STUDIES ON TRANSITION METAL COMPLEXES OF SCHIFF BASES DERIVED FROM AMINOACIDS

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By

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CERTIFICATE

This is to certify that the thesis entitled STUDIES ON TRANSITION METAL COMPLEXES OF SCHIFF BASES DERIVED FROM AMINOACIDS is an authentic record of the research work carried out by Mrs. G. INDIRA DEVI under my supervision in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry of the University of Calicut and further that no part thereof has been presented before for any other degree

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DECLARATION

I here by declare that this thesis entitled STUDIES ON TRANSITION METAL COMPLEXES OF SCHIFF BASES DERIVED FROM AMINOACIDS submitted to the University of Calicut in partial fulfillment of the requirements for the Doctoral Degree in Chemistry is a bonafied research work done by me under the supervision and guidance of Dr. Geetha Parameswaran.

I further declare that this thesis has not previously formed the basis for the award of any degree, diploma, or other similar title

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G. INDIRA DEVI

DEDICATED
TO
THE EVERLOVING MEMORY
OF
MY BELOWED

FATHER

PREFACE

Coordination compounds have been a challenge to the inorganic chemist since they were identified in the nineteenth century. Transition metal complexes with Schiff bases as ligands have been amongst the most widely studied coordination compounds. The chelating characters of Schiff bases towards transition metals have been very interesting. Schiff may be regarded as the first to have defined the composition of a metal complex with such a ligand. Researches in this field of chemistry possess greater attention now a day.

In the present course of studies the complexation of five new Schiff bases anthracene carboxaldehyde L-histidine, anthracene carboxaldehyde L-tyrosine, anthracene carboxaldehyde glycine, anthracene carboxaldehyde DL - alanine and anthracene carboxaldehyde L - phenyl alanine have been studied extensively. Their metal chelates were synthesized and characterized. Characterization of metal complexes has been done based on physicochemical studies. These results are presented in Part I.

The thermal studies of fifteen metal complexes were carried out on the basis of mechanistic and non mechanistic equations. The results of these studies have been reported in Part II.

Based on the X-ray powder diffraction pattern the crystal lattice and cell dimensions of Cr(III), Ni (II) , Cu (II), Zn (II) , Fe (III) and Ag (I) complexes have been reported in Part III.

Part IV explores the application of selected complexes as antifungal agents. The antifungal activities were studied by using *phytophthora capsici*. For the sake of brevity, symbols and formulae instead of names have been used in this thesis, which are given in the abbreviations at the beginning of the thesis. The summary and the references can be had from the last pages of the thesis.

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Above all I submit all my thoughts and actions to the Almighty who always guides me in the path of righteousness

G. INDIRADEVI

ABBREVIATIONS

ACA - Anthracene Carboxaldehyde D L Alanine

ACG - Anthracene Carboxaldehyde glycine

ACH - Anthracene Carboxaldehyde L histidine

ACPA }
ACP } - Anthracene Carboxaldehyde phenyl alanine

ACT - Anthracene Carboxaldehyde L tyrosine

AC - Anthracene Carboxaldehyde

B. M - Bohr Magnetone

L - Ligand moiety in a complex

M - Central metal ion in a complex

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SYNTHESIS AND CHARACTERIZATION

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PART I
INTRODUCTION

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

PART I

SYNTHESIS AND CHARACTERIZATION

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CHAPTER 1

INTRODUCTION

The world is so beautiful, because of its colors. The main reason for these colors is due to coordination compounds. The transition metal complexes are one of the major contributors of color in our lives. The world of transition metal compounds is a familiar and unfamiliar, a new and an old world. These compounds represent a world that is old, in terms of its use, new in terms of our understanding

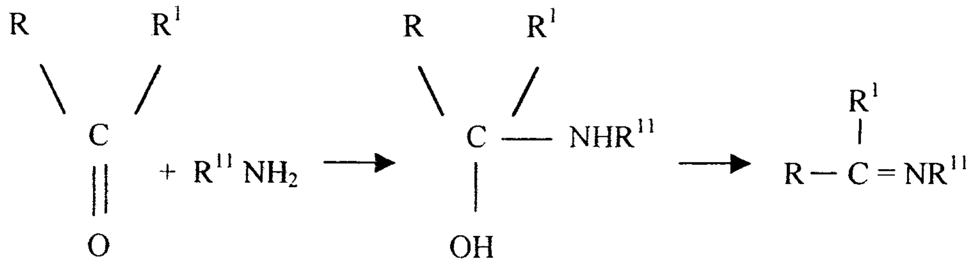
As early as 1798,Tassert carried out a reaction between cobalt chloride hexa hydrate, $CoCl_3.6H_2O$, and ammonia. He obtained orange colored crystals corresponded to have the composition, $CoCl_3.6NH_3$ [1] .This experimental observation was a puzzle to the chemists and this discovery marks real beginning of coordination chemistry. Later after 100 years, Alfred Werner who was the first Nobel Prize winner in chemistry made a real break through in the world of coordination chemistry. Werner's famous coordination theory [2] was a watershed in the history of coordination compounds. It is the number and diversity of the metal complexes that provide the wealth of transition metal chemistry. Transition metal ions were classified on the basis of their electron accepter properties as "class a and class b" by Ahrland et al[3] and Pearson[4] has suggested the terms "hard" and "soft" to describe the members of "class a and class b". Hard acid is a type [a] metal ion like Mn^{2+} ,$Fe^{3+}$and, hard base is a ligand such as ammonia or fluoride ion. Conversely a soft acid is a type [b] metal ion such as Cu^{+}, Cd^{2+}, Hg^{2+} and a soft base is a ligand like SCN^{-}, CN^{-} or the iodide ion. Since there is no sharp demarcation line between the two, a borderline class also exists, which include the Lewis acids like Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} . The hard species, both acids and bases are slightly polarizable small species, and soft acids and bases tend to be larger and more polarizable. For a given ligand stability of complexes with dipositive transition metal ions follows a stability order called, natural order of stability or Irving - Williams series of stability[5], which is $Mn < Fe < Co < Ni < Cu > Zn$ for the first transition series. Most dramatic reactions of coordination ligands occur in the complexes of transition metals are because of the inherent stability of these complexes and also due to the high nuclear charge of metal ions.

Coordination chemistry is currently one of the most significant and rewarding area of research in inorganic chemistry and it provide many contributions to humanity. Coordination compounds have a key roll in the existence and development of mankind. Manganese has an important roll in photosynthesis.[6] Amino acid complexes are involved in the active transport of metal ions across various biological membranes .[7] Rubridoxin contain $(Cys - S)_4$ Fe and low molecular weight proteins known as metalothioneins [8] contain large number of amino acid residues bonded to metal ions. The physiological importance of dihydroxy phenyl alanine and its use as a therapeutic agent for manganese poisoning [9] reveal the significance of amino acid complexes. Blue copper proteins occur in some bacteria known as cyano bacteria. Red sea is so named because of these red pigmented cyano bacteria, which is a complex that float on the surface. The colored rain falls in the recent period occurred, in different parts of Kerala are also due to the presence of protein complexes with metal ions. The greater zinc nutritional value of human milk as opposed to bovine milk is related to the nature of zinc complex[10], which is present as labile citrate complex in the former, but as a tightly bound protein complex in the later. Vitamin

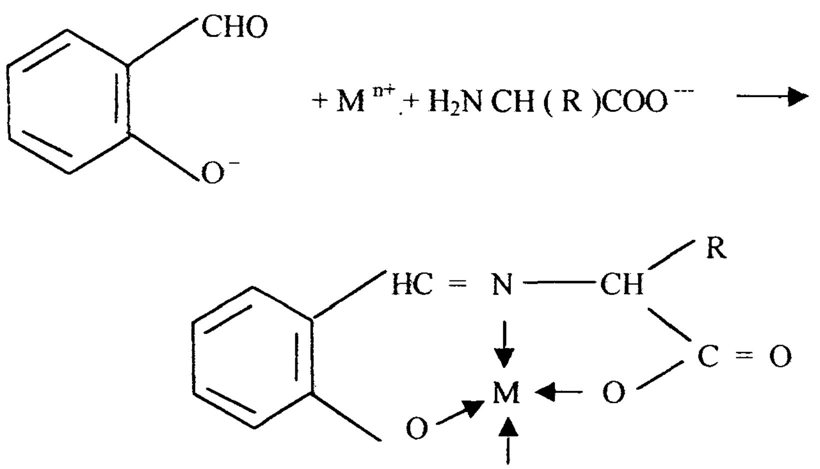
B_{12} is a red crystalline cobalt-containing compound and has a functional role in preventing pernicious anemia. It also serves as a co enzyme in hydrogen and methyl transfer reactions and as a growth-promoting factor for several microorganisms. A number of metal ions are essential for the proper functioning of all living cells, which is achieved by selective chelation. Due to miscoordination[11], accumulation of these metal ions causes physiological disorders producing disease like Wilson's disease. The transition metal complexes have a wide use in different areas such as catalyst, qualitative and quantitative study, biological systems etc.

SCHIFF BASE COMPLEXES

Transition metal complexes with Schiff bases as ligands have been amongst the most widely studied coordination compounds. Schiff bases and their metal compounds have found a multitude of uses. [12,13] Azo methine group >C=N is the functional group of Schiff base. The condensation of primary amines with aldehyde and ketones, give a product, known as imine, which contains >C=N.



If there is an aryl group bonded to the nitrogen atom or to the carbon atoms, the imines formed are called Schiff bases. Schiff [14] may be regarded as the first who reported the synthesis of complexes with such ligands. In the present day usage, the term Schiff base denotes all compounds, possessing azo methine group $> C = N$, which is intermediate between $>C=C<$ and $>C=O$ group[15] . By the presence of a lone pair of electrons on the nitrogen atom and the general electron donating character of double bond, compounds containing $>C=N$ group possess basic property, in which Azo methine group can act as a Π accepter [16] . Schiff base compounds generally show hard character and are effective, as coordinating ligands if they bear functional group, usually -OH or -COOH sufficiently near the site of condensation. They are capable of forming five or six membered chelate ring during the complexation with a metal ion in which, the $> C = N$, and $> C = C <$ can be located in internal positions in chains or rings.[15] Tridentate Schiff base ligands containing two annulated rings form stable complex[17]. A few studies have revealed that electron releasing methyl and methoxy substituents increases, while electron withdrawing nitro and halo substitituents decreases the basic strength of the azo methine group.[18] Salicylaldimine complexes are reported to be first synthesized in this field by Schiff [19]. Snell et al[20] have pointed out that similar reactions occurred, if pyridoxal was used instead of salicylaldehyde. The principal structural type complex formed between metal ion, salicylaldehyde and amino acids are shown below.



The synthesis and properties of Schiff bases have been widely reviewed [21,22]. The systematic study of Schiff base complexes done by Pfeiffer et al [23-27] was utilized by the chemists for the last few years.

In this dissertation, formation and characterization of metal complexes derived from amino acids and carbonyl compounds are described. So besides > C = N, in these types there is an additional carboxylic acid functional group. Schiff bases derived from amino acids are potential metal chelating agents. Chelating ligands generally formed stabler complexes than those formed by their mono dentate analogues. [28] A sudden change in solubility, drop in conductivity, or color change is an indicative of a complex compound between metal ion and ligand. Bonding ability of ligand depends on nature of atoms, which act as coordination sites, their electro negativity and steric factors. Thermodynamic stability of metal complex depends considerably on the nature of ligand and metal ion[29] . No stable coordination compound of any monodentate Schiff base has been reported [30,31]

There are many published papers, which contain the methods of preparation of Schiff base complexes. [32-41,19]. Stability and solubility vary from ligand to ligand and from one metal complex to other. Some methods of synthesis of Schiff base complexes are summarized as follows

a) Addition of metal salt in aqueous methanol to a methanolic solution of the ligand, which is suitable for complexes which possess high hydrolytic stability.[32]

b) In Schiff's method[19,] refluxing the metal salt, usually acetate, with a preformed Schiff base in aqueous ethanol or similar solvents carried out, and it is not convenient, if the Schiff base is readily hydrolyzed and this method is limited to complexes of *o* - hydroxyarylidene amines.

c) The direct addition of a primary amine with a preformed aldehyde / ketone-metal complex. This method was developed by Pfeiffer[42] and is probably the most general method available.

d) Template method involves the refluxing of metal amine complex and the appropriate carbonyl compound[43] and complexes of almost all types can be synthesized by this method.

e) Reacting metal alkoxide with Schiff base in non aqueous medium.[44-47] and a variation of this procedure includes strong alkoxide base, dissolves the ligand in this solution and then added an appropriate amount of anhydrous salt of the metal.[48]

f) New mechanochemical method which involves rubbing of metal surfaces with ligand in solution, were also reported[49] .An indirect synthetic route to Schiff base complex can be written as

$$[\,M(acac)_2\,] + \text{amino acid} \xrightarrow{h\upsilon \text{ reflux in 95 \% alcohol}} [M\,(\text{tridentate})\,H_2O\,]$$

Pfeiffer et al have published a series of papers [42] which explains the studies on the complexes of Schiff base derived from salicylaldehyde and related compounds[50]. Metal chelates derived from salicylaldehyde are numerous than those derived from other carbonyl compounds. Amino acid - Schiff bases would have considerable biological significance since amino acids are the building blocks of proteins. When we consider the importance of azo methine group, its biological importance is significant. The visual pigment rhodopsin contains an azomethine linkage [51]. It has been reported that certain amino acid Schiff bases are excellent analytical reagents for the estimation of metals like Cu(II) and Zr(IV)[52 - 55]. Mukerjee[56] used the Schiff base ligand derived from salicylaldehyde - glycine oxamic acid as a colorimetric reagent for Fe(III). Vanillidene anthranilic acid was used to prepare new uranyl complexes having different metal to ligand ratios[57]. Mehta et al recommended that N (2 – hydroxy – 1 – naphthylidene) anthranilic acid and N – acetyl acetone anthranilic acid are effective gravimetric reagents for copper. Schiff bases of pyridoxal are involved in transamination and racemisation reactions of amino acids [58,59]. Metal chelates of certain Schiff bases have been found volatile enough for their separation using vapour phase chromatography [60,61] . Now a days nuclear medicinal application of technetium (V) complexes of Schiff base is receiving attention [62,63]. The review of Holm et al [65] and other important reviews[64,65-72] give explanations of synthetic biological and physico chemical studies of Schiff base complexes and their applications. The Schiff base complexes have influenced the every day life of modern man as drugs against tuberculosis bacteria fungi microbs and cancer[73-80] . They also play a dramatic roll in chemical analysis [81] and selective separation and enrichment of metals [82, 83]

REVIEW

The world of Schiff bases is very wide, but the works on amino acid Schiff bases are very few. Relevant work reported in this area is on the condensation of amino acids with salicylaldehyde, pyridoxal, *o*-vanillin, and hydroxy naphthaldehyde. This review has been restricted to transition metal complexes of tridentate ONO- and tetradentate ONNO-type donor ligand, since only such ligands are pertinent to the present investigation. The work done in the field of complexation of Schiff bases is very few, but the parent amino acids were found to form complexes with almost all metal ions.[84-88] Amino acid complexes have been attracted by the biochemists, because of its vast application.[89- 94] In ceruloplasmin[95] histidine residues are involved in copper ion bonding where as in ferritin, and transferin, tyrosine is bonded to Fe(III)[96]

The study of tridentate Schiff bases of salicylaldehyde with aliphatic amino acids are in the forefront now.[97] N- salicylidene glycine and similar ligands have been reported to form dinuclear nickel (II) complexes. [98] In these complexes, metal ion acquires octahedral environment through two coordinated water molecules per metal ion. Dutta and Ray[99] in 1977 reported the preparation and characterization of Mn(II) complexes derived from the condensation products of glycine, β alanine and L – leucine with salicylaldehyde, and its derivatives. These complexes, similar to Ni (II) complexes mentioned above, have been formulated as $[MnL(H_2O)_2]_2$.

