^-$	Redish	250^0C	33.321	0.319

Where :

d	=	Decomposition
Dia	=	Diamagnetic
oxa	=	Oxalic acid
Mal	=	Malic acid
MA	=	Methanoic acid
EA	=	Ethanoic acid
PA	=	Propanoic acid
ala	=	Alaline
2,2′ – Bipy	=	2,2'–Bipyridyl

Table-6.2: Data of the elemental analysis of the complexes

Complex No	Complexes	Molecular weight		Metal %		Carbon%		Nitrogen%		Hydrogen%	
		Cal	Found	Cal	Found	Cal	Found	Cal	Found	Cal	Found
1	$K^+[V(IV)(oxa)_2(ala)]^-$	404.94	404.70	12.57	12.63	29.63	29.70	6.91	6.99	3.46	3.51
2	$[V(IV)(MA)_2(ala)_2]$	318.94	318.82	15.97	15.72	30.10	30.18	8.78	8.88	5.02	5.07
3	$[V(IV)(EA)_2(ala)_2]$	346.94	346.72	14.68	14.71	34.59	34.61	8.07	8.10	5.76	5.77
4	$[V(IV)(PA)_2(ala)_2]$	374.94	374.10	13.95	13.99	38.41	38.50	7.47	7.51	6.40	6.44
5	$K^+[V(IV)(oxa)_2(2,2'-Bipy)]^-$	538.94	538.34	9.45	9.49	53.43	53.48	10.39	10.42	2.97	2.61
6	$K^+[V(IV)(Mal)_2(ala)]^-$	492.94	492.73	10.33	10.40	34.08	34.12	5.68	5.74	4.46	4.53

Where :

oxa = Oxalic acid
Mal = Malic acid
MA = Methanoic acid
EA = Ethanoic acid
PA = Propanoic acid
ala = Alaline
$2,2'-Bipy$ = 2,2'–*Bipyridyl*

Table-6.3: Electronic spectral data of the complexes

Complex No.	Complexes	λ max (nm)
1	$K^+[V(IV)\ (oxa)_2\ (ala)]^-$	430
2	$[V(IV)\ (MA)_2\ (ala)_2]$	420
3	$[V(IV)\ (EA)_2\ (ala)_2]$	340
4	$[V(IV)\ (PA)_2\ (ala)_2]$	350
5	$K^+[V(IV)\ (oxa)_2\ (2,2'-Bipy)]^-$	380
6	$K^+[V(IV)\ (Mal)_2\ (ala)]^-$	370

Where :

oxa = Oxalic acid
Mal = Malic acid
MA = Methanoic acid
EA = Ethanoic acid
PA =Propanoic acid
ala =Alaline
2,2′ – Bipy = 2,2'–*Bipyridyl*

Table-6.4: IR data of the complexes (Band Maxima in Cm^{-1})

Complex No	Complexes	υ(N – H)	υ(C = O)	υ(C = N)	υ(C – O)	υ(M – O)	υ(M – N)
1	$K^+[V(IV)\ (oxa)_2\ (ala)]^-$	-	1680	1440	1330	520	415
2	$[V(IV)\ (MA)_2\ (ala)_2]$	-	1650	1460	1340	490	412
3	$[V(IV)\ (EA)_2\ (ala)_2]$	3320	1630	1450	1355	525	450
4	$[V(IV)\ (PA)_2\ (ala)_2]$	-	1660	1455	1345	515	430
5	$K^+[V(IV)\ (oxa)_2\ (2,2'-Bipy)]^-$	3180	1670	1430	1350	530	430
6	$K^+[V(IV)\ (Mal)_2\ (ala)]^-$	3160	1620	1480	1340	510	420

Where :

oxa = Oxalic acid
Mal = Malic acid
MA = Methanoic acid
EA = Ethanoic acid
PA = Propanoic acid
ala = Alaline
2,2' – Bipy = 2,2'–*Bipyridyl*