Monomeric 1 : 1 complexes of type [MLX] of Fe (II) with Schiff bases derived from salicylaldehyde and the amino acid, β alanine or anthranilic acid have been synthesized ,[100,101] Co (II), Ni (II) , Zn (II), and Cd (II) may also form complexes with same ligand. Complex of Ni (II) with Schiff bases, derived from the condensation with the bidentate amino acids β alanine, DL – 2 – aminobutyric acid and the potential tri dentate amino acids like DL – aspargines and L – glutamine have been prepared and characterised[102]. Crystalline complexes of Cu(II), Co(II), and Fe(II) complexes of pyridoxylidene amino acids have been reported [103]According to Holm, pyridoxylidine amino acids possess catalytic property. [104] Copper (II) complexes[105] having the formula $[CuL(H_2O)].nH_2O$ with salicylaldehyde, and amino acids like alanine, valine, leucine, iso leucine, phenyl alanine, phenyl glycine and serine were reported. Cu(II) readily forms a colored complex with salicylaldehyde and glycine.[106] Hamalainen and coworkers[107] reported the synthesis and characterization of copper chelate of Schiff base derived from phenyl alanine. Anionic complexes of iron and cobalt having the formula $[FeL_2]^-$ and $[CoL_2]^-$ obtained from their salts by salicylaldehyde - aminoacid (ligand) replacement.[108] Mixed ligand complex of Ni having the formula $[Ni L (Py)_2]_2$. [109] have been prepared, where, LH is the Schiff base derived from N-salicylidene amino acids and Py is pyridine. Oxovanadium(IV) which form stable complexes with ligands derived from amino acids and $[VOL(H_2O)]$ type complexes of N salicyidene amino acids (glycine, alanine, leucine) have been prepared and characterized [110]. By similar methods, mixed ligand complexes of oxovanadium (IV) have been obtained from anthranilic acid. [111] A series of oxovanadium(IV) and oxovanadium(V) complexes with 2-hydroxy-1-naphthalidene amino acids have been reported by Syamal et al. [112]. Dimeric Mn (II) [113] complex of 5 –

nitro and 5-chloro salicylidene amino acids having the formula $[MnL(H_2O)_2]_2.nH_2O$ are reported. These are prepared with 5-bromo salicylidene glycine, 3,5–dibromo salicylidene glycine and 5–nitro salicylidene glycine. Mixed ligand complexes of copper having the formula [CuLA] have been prepared where LH is the Schiff base derived from the above ligand and A is pyridine or α picoline or γ picoline. Oxovanadium(IV) can form stable complexes with ligands derived from amino acids $[VOL(H_2O)]$ type complexes of N–salicylidene amino acids have been prepared and characterized. Salicylidene amino acids and 2 hydroxy naphthalidene amino acids have also found to form complexes with Cu (II)[114].

A series of new poly crystalline Cu (II) complexes with N- nicotinyl amino acids ligand were prepared[115]. A notable piece of work have been reported by Jessy et al[116 - ,120] on a novel series of metal chelates of vanillidene anthranilic acid and its 5 – bromo derivatives with almost all metal ions of first transition series and some lanthanide ions . Co (II), Ni (II), Zn (II) and Cu (II) complexes of two Schiff bases citronellal anthranilic acid and citronellal – 5 – bromo anthranilic acid have also been synthesized[121] by Rehina. Shanti et al [122]prepared octahedral Cr(III) complexes of N-salicylidene amino acids of type $K[Cr(Sal.aa)_2].nH_2O$. Isolation and characterization of VO(II) complexes of Schiff bases of anthranilic acid with salicylaldehyde, 5-bromo salicylaldehyde and 2–hydroxy–1-napthaldehyde have been reported by Mohanty et al[123]. Chakravarthy and coworkers[124] have studied the transition metal complexes of vanilline anthranilic acid. In 1974 Shivahare and Rao [125]have synthesized Ni(II) , Fe(II), and Co (II) complexes of salicylaldehyde 5- bromo anthranilic acid. Nakao [126] et al reported synthesis and characterization of thirteen Cu (II) complexes of Schiff bases derived from some amino acids, having the formula [$CuL(H_2O)$]. N – salicylidene anthranilic acid and N–salicylidene β alanine forms a non planar dimeric bridged structure[127] with Cu(II) ions with no direct spin change. Salicylidene amino acids and 2–hydroxy napthalidene amino acids have found to form complexes with Cu (II) [128]

Solid state chelates of Fe (II), Co (II) and Ni(II) with a tri dentate ligand of 5–bromo salicylidene anthranilic acid have been synthesized and characterized.[129] Chandra et al[130] have reported Mn(II) complexes of Schiff bases derived from salicylaldehyde and β alanine or anthranilic acid or 2–hydroxy naphthaldehyde and anthranilic acid of the type $Mn\ L_2$. In this the reaction of the ligand H_2L with [$Mn(OAc)_3.2H_2O$] affords [$KMnL_2.H_2O$] , which upon chemical or electro chemical oxidation in methanol gave $Mn\ L_2$ in high yield, and among this, the structure of β alanine complexes was detected by X–ray crystallography. Preparation and oxygenation of Mn (II) complexes of imines derived from salicylaldehyde and amino acids (L–alanine, L–valine, L–phenyl alanine, L–histidine and glycine) of the type[MnL.nQ]have been reported[131], where Q is H_2O or EtOH. Most of these compounds are stable towards dry air but absorb oxygen readily in many organic media to the extent of O_2 / Mn , equal to1or 0.5

Eleven Fe (III) complexes of tridentate di basic salicylidene / substituted salicylidene aminoacids were prepared by Ray[132]. They are represented by general formula [$FeL(H_2O)_2]_2.(OH)_2$. All Fe (III) complexes possess dimeric pseudo octa hedral structure. These are characterized by elemental analysis, magnetic moment studies and TGA. IR spectra of these complexes are super impossible with those of Ni (II), Co (II), Mn (II) and

Zn(II) complexes. Thermal studies on Co (II), Ni (II), and Cu (II) complexes of Schiff bases derived from salicylaldehyde and glycine were carried out by Nathmala[133]. Physico chemical investigations on complexes of Mn (II), Fe (II), Co (II), Ni (II), Cu (II), and Cd(II) with N – 5 - bromo salicylidene, 5 – bromo anthranilic acid have been carried out[134] .Octahedral Ni(II) complexes with Schiff bases derived from serine and salicylaldehyde have been prepared and characterized [135]. Li Taishan et al [136] reported the synthesis and properties of five Schiff bases obtained by the reaction of salicylaldehyde with glycine, DL valine, L isoleucine, L leucine and L phenyl alanine. Analysis of IR, ^{H}NMR and electronic spectra indicate that the tautomeric equilibrium between the enol imine and keto enamine exist in the Schiff bases .A review with five references includes a listing of the odour properties of methyl anthranilate based Schiff bases commonly employed in perfume industry[137]. Ruthenium salicylaldehyde amino acid complexes were synthesized and their reaction with Π accepter ligands such as 2, 2^1 bi pyridine and 1,10 phenanthroline have been studied by Kureshy and Khan[138]. Dimeric complexes of Cu(II) anthranilate ,benzoate, acetate and oxalate derived from Schiff bases were prepared.[139] Salicylidene amino carboxylate complexes of Cu(II), [Cu(X–SA)L.nH_2O], where SA is salicylidene glycinate and salicylidene anthranilate, X is substituents on the salicylidene moiety (X = H, 5 – bromo, 3, 5 – dibromo, 5 – nitro, 3, 5 – dinitro) and L = monoamines (pyridine, picoline, quinoline and triethyl amine) and diamines like ethylene diamine, O – phenanthroline have been prepared [140] . Cinnamaldehyde complexes of Mn (II), Fe (II), Co (II), Ni (II) and Cu (II) with anthranilic acid were synthesized and analysed[141,142]

Synthesis and characterization of N–salicylidene amino acids Zn(II) complexes of the type ZnL(H_2O) have been reported.[143] Crystal studies, molecular structure and spectroscopic properties of oxovanadium complexes with salicylidene aminoacids have been studied by Cavaco et al [144] . Some new Cu (II) and Zn (II) complexes of Schiff bases derived from ortho vaniline and glycine, DL alanine, DL valine, DL methionine, L leucine, L phenyl alanine were synthesized and characterized by Wang et al[145] . The Schiff bases are bivalent anions with tri dentate ONO donors derived from carboxylate O, imino N and phenolic O. Cai Dongmei et al[146] have synthesized and characterized monodentate germanium(IV) complexes of Schiff bases derived from amino acids and salicylaldehyde. Condensation of equimolar quantities of salicylaldehyde and amino acids (glycine, alanine, valine, leucine, phenyl alanine, serine, cysteine) in absolute MeOH–KOH gives amino acid Schiff bases as their potassium salts. From this germanium tetra chloride adducts having the formula $GeCl_4(Sal.aa)_2$ were prepared and characterized by elemental analysis, conductance measurement, IR, ^{1}H–NMR spectra and electronic spectra. Synthesis, spectral and electro chemical studies of mixed ligand complexes of ruthenium(III) chiral Schiff base complexes with nitrogen donors have been reported[147] . Eighteen mixed ligand complexes of ruthenium having the formulae [RuL(PPh_3)Y] and [RuL(PPh_3)(H_2O)Y] type were prepared, where LH is the Schiff base derived from L alanine , L valine, L serine, L cysteine, L argenine or L aspartic acid with salicylaldehyde and , Y is 2 – 2^1 bi pyridine or 1,10 phenanthroline. According to Jursik and his coworker[148] Co(III) complex derived from salicylaldehyde- amino acid help to elucidate the iron binding site in trasferrins. Nathmala et al[149] have reported Cu (II) complexes of salicylidene amino acid Schiff bases of the type [Cu(Sal.aa)H_2O].nH_2O. The activities of these were tested towards the decomposition of H_2O_2 at 40^0 over a pH range 6 – 11. Dis proportionation of H_2O_2 catalyzed by these complexes at 40 ^{0} at pH 9 are reported. Synthesis and anti tumor activity of Schiff base coordination compounds containing Cu, Ni , Zn and Co synthesized from salicylaldehyde, 2,4 di hydroxy naphthaldehyde, with glycine and L alanine have been reported.[150]. Potentiometric determination of equilibrium constants and species distribution of Schiff base complexes in aqueous solution involving salicylaldehyde and tri dentate α amino acids with metal ions, Cu (II), Ni (II) and Zn (II) were reported. [151]

Some new diphenyl tin (IV) complexes having the general formula Ph_2 Sn L where LH, the Schiff bases derived from the condensation of 2- hydroxy – 1 – napthaldehyde with amino acids have been synthesized and characterized .[152] A series of Schiff bases of α and ω amino acids with salicylaldehyde was synthesized and their hydrolysis constants at pH 6 , 7 and 8 were determined [153]. Synthesis and characterization of complexes of Cu (II) with N salicylidene - phenyl alanine and N salicylidene alanine have been carried out by Shen wiang [154] et al . There are reports [155] on synthesis of N salicylidene leucine 3d metal complexes and their studies on thin layer chromatography and ultra violet spectra studies. Seven complexes of Co(II), Ni(II), Zn(II) and Cd(II) by metal ion template condensation of amino acids and aldehyde / ketone (salicylaldehyde ortho hydroxy naphthaldehyde, *ortho* vanillin, isatin)have been reported by Sharma et al[156].

Thermo chemical behavior of salicylidene - valine and its complexes with Co (II) and Ni(II) of molecular formula $[Co(HL)(H_2O)_2Cl]$ and $[Ni(HL)Cl]$ were characterized by Emam et al[157] . Four kinds of Schiff base complexes of Cu (II), Zn (II) and Ni (II) derived from *ortho* vanillin and alanine, leucine and phenyl alanine were reported[158]. A review with 46 references is given on the synthesis, structure, and reactions of chiral metal complexes with Schiff bases derived from amino acids[159]. Another set of 41 references based on Schiff base complexes of salicylidene amino acid were published. Their properties and application in many region such as fluoroescene, chromatographic behaviour, anti bacterial, anti cancer, and catalysis study has also been summarized in it[160] . Abdel and coworkers have synthesized[161] Co (II) and ternery Ni(II), Cu(II) complexes of salicylidene amino acids (Sal. aa) with imidazole or substituted imidazole. Christensen prepared crystalline complexes of Fe(II),Co(II) and Cu(II) with pyridoxylidene amino acids[162]. Cu(II) complexes of Schiff base derived from amino acids were prepared and studied[163]. Singh have characterized Co(II), Ni(II)and Cu(II) complexes of Schiff base derived from amino acids.[164]. Octahedral and tetrahedral Ni(II) complexes were reported with Schiff base derived from serine and salicylaldehyde .[165] Bertrand and Eller[166] in their broad review have reported that amino acids on deprotonation shows an increased tendency to chelate and to form additional bond and bridge with metal ions. According to Butler[167] manganese (II) form complexes with 5-bromo or 5-chloro salicylidene anthranilic acid. Similar complex formation have been reported with vanillin anthranilic acid.[168,169] Sharma and Dubay have synthesized and characterized Fe(II) complexes with N-salicylidene and N-(2-hydroxy –1-naphthaldehyde)-amino acids.[170] Solid state chelates of some inner transition metal ions with a tridentate ligand of anthranilic acid have been reported[171] .Some square planar complexes of Ni(II) with N-naphthylidene amino acids have been isolated by Mohmoud and coworkers.[172] Successful synthesis and characterization of transition metal complexes of hydroxy naphthaldehyde - anthranilic acid were carried out.[173] Physicochemical studies and thermal decomposition kinetics of Co(II), Ni(II), Cu(II), and Zn(II) complexes of camphor anthranilic acid and camphor 5-bromo anthranilic acid have been reported.[174] Coenzyme behavior of Schiff bases of pyridoxal 5^1- phosphate and 5^1–deoxy pridoxal with leucine in pure water and aqueous solution containing, different amounts of surfactants have been studied.[175] Synthesis characterization and antitumour studies of N-(2-hydroxy naphthylidene) – Gly - K Schiff base and its Cu(II) and Ni(II) complexes were carried out.[176]. Formulas of these compounds are $[K(C_{13}H_{12}NO_4)]$, $[Cu(C_{13}H_{11}NO_4)]$ and $[Ni(C_{13}H_{15}NO_6)]$. Cu(II) complex had one molecule of coordinated water and it showed 27.5% anti tumor activity. Recently detailed studies like antibacterial activity, stability constants etc of N salicylidene amino acids and their 3d metal complexes have been reported. [177]