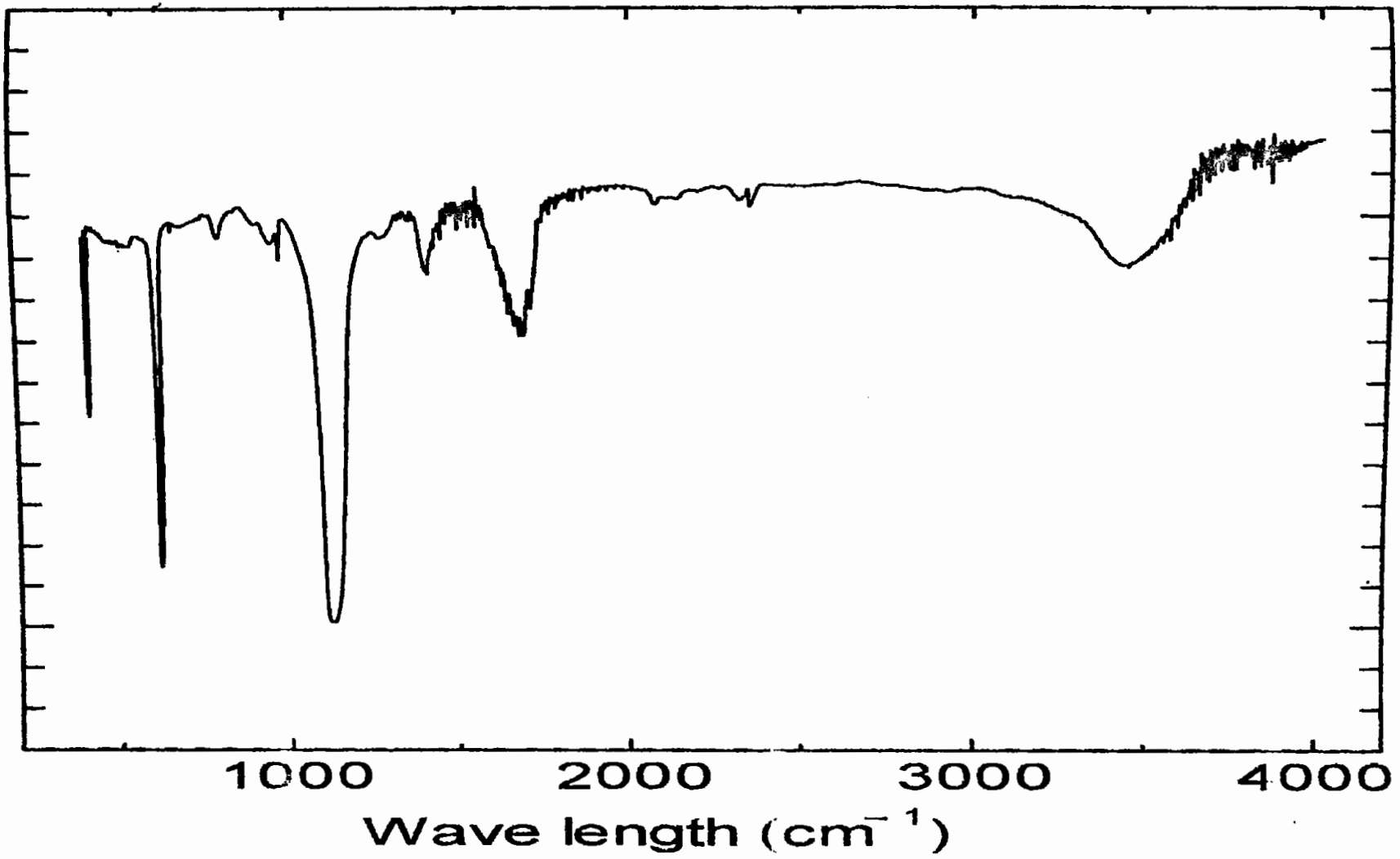


Fig. 6.1: IR spectrum of $K^+[V(IV)(oxa)_2(ala)]^-$

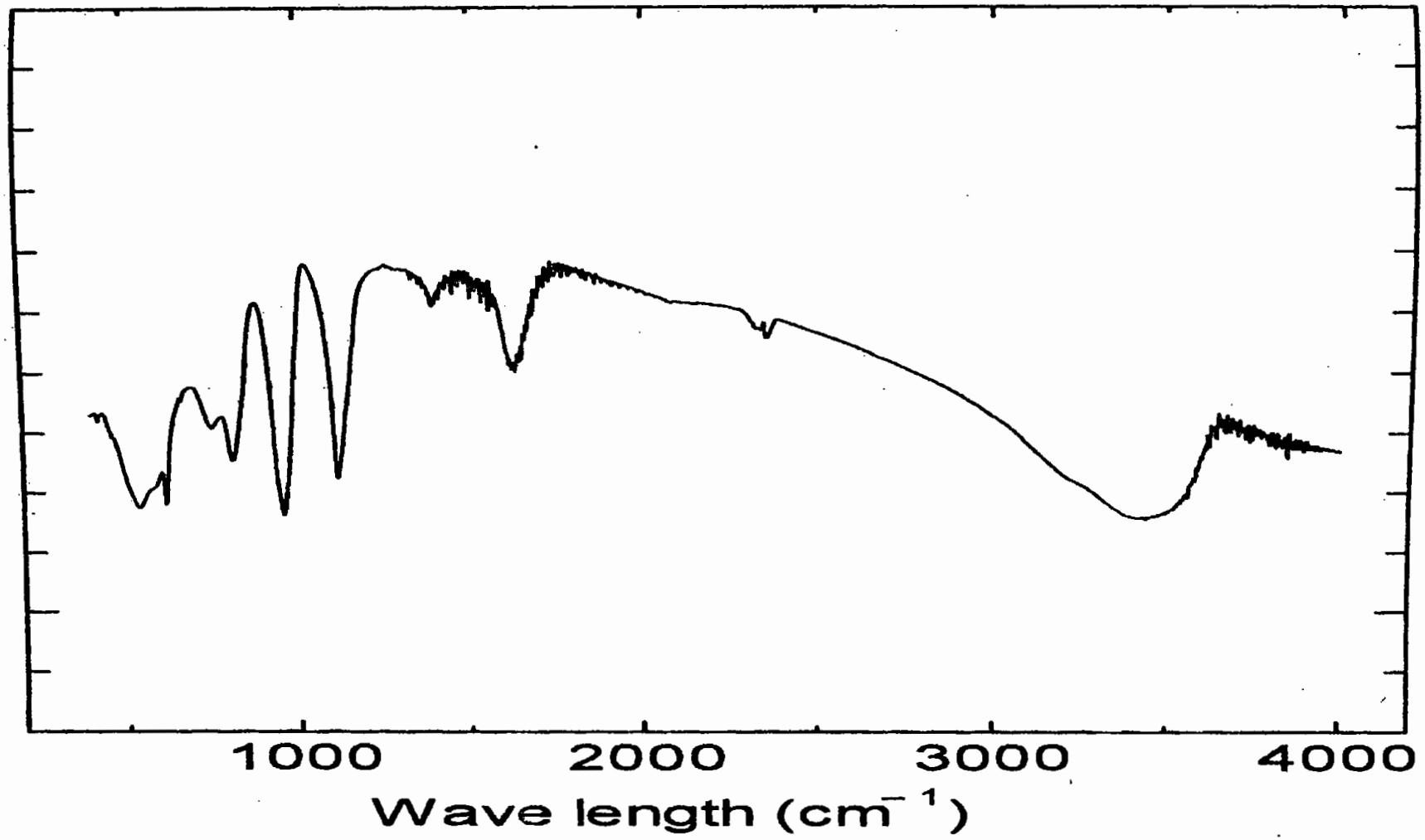


Fig. 6.2: IR spectrum of $[V(IV)(EA)_2(ala)_2]$

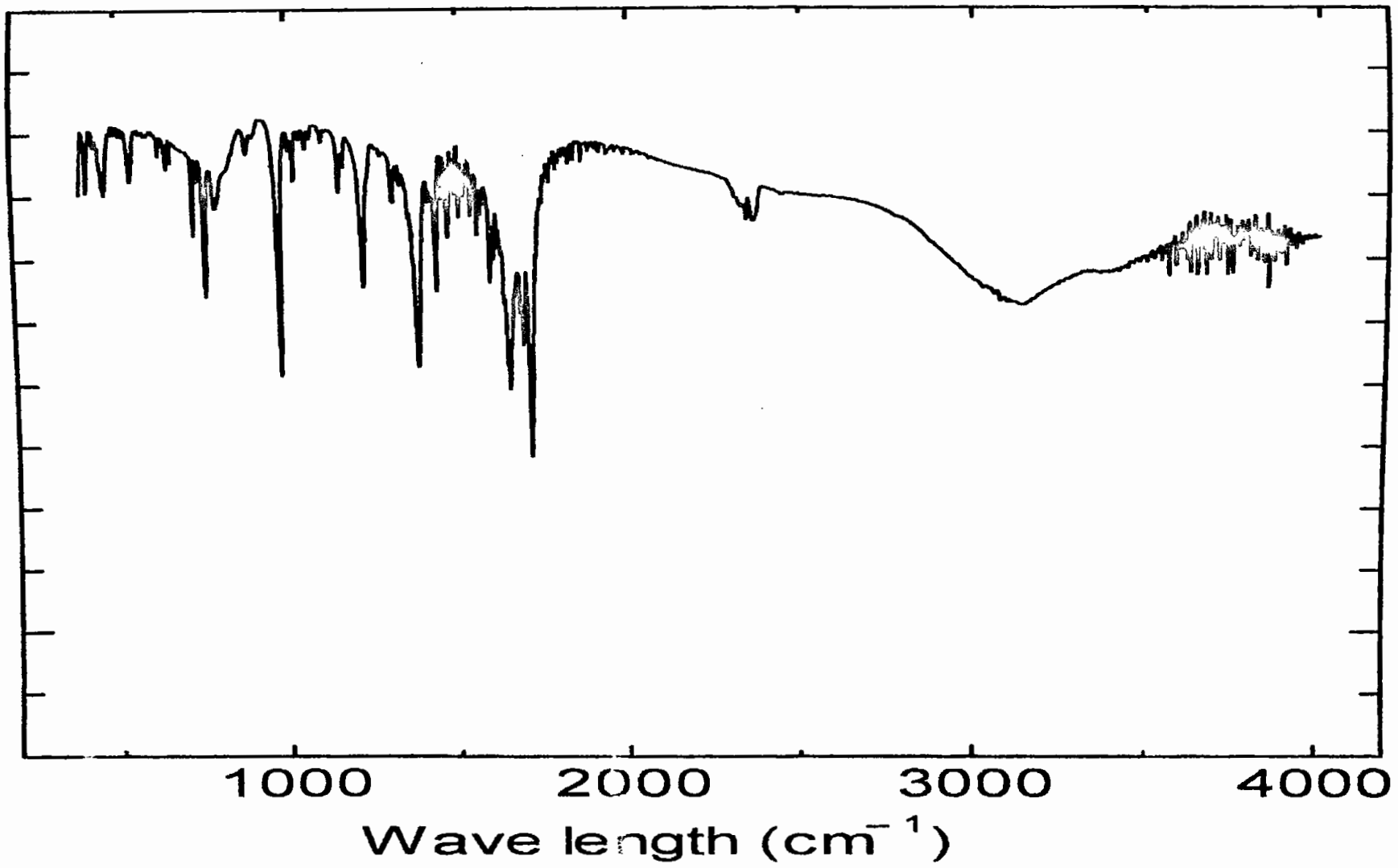


Fig. 6.3: IR spectrum of $K^{+}[V(IV)(oxa)_2(2,2'\text{-Bipy})]^{-}$

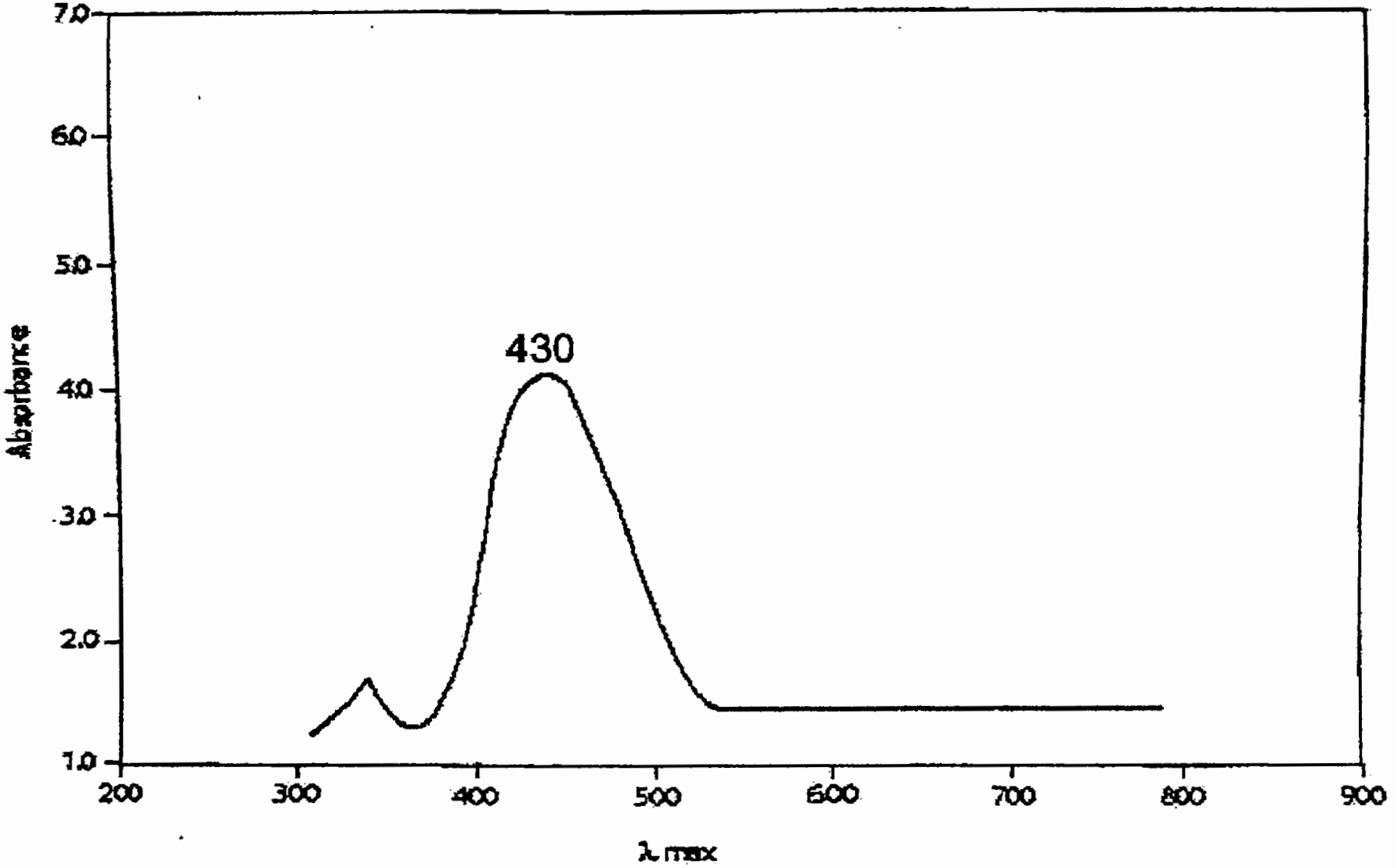


Fig.-6.4 : UV-Visible spectrum of $K^+[V(IV)\ (oxa)_2\ (ala)]^-$ Complex-1

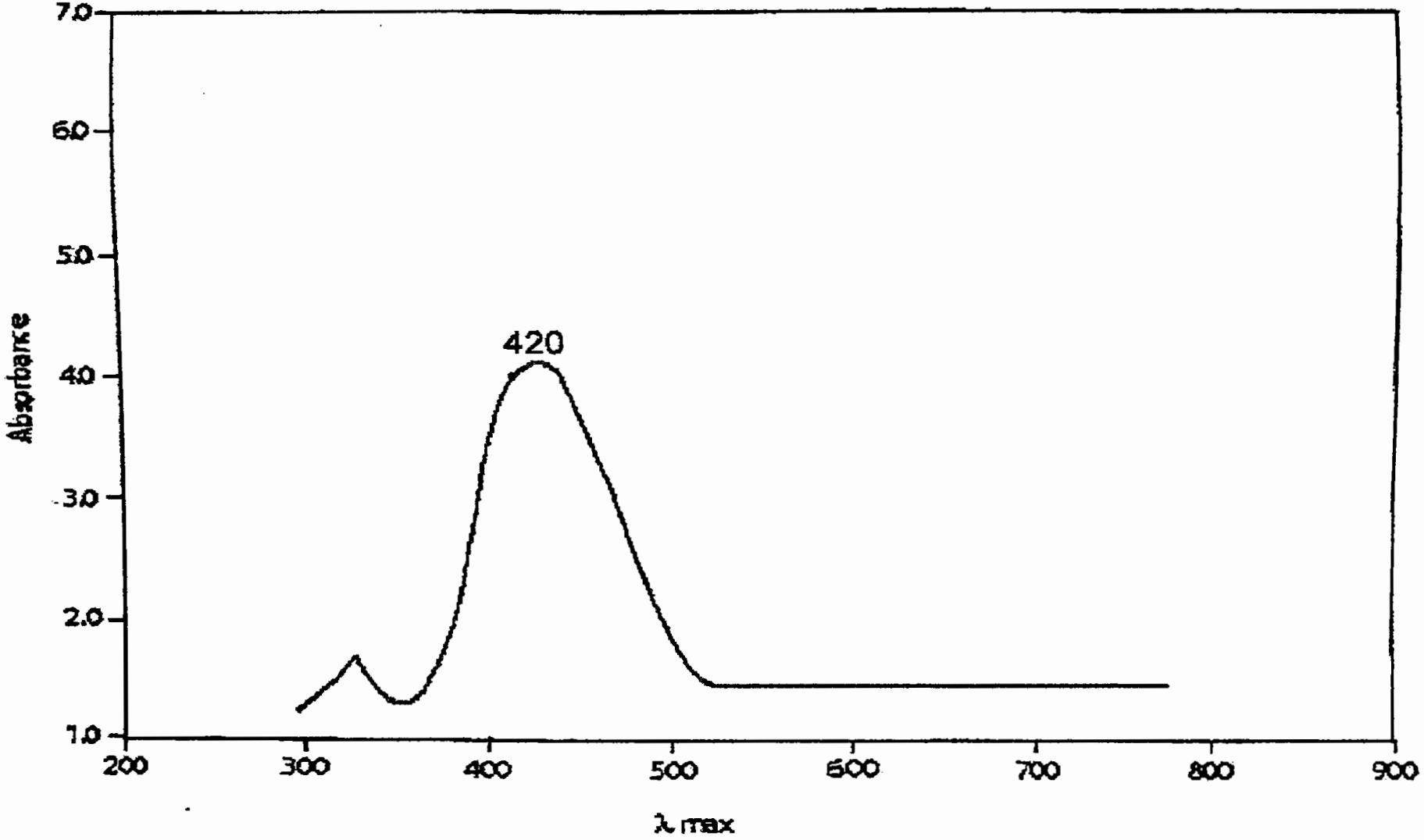


Fig.-6.5 : UV-Visible spectrum of [V(IV) $(MA)_2$ $(ala)_2$] Complex-2

6.4 Conclusion:

From the above discussion the structure of vanadium (IV) Complexes are assignable to octahedral stereochemistry. On the basis of the above discussion the possible structure of the complex (5) is given in the figure (6.4). Similarly the structure of other complexes may also be given.

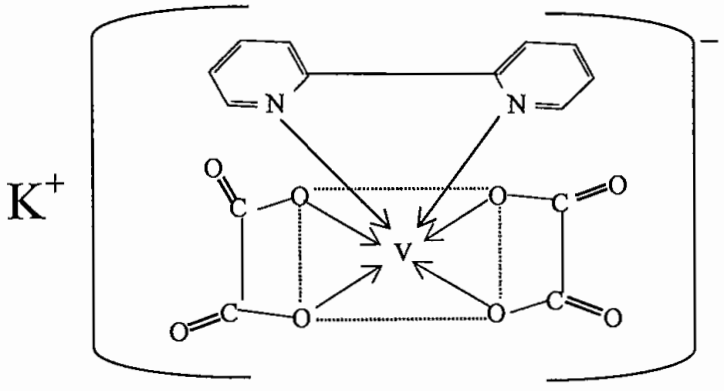


Fig-6.4: Possible structure of the Complex (5) $K^+[V(IV)\ (oxa)_2\ (2,2'-Bipy)]^-$

CHAPTER SEVEN

SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF VANADIUM (IV) WITH ORGANIC ACID AND PHENYL ALALINE

CHAPTER – 7

SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF VANADIUM (IV) WITH ORGANIC ACID AND PHENYLALALINE

7.1 Introduction:

There are many reports on the transition metal malonate, oxalate and Phthalates with structural and magneto structural characterization. New mixed ligand complexes of Vanadium (IV) with organic acids and β-Phenyl alanine, amines have been prepared and characterized by Islam[164-170]. Sharma *et. al.*,[171,172] determined the stability of mixed ligand complexes of V (IV), with organic acid. Mixed ligand complexes of V(IV) with organic acid and amines have been prepared by Islam[173].

With this additional information over the topic in continuation of the work. We prepared some new mixed ligand complexes of V(IV) with Malic acid, Oxalic acid, Methanoic acid, Ethanoic acid, propanoic acid and amine bases, e.g. β-phenyl alanine.

7.2 Experimental:

7.2.1 Chemicals and reagents:

As stated in Chapter-2, Page No.-22

7.2.2 Physical measurements:

As stated in Chapter-2, Page No.-24

7.2.3 Preparation:

General Method for preparation of [V(IV) L_2(β-Ph-ala)$_2$]

Where L = Malic acid, oxalic acid, Methanoci acid, Ethanoic acid, propanoic acid β-Ph-ala = β-phenyl alanine;

As earlier described in Page No.-34

7.3 Results and Discussion:

The Vanadium Complexes were obtained according to the following reactions:

$VOSO_4$ +2L + 2(β-phala)+4KOH → k [V(IV)L_2 (β-phala)$_2$]

Where:

L = Malic acid, Oxalic acid, Methanoic acid, Ethanoic acid, Propanoic acid and β-Ph-ala= β-phenyl alanine.

7.3.1 Elemental Analysis and Conductivity measurements:

The analytical data and other physical. Properties of the complexes are given in table 7.1 Vanadium Complexes were soluble in DMF and

DMSO. The analytical data are in good agreement with the proposed, empirical formulae of the present complexes. Their structures have been confirmed by conductivity, Magnetic measurements and electronic spectral data.

The molar conductance of 10^{-3}M Solutions of the complexes in DMSO were measured 28°C. The molar Conductance values indicate that all the complexes are non-electrolytic in nature.

7.3.2 Magnetic measurements:

The Observed values or the effective magnetic moments of the complexes at room temperature are given in table 7.1 Vanadium(IV) complexes were found to be diamagnetic in nature.

7.3.3 Electronic Spectra:

All the complexes of Vanadium were diamagnetic in nature which indicated no change in the oxidation state of the metal ions on complex formation. The Spectra of the solution of Vanadium (IV) complexes showed bands at (330-360) nm region due to the charge transfer only. The UV-visible spectra of the complexes (1,2) are shown in Fig. (7.1,7.2).

7.3.4 IR spectra:

As earlier described in Page No.-53

Major IR spectral data for the complexes are given in table 7.4.

Table-7.1: Physical properties of complexes

Complex No	Complexes	Colour	Melting point or d temperature ($\pm 5^0$C)	Molar conductance (ohm^{-1} Cm^2 mol^{-1})	Magnetic moment (μ_{eff}) B.M.
1	$K^+[V(IV)(Mal)_2(\beta\text{-phala})]^-$	Light grey	160^0C	30.412	Dia
2	$K[V(IV)(oxa)_2(\beta\text{-phala})]^-$	Grey	170^0C	32.321	Dia
3	$[V(IV)(MA)_2(\beta\text{-phala})_2]$	Cream	162^0C	1.371	Dia
4	$[V(IV)(EA)_2(\beta\text{-phala})_2]$	Cream	215^0C	0.121	Dia
5	$[V(IV)(PA)_2(\beta\text{-phala})_2]$	Grey	230^0C	0.358	Dia

Where :

d = Decomposition
Dia = Diamagnetic
oxa = Oxalic acid
Mal = Malic acid
MA = Methanoic acid
EA = Ethanoic acid
PA = Propanoic acid
ala = Alaline
β-phala = β-Phenalyalanine

Table-7.2: Data of the elemental analysis of the complexes

Complex No	Complexes	Molecular weight		Metal %		Carbon%		Nitrogen%		Hydrogen%	
		Cal	Found	Cal	Found	Cal	Found	Cal	Found	Cal	Found
1	$K^+[V(IV)(Mal)_2(\beta\text{-phala})]^-$	547.94	547.20	9.30	9.37	35.04	35.12	5.11	5.19	5.47	5.54
2	$K[V(IV)(oxa)_2(\beta\text{-phala})]^-$	556.94	556.70	9.15	9.20	47.40	47.48	5.03	5.09	3.95	3.11
3	$[V(IV)(MA)_2(\beta\text{-phala})_2]$	470.94	470.21	10.82	10.91	50.96	50.13	5.94	5.72	5.10	5.17
4	$[V(IV)(EA)_2(\beta\text{-phala})_2]$	498.94	498.80	10.21	10.30	52.91	52.40	5.61	5.70	5.61	5.68
5	$[V(IV)(PA)_2(\beta\text{-phala})_2]$	528.94	528.75	9.63	9.70	54.45	54.50	5.29	5.30	6.05	6.12

Where :

oxa = Oxalic acid
Mal = Malic acid
MA = Methanoic acid
EA = Ethanoic acid
PA = Propanoic acid
ala = Alaline
β-phala = β-Phenaly alanine

Table-7.3: Electronic spectral data of the complexes

Complex No.	Complexes	λ max (nm)
1	$K^+[V(IV)\ (Mal)_2\ (\beta\text{-phala})]^-$	430
2	$K[V(IV)\ (oxa)_2(\beta\text{-phala})]^-$	450
3	$[V(IV)\ (MA)_2(\beta\text{-phala})_2]$	360
4	$[V(IV)\ (EA)_2(\beta\text{-phala})_2]$	380
5	$[V(IV)\ (PA)_2(\beta\text{-phala})_2]$	410

Where :

oxa = Oxalic acid
Mal = Malic acid
MA = Methanoic acid
EA = Ethanoic acid
PA = Propanoic acid
ala = Alaline
β-phala = β-Phenaly alanine

Table-7.4: IR data of the complexes (Band Maxima in Cm^{-1})