Metal chelates of tridentate Schiff bases derived from pyridoxal and aminoacids were isolated by Wrableski and Long[178]. Baddiley[179] synthesized and characterized Cu(II) complex of the Schiff base derived from pyridoxal and valine. Mn (II) complexes having the formula Mn $(HL)_2$ with the above ligand was also synthesized [180]. Cu (II) chelate of Schiff base was deduced from phenyl alanine by Bentley and coworkers [181]. Pyruvic acid amino acids, glyoxalic acid - amino acids and 3–(hydroxy methylene) camphor amino acids have been found to form complexes with Cu(II).[182, 183, 184] Some work has been reported on the complexation abilities of benzoin anthranilic acid with Cu(II), Co(II), Ni(II), Zn (II), Cd(II), and Hg(II). [185] A notable piece of work have been reported by Mohan on metal chelates of hydroxy naphthaldehyde amino acid and N acetyl acetone amino acids with almost all metal ions of first transition series. Preparation and X ray diffraction studies were reported for two novel N salicylidene tryptophanato di aquo Cu

(II) complexes .[186] Mg (II) chelate [187] of N salicylidene glycine alkyl ester when heated under reflux in methanol gave 3 – amino coumarin and the same chelate yielded an amine on treatment with sodium methoxide in methanol. N- salicylidene glycine esters have been reported to undergo transesterification and aminolysis reactions.[188] Studies on model systems utilizing N – pyridoxylidene amino acids and their metal complexes have been carried out and the results have been reviewed.[189,190 ,191] The complexes formed between transition metal ions and the Schiff bases synthesized from salicylaldehyde, 2 ,4 dihydroxy naphthaldehyde and aminoacids were isolated and their anti tumor activity were studied by Zhao et al. [192] The order of antitumor activity of compounds is Ni > Cu > Zn > Co. Some transition metal complexes of amino acid Schiff base were synthesized and their purity was confirmed by Li Huaina and coworkers [193] . Blue crystalline mixed ligand complex of Cu (II) having the formula Cu $[L(Py)_2]$ where H_2L is salicylidene L valine and Py is pyridine was synthesized and its structure determined by single crystal X ray diffraction method[194]. The synthesis and X ray crystal structure of Schiff bases prepared from salicylaldehyde and di amino acids were studied[195]. Cluster complexes of salicylidene glycine and salicylidene anthranilic acid complexes of Cu(II) with metal halides and per chlorates were isolated.[196] Das and coworkers have prepared and characterized a series of planar or octahedral complexes of salicylidene amino acids [197] . 1 : 2 chelates of 2 hydroxy naphthaldehyde – anthranilic acid were isolated in solid form and analysed by electronic, spectral, and thermal studies.[198] Synthesis and properties of Mn (II) , Co (II), NI (II), Cu (II) and Zn (II), complexes with amino acid Schiff bases have been reported by Tian et al [199]. Complexes of N salicylidene anthranilic acid, 2 bromo salicylidene anthranilic acid and N – (2 hydroxy benzyl) anthranilic acid with Cu (II) were prepared and characterized.[200] A series of transition metal complexes with two Schiff bases, fluorenone anthranilic acid and anthracene carboxaldehyde anthranilic acid were prepared and characterized on the basis of physico chemical[201,202] studies. Solid state complexes of L – histidine with first row of d – block was separated and studied[203]

The review reveals that while the coordination chemistry of N – salicylidene amino acids, N- pyridoxylidne amino acids and N - (2 hydroxyl – naphthylidene)amino acids has received considerable attention in recent years, that of anthracene carboxaldehyde has received only scanty and sporadic attention.

Scope of present investigation

Even though extensive studies were done on metal complexes of Schiff bases derived from various aldehydes and ketones, the importance of transition metal complexes of Schiff bases derived from amino acid with anthracene carboxaldehyde is yet to be studied. In the present investigation aromatic Schiff base ligands anthracene carboxaldehyde-L histidine (ACH), anthracene carboxaldehyde-L tyrosine (ACT), anthracene carboxaldehyde glycine (ACG), anthracene carboxaldehyde DL- alanine (ACA) and anthracene carboxaldehyde –L phenyl alanine (ACPA) have been synthesized and characterized. Their complexes with many transition and inner transition metal ions have already been isolated. Generally used metal ions ,during the current course of studies are Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Ag(I).

The solid complexes were characterized by various physicochemical methods like IR, electronic spectra, molar conductance and magnetic moment data. The thermal decomposition behavior of certain representative complexes in static air has been studied by TGA techniques to understand their thermal stability and decomposition pattern. Crystalline state of seven complexes was established by indexing its X-ray powder diffraction pattern.

PART I

MATERIALS, METHODS AND INSTRUMENTS

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER II

MATERIALS, METHODS AND INSTRUMENTS

MATERIALS

Chemicals used were Analar Grade (B.D.H, E.Merck or Sisco). For synthetic purposes commercial solvents were distilled and used. Analar grade metal salts (chloride, acetate) were used for synthesizing the complexes. For physical and physiochemical measurements, solvents used were purified by methods recommended by Weissberger[204].

Only complexes obtained analytically pure are reported in this thesis. Metal complexes reported herein are stable and have good keeping qualities.

METHODS

Standard methods [205] like volumetric, gravimetric or pyrolytic techniques and atomic absorption spectroscopy were adopted for the estimation of metal content in the complexes.

For these estimations, about 0 .2 g of the complex was digested with concentrated nitric acid – perchloric acid mixture and then with concentrated hydrochloric acid. The resultant solution was then qualitatively made up to 100 ml. Using a definite volume of the solution the metal content in the complex was determined.

Carbon, hydrogen, and nitrogen content of the ligands and their metal complexes were carried out at I. I. T. Madras, on a Heraous – CHN – O – rapid analyzer. The observed percentage of carbon , hydrogen and nitrogen were in agreement with the calculated values.

The molar conductance[206] of the complexes were determined in methanol, at 28 ± 2 ^{0}C, using a solution of 0.001 M concentration. The conductance measured can be used to find out the electrolytic or non-electrolytic nature of the complexes.

Magnetic susceptibility was determined at room temperature 28 ± 2^0. $Hg[Co(NCS)_4]$ was used as standard [207] and diamagnetic corrections were carried out using Pascals's constant [208].

The UV-Visible spectra of the present ligands and complexes were recorded on a Shimadzu recording spectrophotometer by using methanol as solvent. For recording UV - visible spectra in solid state the Nujol Mull technique recommended by Venanzi et al[209] was used.

IR spectroscopy is a fingerprint for identification and a powerful tool for studying molecular structure. Fourier transform infrared spectrometer[210, 211] was used.

The X-ray diffraction pattern of some complexes were recorded with the powdered sample for 2θ values from 5-60^0 at a scan speed of 0.01^0 per 0.2 S. The unit cell determination, calculation and elucidation of cell dimensions from the crystallographic pattern can be used to confirm the structure of complexes assigned.

Thermal analysis was carried out in static air atmosphere maintaining the rate of heating at 10 degree per minute. Thermo analytical curves were drawn with mass versus temperature. Using the programming language C^{++} the computational work was done.

Anti fungal studies were carried out at I I S R Calicut. Four different phases of study on *phytophthora capsici* was done. Four phases are mycelia growth , sporulation study, zoospore release and zoospore germination.

Melting points of ligand and complexes were determined using melting point apparatus.

The instruments used for the above studies are listed below.

1. Atomic absorption spectrophotometer
2. Heraous –CHN-Orapid CHN analyzer
3. Toshniwal conductivity bridge
4. Gouy type magnetic type balance
5. UV-visible ---Varian E-4 band spectrometer
6. Shimadzu –IR 470 infrared spectrophotometer
7. Philips X-ray powder diffractometer
8. Perkin Elmer 7 series thermal analysis system
9. Intel Pentium III PC
10. Laminar floor
11. Microscope (Nikon)
12. Melting point apparatus

PART I

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L - HISTIDINE

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER III

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L – HISTIDINE (L_H^1)

The Schiff bases derived from anthracene – 9 - carboxaldehyde and amino acids are very interesting due to their ability to form various types of metallic complexes. Comparatively less work has been done on the complexes of anthracene – 9 - carboxaldehyde (AC)[201,212]. A recent work on ortho vanillin L histidine has been reported[213]. In this chapter, the synthesis, spectral and magnetic behavior of anthracene – 9 - carboxaldehyde –L - histidine (ACH) complexes of Cr (III), Mn (II), Fe (III), Co (II) , Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Ag (I) are described.

Synthesis of ligand

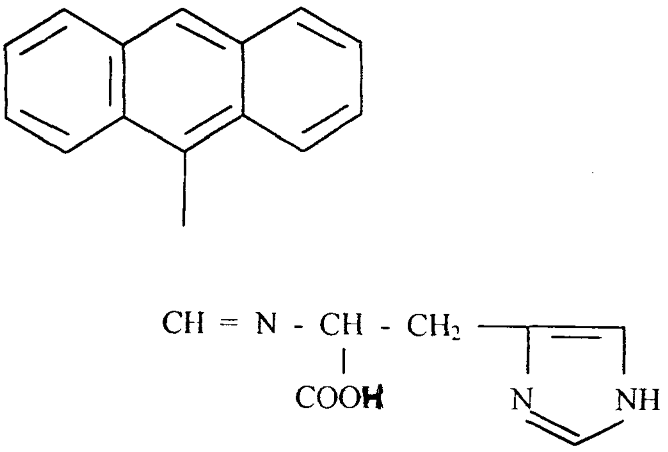
Histidine (3.1 g, 0.02 mol) was added to a solution of potassium hydroxide (1.12 g, 0.02 mol) in 95 % hot ethanol (50 ml). This mixture is stirred well until it became homogeneous. Anthracene – 9 – carboxaldehyde (4.1 g, 0.02 mol) in ethanol was then added drop wise with shaking. The mixture was refluxed on a water bath for 3 hours. On cooling the mixture in ice, needle shaped yellow crystals of potassium salt of the ligand were obtained. It was then filtered, washed with dilute alcohol, dried in a desiccator over anhydrous calcium chloride. The ligand obtained is recrystallised from ethanol. (Yield 95 % , melting point 98 °C). Acid form of the ligand was used for CHN analysis.

Characterization of ligand

The ligand anthracene – 9 – carboxaldehyde – L – histidine was characterized on the basis of elemental analysis and spectral data.

	C%	H%	N%
Analytical data found	73.62	4.95	12.24
Calculated value for $C_{21}H_{17}N_3O_2$	73.41	4.19	11.02

The UV and IR spectra of the ligand showed the characteristic bands. Based on the above results, the structure of the ligand was confirmed as



Studies on Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Ag(I) complexes of anthracene–9–carboxaldehyde–L histidine

In this section the preparation and characterization of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Ag(I) complexes of anthracene–9–carboxaldehyde-L histidine are described.

Synthesis of metal complexes

A solution of cobalt acetate (0.01 mol) in ethanol was added drop wise to a refluxing solution of potassium salt of ligand (0.02 mol) in ethanol. Sodium acetate (1 g) in ethanol was added and refluxed further for 5 hours. The pale yellow precipitate separated was filtered, washed with 50 % ethanol and dried over anhydrous calcium chloride. (Yield 85 %)

Mn(II), Ni(II), Cu(II) and Zn(II) complexes of anthracene–9–carboxaldehyde–L histidine were prepared from their acetates by adopting the same procedure (Yield 85%).

Cd(II) complex was prepared by mixing an ethanol solution of the metal acetate with a solution of the ligand in ethanol. The mixture was refluxed for 8 hours. The separated complex was filtered, washed with aqueous ethanol and dried in a desiccator over anhydrous calcium chloride, (Yield 80 %).

Cr(III) and Fe(III) complexes were prepared from their chlorides. To the boiling ethanolic solution of the ligand after adjusting pH to nearly 7, an ethanolic solution of metal chloride was added and boiled for 3 hours. Reddish brown precipitate of iron complex and yellow colored chromium complex were formed. They were filtered, washed with aqueous ethanol and dried over anhydrous calcium chloride. (Yield 90 %)

Hg(II) complex was prepared from mercury(II) chloride by following the same synthetic procedure employed for Co(II) complex (Yield 85 %).

Ag(I) complex was prepared in the dark using silver acetate. An ethanolic solution of silver acetate and ethanolic solution of ligand were refluxed together for 3 hours after adding 1 g sodium acetate. A dark green precipitate of the complex was separated. The complex separated was filtered, washed with aqueous solution of ethanol and dried. (Yield 90 %).

Characterization of complexes

The complexes were characterized on the basis of elemental analysis, magnetic measurements, electronic and infrared spectral data, conductance measurements and thermal data.

Results and discussion

The complexes are stable and colored. They are insoluble in water but soluble in ethanol and methanol.

Elemental analysis

Percentage of carbon, hydrogen and nitrogen were determined by micro analytical methods. Anthracene – 9 – carboxaldehyde – L histidine acts as a bidentate ligand in the reaction with common transition metal ions. Complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)'possess 1 : 2 metal to ligand ratio, but in Ag(I) there is 1 : 1 ratio. The analytical data, physical appearance and melting point are summarized in the Table 1.3.1.

Molar conductance

The molar conductance measurements in methanol were carried out at a concentration of 10^{-4} mol $^{-1}$ at 28 ± 2 ^{0} C. Molar conductance of on Cr (III), Mn (II), Fe (III), Co (II) , Ni (II), Cu (II), Zn (II), Cd (II), Hg (II), and Ag (I) were found to be in the range of 3 – 13 ohm $^{-1}$ cm ^{2} mol $^{-1}$,indicating their non electrolytic nature in methanol.

Magnetic measurements

The values of magnetic moments were tabulated in Table 1. 3. 1. A magnetic moment of 6.3 B.M for Mn (II) complex[214] suggested the geometry as octahedral . The room temperature magnetic moment of Fe(III) complex is 6 BM. This indicates an octahedral geometry around the metal ion[214]

Co(II)[214] complex has a magnetic moment value of 4.9 B M. An octahedral geometry is suggested around the metal ion. Ni(II) complex has a magnetic moment value of 3.36 B.M which is very close to the spin only values of octahedral Ni(II) complex, indicating the presence of two unpaired electrons with an electronic configuration of t_{2g}^{6} $e_g^{2}(^{3}A_2)$. Therefore an octahedral geometry can be assigned to the Ni(II) complex. Cu(II) complex give a magnetic moment value of 1.54 B M, which is expected for one unpaired electron of the d^9 electronic configuration indicating octahedral geometry[214,215]. Cr(III) [216] complex gave a magnetic moment of 4.1 B M, expected for three unpaired electrons, indicating octahedral geometry. The remaining complexes are diamagnetic as expected.

Infrared spectral studies

The infrared spectroscopic results provide support for the molecular constitution of these complexes. The assignments are made on the basis of comparison with the spectra of similar type of compounds. Selected infrared frequencies of the ligand and complexes are represented in Table 1. 3. 2.

A broad feature at 3410 – 3250 cm^{-1} in the spectra of several complexes is attributed to the hydroxyl-stretching mode of water molecules. [217 - 220] In addition a medium band approximately at 870 – 950 cm^{-1} suggests that water molecules are coordinated. [221]

The other very strong hands are observed in the 1700 – 1300 cm^{-1} region, one at ≈1660 cm^{-1} and the other at ≈1405 cm^{-1}. These are attributed to the asymmetric and symmetric stretching vibration respectively of carboxylate ion. Further the separation value, $\Delta\gamma\ COO^-$ (γ asy COO^- - γ sy COO^-) of ≈ 250 cm^{-1} rules out the possibility of a bridged or coordinated carboxylate group.

A strong band approximately at 1546 cm^{-1} in the spectrum of the ligand anthracene carboxaldehyde – L histidine may be assigned to γ C = N stretch. This band shows a down ward shift by about 19 – 39 cm^{-1} in the spectra of all the metal complexes, indicating the participation of the azo methine nitrogen in coordination with metal ions [222]. The shifted band in many cases is coincident with the C = C band, which then shows greater intensity or broadening.

Further evidence for broadening by nitrogen and oxygen atoms is provided by far IR spectra of the complexes. Due to the interference of skeletal vibrations of the ligands, with M – N and M – O vibrations, definite assignments of bands is difficult as a result of metal ligand vibration. Therefore only tentative assignments are made on the basis of information available in literature. Spectra of all complexes prepared in this investigation showed intense broad bands at 590 – 530 cm $^{-1}$ and 510 - 490 cm $^{-1}$ assignable to γM – N and γ M – O [223-225]The aromatic out of plane vibration [226, 227] is seen near 810 cm $^{-1}$ and in plane vibration at 770 cm $^{-1}$ and 720 cm $^{-1}$.

Electronic spectra

Electronic spectra of the ligand anthracene carboxaldehyde L – histidine is characterized by two bands lying around 32365 cm^{-1} and 24270 cm^{-1} . These bands can be assigned to n $\longrightarrow$ σ^* and n $\longrightarrow$ π^* transitions. During complex formation a red shift is detected for these bands, which indicate the involvement of Schiff base in co ordination

The band appearing at 25000 cm^{-1} in the electronic spectrum of Mn (II) complex is a support for the assigned octahedral geometry[228]. In this complex, all the weak transitions are masked by strong charge transfer bands. Cr (III) complex shows a weak band at 17930 cm^{-1} due to transition of $^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ in the spectrum, which is suggestive of its octahedral geometry.

The electronic spectrum of Fe (III) complexes at 24857 cm^{-1}, which is due to charge transfer transition. A weak shoulder is located at 16000 cm^{-1} . Martin and White[229] have observed these bands. Since the ground state for Fe (III) high spin complexes is $^{6}A_{1}$, all transitions are expected to be weak and frequently obscured by charge transfer bands.

The electronic spectrum of Co (II) complex gives two bands at 17000 cm^{-1} and 21130 cm^{-1} due to $^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$ and $^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ transitions. The expected octahedral transitions of Co (II) are

$^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$
$^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and
$^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$

The middle band is due to a transition of two electron which is forbidden, and give a weak band. And again, $^{4}A_{2g}(F)$ and $^{4}T_{1g}(P)$ are very close in octahedral geometry. Due to these factors, detection of middle band is very difficult.

Ni (II) complex exhibit two d – d transitions in the electronic spectrum at about 16,700 cm^{-1} and 22500 cm^{-1} due to $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ transitions. The electronic spectrum of Cu (II) complex showed absorption maximum at about 15380 cm^{-1} which supports a distorted octahedral geometry [230]. The remaining Zn (II), Cd (II), Hg (II) and Ag (I) and complexes do not show any characteristic d – d transition bands.

X-ray studies

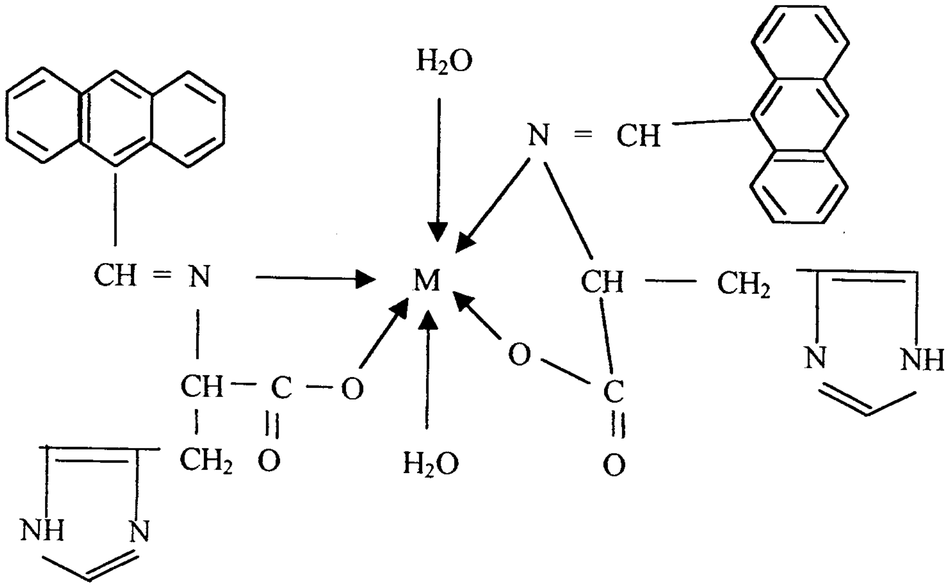
The Cu(II) and Ni(II) complexes of anthracene carboxaldehyde-L-histidine were subjected to X-ray crystallographic studies to determine their crystal structure in solid state. The investigations shows that Cu(II) and Ni(II) complex of ACH form orthorhombic crystals in solid state. The studies have confirmed 1 : 2 metal ligand ratio. $[ML_2(H_2O)_2]$ being the general formula.

Thermal studies

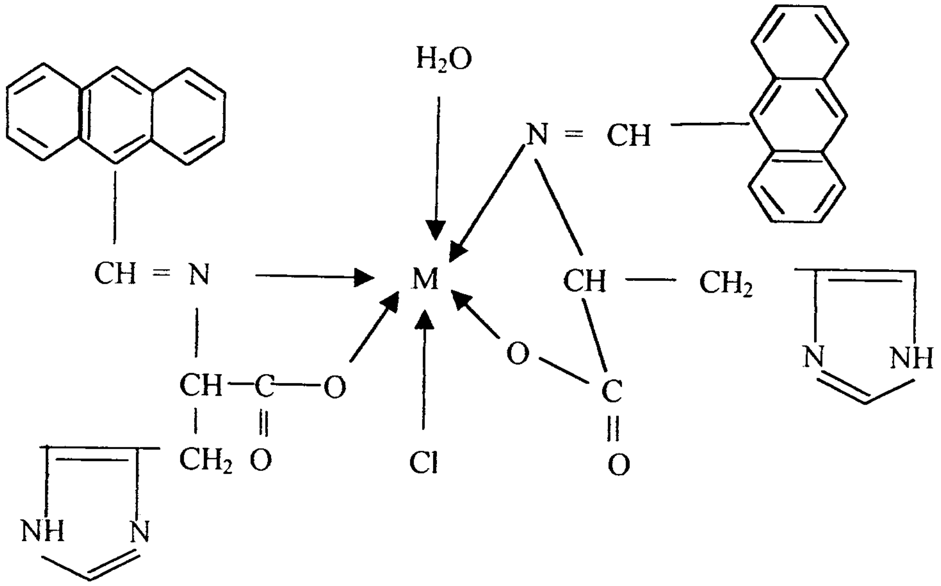
Co(II) , Ni (II) and Cu(II) complexes were subjected to thermal studies by non isothermal methods. The complexes decomposed in different stages, finally converted to their oxides. The determination of kinetic parameters, mechanism of decomposition and probable assignment of each decomposition are discussed in Part II.

Above results reveal that all these complexes except Zn(II), Cd(II), Hg(II) , and Ag(I) possess octahedral orientation which can be depicted as shown below. Zn(II), Cd(II), Hg(II) and Ag(I) complexes possess tetrahedral geometry.

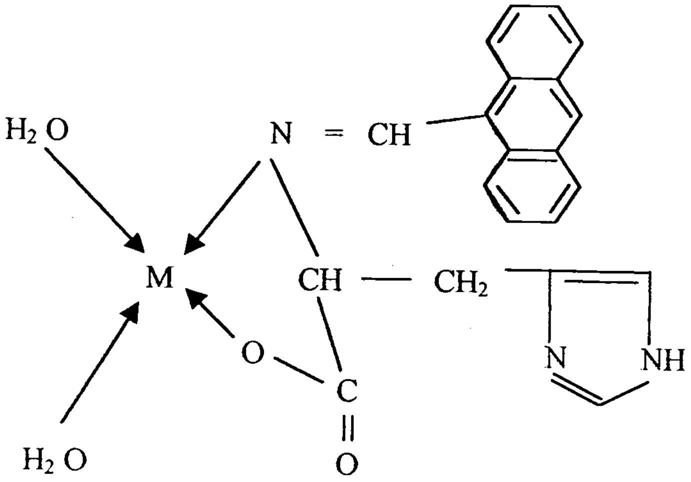
The structure of the complexes are as shown below.



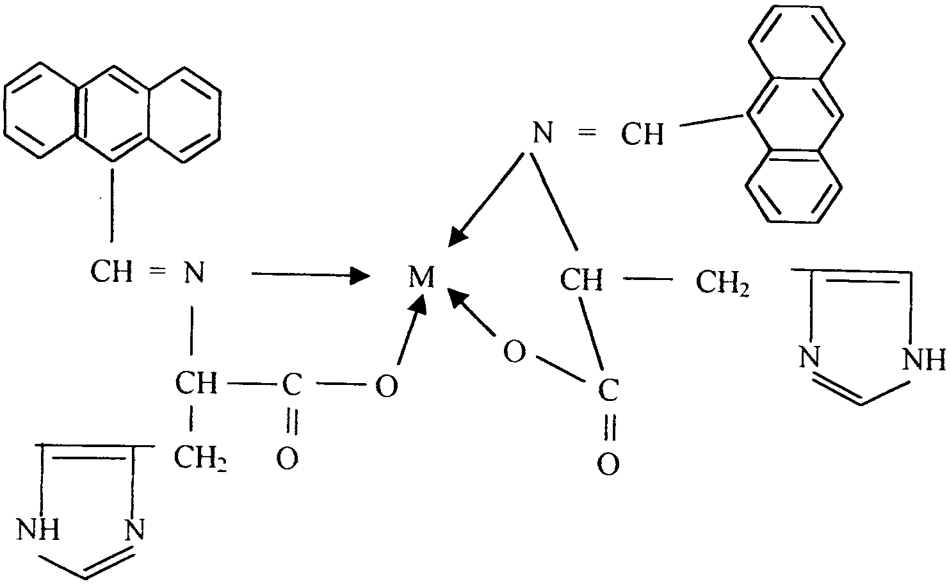
M = Mn (II), Co (II), Ni (II), Cu (II)



M = Cr (III) or Fe (III)



M = Ag (I)



M = Zn (II), Cd (II), Hg (II)

TABLE 1.3.1

Micro analytical, magnetic moment and conductance data of transition metal chelates of Anthracene-9-carboxadehyde-L histidine

Metal Complexes	Colour	Melting point	M%	C%	H%	N%	μ_{eff} B.M.	Ω_m^{-1}
$[CrL'_2(H_2O)Cl]$	Greenish Yellow	176	6.73 (6.58)	64.24 (63.79)	4.66 (4.3)	10.87 (10.63)	4.1	4.27
$[MnL'_2(H_2O)_2]$	Brown	132	6.73 (7.08)	65.22 (64.99)	4.601 (4.64)	10.13 (10.83)	6.3	9.015
$[FeL'_2(H_2O)Cl]$	Reddish Brown	97	7.2 (7.03)	64.91 (63.49)	4.64 (4.28)	10.82 (10.52)	6	3.97
$[CoL'_2(H_2O)_2]$	Yellow	240	8.24 (7.56)	64.51 (64.66)	4.58 (4.62)	10.75 (10.78)	4.9	5.51
$[NiL'_2(H_2O)_2]$	Pale Yellow	194	7.3 (7.53)	63.98 (64.62)	4.81 (4.62)	10.76 (10.78)	3.36	8.63
$[CuL'_2(H_2O)_2]$	Bluish Green	185	7.4 (8.09)	64.62 (64.28)	4.2 (4.52)	10.9 (10.71)	1.54	9.23
$[ZnL'_2]$	Yellow	91	8.31 (8.72)	66.93 (67.21)	4.58 (4.27)	10.69 (11.2)	D	4.5
$[CdL'_2]$	Pale yellow	190	13.82 (14.11)	62.66 (63.24)	4.015 (4.07)	10.1 (8.56)	D	6.02
$[HgL'_2]$	Yellow	170	21.78 (22.6)	55.72 (56.94)	3.91 (3.62)	9.12 (9.49)	D	6.32
$[AgL'(H_2O)_2]$	Dark Green	80	23.01 (22.19)	50.27 (51.83)	4.32 (4.11)	7.98 (8.63)	D	13.25

The calculated values are given in parentheses; D dia magnetic; M metal; Ω_m^{-1} molar conductance in $ohm^{-1}\ cm^2\ mol^{-1}$

TABLE 1. 3. 2

Selected absorption frequencies (cm $^{-1}$)of transition metal chelates of Anthracene carboxaldehyde L – histidine (ACH)

Complex	γ H_2O	γ asyCOO	γ syCOO$^-$	γ C = N	In Plane deform	Out of plane deform	γ M - N	γ M - O
Ligand	---	1660	1407	1546	896	777 724	---	---
$[Cr\,L^1{}_2Cl(H_2O)]$	3409	1666	1401	1527	870	778 738	598	506
$[Mn\,L^1{}_2(H_2O)_2]$	3423	1659	1374	1520	877	778 724	592	506
$[Fe\,L^1{}_2Cl(H_2O)]$	3423	1659	1381	1507	870	777 724	592	499
$[Co\,L^1{}_2(H_2O)_2]$	3390	1666	1381	1513	870	777	585	506
$[Ni\,L^1{}_2(H_2O)_2]$	3436	1666	1380	1518	872	778 731	598	507
$[Cu\,L^1{}_2(H_2O)_2]$	3443	1666	1401	1513	870	771 731	598	499
$[Zn\,L^1{}_2]$		1662	1383	1511	872	778 724	592	505
$[Cd\,L^1{}_2]$		1666	1381	1520	890	784 724	546	506
$[Hg\,L^1{}_2]$		1662	1401	1518	872	778 731	546	499
$[Ag\,L^1(H_2O)_2]$	3443	1666	1380	1520	890	784 724	592	499

PART I

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE-L-TYROSINE

G. Indira Devi “ Studies on transition metal complexes of schiff bases derived from aminoacids” Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER IV

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE-L–TYROSINE [L^{11}_{H}]

Tyrosine is a potential chelating agent, because this forms stable and colored complexes with various metal ions. Schiff bases derived from tyrosine and their metal complexes have wide application in biological science. A review by He yufeng et al [160] on the metal complexes of Schiff bases derived from amino acids and salicylaldehyde point out the current interest of this type of complexes. Therefore it was thought worthwhile to study about some transition metal complexes derived from tyrosine and anthracene – 9 – carboxaldehyde.