Complex No	Complexes	υ(N – H)	υ(C = O)	υ(C = N)	υ(C – O)	υ(M – O)	υ(M – N)
1	$K^+[V(IV)\ (Mal)_2\ (\beta\text{-phala})]^-$	-	1660	1430	1355	590	410
2	$K[V(IV)\ (oxa)_2(\beta\text{-phala})]^-$	-	1630	1460	1340	530	450
3	$[V(IV)\ (MA)_2(\beta\text{-phala})_2]$	3340	1670	1435	1345	510	430
4	$[V(IV)\ (EA)_2(\beta\text{-phala})_2]$	-	1620	1480	1330	525	420
5	$[V(IV)\ (PA)_2(\beta\text{-phala})_2]$	-	1665	1470	1335	515	410

Where :

oxa = Oxalic acid
Mal = Malic acid
MA = Methanoic acid
EA = Ethanoic acid
PA = Propanoic acid
ala = Alaline
β-phala = β-Phenaly alanine

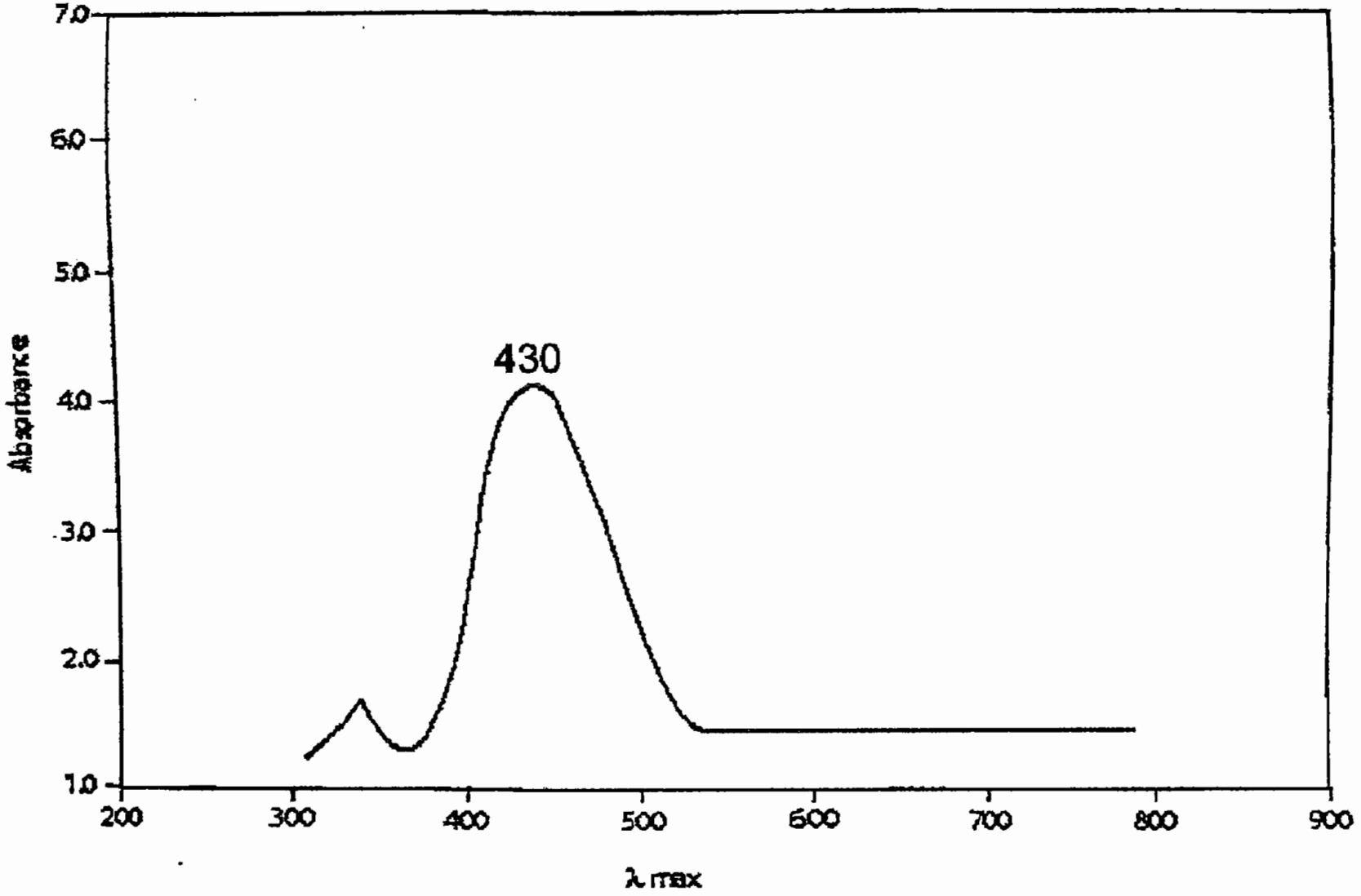


Fig.-7.1 : UV-Visible spectrum of $K^{+}[V(IV)\ (Mal)_2\ (\beta\text{-Ph-ala})]^{-}$ Complex-1

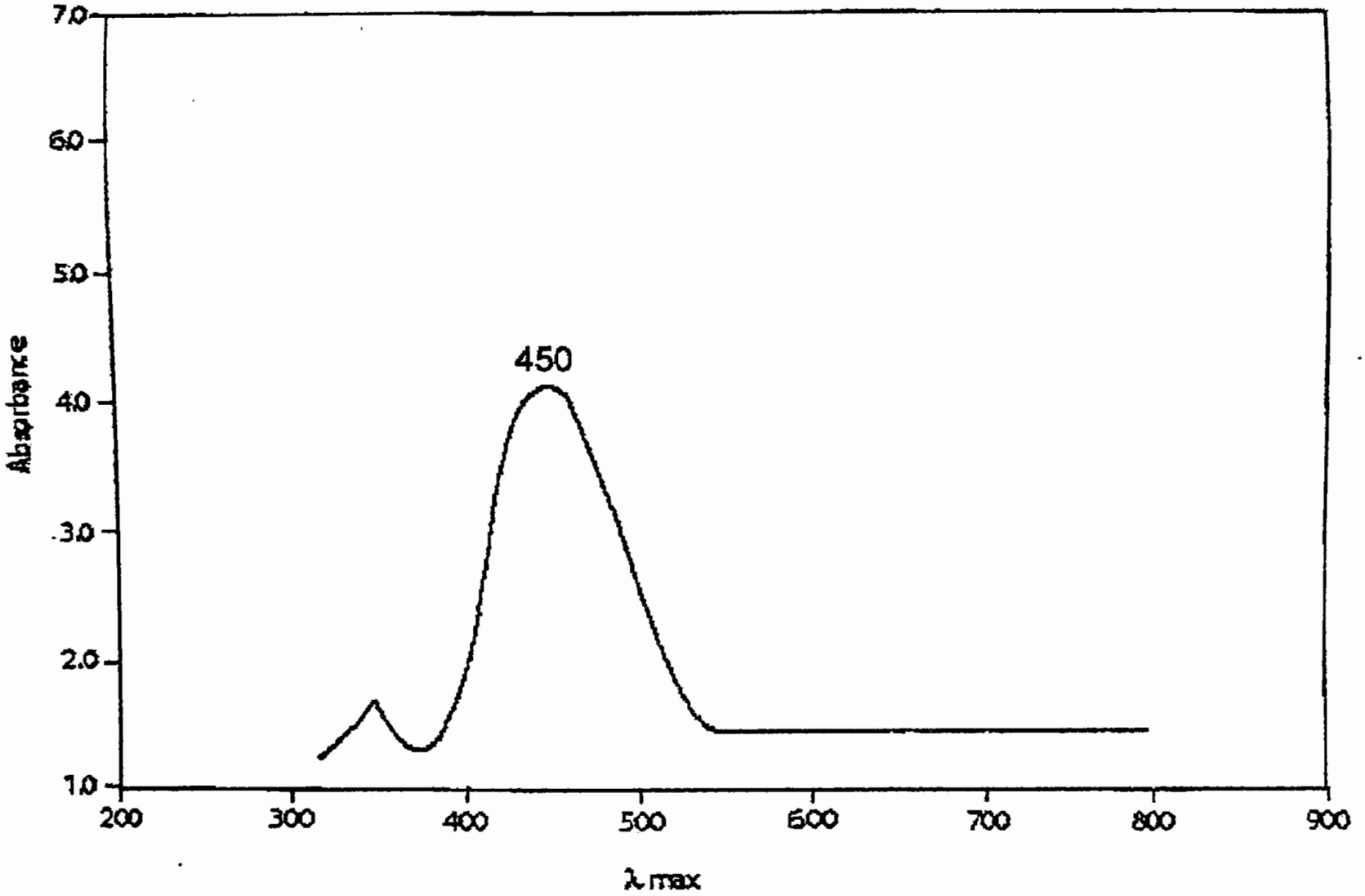


Fig.-7.2 : UV-Visible spectrum of K[V(IV) $(oxa)_2$ (β-Ph-ala)]$^-$ Complex-2

7.4 Conclusion:

From the above discussion the structure of Vanadium (IV) Complexes are assignable to octahedral geometry. On the basis of the above discussion the possible structure of the complex (2) is given in the figure (7.1). Similarly the structure of other complexes may also be given.

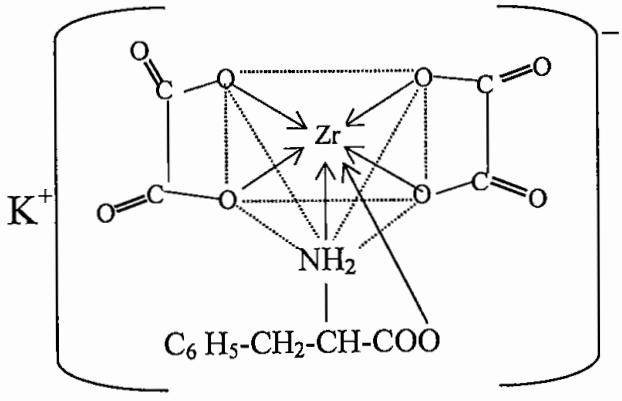


Fig. 7.1: Possible structure of the Complex (2) $K^+[V\ (IV)\ (oxa)_2\ (\beta\text{-Phala})]^-$

CHAPTER EIGHT

SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF Zr(IV) WITH IMIDES AND AMINE BASES

CHAPTER – 8

SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF Zr(IV) WITH IMIDES AND AMINE BASES

8.1 Introduction:

The studies of simple metal imide complexes are available in the literature but a very little work has been done on their mixed ligand complexes. The salts of imides with various metal ions were prepared under anhydrous conditions[174,175] because of their hydrolysable nature. Mercuric acetate with Phthalimide in presence of potassium hydroxide gave a golden yellow compound $(C_8H_4O_2N)_3$ HgK and reacts with gold salts or fulminating gold to give its complexes.[176] The copper complexes having the formula $(C_8H_4O_2N)_4$ Cu. M. nH_2O were prepared by the interaction of Phthalimide solution and copper acetate or chloride containing minimum amount caustic alkalies[177-179], where M= Li, Na, K, Rb, or Cs ions and n = 1,2,3 or 6 to prepare the brownish red Ba, copper Phthalimide complexes [Ba Cu $(C_8H_4O_2N)_4$]. In the same manner the metal complexes of succinimide have been studied in relation to their preparation, chemical analysis, magnetic properties and Infrared studies The preparation and characterization of mixed ligand complexes of Zr (IV) imides[180], homophthalate[181] and diphenates[182] have been carried out in this laboratory. Scanty information is found in recent literature about the mixed ligand complexes of amine bases.[183,184]

We report here in the preparation and characterization of some mixed ligand complexes of Zr (IV) with Phthalimide as primary and amine bases viz. Quinoline, 2-amino pyridine, 8-Hydroxy quinoline, pyridine, α-Picoline as secondary ligands.

8.2 Experimental:

8.2.1 Chemicals and reagents:

As started in Chapter-2, Page No.-22

8.2.2 Physical measurements:

As described earlier is Chapter-2, Page No.-24

8.2.3 Preparation of the imide salts:

A saturated solution of Phthalimide in alcohol was mixed with alcoholic solution of potassium hydroxide, white precipitates were immediately formed which were filtered, washed several times with alcohol and then dried in the oven at 50°C. This potassium succinimide was also similarly prepared by taking the saturated solution of succinimide in acetone. The precipitates ware also washed finally with acetone.

8.2.4 Preparation of the Zr(IV) Complexes:

The freshly prepared Zirconium Chloride 0.001 mol was dissolved in water 25 ml and the potassium salt of the imides 0.001 moles for complex-1 and 0.002 mole for complexes-2, 3, 4, 5 were mixed in the calculated ratio with constant stirring. Then 25ml of an ethanolic solution of heterocyclic amine bases was added to the resulting mixture under stirring. The precipitates formed and were filtered, washed several times with ethanol and then dried in a desiccator over silica gel.

8.3 Results and Discussion:

The Zirconium Complexes were obtained according to the following reactions:

$ZrOCl_2 . 8H_2O + 2\ Phtha + 2L + 4KOH \rightarrow [Zr(IV)(Phtha)_2L_2] + KCl + H_2O$

Where,

Phtha = Phthalimide

L = Quinoline, 8-Hydroxy quinoline, pyridine, 2-Amino pyridine, α-Picoline.

8.3.1 Elemental analysis and conductivity measurements:

The analytical data and other physical properties of the complexes are given in table 8.1. Zirconium complexes were soluble in DMF and DMSO. The values of molar conductance in DMF ranging from 2.93-10.7 $Ohm^{-1}\ cm^2\ mol^{-1}$. The molar conductance values indicate that all the complexes are non electrolyte nature.

8.3.2 Magnetic measurements:

The observed values of the effective magnetic moments of the complexes at room temperature are given in table 8.1. Zirconium (IV) Complexes were found to be diamagnetic in nature.

8.3.3 Electronic spectra:

All the complexes of Zirconium were diamagnetic in nature which indicates no change of the oxidation states of the metal ions complex formation. The spectra of the solution of Zirconium (IV) complexes showed bands at (280-330) nm region due to the charge transfer band only.[185,186] The UV-visible spectra of the complexes (1,3) are shown in Fig. (8.1,8.2).

8.3.4 IR Spectra

The distinction between O and N^- coordination of imides is not readily made by IR spectroscopy because shifts in ν(C=O) may results either from coordination through O or from the formation and coordination of the imides (N^-) nitrogen. It is expected that coordination will occur preferentially through nitrogen[187] and coordination through oxygen will be inhibited by steric hindrance. In the complexation ν (C=O) is found at about 1610-cm^{-1} compared with 1730cm^{-1} in Phthalimide, the ν(C=N) stretching frequency at 1450cm^{-1} for the imides is shifted to about 1490cm^{-1} in the complexes indicating thereby N^- formation and coordination[188]. The band about 3360cm^{-1} due to ν(N-H) disappeared in the spectra of complexes. For complexes (2) and (3) this region is observed by ν (O-H) from coordination water. Band at bout 600cm^{-1} in these cases confirmed the presence of water molecules inside the coordination sphere.[189]

The characteristic ring vibrations of the heterocyclic bases in the range (1610-1440) cm^{-1} generally show significant changes on complexation, but in complexes no (2), (3), (4) these band could not be distinguished because of overlap with ν(C=O) and ν(C=N) bands.

The in-plane and out-of-plane ring deformation modes at 501 (Phtha) and 710 cm^{-1} (succ) under positive shifts in the complexes indicating coordination through nitrogen.

Major IR data for the complexes are given in table 8.4.

Table-8.1: Physical properties of complexes

Complex No	Complexes	Colour	Melting point or d temperature ($\pm 5^0$C)	Molar conductance (ohm^{-1} Cm^2 mol^{-1})	Magnetic moment (μ_{eff}) B.M.
1	$[Zr(IV)\ (Phtha)_2\ Q_2]^{2+}$	Blue	280 d	2.93	1.73
2	$[Zr(IV)\ (Phtha)_2\ (2\text{-}Apy)_2]^{2+}$	Green	240 d	3.10	1.60
3	$[Zr(IV)\ (Phtha)_2\ (8\text{-}HQ)_2]$	Black	260 d	10.71	1.67
4	$[Zr(IV)\ (Phtha)_2\ (py)_2]^{2+}$	Brown	310 d	4.13	1.63
5	$[Zr(IV)\ (Phtha)_2\ (\alpha\text{-}Pic)_2]^{2+}$	Black	320 d	5.23	1.67

Where:

d	=	Decomposition
Dia	=	Diamagnetic
Phtha	=	Phthalimide
Q	=	Quinoline
2-Apy	=	2-Amino-pyridine
8-HQ	=	8-Hydroxy quinoline
α-Pic	=	α-Picoline
Py	=	Pyridine

Table-8.2: Data of the elemental analysis of the complexes

Complex No	Complexes	Molecular weight		Metal %		Carbon%		Nitrogen%		Hydrogen%	
		Cal	Found	Cal	Found	Cal	Found	Cal	Found	Cal	Found
1	$[Zr(IV)\ (Phtha)_2\ Q_2]^{2+}$	671.22	671.10	14.00	13.80	51.25	51.21	4.32	4.10	3.60	3.5
2	$[Zr(IV)\ (Phtha)_2\ (2\text{-}Apy)_2]^{2+}$	641.22	641.01	10.32	10.10	57.61	57.52	4.07	4.00	3.75	3.6
3	$[Zr(IV)\ (Phtha)_2\ (8\text{-}HQ)_2]$	667.22	667.20	6.82	6.71	68.24	64.14	5.32	5.20	3.88	3.7
4	$[Zr(IV)\ (Phtha)_2\ (py)_2]^{2+}$	642.22	642.13	12.03	12.00	53.13	53.03	6.17	6.11	4.13	4.0
5	$[Zr(IV)\ (Phtha)_2\ (\alpha\text{-}Pic)_2]^{2+}$	650.22	650.17	8.70	8.62	54.32	54.12	5.11	5.01	4.27	4.20

Where:

Phtha = Phthalimide
Q = Quinoline
2-Apy = 2-Amino-pyridine
8-HQ = 8-Hydroxy quinoline
α-Pic = α-Picoline
Py = Pyridine

Table-8.3: Electronic spectral data of the complexes

Complex No.	Complexes	λ max (nm)
1	$[Zr(IV)\ (Phtha)_2\ Q_2]^{2+}$	330
2	$[Zr(IV)\ (Phtha)_2\ (2\text{-}Apy)_2]^{2+}$	280
3	$[Zr(IV)\ (Phtha)_2\ (8\text{-}HQ)_2]$	300
4	$[Zr(IV)\ (Phtha)_2\ (py)_2]^{2+}$	290
5	$[Zr(IV)\ (Phtha)_2\ (\alpha\text{-}Pic)_2]^{2+}$	285

Where

Phtha	=	Phthalimide
Q	=	Quinoline
2-Apy	=	2-Amino-pyridine
8-HQ	=	8-Hydroxy quinoline
α-Pic	=	α-Picoline
Py	=	Pyridine

Table-8.4: IR data of the complexes (Band Maxima in Cm^{-1})

Complex No	Complexes	$\upsilon(O-H)$	$\upsilon(N-H)$	$\upsilon(C=O)$	$\upsilon(C=N)$	$\upsilon(C-O)$	$\upsilon(M-O)$	$\upsilon(M-N)$
1	$[Zr(IV)\ (Phtha)_2\ Q_2]^{2+}$	-	-	1630	1450	1330	500	410
2	$[Zr(IV)\ (Phtha)_2\ (2\text{-}Apy)_2]^{2+}$	-	-	1640	1440	1310	490	400
3	$[Zr(IV)\ (Phtha)_2\ (8\text{-}HQ)_2]$	3420	3340	1670	1490	1330	510	405
4	$[Zr(IV)\ (Phtha)_2\ (py)_2]^{2+}$	-	3380	1705	1465	1345	520	415
5	$[Zr(IV)\ (Phtha)_2\ (\alpha\text{-}Pic)_2]^{2+}$	-	-	1690	1465	1350	530	530

Where:

Phtha = Phthalimide
Q = Quinoline
2-Apy = 2-Amino-pyridine
8-HQ = 8-Hydroxy quinoline
α-Pic = α-Picoline
Py = Pyridine

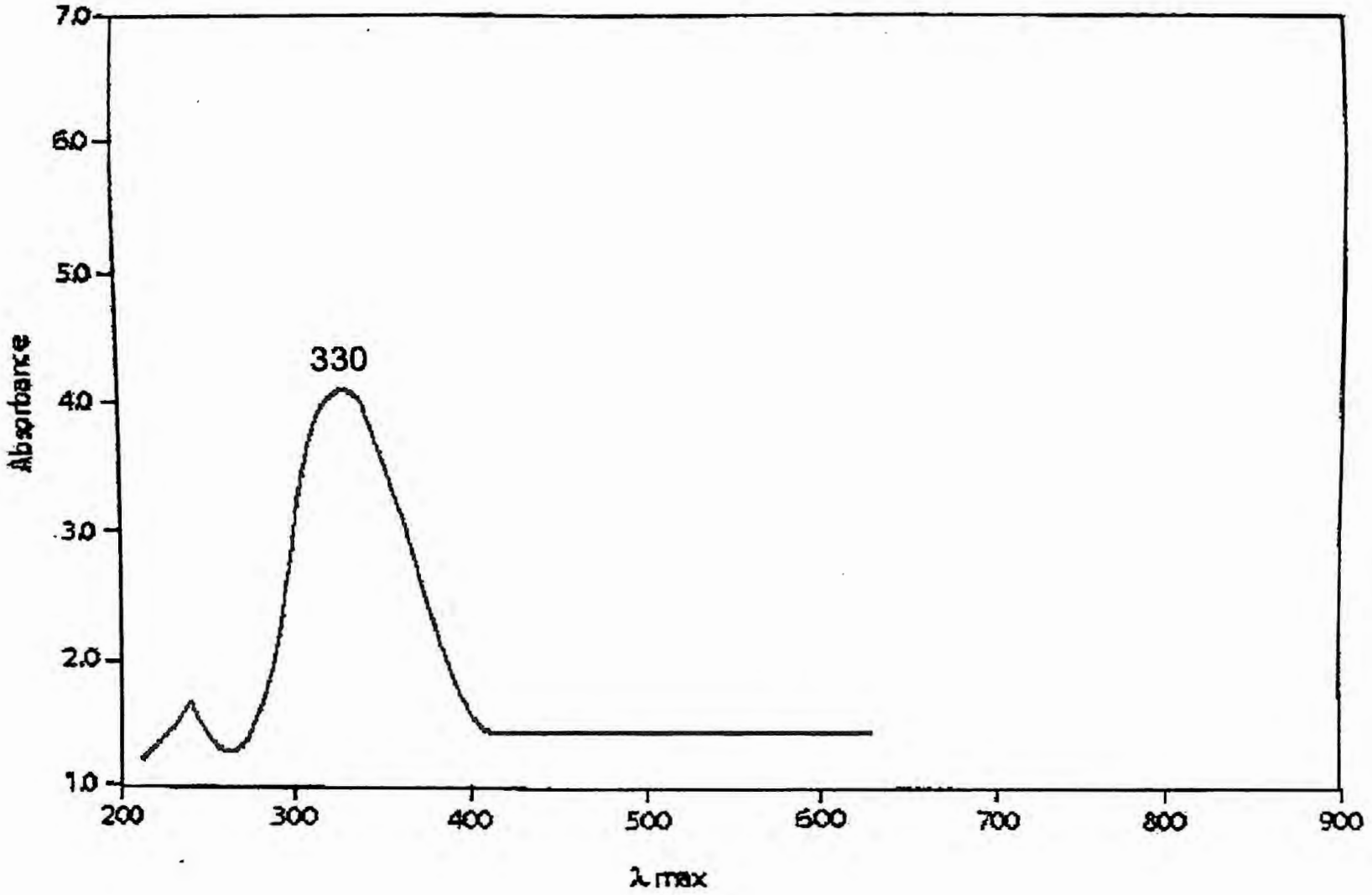


Fig.-8.1 : UV-Visible spectrum of $[Zr(IV)\ (Phtha)_2\ Q_2]^{2+}$ Complex-1

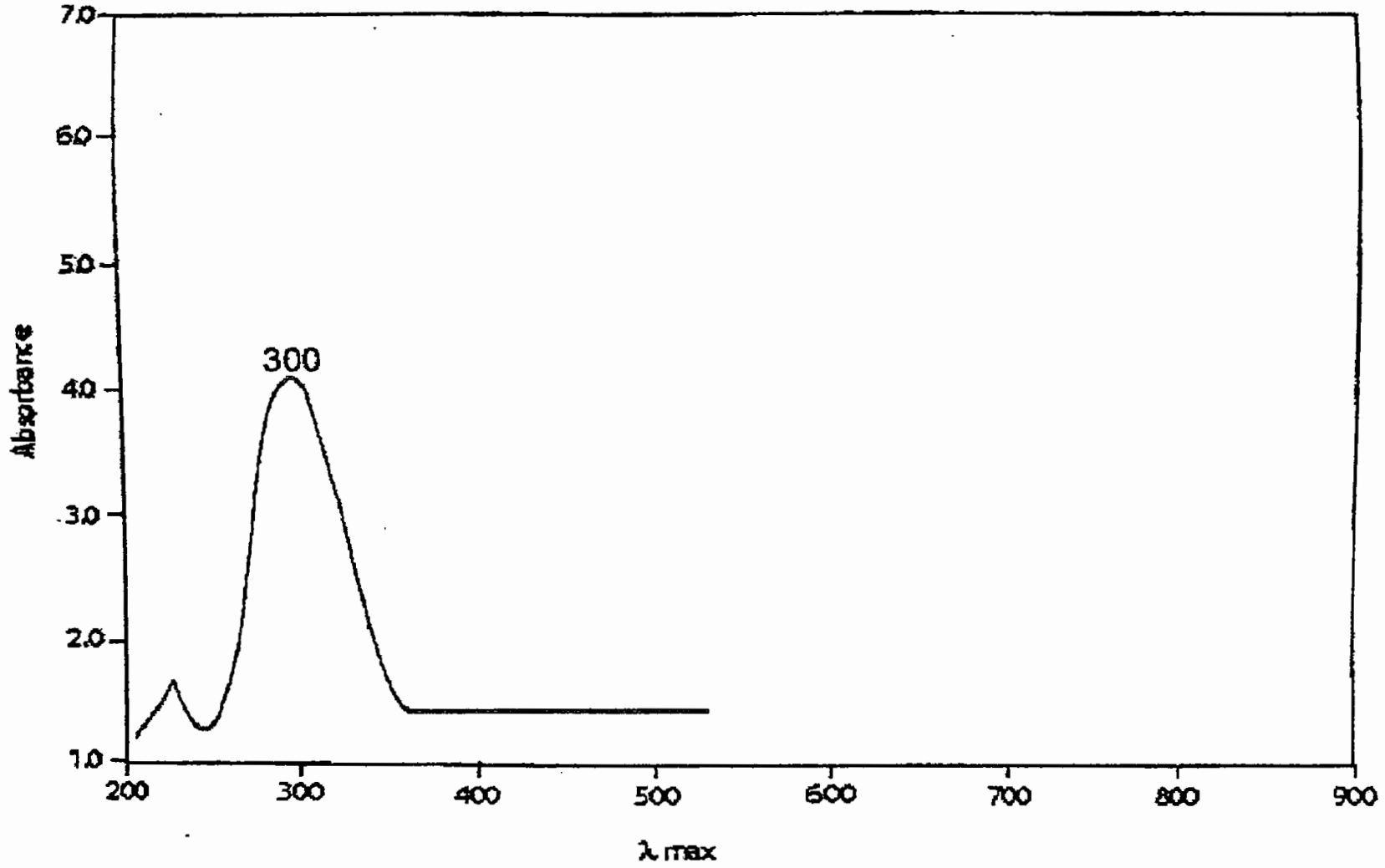


Fig.-8.2 : UV-Visible spectrum of [Zr(IV) $(Phtha)_2$ $(8\text{-}HQ)_2$] Complex-3

8.4 Conclusion:

From the above discussion octahedral structure is assignable to the prepared Zr(IV) complexes. The possible structure of cemplex-3 is in the Fig. 8.1. Similarly the structure of other complexes may also be given.

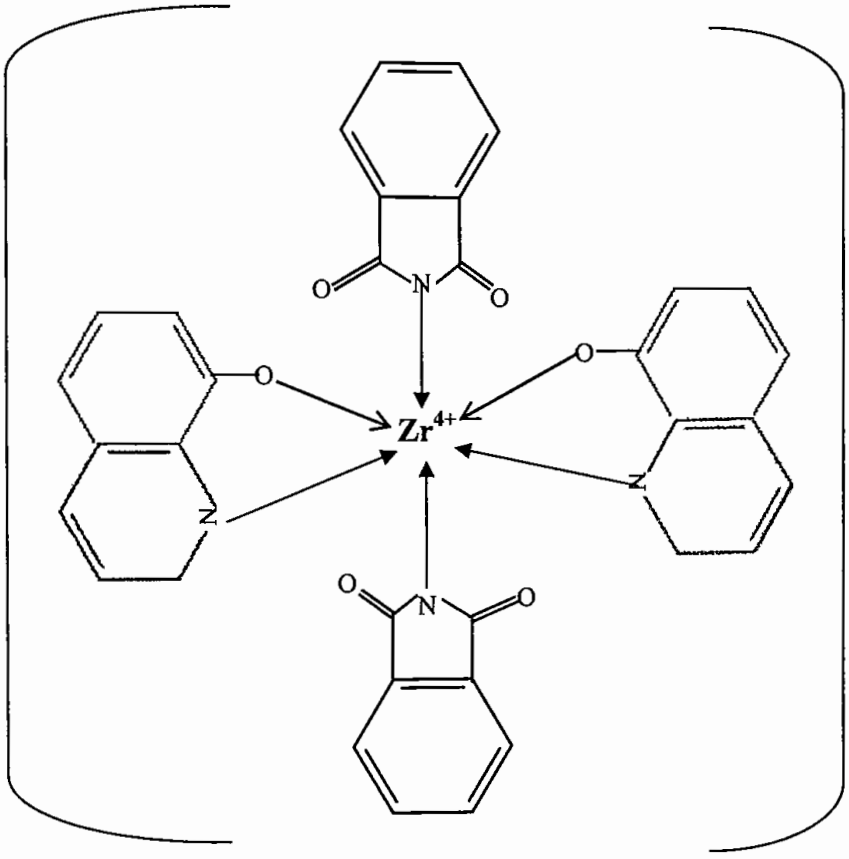


Fig 8.1: Possible structure of the complex [Zr(IV) $(Phtha)_2$ $(8\text{-}HQ)_2$]

CHAPTER NINE

ANTIMICROBIAL ACTIVITY OF SOME TRANSITION METAL COMPLEXES OF Zr(IV) AND V(IV) WITH ORGANIC ACIDS AND HETEROCYCLIC AMINES

CHAPTER – 9

ANTIMICROBIAL ACTIVITY OF SOME TRANSITION METAL COMPLEXES OF Zr(IV) AND V(IV) WITH ORGANIC ACIDS AND HETEROCYCLIC AMINES

(Part-A: Methods & Materials)

9.1 Antibacterial Screening:

9.1.1 Introduction

Antibiotic is a chemical substance which produce by microorganism or synthesized to inhibit selectively or even to destroy bacteria and other microorganisms through an antimetabolic mechanism.