Preparation of ligand

KOH (0.56 g, 0.01 mol) dissolved in methanol and tyrosine (1.81g, 0.01 mol) were mixed, and stirred vigorously . A hot methanolic solution of anthracene – 9 – carboxaldehyde (2.06 g , 0.01 mol) was added to it with constant stirring. The orange yellow precipitate obtained was filtered, recrystallized from methanol and dried in vacuum desiccator. Melting point was found to be 79^{0}C

The reaction involved in the formation of the ligand can be represented as follows

$$C_{14}H_9CH = O + C_9H_{10}O_3NK \longrightarrow C_{14}H_9CH=NO_3H_8C_9K + H_2O$$

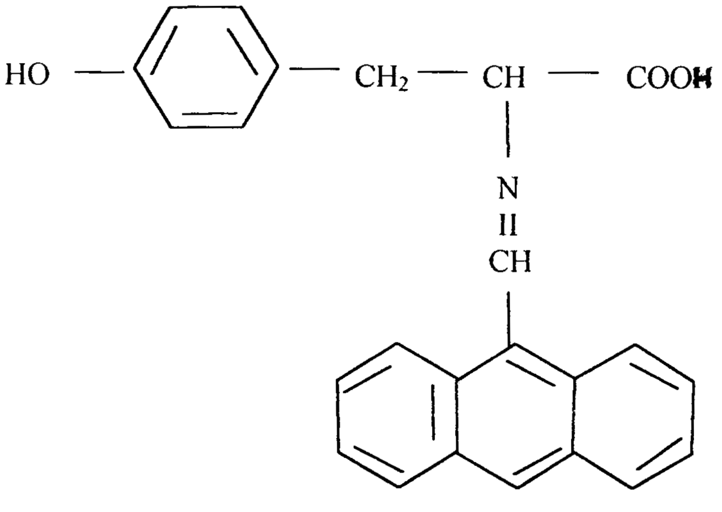
Acid form of the ligand was used for CHN analysis

Characterization of ligand

The ligand anthracene – 9 – carboxaldehyde - tyrosine was characterized on the basis of CHN analysis and spectral data. The calculated and observed percentages of carbon, hydrogen and nitrogen were in good agreement.

Ligand [ACT]	C%	H%	N%
Analytical data found	78.59	4.41	3.43
Calculated for $C_{24}H_{19}NO_3$	78.19	4.89	3.8

The UV and IR spectra of the ligand showed the characteristic bands. On the basis of these results, the structure of the ligand ACT was confirmed as



Studies on Cr(III), Mn(II), Fe(III) , Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Ag(I) complexes of anthracene–9–carboxaldehyde–L- tyrosine

The Schiff base derived from anthracene – 9 – carboxaldehyde and – L – tyrosine is found to be highly stable. The presence of - COO^- group adjacent to >C = N linkage stabilizes the complex by chelation. In this section studies on some transition metal complexes of anthracene – 9 – carboxaldehyde are described.

Preparation of complexes

The complexes were generally prepared by adding slowly a hot aqueous methanolic solution of the metal acetate or chloride to a refluxing solution of the ligand in the methanol medium. The complexes possess 1 : 2 stoichiometry except Ag (I), which is 1 : 1 in nature. The details of preparation and characterization of complexes are given below:

Ni(II), Cu(II), Zn(II), Cd(II) and Co(II) were prepared by adding methanolic solution of the metal acetate, (0.005 mol) to a refluxing solution of the ligand (0.01 mol), in methanol after adjusting its pH (7- 7.5) with acetic acid. The precipitated complex was filtered, washed with methanol – water (1 : 1 mixture) and dried in a vacuum desiccator.

Cr(III), Hg(II) and Fe(III) complexes were also prepared by the same procedure, as above using their chloride. Approximately 80% yield obtained for these complexes.

Ag(I) complex was prepared in 1 : 1 metal to ligand ratio by adopting the same procedure as above.

Characterization of the complexes

The complexes were characterized on the basis of micro analytical, UV, IR data, magnetic, conductance, X – ray and thermal studies.

Results and discussion

Elemental analysis

The hydrogen, carbon and nitrogen percentages were determined by micro analytical methods. ACT act as bidentate ligand in reaction with common transition metal ions. All the complexes were found to possess 1 : 2 stoichiometry except Ag (I) which exhibited 1:1 metal to ligand ratio. Physicochemical characteristics are given in Table 1. 4.1

Molar conductance

The molar conductance values of the complexes in methanol at a concentration of 1 x 10 $^{-4}$ M at 28 ± 2^0 C were indicative of their non electrolytic nature.

Magnetic measurements

The values of magnetic moments are tabulated in Table 1.4.1 The magnetic moment of Mn(II) complex was 5.92 BM and it was consistent with octahedral geometry around the metal ion. In Co(II) complex the ligand possess magnetic moment of 5.06 BM. The observed magnetic moment for the spin free octahedral Co(II) ($^4T_{1g}$) have excess of spin only value and it may be due to the orbital contribution of the ground state (t_{2g}^5 e_g^2).

It is reported that octahedral high spin geometry can be assigned to Co(II) complex, if the measured μ_{eff} value is in the range 4.7 – 5.2 BM. Ni(II) complex shows a magnetic moment value of 3.2 which is very close to the spin only value of octahedral complexes (2.9 – 3.4 BM), depending on the magnitude of the orbital contribution. Therefore an octahedral geometry can be assigned to the Ni(II) complex. Cu(II) complex gives magnetic moment value 2.28 BM , expected for one unpaired electron of the d^9 electronic configuration indicating octahedral geometry. Fe(III) complex gave a magnetic moment of 5.91 BM This shows an octahedral geometry around the metal ion. Cr(III) [25] gave a magnetic moment 3.94 BM, expected for three unpaired electrons, indicating octahedral geometry. Remaining complexes are found to be diamagnetic.

Infrared spectra

Infra red spectra of the free Schiff base and the metal complexes studied are given in Table 1.4.2 The ligand anthracene carboxaldehyde – L – tyrosine shows strong bands at $\approx$ 1659 cm^{-1} due to carbonyl stretching frequency of carboxylate group, another band at $\approx$1520 cm^{-1} due to C = N and C = C stretches and a third band at $\approx$1440 cm^{-1} corresponding to γ syCOO^- vibration.

In the metal chelate, the presence of coordinated water is confirmed by the observation of a broad band appearing in the region 3450 – 3000 cm^{-1}. The coordinated nature of the water molecule is further supported by the appearance of a rocking mode of medium intensity at 860 cm^{-1}

The strong bands observed in the region 1700 – 1300 cm $^{-1}$, one at 1660 and the other at ≈ 1410 cm $^{-1}$ are attributed to the asymmetric and symmetric stretching vibrations respectively of the carboxylate ion. The presence of monodentate carboxylate group is indicated here.

The sharp band at 1520 cm $^{-1}$ in the IR spectrum assignable to γ (C = N) of the Schiff base residue, shifts to lower frequencies around 1513 cm $^{-1}$ in the complexes indicating a reduction of electron density in the azomethane linkage as the nitrogen coordinates to the metal ion.

Further evidence for the coordination of nitrogen and oxygen arises from the IR spectral data. In all the above complexes new absorption bands are observed in the regions 585 – 598 cm $^{-1}$ and 420 – 460 cm $^{-1}$. These bands are assigned to γ M – N and γ M – O stretching vibrations respectively.

The region 1600 – 1450 cm $^{-1}$ also showed bands / shoulders due to the skeletal vibrations of aromatic nucleus.

Electronic spectra

The electronic spectral data was found to agree with conclusions arrived from magnetic susceptibility measurements. The spectrum of Co (II) complex with octahedral geometry was very clear in the spectrum at 20500 cm^{-1} and 13225 cm $^{-1}$ which are assigned to the transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ respectively of Co (II) complex [231]. The electronic spectrum of the Mn(II) complex containing a band at 25000 cm^{-1} which was taken as evidence to support the presence of Mn (II) in the octahedral environment. A weak shoulder observed at 18181 cm^{-1} may be attributed to $^5T_{2g} \longrightarrow {}^5E_g$ transition characteristic of octahedral stereo chemistry around Fe(III) metal ion [232]. Ni(II) complex shows three bands in the electronic spectrum which can be attributed to spin allowed d – d transition at 26954 cm^{-1}, 25000 cm^{-1} and 17452 cm^{-1} assigned to $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$, respectively Cu(II) complex shows a strong band at 24938 cm^{-1} attributed to charge transfer transition [233]

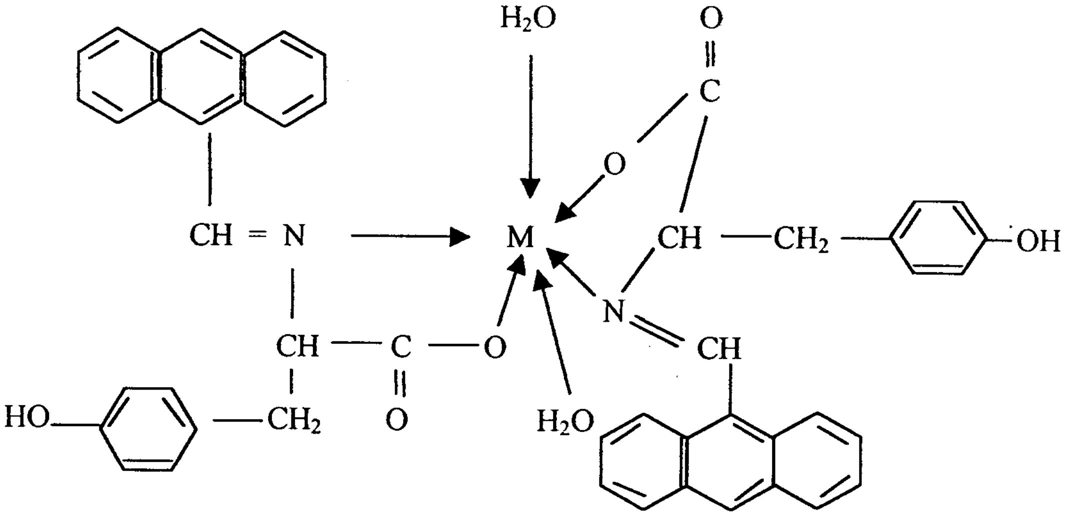
X – Ray studies

Zn (II) complex of ACT was subjected to X – Ray analysis to determine its structure in solid state. A detailed study is given in part III. Investigation shows that Zn(II) complex of ACT is orthorhombic.

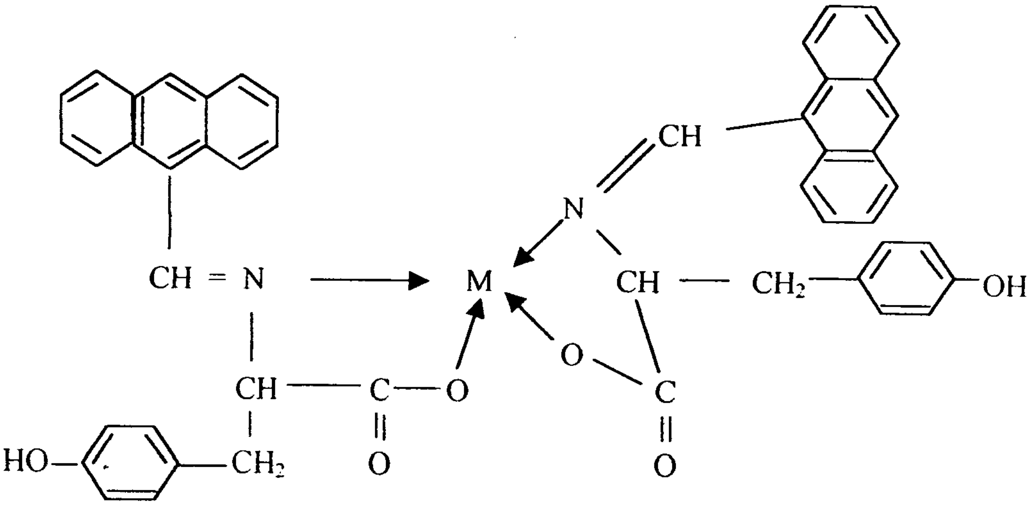
Thermal studies

Co(II) , Ni (II) and Cu(II) complexes were subjected to thermal studies by non isothermal methods. Single stage decomposition is observed in Co(II) and Ni(II) complex, where as Cu (II) complex undergoes a two stage decomposition. The determination of kinetic parameters, mechanism of decomposition and probable assignment of each decomposition are discussed in Part II