The frequency of life threatening infections such as tuberculosis, cancer, AIDS etc caused by pathogenic microorganisms is increasing world-wide and becoming an important cause of morbidity and mortality in immune compromised patients. Synthetic chemical compounds constitute important sources of various bioactive compounds such as antibacterial[190] antifungal[191] and anticancer[192] compounds. The synthesized chemical compounds which are used for the treatment of infectious diseases are known as chemotherapeutic agents. Every year thousands of compounds are synthesized with an aim to find a potential chemotherapeutic agent to combat pathogenic microorganisms. But a very few compounds withstand as therapeutic agent for various methodological tests. Antimicrobial screening is one of these tests required to perform for primary selection of compounds as the therapeutic agents.

Most of the insecticides in their early stage of the inorganic compounds having bad odor and very ugly to look at.[193] The production of effective poisons in this regard began from the middle of 19th century. The arsenate compounds of Ca, Pd, S and paris green [$Cu(C_2H_3O_2)_2$ 3Cu(AsO2)] were remarkable among them.

The complexes of platinum metals are very important from medicinal point of view. Some complexes of platinum inhibit potent antitumor activity[194] and ehrlich ascities carcinoma and leukemias.[195] Kaur and co-workers reported Ni(II), Co(II), Fe(III) and Cu(II) complexes with theazoline and their fungicidal activity has been evaluated.[196]

The metal complexes of phthalic have been studied both from pharmacological[197,198] and industrial[199-203] paint of view as indicated by available literature. Bhatia *et al.* (1993) reported that all of tested forty-nine strains of fungi were reduced 2.35 triphenyl tetrazolium chloride (T.T.C.). But when malonic acid and iodoacetic acid were used as inhibitors of endogenous substrate respiration, only 50% of strains could reduce TIC.[204] Paajanen *et al.* (1999) investigated on the weather resistance of specimens treated with a mixture of tall oil and maleic anhydride in a one-year exposure test and a 670 hour ageing test in a weather chamber was superior to that of untreated specimens of wood. A fairly hard hydrophobic film developed on the wood surface during the ageing process. The treatment inhibited the growth of blue stain and mould fungi.[205]

Heterocyclic bases have a great importance in biological and industrial fields. Most of the heterocyclic bases are used as corrosion inhibitors[206] and as antibacterial, anticonvulsive, antifungal and antifouling agents.[207] The chlorinated species of 8-hydroxyquinoline has been proved as antibacterial and antifungal agents[208] and the diode derivative is administered to overcome Zn deficiency in animals.[209] Derivatives of Cu with 8-hydroxyquinoline are antifouling agents[210] and it itself protects the industrial and fungi in them.[211,212] 3-AminoPyridine has strong anti-convulsive effects.[213,214]

Some mixed ligand transition metal Zr (IV) and V(IV) complexes with some dibasic acids, viz. Oxalic acid (oxa), malic acid (Mal),

as primary and heterocyclic bases, viz. quinoline (Q), Iso-quinoline (IQ), Pyridine (Py), 2-Amino Pyridine (2apy) and 8-hydroxyquinoline (8-HQ), 2-2′-Bipyridyl as secondary ligands have been prepared and their antimicrobial studies have been carried out to perform primary selection of these complexes as the therapeutic agents.

Antibacterial screening is used to perform for primary selection of the compounds as therapeutic agent. In general, antimicrobial screening is under taken in two phases described as follows:

It is a qualitative assay to detect the presence or absence of the antimicrobial activity. The primary assay can be performed in vitro by disc diffusion assay technique.

Disc diffusion assay technique include:

(a) Plate diffusion test &

(b) Streak test.

The streak test permits the determination of the antibacterial effect of a test compound on several microorganisms simultaneously and is tensing suitable for the determination of the spectrum of the activity. But the plate diffusion test is commonly used.

Secondary assay:

It quantifies the relative potency such as minimum inhibitory concentration (MIC). The lowest concentration of antimicrobial agent required to inhibit the organism in vivo is referred to as minimum inhibitory concentration (MIC). It is done by serial dilution technique.

Antimicrobial Activity of mixed ligand complexes of Zr(IV) and V(IV) with dibasic acids and heterocyclic amines.

Ten pathogenic bacteria and eleven fungi from the department of pharmacy & department of Bio-Chemistry, University of Rajshahi

respectively and selected for antimicrobial test. Nutrient agar and potato dextrose-agar were used as bacteriological and fungicidal media respectively. The complexes were dissolved separately in dimethylsalfoxide (DMSO) to get a Concentration of 30 μg /disc; 200 μg /disc, 400 μg per/ disc, 600 μg / disc respectively. Then in vitro antimicrobial activity of these complexes were carried out by disc diffusion method. The diameter of the Zone inhibition produce by the Complexes was compared with Kanamycin (30 μg/disc) and Nystatin (200 μg/disc) for bacteria and fungi respectively.

We have also prepared their thirteen new complexes but their are six antimicrobial activity was done.

Table-9.1: List of the Complexes

Sl.No	Complex	Complexes	Active Complexes
1	02	$K^+[Zr(IV)(oxa)_2(2\text{-}Apy)]^-$	$K^+[Zr(IV)(oxa)_2(2\text{-}Apy)]^-$
2	03	$2K^+[Zr(IV)(oxa)_2\ (8\text{-}HQ)]^{2-}$	$2K^+[Zr(IV)(oxa)_2\ (8\text{-}HQ)]^{2-}$
3	04	$[Zr(IV)(oxa)_2(Py)_2]$	$[Zr(IV)(oxa)_2(Py)_2]$
4	06	$[Zr(IV)(oxa)_2(\alpha - Pic)_2]$	-
5	08	$K^+[Zr(IV)(oxa)_2\ (2,2'\text{-}Bipy)]^-$	-
6	10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$
7	12	$K^+[Zr(IV)(Mal)_2\ (2,2'\text{-}Bipy)]^-$	-
8	13	$[Zr(IV)(Mal)_2(IQ)_2]$	-
9	15	$[Zr(IV)(Mal)_2(\alpha - Pic)_2]$	-
10	20	$K^+[V(IV)(oxa)_2(ala)]^-$	$K^+[V(IV)(oxa)_2(ala)]^-$
11	22	$[V(IV)(EA)_2\ (ala)_2]$	-
12	25	$K^+[V(IV)(oxa)_2\ (2,2'\text{-}Bipy)]^-$	$[V(IV(oxa)_2\ (2,2'\text{-}Bipy)_2]$
13	29	$K^+[V(IV)(Mal)_2(ala)]^-$	-

Table-9.2: Test organisms used for the study

Sl.No	Name of The Bacteria	Nature	Bacteria Code
1	Shigella sonnei	Gram negative	M006
2	Shigella dysenteria	Gram negative	M007
3	Shigella shiga	Gram negative	M008
4	Escherichia Coli	Gram negative	M009
5	Klebsiella SP.	Gram negative	M010
6	Sarcina. Lutea	Gram Positive	M012
7	Bacillus Megterium	Gram Positive	M013
8	Bacillus Subtilis	Gram Positive	M014
9	Staphylococcus aurous	Gram Positive	M015
10	Streptococcus-β-haemolyticus	Gram Positive	M016

9.1.2 Principle of disc diffusion assay method:

In the diffusion assay, the surface of a nutrient agar medium contained in a petridish, is uniformly inoculated with the test bacterial culture. The test solution of compounds are added to such a plate by pipetting them either into circular holes cut into the agar or into previously applied glass or metal cylinders or they are absorbed on the filter paper discs, which are put on the surface of the agar. The test substances diffuse into the agar with decreasing concentration towards the periphery. In the case of positive reaction, an inhibitory zone can be observed after incubation for several hours where the concentration exceeds the MIC for that particular organism. The diameter of the zone of inhibition is proportional to the logarithm of the concentration of the antibiotic. The diameter of the zone

of inhibition under constant experimental conditions depends on the following factors:

(a) Thickness of the agar medium.

(b) Diffusion rate of the test compound.

(c) Inoculum time.

(d) Temperature of cultivation.

(e) Culture medium composition.

(f) Growth rate of the test organism.

(g) Concentration of test organisms inoculated in the medium.

(h) Concentration of drug per disc.

9.1.3 Mechanism by which disc diffusion assay technique acts

A number of events occur simultaneously during this process:

(i) Initially the dried disc absorbs water from the surrounding test medium and the drug becomes dissolved in it.

(ii) The drug migrates through the adjacent test medium due to concentration gradient.

(iii) This results in a gradual change of the drug concentration in the agar surrounding each disc.

The plates seeded with test organism disc containing antibiotics were kept at low temperature (4°C) for 24 hours and then incubated at 37.5 for 24 hours in an incubator. A clear zone of inhibition was observed where the drug was present higher than the inhibitory concentration.

9.1.4 Apparatus and reagents

(i) Filter paper for disc making.

(ii) Standard disc (Kanamycin K- 30).

(iii) Sample

(iv) DMSO

(v) Alcohol (95%)

(vi) Nutrient Agar (DIFCO)

(vii) Petridishes

(viii) Inoculating loop

(ix) Sterile cotton

(x) Sterile Forceps

(xi) Spirit lamp and match box

(xii) Test-tubes

(xiii) Micropipette.

(xiv) Laminar air flow unit

(xv) Autoclave (KT-30L)

(xvi) Refrigerator

(xvii) Incubator (OSK 9639A)

9.1.5 Sterilization procedure

Antimicrobial screening was carried out in laminar air flow unit and all types of precautions were highly maintained to avoid any contamination during the test. UV light has switched on before working in laminar hood for one half hour to avoid any accidental contamination. Petridishes and other glass wares were sterilized by autoclaving at a temperature of 121°C at pressure of 1 5 lbs/sq inch for 1 5 minutes.

9.1.6 Test materials used for the study:

The isolated antibiotics were used for the investigation of antibacterial activity. The antibiotic was dissolved in DMSO and concentration (100 µg/disc) was used to make a better correlation of the antibacterial activities. Kanamycin (30µ/disc) was used as a standard.

9.1.7 Method :

As the test bacteria are pathogenic. These bacteria were collected from Department of Bio-chemistry Microbiology, Rajshahi Medical College and Hospital, Botany Department, Rajshahi University, Bangladesh. All steps of the work were done with high precaution and aseptic condition which are mentioned below. These antibacterial activity test was carried out at the Bio-chemistry Department, Rajshahi University.

9.1.8 Culture media :

The following media were used to demonstrate the antibacterial activity and for subculture of the organisms.

(i) Nutrient agar medium.

(ii) Nutrient broth medium.

(iii) Mueller-Hinton medium

In the present case, Nutrient agar media (D1FCO) was used for testing the sensitivity of the organisms to the test materials and to prepare fresh cultures.

Composition of the Nutrient Agar medium (DIFCO) for 1000 ml is as follows:

Ingredients	Amounts
Peptons A	5 gm
Beef extract	5 gm
Yeast extract	15 gm
Sodium chloride	5 gm
Agar powder	15 gm
Distilled water q.s.	1000 ml

pH is maintained at about 7.2 ± 1 at 25°C.

9.1.9 Media preparation:

The Instant nutrient agar (Difco) medium was weighted and then reconstituted with distilled water in a conical flask according to specification (2.3% w/v). It was then heated in a water bath to dissolved the agar until a transparent solution was obtained.

9.1.10 Preparation of the fresh culture of the pathogenic bacteria:

The media prepared in the above section were dispensed to a number of clean test tubes, each containing 5 ml, to prepare slants. The test tubes were plugged with cotton and sterilized in an autoclave at 121°C and 15 lbs/sq-inch pressure for 15 minutes. After sterilization, the test tubes were kept in an inclined position for solidification. These were then incubated at 37.5°C to ensure sterilization. Finally, the slants were streaked with pure culture of the test organisms under a laminar air flow unit and incubated at 37.5°C for 24 hours to assure the growth of test organisms.

9.1.11 Preparation of test plates:

(i) A number of Petridishes were washed and sterilized by dry heat.

(ii) Nutrient agar media prepared in the previous section was poured in 15 ml quantity in clean test tubes and plugged with cotton.

(iii) The test tubes were sterilized by autoclaving and allowed to cool at about 50°C.

(iv) The media in the test tubes inoculated with fresh culture of the test bacteria by means of a sterile loop in aseptic condition and agitated to ensure uniform dispersion of organisms into the media.

(v) Finally, the media were poured into sterile Petridishes in aseptic condition. The Petridishes were rotated several times, first clockwise and then anticlockwise, to assure homogeneous distribution of test organisms. Thus, plates were ready for sensitivity test and stored in refrigerator at 4°C.

9.1.12 Preparation of discs containing samples:

For the preparation of discs containing samples the following procedure was utilized.

(a) Sample discs:

(i) Solution of the antibiotic was prepared in DMSO in such a manner that 10 µL contained 100 µg of the antibiotic.

(ii) Filter paper discs were taken in a petridish and sterilized by autoclaving.

(iii) µL of the test solution was applied on a disc with the help of a micropipette. Thus disc containing 100 µg of antibiotic was prepared.

(iv) These discs were left for a few minutes in aseptic condition for complete removal of the solvent.

(b) Standard discs:

These were used as positive control to ensure the activity of standard antibiotic against the test organisms as well as for comparison the response produced by the known antibacterial agent with that produced by test samples. In our investigation, Kanamycin (k-30 µg/disc) standard disc was used as reference.

9.1.13 Placement of disc, diffusion and incubation:

Precaution:

The discs were placed in such that the discs were no closer than 15 mm to the edge of the place and for enough apart to prevent overlapping the zones of inhibition.

Procedure:

(i) The sample impregnated discs and standard antibiotic discs were placed gentle on the solidified agar plates seeded with test organisms to ensure contact with the media, with the help of sterile forceps.

(ii) The plates were then kept in a refrigerator for at 4°C for 24 hours in order to provide sufficient time to diffuse into the medium.

(iii) They were finally incubated at 37.5°C for 24 hours in an incubator.

9.2 Results and Discussion:

It has been observed that some drugs (ligands) increase the activity when administered as metal complexes or their metal chelates. The antibactireal activity of the metal complex 2, 3, 4, 10, 20, 25 and the ligand are studied against eight pathogenic bacteria viz.

1. Shigella sonnei
2. Shigella dysenteriae
3. Shigella shiga.
4. Escherichia coli
5. Klebsialla SP.
6. Sarcina lutea.
7. Bacillus megterium
8. Bacillus Subtilis

And the results are given in table (9.3-9.10). It is seen that the complex 3 showed the most activities above eight pathogenic bacteria as shown in Fig. (9.4-9.9)

The complex 3 showed the best activity against shigella shiga and less activity 3 against Escherichia coli (-ve) and the complex 20 showed the best activity against Shigella dysenteriae (-ve) and less activity against Sarcina lutea.

All the results are compared with the standard compound kanamycin as shown in the table (9.3-9.10). From these result it is concluded that the complexes showed good activities against the eight pathogenic bacteria as compared to the standard compound, kanamycin. It is evident that the metal ion plays the key role to show good activities, because the ligands did not show activity.

Table-9.3: Antibacterial activity of the complexes 2, 3, 4, 10, 20, 25 against shigella sonnei (-ve) (M006)

Complex No.	Complexes	Diameter of inhibition zone of bacteria in different complexes. (mm)			
		200 μg / disc	400 μg / disc	600 μg / disc	Kanamycin 30 μg / disc
2	$K^+[Zr(IV)(oxa)_2(2Apy)]^-$	14	16	18	26
3	$2K^+[Zr(IV)(oxa)(8\text{-}HQ)]^{2-}$	22	21	19	24
4	$[Zr(IV)(oxa)_2(py)_2]$	14	15	19	27
10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	12	16	13	28
20	$K^+[V(IV)(oxa)_2(ala)]^-$	17	19	22	12
25	$K^+[V(IV)(oxa)_2\ (2,2' - Bipy)]^-$	9	10	11	28

Where :

oxa = Oxalic acid
2-Apy = 2-Amino Pyridine
8-HQ = 8 Hydroxy quinoline
py = Pyridine
ala = Alanine
2,2′-Bipy = 2,2′-Bipyridyl

Table-9.4: Antibacterial activity of the complexes 2, 3, 4, 10, 20, 25 against shigella dysenteria (-ve) (M007)

Complex No.	Complexes	Diameter of inhibition zone of bacteria in different complexes. (mm)			
		200 µg / disc	400 µg / disc	600 µg / disc	Kanamycin 30 µg / disc
2	$K^+[Zr(IV)(oxa)_2(2Apy)]^-$	09	12	16	25
3	$2K^+[Zr(IV)(oxa)(8\text{-}HQ)]^{2-}$	23	13	24	21
4	$[Zr(IV)(oxa)_2(py)_2]$	11	13	10	26
10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	11	24	17	27
20	$K^+[V(IV)(oxa)_2(ala)]^-$	24	26	18	26
25	$K^+[V(IV)(oxa)_2\ (2,2' - Bipy)]^-$	10	13	15	25

Where :

oxa = Oxalic acid
2-Apy = 2-Amino Pyridine
8-HQ = 8 Hydroxy quinoline
py = Pyridine
ala = Alanine
2,2'-Bipy = 2,2'-Bipyridyl

Table-9.5: Antibacterial activity of the Complexes 2, 3, 4, 10, 20, 25 against shigella shiga (-ve) (M008)

Complex No.	Complexes	Diameter of inhibition zone of bacteria in different complexes. (mm)			
		200 μg / disc	400 μg / disc	600 μg / disc	Kanamycin 30 μg / disc
2	$K^+[Zr(IV)(oxa)_2(2Apy)]^-$	13	14	16	22
3	$2K^+[Zr(IV)(oxa)(8\text{-}HQ)]^{2-}$	25	22	21	26
4	$[Zr(IV)(oxa)_2(py)_2]$	14	16	18	26
10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	10	15	16	19
20	$K^+[V(IV)(oxa)_2(ala)]^-$	18	20	24	28
25	$K^+[V(IV)(oxa)_2\ (2,2' - Bipy)]^-$	8	9	10	27

Where :

oxa = Oxalic acid
2-Apy = 2-Amino Pyridine
8-HQ = 8 Hydroxy quinoline
py = Pyridine
ala = Alanine
2,2′-Bipy = 2,2′-Bipyridyl

Table-9.6: Antibacterial activity of the complexes 2, 3, 4, 10, 20, 25 against Escherichia coli (-ve) (M009)

Complex No.	Complexes	Diameter of inhibition zone of bacteria in different complexes. (mm)			
		200 µg / disc	400 µg / disc	600 µg / disc	Kanamycin 30 µg / disc
2	$K^+[Zr(IV)(oxa)_2(2Apy)]^-$	12	14	17	23
3	$2K^+[Zr(IV)(oxa)(8\text{-}HQ)]^{2-}$	23	27	19	21
4	$[Zr(IV)(oxa)_2(py)_2]$	11	13	19	26
10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	11	17	13	27
20	$K^+[V(IV)(oxa)_2(ala)]^-$	26	21	18	21
25	$K^+[V(IV)(oxa)_2\ (2,2' - Bipy)]^-$	12	11	13	26

Where :

oxa = Oxalic acid
2-Apy = 2-Amino Pyridine
8-HQ = 8 Hydroxy quinoline
py = Pyridine
ala = Alanine
2,2′-Bipy = 2,2′-Bipyridyl

Table-9.7: Antibacterial activity of the complexes 2, 3, 4, 10, 20, 25 against Klebsiella SP(-ve) (M010)

Complex No.	Complexes	Diameter of inhibition zone of bacteria in different complexes. (mm)			
		200 µg / disc	400 µg / disc	600 µg / disc	Kanamycin 30 µg / disc
2	$K^+[Zr(IV)(oxa)_2(2Apy)]^-$	13	15	19	27
3	$2K^+[Zr(IV)(oxa)(8\text{-}HQ)]^{2-}$	19	23	25	24
4	$[Zr(IV)(oxa)_2(py)_2]$	12	13	17	22
10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	9	24	16	28
20	$K^+[V(IV)(oxa)_2(ala)]^-$	17	19	22	12
25	$K^+[V(IV)(oxa)_2\ (2,2' - Bipy)]^-$	0	0	0	9

Where :

oxa = Oxalic acid
2-Apy = 2-Amino Pyridine
8-HQ = 8 Hydroxy quinoline
py = Pyridine
ala = Alanine
2,2′-Bipy = 2,2′-Bipyridyl

Table-9.8: Antibacterial activity of the complexes 2, 3, 4, 10, 20, 25 against Sarcina Lutea (+ve) (MO12)

Complex No.	Complexes	Diameter of inhibition zone of bacteria in different complexes. (mm)			
		200 μg / disc	400 μg / disc	600 μg / disc	Kanamycin 30 μg / disc
2	$K^+[Zr(IV)(oxa)_2(2Apy)]^-$	12	14	15	23
3	$2K^+[Zr(IV)(oxa)(8\text{-}HQ)]^{2-}$	24	23	17	26
4	$[Zr(IV)(oxa)_2(py)_2]$	10	12	14	24
10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	10	27	18	29
20	$K^+[V(IV)(oxa)_2(ala)]^-$	19	21	24	29
25	$K^+[V(IV)(oxa)_2\ (2,2' - Bipy)]^-$	12	13	16	26

Where :

oxa = Oxalic acid
2-Apy = 2-Amino Pyridine
8-HQ = 8 Hydroxy quinoline
py = Pyridine
ala = Alanine
2,2′-Bipy = 2,2′-Bipyridyl

Table-9..9: Antibacterial activity of the complexes 2, 3, 4, 10, 20, 25 against Bacillus Megterium (+ve) (M013)

Complex No.	Complexes	Diameter of inhibition zone of bacteria in different complexes. (mm)			
		200 μg / disc	**400** μg / disc	**600** μg / disc	**Kanamycin 30** μg / disc
2	$K^+[Zr(IV)(oxa)_2(2Apy)]^-$	12	16	19	27
3	$2K^+[Zr(IV)(oxa)(8\text{-}HQ)]^{2-}$	21	30	16	22
4	$[Zr(IV)(oxa)_2(py)_2]$	14	16	20	23
10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	10	23	12	28
20	$K^+[V(IV)(oxa)_2(ala)]^-$	20	25	22	30
25	$K^+[V(IV)(oxa)_2\ (2,2' - Bipy)]^-$	24	26	28	31

Where :

oxa = Oxalic acid
2-Apy = 2-Amino Pyridine
8-HQ = 8 Hydroxy quinoline
py = Pyridine
ala = Alanine
2,2′-Bipy = 2,2′-Bipyridyl

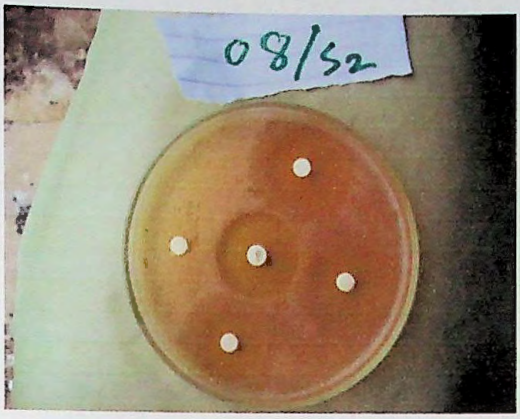
Table-9.10: Antibacterial activity of the complexes 2, 3, 4, 10, 20, 25 against Bacillus Subtilis (+ve) (MO14)

Complex No.	Complexes	Diameter of inhibition zone of bacteria in different complexes. (mm)			
		200 μg / disc	400 μg / disc	600 μg / disc	Kanamycin 30 μg / disc
2	$K^+[Zr(IV)(oxa)_2(2Apy)]^-$	8	10	15	23
3	$2K^+[Zr(IV)(oxa)(8\text{-}HQ)]^{2-}$	20	22	29	21
4	$[Zr(IV)(oxa)_2(py)_2]$	13	15	19	23
10	$2K^+[Zr(IV)(Mal)_2\ (8\text{-}HQ)]^{2-}$	9	11	14	28
20	$K^+[V(IV)(oxa)_2(ala)]^-$	19	21	28	31
25	$K^+[V(IV)(oxa)_2\ (2,2' - Bipy)]^-$	23	25	29	31

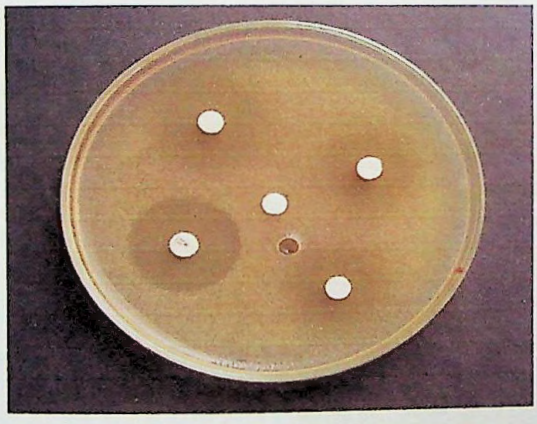
Where :

oxa = Oxalic acid
2-Apy = 2-Amino Pyridine
8-HQ = 8 Hydroxy quinoline
py = Pyridine
ala = Alanine
2,2′-Bipy = 2,2′-Bipyridyl

Complex-2



Complex-3



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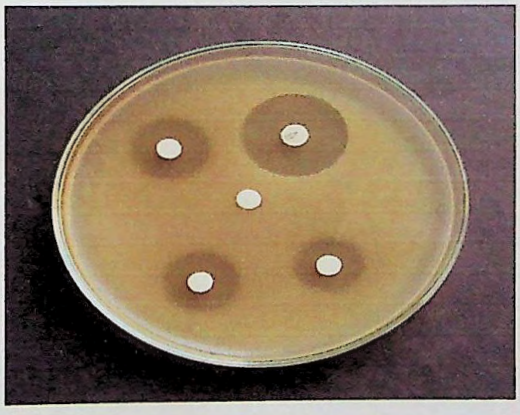
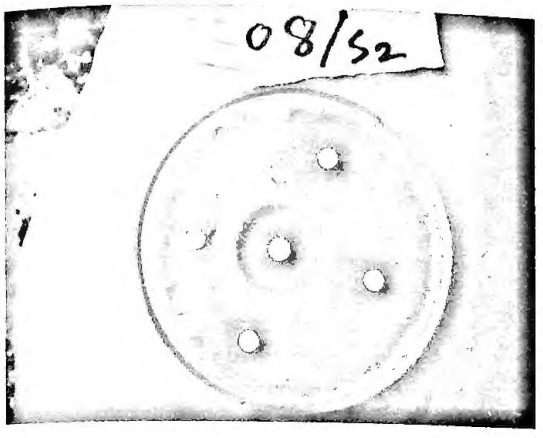
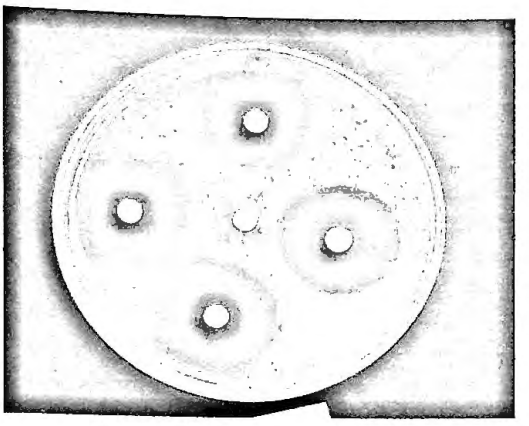


Complex-25

Fig-9.4: Antibacterial activity of the Complexes 2, 3, 4, 10, 20, 25 against shigella sonnei (-ve) (M006)



Complex-2



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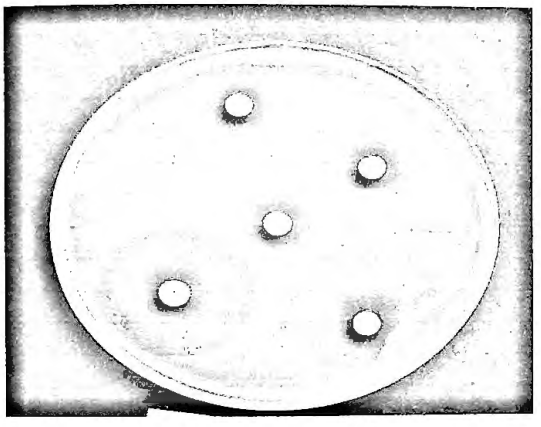
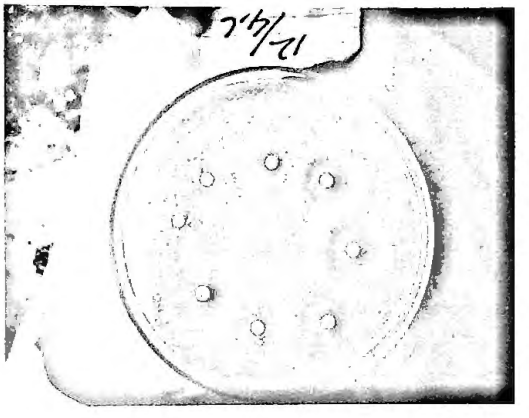