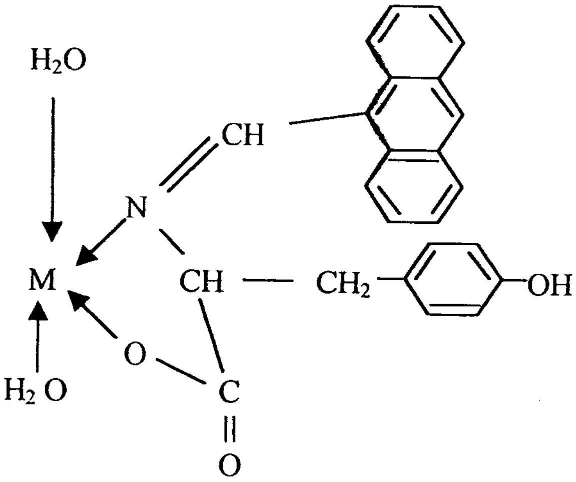
Based on the above results, hexa coordinated structure is assigned to all chelates except Zn (II) , Cd (II) , Hg (II) and Ag (I). The general structure of these ten complexes are shown below



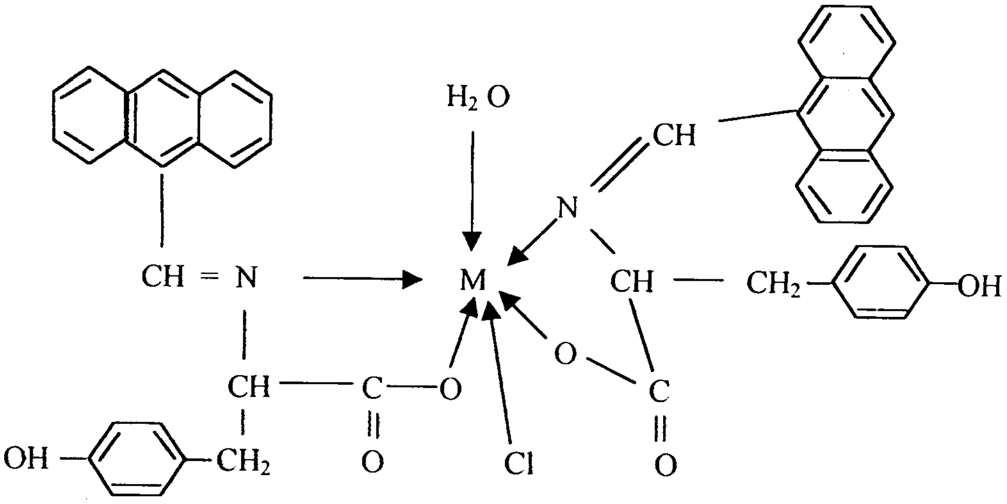
M = Mn (II), Co (II), Ni (II), Cu (II)



M = Zn (II) , Cd (II) and Hg(II)



M = Ag (I)



M = Cr (III), Fe (III)

TABLE 1.4.1

Micro analytical, magnetic moment and conductance data of transition metal chelates of Anthracene-9-carboxadehyde-L tyrosine

Metal Complexes	Colour	Melting point	M%	C%	H%	N%	μ_{eff} B.M.	Ω_m^{-1}
$[CrL''_2(H_2O)Cl]$	Green	190	5.83 (6.18)	69.87 (68.42)	4.85 (4.75)	3.4 (3.32)	3.94	8.92
$[MnL''_2(H_2O)_2]$	Brown	142	6.5 (6.64)	70.52 (69.62)	4.62 (4.83)	3.1 (3.38)	5.92	3.78
$[FeL''_2(H_2O)Cl]$	Reddish Brown	134	6.79 (6.66)	69.53 (68.09)	4.83 (4.73)	3.38 (3.31)	5.91	2.2
$[CoL''_2(H_2O)_2]$	Yellow	95	6.61 (7.1)	69.96 (69.29)	4.52 (4.81)	3.4 (3.37)	5.06	8.2
$[NiL''_2(H_2O)_2]$	Orange	160	6.85 (7.06)	68.84 (69.31)	4.58 (4.81)	3.91 (3.37)	3.2	12.7
$[CuL''_2(H_2O)_2]$	Brown	104	8.8 (7.06)	69.21 (68.90)	4.52 (4.78)	3.1 (3.35)	2.28	15.51
$[ZnL''_2]$	Yellow	195	8.16 (7.6)	69.75 (71.83)	4.77 (4.49)	3.34 (3.49)	D	4.32
$[CdL''_2]$	Pale yellow	235	12.35 (13.24)	65.47 (67.85)	4.26 (4.24)	4.41 (3.3)	D	9.3
$[HgL'_2]$	Orange	100	20.88 (21.44)	59.2 (61.47)	4.11 (4.27)	2.9 (2.99)	D	7.3
$[AgL''(H_2O)_2]$	Dark Green	84	20.7 (21.1)	55.96 (56.23)	4.09 (4.3)	2.71 (2.73)	D	6.09

The calculated values are given in parentheses; D dia magnetic; M metal; Ω_m^{-1} molar conductance in ohm^{-1} cm^2 mol^{-1}

TABLE 1.4.2

Selected absorption frequencies (cm $^{-1}$)of transition metal chelates of Anthracene carboxaldehyde L – tyrosine (ACT)

	γ H_2O	γ asyCOO^-	γ syCOO^-	γ C = N	In Plane deform	Out of plane deform	γ M - N	γ M – O
Ligand	---	1659	1440	1520	897	777 731	---	---
$[CrL^{11}{}_2Cl(H_2O)]$	3449	1664	1447	1516	890	777 738	593	425
$[Mn\,L^{11}{}_2(H_2O)_2]$	3426	1666	1414	1513	870	777 725	592	426
$[Fe\,L^{11}{}_2Cl(H_2O)]$	3409	1659	1414	1513	877	777 738	585	433
$[Co\,L^{11}{}_2(H_2O)_2]$	3443	1666	1401	1513	870	784 724	585	433
$[Ni\,L^{11}{}_2(H_2O)_2]$	3436	1664	1438	1518	895	781 731	593	426
$[Cu\,L^{11}{}_2(H_2O)_2]$	3416	1660	1434	1513	890	777 731	592	425
$[Zn\,L^{11}{}_2]$		1666	1440	1513	870	771 731	598	459
$[Cd\,L^{11}{}_2]$		1664	1414	1510	870	781 724	592	426
$[Hg\,L^{11}{}_2]$		1659	1401	1518	872	777 731	590	425
$[Ag\,L^{11}(H_2O)_2]$	3449	1659	1401	1513	850	778 731	598	420

PART I

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEAME-GLYCINE

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER V

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE-GLYCINE [L^{111}_{H}]

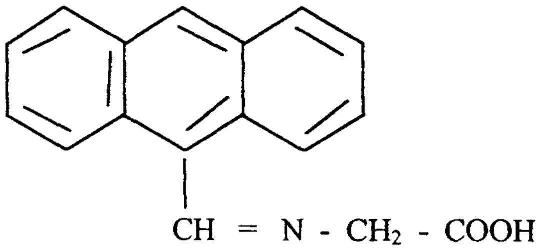
Transition metal complexes of amino acids have a variety of applications including biological, clinical and analytical. The coordinating possibilities of amino acid like glycine have been improved by condensing with carbonyl compound like anthracene-9-carboxaldehyde. No work has been reported so far on the Schiff base derived from anthracene-9-carboxaldehyde and glycine. In this chapter the studies made on anthracene-9-carboxaldehyde – glycine and its metal complexes are discussed.

Preparation of ligand

Glycine (0.75 g, 0.01 mol) in water was mixed with anthracene-9-carboxaldehyde (2.06 g, 0.01 mol) in ethanol. This mixture was refluxed for two hours. It was then concentrated by evaporation. On cooling yellow precipitate was separated. This precipitate was then filtered, washed with aqueous alcohol, and dried over anhydrous calcium chloride. Melting point was found to be 84^{0}C. The ligand was soluble in hot methanol and ethanol.

Characterization of ligand

The ligand anthracene - 9 - carboxaldehyde glycine was purified by repeated recrystallization from ethanol. The ligand was characterized on the basis of elemental analysis and IR spectral data .The proposed structure of the ligand is as follows.



:	C %	H %	N %
Analytical data found for ACG	77.54	4.82	5.81
Calculated value for$C_{17}H_{13}NO_2$	77.57	4.94	5.32

Studies on Cr(III), Mn (II), Fe(III), Co(II), Ni(II) ,Cu(II) Zn(II) Cd(II), Hg(II) and Ag(I) complexes of anthracene-9-carboxaldehyde glycine

General method of preparation

Most of these complexes were prepared by refluxing hot ethanolic solution of anthracene - 9 - carboxaldehyde with aqueous solution of glycine and metal salts in the 1 : 2 molar ratio For the preparation of Ag(I) complex the whole reaction was carried out at dark in which the metal to ligand ratio is 1:1.

To an ethanolic solution of anthracene - 9 - carboxaldehyde (2.06 g, 0.01 mol), aqueous solution of glycine (0.75 g, 0.01 mol) and 1 gm sodium acetate were added. It was refluxed for 1 hour. To this refluxing solution aqueous Cr (III) chloride solution (1.23 g, 0.005 mol) was added and again refluxed for 1 hour and cooled. The precipitate was filtered and washed with water alcohol mixture and dried. Yield : 65 %

Hot ethanolic solution of anthracene - 9 - carboxaldehyde (2.06 g, 0.01 mol) was mixed with aqueous solution of manganese acetate (1.23 g, 0.005 mol), glycine (0.75 g, 0.01 mol) and sodium acetate (1 g). This mixture was refluxed for 3 hours. The brown colored precipitate of the complex was filtered, washed with ethanol - water mixture and dried in vacuum desiccator. The yield was 80 %

A mixture of anhydrous Fe (III) chloride (1.62 g, 0.01 mol), the ligand (5.26g, 0.02 mol) in ethanol and 1 g sodium acetate were refluxed for 3 hours. The reddish brown complex was filtered, washed, with aqueous ethanol and dried in desiccator. Yield : 90 %

Co (II) complex was prepared similarly as Cr (III) complex using Co(II) acetate solution Its yield was 86 %.

Ni (II) complex was prepared by following the same procedure as that of the Co (II) complex. 85 % yield obtained.

The green Cu (II) complex was prepared from Cu (II) acetate by refluxing together a mixture of ethanolic solution of anthracene - 9 - carboxaldehyde (2.06 g, 0.01 mol) aqueous solution of glycine (0.75 g , 0.01 mol), 1 gm sodium acetate solution and aqueous solution of Cu (II) acetate (0.998 g, 0.005 mol) for 1 hour. Yield : 90%

For the preparation of Zn(II) complex, ligand (2.6 g, 0.01 mol) and zinc acetate (1.28 g , 0.005 mol) were taken. Ligand was dissolved in ethanol by refluxing on a water bath and to this solution hot ethanolic solution of the metal salt and sodium acetate were added with constant shaking and the mixture was refluxed for 3 hours. The complex separated was filtered, washed with 1 : 1 ethanol water mixture and dried. Yield : 65 %

Cadmium acetate (2.67 g, 0.01 mol) was dissolved in water. To this added an ethanolic solution of ligand (2.6 g , 0.01 mol) and the mixture was refluxed for 4 hours. The solution was concentrated by evaporation and cooled. Yellow precipitate was filtered, washed with 1 : 1 ethanol water mixture, and dried. Yield 80 %.

Mercuric chloride (1.36 g , 0.005 mol) dissolved in minimum water was added drop wise to a hot solution of the ligand (2.6 g , 0.01 mol) in ethanol. Sodium acetate (1 g) was added , and the mixture refluxed for 2 hours. The solid complex precipitated on cooling was filtered, washed with aqueous ethanol and dried in a vacuum desiccator. yield: 65 %.

To the ligand anthracene - 9 - carboxaldehyde – glycine (2.6 g, 0.01 mol) dissolved in hot ethanol , an ethanolic solution of silver acetate (0.01 mol) was added and refluxed for 3 hours. The precipitate was filtered and washed with aqueous ethanol and dried . Yield : 85 %

Characterization of the complexes

The complexes were characterized on the basis of elemental analysis, magnetic and conductance measurements and UV visible and IR spectra.

Results and discussion

Elemental analysis

Percentage of carbon, hydrogen and nitrogen were determined by micro analytical methods. The results are summarized in Table 1: 5 : 1 , The complexes are stable and colored and possess 1 : 2 stochiometry except Ag (I)

Molar conductance

Molar conductance data of the complexes in methanol are tabulated in Table 1: 5: 1. The conductance value for Mn (II) complex was found to be 24.9. Remaining complexes have conductance value in the range of 1 to 10 ohm $^{-1}$ mol $^{-1}$ cm ^{2} which indicate that these complexes are non electrolytes in methanol.

Magnetic studies

The magnetic moments of the complexes are given in Table 1.:5. 1. Mn (II) complex shows a µeff value of 6.2 1 BM , which reveals the high spin octahedral geometry around manganese.[135] .Co (II) complex possess a magnetic moment value of 4.77 BM. The observed magnetic moment value for the spin free octahedral Co(II) ($^4T_{1g}$) have spin only value . It may be due to the orbital contribution of both the ground state ($t_{2g}^5\ eg^2$) and the first excited state ($t_{2g}^4\ e_g^3$). It is reported that high spin symmetry can be assigned to Co (II) complex , because the measured µ eff value is in the range of 4.7 to 5. 2 BM[39]. Ni (II) complex possess magnetic moment of 2.92 BM indicating the presence of two unpaired electrons with electronic configuration of $t_{2g}^6\ e_g^{\ 2}$. An octahedral geometry can be assigned to Ni (II) complex also. Observed magnetic moment of 1.74 BM for Cu (II) complex indicated the presence of one unpaired electron. This corresponds to $d^{\ 9}$ electronic configurations. Cr complex with magnetic moment 3.97 BM suggested that Cr is in trivalent state, and has an octahedral geometry. A magnetic moment of 5.84 BM suggested an octahedral geometry for Fe (III) complex. All other complexes were found to be dia magnetic.

Infrared spectra

Comparison of the infrared spectra of the chelates and ligand reveal that the spectra of chelates differ from that of the ligand in some characteristic frequencies. The presence of coordinated water molecules in the complexes is confirmed by the appearance of a double hump between 3400 – 3450 cm $^{-1}$ and is followed by a sharp rocking mode of vibration between 840 and 850 cm $^{-1}$

The band appearing in the spectra of ligand at 1613 cm $^{-1}$ is due to γ C = N, which undergoes to lower frequency region in the complexes indicating coordination through azomethine nitrogen.

The aromatic out of plane vibration is seen near 870 cm $^{-1}$ and in plane vibration at 770 cm $^{-1}$ and 725 cm $^{-1}$. The asymmetric stretching vibrations of COO^- group is seen at 1659 cm^{-1}, while symmetric stretching vibrations occur at 1407 cm $^{-1}$ in ligand spectra. Upon complexation, both these bands shift to lower frequency region, ≈1610 to 1630 cm $^{-1}$ and ≈1355 to 1405 cm $^{-1}$

The conclusive evidence of bonding of the ligand to the central metal ion is provided by the appearance of bands at ≈ 500 cm $^{-1}$ and ≈ 450 cm $^{-1}$, which can be assigned to M – N and M – O bands respectively.

Selected infrared frequencies of the ligand and the complexes are represented in Table 1 . 5 . 2.

Electronic spectra

The ligand spectra showed two characteristic bands near 33115 cm^{-1} and 22173 cm^{-1}. The shift of these bands exhibited in the spectra of complexes can be taken as a proof of coordination of the ligands to metal ions [230]

The Cu(II) complex shows a broad band at 16670 cm $^{-1}$ indicating octahedral stereo chemistry. Ni (II) complex displays a band at 25906 cm $^{-1}$ that indicates an octahedral geometry. The green color and the absorption in the region 16000 cm $^{-1}$ and

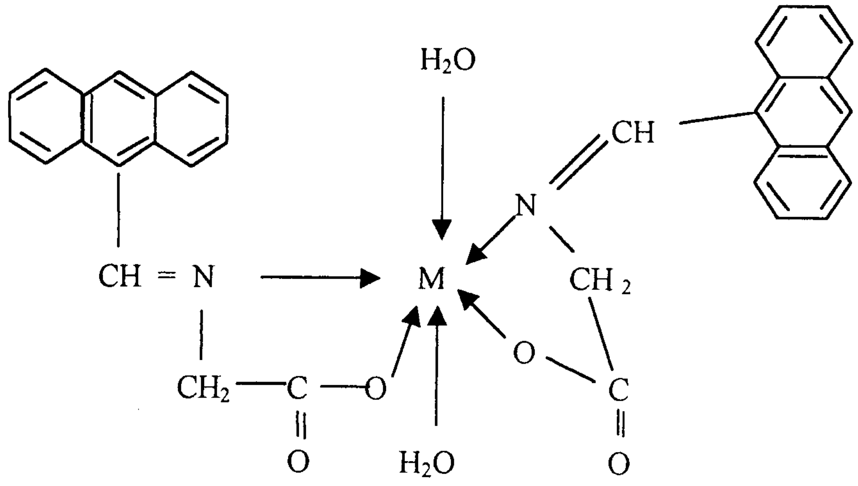
23250 cm $^{-1}$ in the case of Cr(III) complex suggests an octahedral nature. Co(II) complexes with octahedral geometry was clear in the spectra at 25000 – 27000 cm $^{-1}$. The band at ≈ 10000 cm $^{-1}$ in Ni (II) complexes are assignable to $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ transition and other at ≈25906 cm $^{-1}$ to $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ transition of octahedral geometry. In the case of Fe (III) complex, an intense band at 25000 cm $^{-1}$ which is due to the charge transfer. Electronic spectrum of manganese complex supports the presence of Mn (II) in octahedral environment. Based on these observations, the structure of complexes can be confirmed to be octahedral. Various thermal and spectral studies of Co(II), Ni(II) and Cu (II) complexes of ACG support octahedral structure.

X – Ray studies

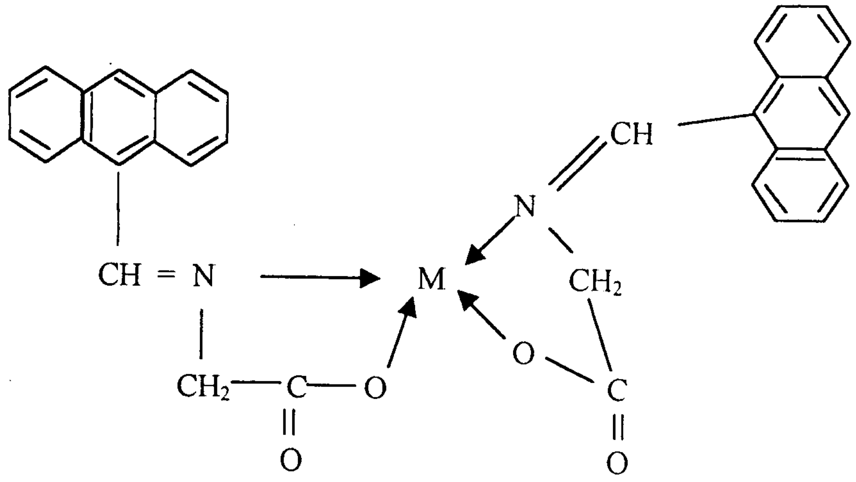
X ray diffraction data of Fe (III) and Ag (I) complex are presented in Part III. These two complexes form orthorhombic crystals in solid state.

Thermal studies

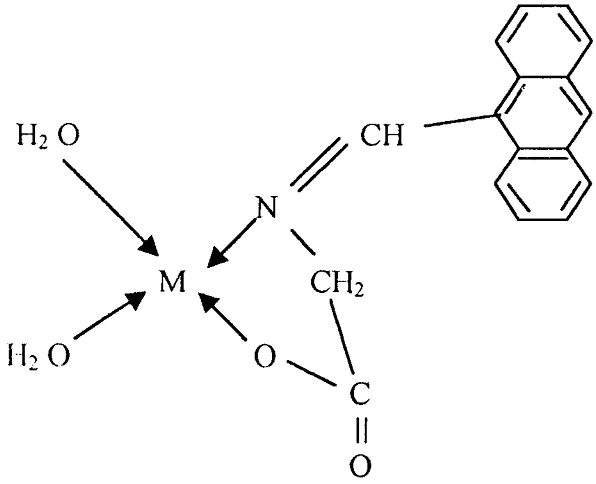
Thermal data of Co (II) , Ni (II) and Cu (II) complexes are presented in Part II. Thermograms of these chelates exhibit mass loss corresponding to water molecules around 150^{0}C, and this evidence further supports the presence of coordinated water. The residues were found to be $Co_3\,O_4$, Ni O and Cu O respectively. Based on the above physico chemical studies, octahedral structure has been assigned to Cr (III) , Mn (II), Fe (III), Co (II) , Ni (II) , Cu (II) , complexes and tetrahedral geometry to Zn (II) , Cd (II), Hg (II) and Ag (I).



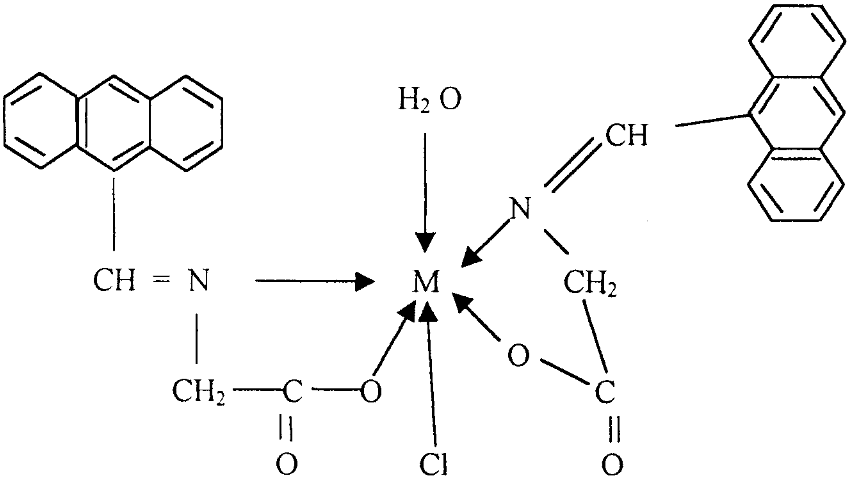
M = Mn (II), Co (II), Ni (II), Cu (II)



M = Zn (II) , Cd (II) and Hg(II)



M = Ag (I)



M = Cr (III), Fe (III)

TABLE 1.5.1

Micro analytical, magnetic moment and conductance data of transition metal chelates of Anthracene-9-carboxadehyde-L glycine

Metal Complexes	Colour	Melting point	M%	C%	H%	N%	μ_{eff} B.M.	Ω_m^{-1}
$[CrL'''_2(H_2O)Cl]$	Green	115	8.26 (8.34)	64.64 (64.7)	4.17 (4.14)	4.5 (4.44)	3.97	4.62
$[MnL'''_2(H_2O)_2]$	Brown	162	9.2 (8.9)	66.5 (66.42)	4.32 (4.5)	5.01 (4.5)	6.21	24.95
$[FeL'''_2(H_2O)Cl]$	Reddish Brown	148	8.82 (9)	65.2 (64.4)	4.55 (4.42)	4.62 (4.42)	5.84	2.46
$[CoL'''_2(H_2O)_2]$	Yellow	208	9.1 (9.31)	69.2 (69.9)	4.5 (4.52)	4.54 (4.52)	4.77	7.1
$[NiL'''_2(H_2O)_2]$	Pale Yellow	118	8.91 (9.4)	65.2 (65.9)	4.6 (4.56)	4.24 (4.32)	2.92	9.14
$[CuL'''_2(H_2O)_2]$	Green	156	10.83 (10.18)	65.62 (65.4)	4.4 (4.48)	4.52 (4.48)	1.74	9.9
$[ZnL'''_2]$	Yellow	106	10.4 (11.09)	70.01 (69.8)	4.17 (4.07)	4.47 (4.74)	D	3
$[CdL'''_2]$	Pale Yellow	100	17.38 (17.65)	64.41 (64.09)	3.89 (3.77)	4.41 (4.39)	D	5.6
$[HgL'''_2]$	Yellow	122	26.86 (27.1)	56.62 (56.29)	3.36 (3.36)	3.78 (3.86)	D	3.12
$[AgL'''(H_2O)_2]$	Dark Green	88	26.2 (26.57)	50.83 (50.24)	4.09 (3.9)	3.23 (3.44)	D	10.09

The calculated values are given in parentheses; D dia magnetic; M metal; Ω_m^{-1} molar conductance in ohm^{-1} cm^2 mol^{-1}

TABLE 1.5.2

Selected absorption frequencies (cm $^{-1}$)of transition metal chelates of Anthracene carboxaldehyde glycine (ACG)

Complex	γ H_2O	γ asyCOO	γ syCOO	γ C = N	In plane deform	Out of plane deform	γ M - N	γ M - O
Ligand	---	1659	1407	1613	864	771 725	---	---
$[Cr\,L^{III}_2Cl\,(H_2O)]$	3449	1625	1378	1557	877	779 730	505	425
$[Mn\,L^{III}_2\,(H_2O)_2]$	3409	1666	1401	1580	877	777 724	506	439
$[Fe\,L^{III}_2Cl\,(H_2O)]$	3423	1619	1381	1580	870	778 725	506	413
$[Co\,L^{III}_2\,(H_2O)_2]$	3423	1613	1388	1560	883	771 738	512	446
$[Ni\,L^{III}_2\,(H_2O)_2]$	3443	1613	1401	1587	877	771 731	500	419
$[Cu\,L^{III}_2\,(H_2O)_2]$	3436	1626	1355	1560	890	771 731	492	439
$[Zn\,L^{III}_2]$		1619	1401	1580	870	771 725	506	413
$[Cd\,L^{III}_2]$		1612	1376	1582	888	771 731	510	418
$[Hg\,L^{III}_2]$		1613	1388	1560	877	770 728	508	415
$[Ag\,L^{III}\,(H_2O)_2]$	3429	1626	1388	1560	870	764 731	499	439

PART I

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - DL - ALANINE

CHAPTER VI

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - DL – ALANINE(L_H^{IV})

Anthracene carboxaldehyde –DL- alanine is a potentially bidentate Schiff base ligand, which has been synthesized for the first time. This ligand forms complexes with various transition metals.

Preparation of the ligand

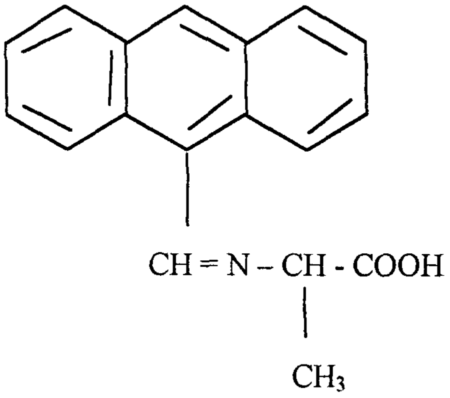
Anthracene carboxaldehyde DL– alanine was prepared from anthracene carboxaldehyde (2.06 g, 0.01 mol) and DL-alanine (.89g,.01mol) following the same procedure adopted for the preparation of the ligand in chapter V. The melting point of the purified sample was found to be 93^{0}C.

Characterization of the ligand

The ligand was found to be soluble in methanol and ethanol. Anthracene carboxaldehyde –DL alanine was then characterized on the basis of elemental analysis and spectral data

Ligand ACA	C %	H %	N %
Analytical data found–	77.2	4.88	5.5
Calculated data for $C_{18}H_{15}NO_2$	77.92	5.41	5.05

Analytical and spectral observations suggest the following structure for the ligand



Preparation of complexes

Hot aqueous solution of DL-alanine was mixed with methanolic solution of anthracene carboxaldehyde in 1:1 molar ratio and refluxed. Appropriate metal salt solution in methanol was added drop wise to the boiling solution and refluxed for 2 hours. Concentrated by evaporation and on cooling complexes were separated.

Fe(III), Cd(II) and Hg(II) complexes were formed only after refluxing the solution for 4 hours. The separated complexes were filtered, washed with water and methanol mixture. It was dried over anhydrous calcium chloride. The yield was found to be approximately 80 %

Characterization of complexes

The complexes were characterized on the basis of elemental analysis, UV and IR spectral data, magnetic studies and conductance measurements

Results and discussion

All complexes are colored. All of them are soluble in hot methanol and ethanol, insoluble in common organic solvents. On the basis of elemental analysis Mn(II), Co (II) , Ni(II), and Cu (II) complexes can be represented by the general formula [ML^{IV}_2 (H_2O)$_2$.]

Zn (II), Cd (II) and Hg (II) are represented by the general formula [ML^{IV}_2]and complexes of Fe (III) and Cr(III) having the formula [ML^{IV}_2(H_2O) Cl.] Complex of Ag(I) can be represented as [Ag L^{IV} (H_2O)$_2$.] The analytical data and physical characteristics of these complexes are tabulated in Table 1 . 6. 1. Magnetic moment value and molar conductivity of the complexes are also reported in this Table.

Molar conductance

Molar conductance measurements of these complexes were carried out in methanol. Values show that they are non-electrolytes.

Magnetic measurements

The observed magnetic moment of the Fe (III) complex was 6.1 BM . For Cu (II) complex, the μ eff value obtained was 1.85 BM therefore octahedral structure can be assigned to both Fe (III) and Cu (II) complexes. The magnetic moment value of Ni (II) complex was 2.82 BM and for Mn(II) it was 6.04BM and these values were in agreement with their octahedral geometry.

For Co (II) complex the observed magnetic moment was 4.93 BM and for Cr (III) it was 3.94 BM. Therefore octahedral structure can be assigned to both Co (II) and Cr (III) complexes. The remaining complexes were found to be diamagnetic.