Complex-4



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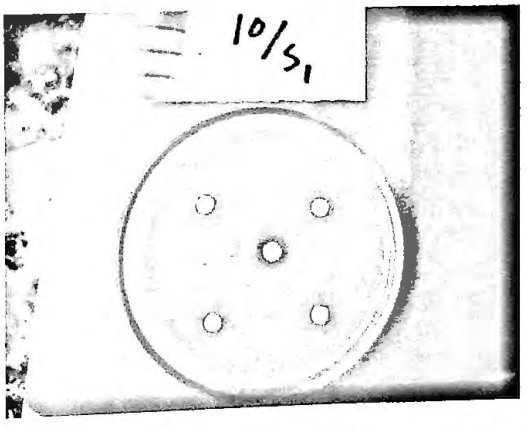
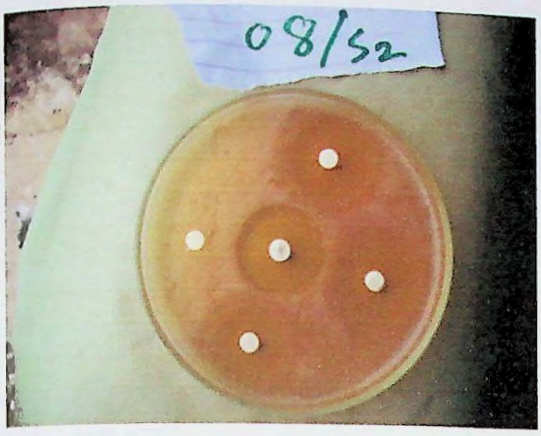


Complex-25

Fig-9.5: Antibacterial activity of the Complexes 2, 3, 4, 10, 20, 25 against shigella shiga (-ve) (M008)



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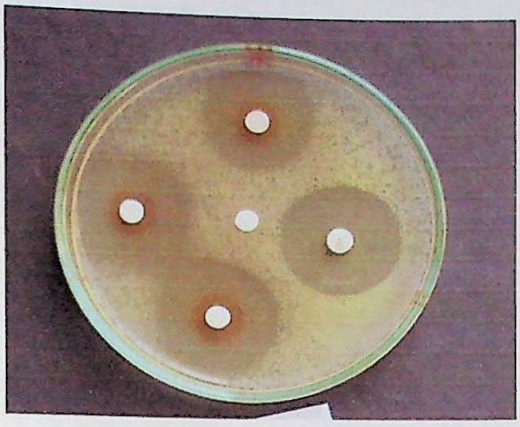

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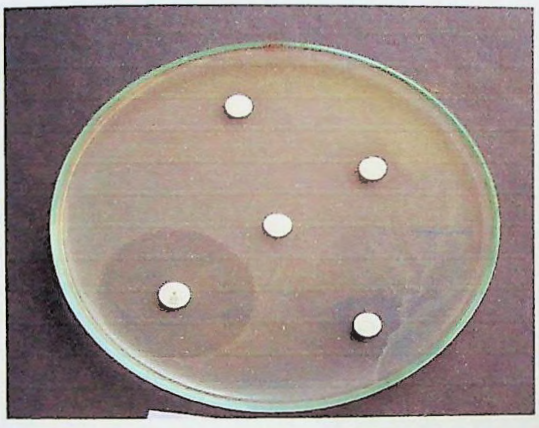
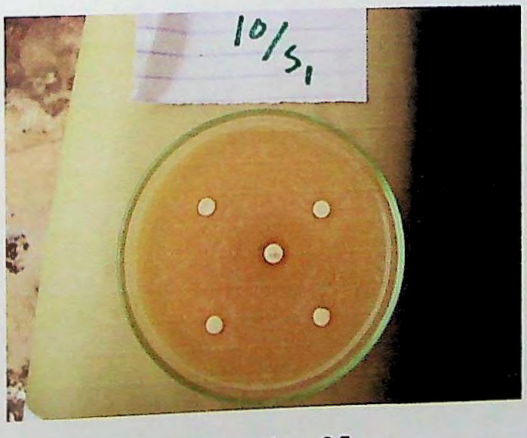


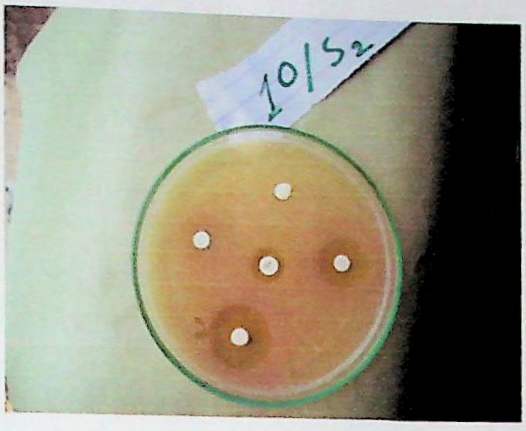
Complex-4

Complex-20



Complex-25

Fig-9.5: Antibacterial activity of the Complexes 2, 3, 4, 10, 20, 25 against shigella shiga (-ve) (M008)



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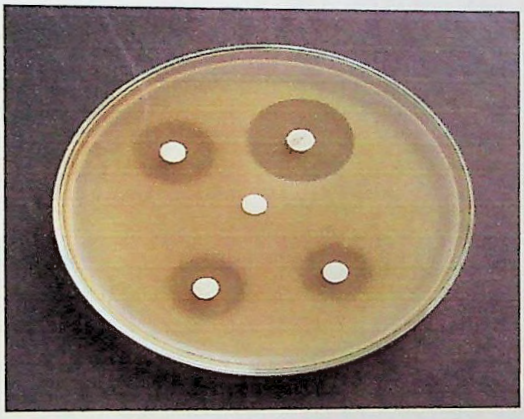

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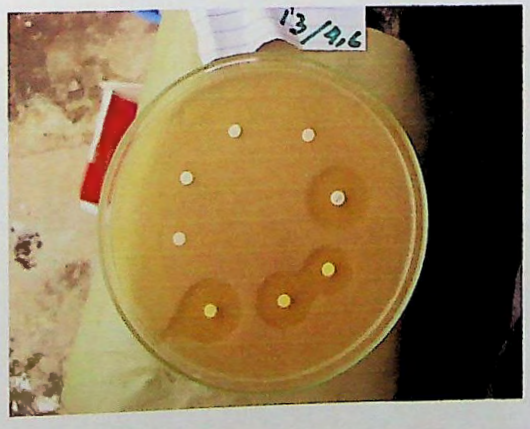
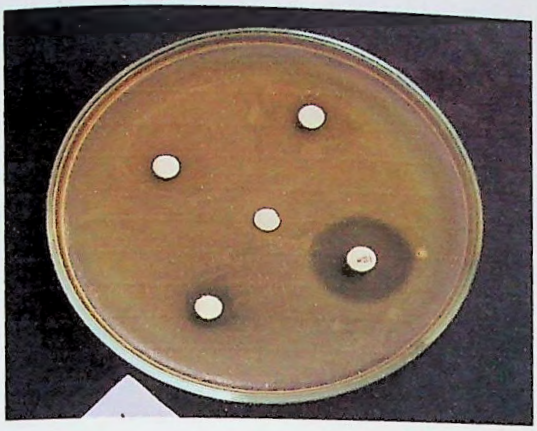
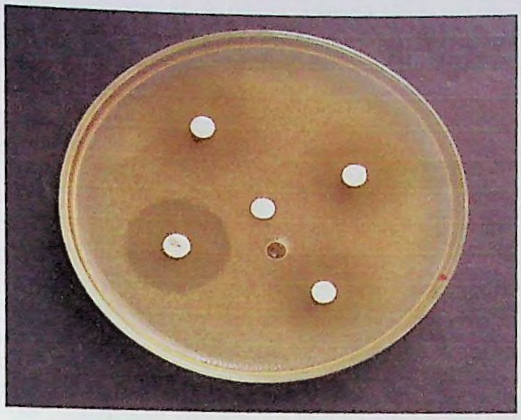


Complex-4

Fig-9.6: Antibacterial activity of the Complexes 2, 3, 4, 10, 20, 25 against Escherichia coli (-ve) (M009)

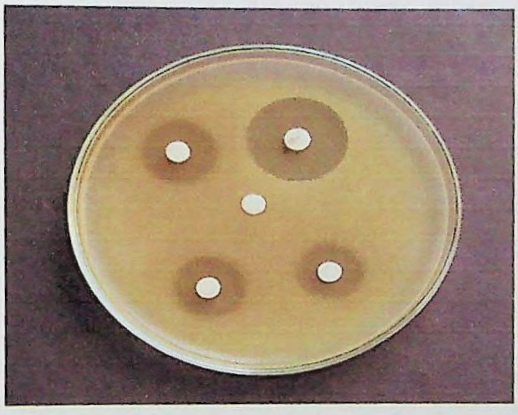


Complex-2

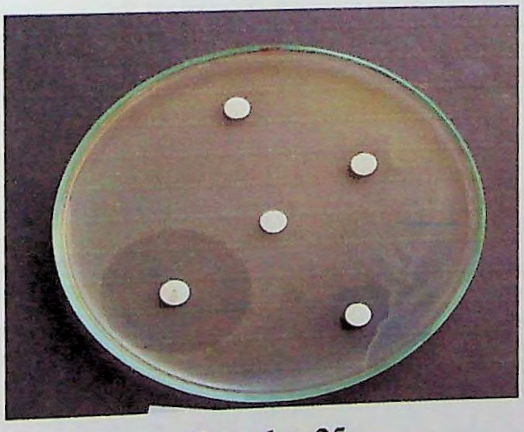


Complex-3

Complex-4

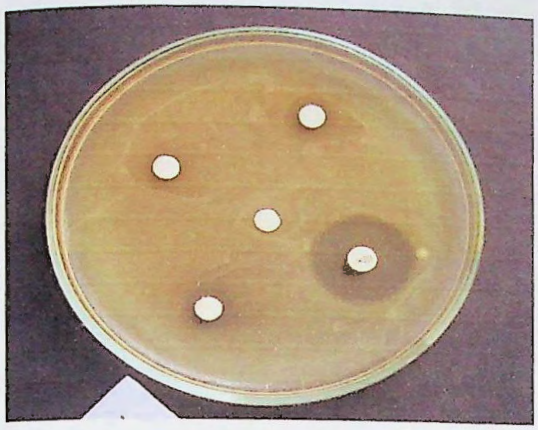


Complex-20

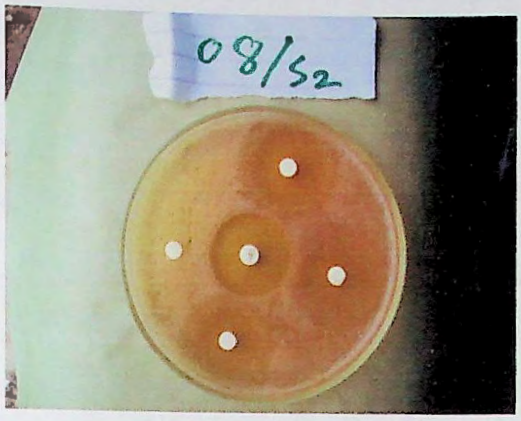


Complex-25

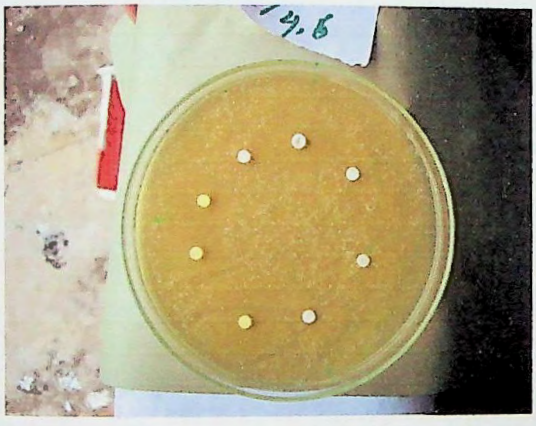
Fig-9.7: Antibacterial activity of the Complexes 2, 3, 4, 10, 20, 25 against Klebsiella SP(-ve) (M010)



Complex-2:



Complex-3:



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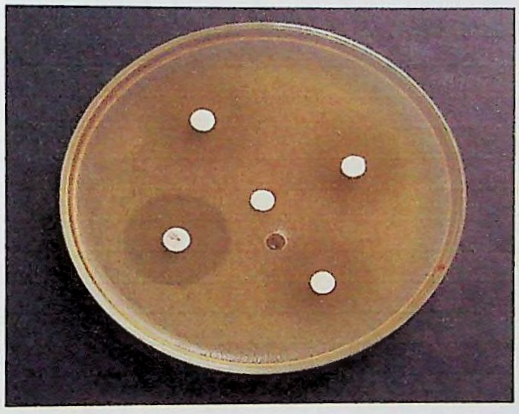
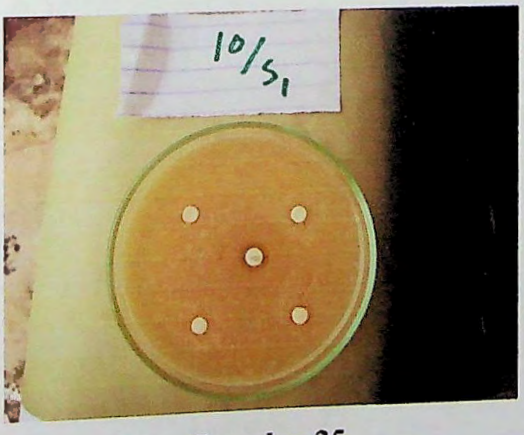
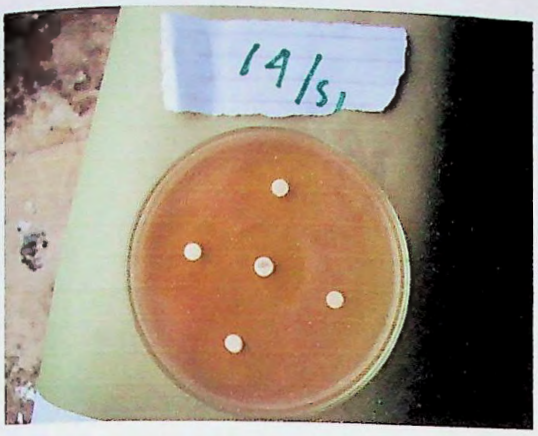


Complex-20:

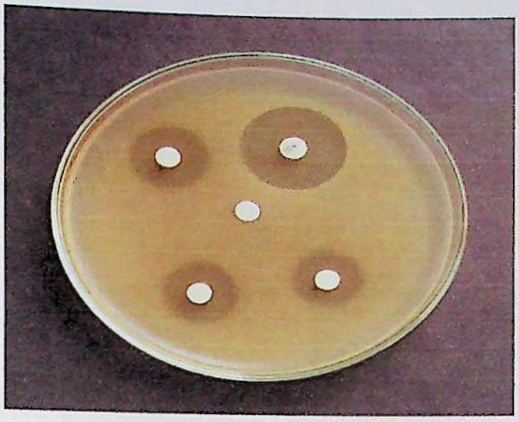


Complex-25

Fig-9.8: Antibacterial activity of the Complexes 2, 3, 4, 10, 20, 25 against Sarcina lutea (+ve) (MO12)

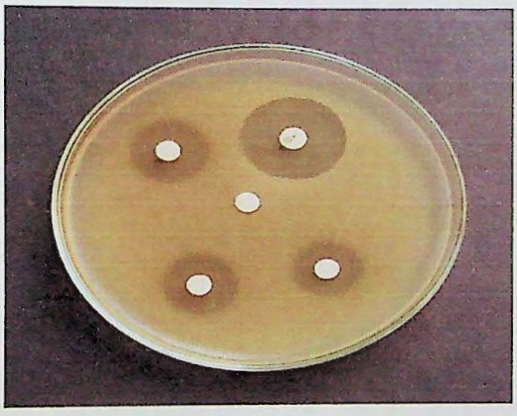


Complex-2:



Complex-3:

Complex-4:



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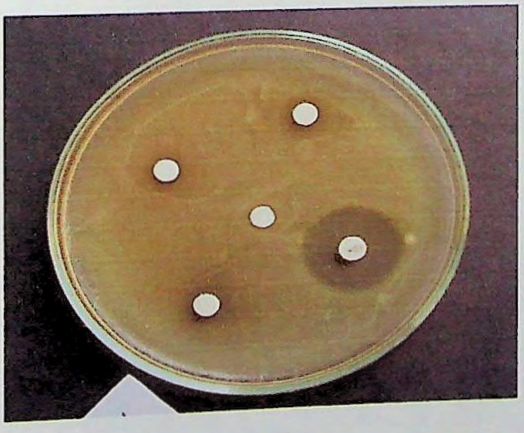


Complex-25:

Fig-9.9: Antibacterial activity of the Complexes 2, 3, 4, 10, 20, 25 against Bacillus Subtilis (+ve) (MO14)

CHAPTER TEN

ANTIFUNGAL ACTIVITY OF SOME TRANSITION METAL COMPLEXES OF Zr(IV) AND V(IV) WITH ORGANIC ACIDS AND AMINE BASES

CHAPTER – 10

ANTIFUNGAL ACTIVITY OF SOME TRANSITION METAL COMPLEXES OF Zr(IV) AND V(IV) WITH ORGANIC ACIDS AND AMINE BASES

10.1 Introduction and principle:

The susceptibility of microorganism to antimicrobial agents can be determined in vitro by a number of methods. The disc diffusion technique[215,216] is widely acceptable for preliminary investigations of compounds which are suspected to possess antimicrobial properties. Diffusion procedure, as normally used in essentially a qualitative test which allocates the organism as susceptible, intermediate (moderately susceptible) or resistant categories.

Diffusion assays are based on the ability of antibiotics to diffuse from a confined source through a PDA gel and create a concentration gradient.

In the disc diffusion technique, dried filter paper discs containing known amount of test compound are placed on agar plates seeded with test organisms. These plates are kept in refrigerator (4°C) for 24 hours.

Initially the dried discs absorb water from the surrounding test medium and the drug is dissolved. The drug migrates through the adjacent test medium by concentration gradient of the drug according to physical law that govern diffusion of molecules through an agar gel.[217] As a result, there is a gradual change of drug concentration in the agar surrounding each discs. Then the plates are incubated in an incubator at 37°C for 24-48 hours.

As the antibiotic diffusion progresses, microbial multiplication also proceeds. After an initial log phase, a logarithmic fungal phase is initiated. At that moment fungal multiplication proceeds more rapidly than the drug can diffuse and fungal cell which are not inhibited by the antimicrobial agents will continue to multiply until a lawn of growth can be visualized. No growth will be appear in the area where drug is present in inhibitory concentration.

Generally, more susceptible the test organism, the larger is the zone of inhibition. Antimicrobial activities of the test samples are expressed by measuring the zone of inhibition observed around the area. The diameter of the inhibition zone is usually measured to understand the extent of inhibition in different concentrations.

The size of the inhibitory zones depends principally on the following factors

1. Intrinsic antimicrobial sensitivity of the test sample.
2. Growth rate of the test microorganisms.
3. Diffusion rate of the drug which is related to its water solubility.
4. Number of inoculumn of the freshly seeded test organisms.
5. Amount of the test sample or disc.
6. Thickness of the test medium in the petridishes.
7. Thickness of the disc paper.
8. Concentration of test organisms inoculated in the medium.
9. Concentration of drug per disc.
10. Composition of the culture medium.

10.2 Apparatus and reagents:

I. Filter paper

II. Samples

III. DMSO

IV. Alcohol (95%)

V. PDA medium

VI. Petridishes

VII. Inoculating loop

VIII. Sterile cotton

IX. Sterile forceps

X. Spirit lamp & match box

XI. Test-tubes

XII. Micropipette

XIII. Laminar flow unit

XIV. Autoclave (KT-30L)

XV. Refrigerator

XVI. Incubator (OSK 9639A).

10.3 Procedure:

The test organisms are pathogenic. For this reason all steps of the work were done with high precaution and aseptic condition which are mentioned below. The test organisms were collected from the Department of Botany, Rajshahi University. All steps of the work were carried out at the plant pathology laboratory, Botany Department, Rajshahi University.

10.4 Test Organisms:

The following fungi have been studied:

a. Plant Pathogens:

i. Trichoderma species

ii. Fusarium species

iii. Botarydiptoden species

iv. Aspergillus flavus

v. Aspergillus species

vi. Mucor species

vii. Penicillium

viii. Bipolaris species

b. Human Pathogen

i. Epidermophton floccosum

ii. Aspergilus niger

iii. Candida albicans

10.5 Sterilization procedure:

Antifungal screening was carried out in a laminar air flow unit and all types of precautions were highly maintained to avoid any contamination during the test. UV light has switched on before working in laminar hood for one half hour to avoid any accidental contamination. Petridishes and other glass wares were sterilize by autoclaving at a temperature of 121°C and a pressure of 15 lbs/sq inch for 15 minutes. Blank discs were first kept in a covered petridish and then subjected to dry heat sterilization at 180°C for 1 hour. Latter, they were kept in laminar hood under UV light for 30 minutes.

10.6 Culture media:

A) PDA (potato, Dextrose, Agar) media:

PDA medium was used as culture media composition of the PDA medium for 1000 ml is as follows

1. Potato(Piece of cutting)	200 gm
2. D-glucose	20 gm
3. Agarto solidify	20 gm
4. Distilled water	1000 ml
5. Adjusted p1-1	5-6

To prepare PDA medium potatoes were cut into small pieces and weighed about 200g and boiled in 500 ml of distilled water for an hour, filtered and volume was made up to 500 ml by adding more distilled water Then glucose and agar added in 500 ml distilled water and stirred and boiled it for a few minutes. And there after this 500 ml solution of agar and glucose added with that 500 ml. The pH of the medium was then adjusted 5 to 6 (by using lactic acid) which is acidic in nature. The medium was then sterilized at I 21°C under pressure for 15 minutes.

B. Sobourand medium

The composition of the sobourand medium for 1000 ml is as follows:

1. Glucose	20 gm
2. Agar powder	20 gm
3. Peptone	10 gin
4. Distilled water	1000 ml

To prepare sobourand rnedium, the amount of each constituent was calculated from above chart. Peptone, glucose of above mentioned amount were taken in a conical flask and distilled water was added (volume should be less than 1000 ml). The contents were heated in a water bath to make a clear solution. The pH of the solution was then adjusted at 6.5. Required amount of agar powder was added to the solution and distilled water was added sufficiently to make the final volume (1000 ml). Again the total volume was heated in a water bath to obtain a clear solution. The medium was then sterilized at 121°C at 1515/sq. inch pressure for 15 minutes.

N.B.

In PDA media plant pathogenic fungi could be grown because potatoes contain starch. Human pathogenic fungi could be grown in Sobourand medium (selective) because it contains protein.

10.7 Preparation of fresh culture:

The media prepared in the above section were dispensed to a number of clean test tubes, each containing 5 ml, to prepare slants. The test tubes were plugged with cotton and sterilized in an autoclave at 121°C and 15 lbs/sq-inch pressure for 1 5 minutes. After sterilization, the test tubes were kept in an inclined position for solidification. These were then incubated at 37.5°C to ensure sterilization. Finally, the slants were streaked with pure culture of the test organisms under a laminar air flow unit and incubated at 37.5°C for 48 hours to assure the growth of test organisms.

10.8 Preparation of test plates:

The test plates were prepared according to the following procedure.

(a) Potato Dextrose-Agar (PDA) prepared in the previous section was poured in 15 ml quantity in clean test tubes and plugged with cotton.

(b) The test tubes were sterilized by autoclaving and allowed to cool at about 50°C.

(c) The media in the test tubes were inoculated with fresh culture of the test fungi by means of a sterile loop in aseptic condition and agitated to ensure uniform dispersion of organizes into the media.

(d) Finally, the media were poured into sterile petridishes in aseptic condition. The petridishes were rotated several times, first clockwise and then anticlockwise, to assure homogeneous distribution of test organisms. Thus, plates were ready for sensitivity test and stored in refrigerator at 4°C.

10.9 Preparation of discs containing samples:

For the preparation of discs containing samples the following procedure was utilized.

(a) Sample discs

(a) Solution of the anitbiotics were prepared in DMSO in such a manner that 20 tl contained 200 ig of the antibiotics.

(b) Filter paper discs were taken in a petridish and sterilized by autoclaving.

(c) 20 jil of the test solution was applied on a disc with the help of a micropipette. Thus disc containing 200 ig of antibiotics were prepared.

(d) These discs were left for a few minutes in aseptic condition for complete removal of the solvent.

(b) Standard discs

These were used as positive control to ensure the activity of standard antibiotic against the test organisms as well as for comparison of the response produced by the known antifungal agent with that produced by test samples. In our investigation, Fluconazol (50 jig/disc) standard disc was used as reference.

(c) Control discs

Sterilized filter paper discs were taken of known concentration was applied on the discs with the help of a micropipette. The solvents from the discs were evaporated by hot air blower.

10.10 Placement of the discs and incubation:

(a) The sample impregnated discs and standard antibiotic discs were placed gently on solidified potato-dextrose agar plates seeded with the organisms to ensure contact with the media, with the help of sterile forceps.

(b) The plates were then kept in a refrigerator at 4°C for 24 hours so that the materials absorbed onto discs could get sufficient time to diffuse into the media.

(c) Finally, the plates were incubated at 37.5°C for 48 hours.

10.11 Measurement of the zone of inhibition:

After 48 hour incubation, the antifungal activities of the antibiotics were determined by measuring the zone of inhibition in term of mm by a transparent scale. Inhibitory zone obtained by samples were compared to that of the standard disc and control disc. Results obtained from these are listed in table from 7.13.

Table-10.1: Results of the antifungal activity of the complexes

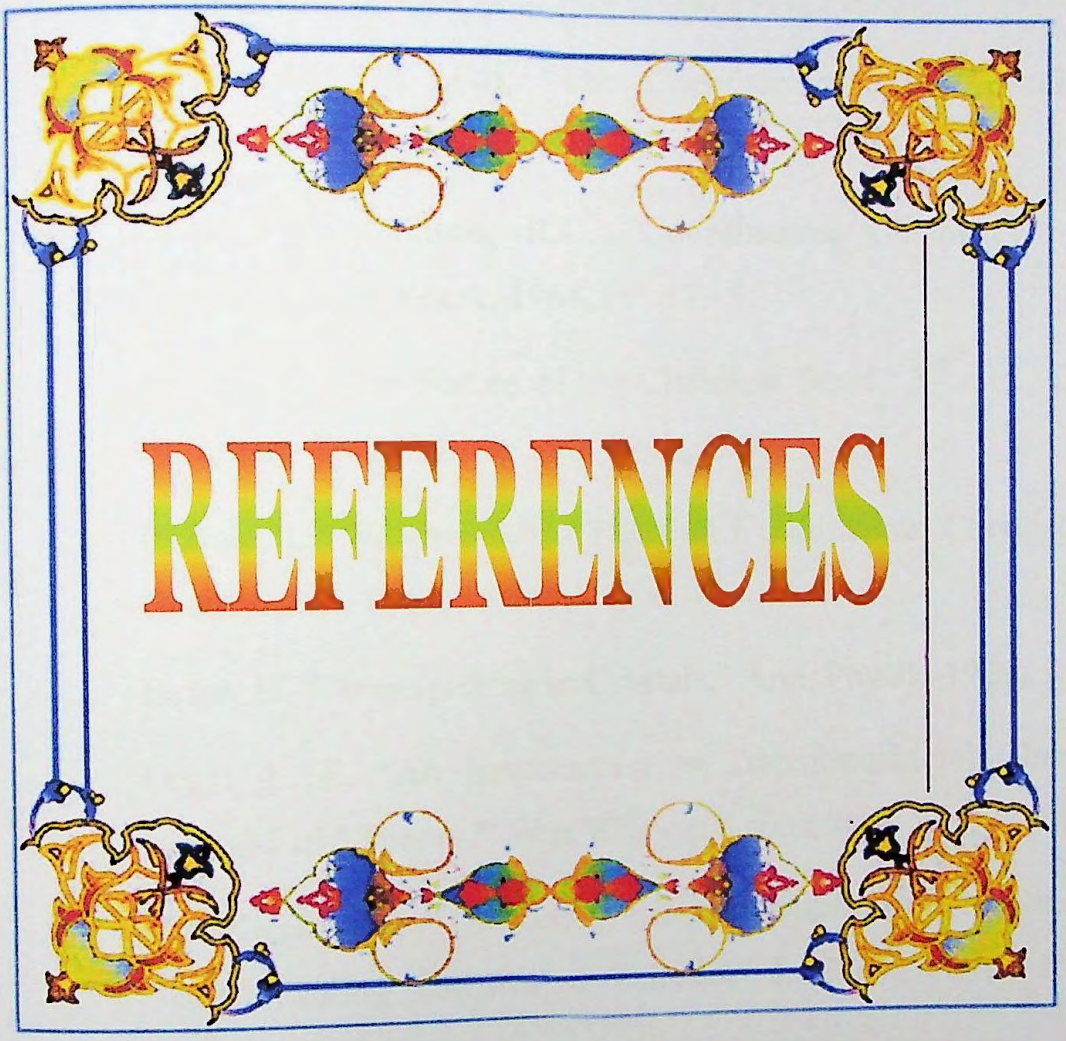
Code No	Test of organisms	Diameter of inhibition zone of fungal in different complexes in (mm)						
		2	3	4	10	20	25	Flucon-azole 200 µg/disc
Plant Pathogen								
R001	Trichoderma species	7	15	20	6	8	5	18
R002	Fusarium species	8	13	25	10	7	9	19
R003	Botarydiptoden species	00	19	8	11	9	7	9
R004	Aspergillus flavus	11	20	14	9	8	13	18
R005	Aspergillus species	9	15	13	7	18	10	12
R006	Mucor species	15	8	10	21	7	00	29
R007	Penicillium	13	9	16	18	10	6	20
R008	Bipolaris species	10	20	35	10	9	16	16
Human Pathogen								
R009	Epidermophton floccosum	8	9	11	10	8	7	22
R010	Aspergilus niger	14	15	17	7	9	00	30
R011	Candida albicans	15	18	19	13	14	00	20

Where,

2. $[Zr(IV)(oxa)_2(2\text{-}Apy)_2]$
3. $2K^+[Zr(IV)(oxa)_2(8\text{-}HQ)]^{2-}$
4. $[Zr(IV)(oxa)_2(Py)_2]$
10. $2K^+[Zr(IV)(Mal)_2(8\text{-}HQ)]^{2-}$
20. $K^+[V(IV)(oxa)_2(ala)]^-$
25. $K^+[V(IV)(oxa)_2(2,2'\text{-}Bipy)]^-$

10.12 Conclusion:

The antifungal activities of the ten metal complexes against 11 pathogenic fungi are presented in table 7. 12. It was found that the metal complexes 4> 3> 20> 10 were moderate active against all pathogenic fungi. The zones of inhibition of the complexes were lower than standard, Fluconozole. The complexes 25>2 were less active against all pathogenic fungi and on comparison with the results of the zone of inhibition with standard in Fluconozole, these activities were much lower than that of standard. On the other hand, the remaining complexes such as 4, 10 and 8 were given positive results against all pathogenic fungi. On comparison with the results of zone of inhibition with standard, Fluconozole, these activities were approximately zero.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