Infrared spectra

Characteristic IR absorption bands of the ligand and complexes are summarized in Table 1.6.2. Comparison of IR spectra of the complexes with that of the free ligand shows significant changes in two areas. Firstly a band of medium intensity of about 1659 cm $^{-1}$ for the ligand which may be attributed to the cabonyl stretching frequency of the carboxylate group, shows a shift in frequencies in the spectra of the complexes indicating chelation of the ligand to the metal atom through the carbonyl oxygen. The second IR region showing important changes upon ligand complexation is the 1700 – 1500 cm $^{-1}$ range. Compounds containing C = N group such as Schiff bases have C = N in the range 1690 – 1470 cm $^{-1}$. In this ligand, the band occurred at 1553 cm $^{-1}$ whereas, in the complexes, the band occurred at 1510 – 1546 cm $^{-1}$. This shift towards the lower frequencies in the complexes indicates the participation of azomethine nitrogen in coordination with metal ions

Since there are two carboxylate groups in the complexes, its effect on the frequencies is not predictable. In all the complexes, the asymmetric and symmetric stretching vibrations of the carboxylate groups occur at 1650 – 1670 cm $^{-1}$ and 1440 – 1493 cm $^{-1}$ showing a $\Delta\gamma$ of about 210 cm $^{-1}$. Monodentate carboxylate group has a $\Delta\gamma$ value of >150 cm $^{-1}$. Monodentate carboxylate groups are therefore indicated in the above chelates.

However exclusive evidence regarding the bonding of nitrogen and oxygen is provided by the occurrence of M – O and M – N in the region ≈ 426 cm $^{-1}$ and ≈ 598 cm^{-1} respectively in the metal complexes. In the chelates the presence of coordinated water is confirmed by the observation of a broad band at 3500 – 3000 cm $^{-1}$.

Electronic spectra

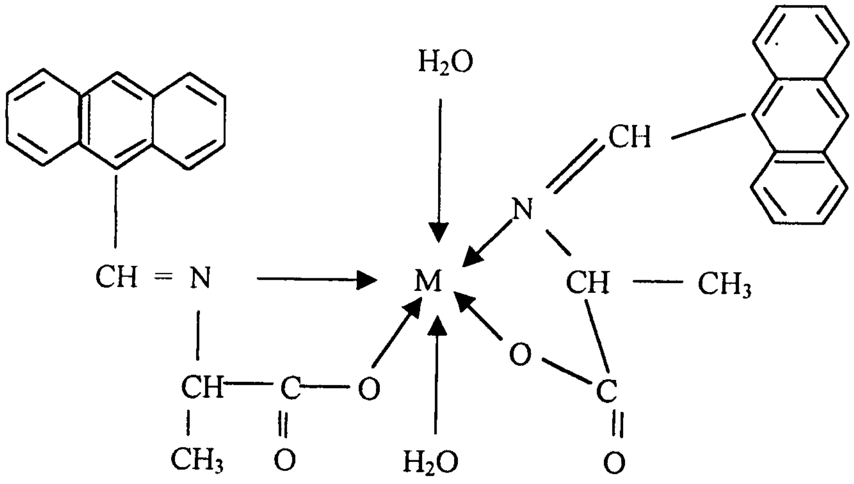
Electronic spectra of ligands are characterized by two bands lying at 24096 cm^{-1} and 32467 cm $^{-1}$. During complex formation a red shift is detected for these bands, which indicate the involvement of Schiff base in coordination. The electronic spectra of Mn(II) complex exhibited a band at 24875 cm $^{-1}$, which was taken as evidence to support the presence of Mn (II) in octahedral geometry. The electronic spectra of Fe (III) complexes show an intense band at 17985 cm $^{-1}$, which is due to charge transfer. A weak shoulder is detected at 18181 cm $^{-1}$. Since ground state of Fe(III) in high spin complexes is in $^6A_1$ all transitions are expected to be weak and frequently obscured by charge transfer band . The electronic spectra of Co(II) complex is characterized by two bands at 10530 cm $^{-1}$ and 23954 cm^{-1} due to $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transitions. Ni(II) complex is also characterized by two bands , one at 10110 cm^{-1} and 22560 cm $^{-1}$. Based on these observations, the structure of complexes can be confirmed to be octahedral. The octahedral geometry of Cu (II) complex is clear from the absorption band at 16155 cm $^{-1}$and Cr (III) the absorption band at 15380 cm $^{-1.}$ In the case of other transition metal complexes no absorption bands other than ligand band is seen.

X ray studies

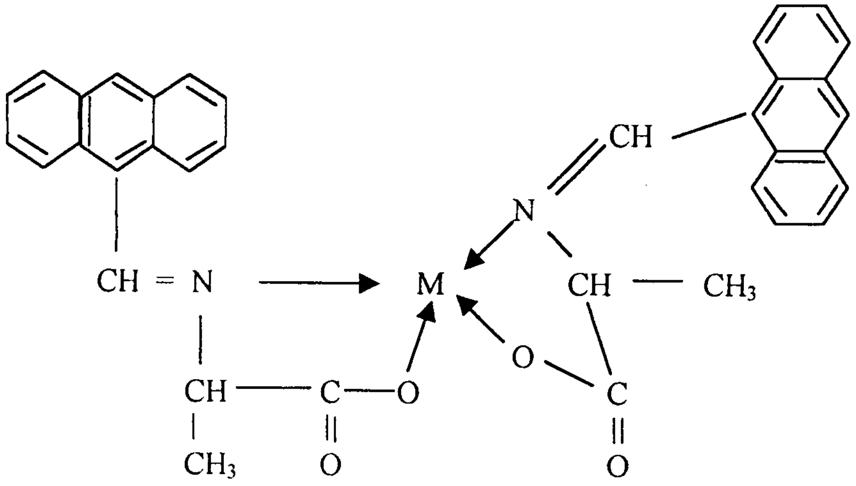
The Cr (III) complex of anthracene carboxaldehyde D L alanine was found to form orthorhombic crystalline lattice. The determination of unit cell dimensions and density calculations confirmed the molecular weight proposed based on the physico chemical studies with metal to ligand ratio. The details of procedure are explained in Part III chapter III .

Thermal studies

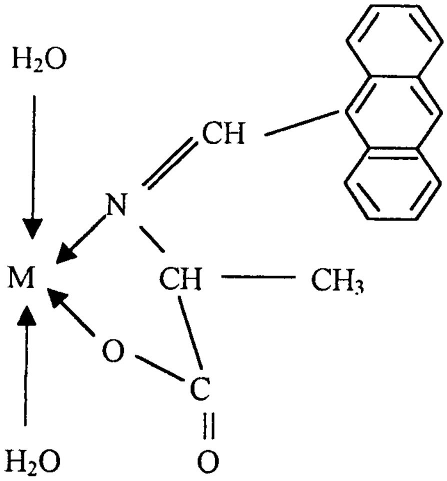
Co(II), Ni(II), and Cu(II) were subjected to non isothermal studies, the heating rate being 10^0 per minute. The mass loss in each stage were in agreement with their 1:2 stochiometry. The detailed study of mechanism of decomposition is given in Part II, Chapter V. Based on the above studies tetrahedral geometry is given for Zn (II) , Cd (II) , Hg (II) and Ag (I) complex. All the other complexes are assigned to have octahedral geometry. The ligand acts as monovalent bidentate one. The probable structures of complexes are given below.



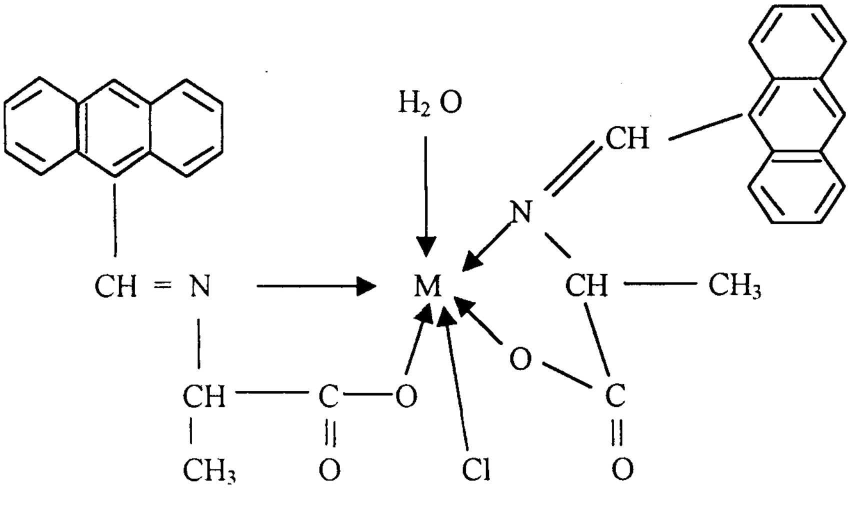
M = Mn (II), Co (II), Ni (II), Cu (II)



M = Zn (II) , Cd (II) and Hg(II)



M = Ag (I)



M = Cr (III), Fe (III)

TABLE 1.6.1

Micro analytical, magnetic moment and conductance data of transition metal chelates of Anthracene-9-carboxadehyde-DL alanine

Metal Complexes	Colour	Melting point	M%	C%	H%	N%	μ_{eff} B.M.	Ω_m^{-1}
$[CrL^{IV}_2(H_2O)Cl]$	Green	160	8.2 (7.9)	65.46 (65.67)	4.7 (4.56)	4.37 (4.26)	3.94	6.31
$[MnL^{IV}_2(H_2O)_2]$	Brown	85	8.01 (8.5)	67.92 (67.15)	5.1 (4.97)	4.43 (4.35)	6.04	5.2
$[FeL^{IV}_2(H_2O)Cl]$	Reddish Brown	118	8.97 (8.44)	65.06 (65.28)	4.97 (4.53)	4.35 (4.23)	6.1	2.6
$[CoL^{IV}_2(H_2O)_2]$	Yellow	160	9.3 (10.1)	66.98 (66.73)	4.83 (4.94)	4.4 (4.33)	4.93	4.64
$[NiL^{IV}_2(H_2O)_2]$	Orange	122	9.24 (9.1)	66.71 (66.76)	4.82 (4.94)	4.4 (4.33)	2.82	9.4
$[CuL^{IV}_2(H_2O)_2]$	Green	118	9.75 (9.74)	66.26 (66.27)	4.91 (4.91)	4.29 (4.3)	1.85	6.5
$[ZnL^{IV}_2]$	Yellow	89	9.51 (10.0)	69.08 (69.92)	4.69 (4.53)	4.48 (4.53)	D	6.7
$[CdL^{IV}_2]$	Pale Yellow	93	16.07 (16.9)	65.2 (64.980	4.76 (4.81)	4.2 (4.21)	D	3.3
$[HgL^{IV}_2]$	Pale Yellow	182	26.3 (26.63)	58.4 (57.37)	3.75 (3.98)	3.55 (3.72)	D	2.6
$[AgL^{IV}(H_2O)_2]$	Dark Green	87	26 (25.69)	51.79 (51.42)	4.19 (4.28)	3.4 (3.33)	D	9.23

The calculated values are given in parentheses; D dia magnetic; M metal; Ω_m^{-1} molar conductance in $ohm^{-1}\ cm^2\ mol^{-1}$

TABLE 1 . 6 . 2

Selected absorption frequencies (cm^{-1})of transition metal chelates of Anthracene carboxaldehyde DL – alanine (ACA)

Complex	γ H_2O	γ asyCOO^-	γ syCOO^-	γ C = N	In plane deform	Out of plane deform	γ M - N	γ M – O
Ligand	----	1659	1440	1553	877	778 731	---	---
$[CrL^{IV}_2(H_2O)Cl]$	3420	1618	1430	1515	868	770 725	580	410
$[Mn L^{IV}_2 (H_2O)_2]$	3423	1666	1447	1546	870	777 731	592	426
$[Fe L^{IV}_2 Cl (H_2O)]$	3416	1619	1434	1513	870	784 738	598	426
$[Co L^{IV}_2 (H_2O)_2]$	3423	1613	1434	1546	870	784 738	592	426
$[Ni L^{IV}_2 (H_2O)_2]$	3448	1619	1434	1546	870	771 731	585	426
$[Cu L^{IV}_2 (H_2O)_2]$	3416	1666	1493	1513	870	784 724	592	426
$[Zn L^{IV}_2]$		1630	1420	1525	872	771 728	580	431
$[Cd L^{IV}_2]$		1618	1431	1513	870	781 735	595	429
$[Hg L^{IV}_2]$		1622	1428	1525	868	775 729	598	426
$[Ag L^{IV} (H_2O)_2]$	3499	1659	1434	1546	870	784 731	598	420

PART I

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L - PHENYL ALANINE

G. Indira Devi “ Studies on transition metal complexes of schiff bases derived from aminoacids” Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER VII

TRANSITION METAL COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L – PHENYL ALANINE (L^{Y}_{H})

In this chapter the studies of the synthesis and characterization of Cr(III), Mn(II), Fe(III), Co(II) , Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Ag(I)complexes of anthracene carboxaldehyde -L- phenyl alanine are reported.

Synthesis of the ligand

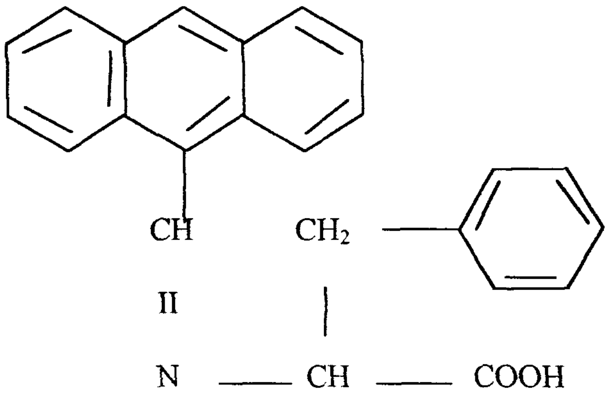
A mixture of methanolic solutions of anthracene – 9 – carboxaldehyde (2.06 g, 0.01 mol) and phenyl alanine (1.65g, 0.01 mol) were refluxed on a water bath for 2 hours. Mixture was concentrated, cooled and the ligand was then separated. It was filtered, washed with aqueous methanol and dried in a desiccator over anhydrous calcium chloride.

Characterization of ligand

The ligand was characterized on the basis of CHN analysis and IR data. The calculated and observed percentage is in good agreement. Melting point of the ligand is found to be 95^{0}C.

	C%	H%	N%
Analytical data found for ACP	81.75	5.41	3.96
Calculated data for $C_{24}H_{21}NO_2$	81.59	5.38	3.97

Based on this, the structure of the ligand was confirmed as



Transition metal complexes of Anthracene – 9 - carboxaldehyde – L - phenyl alanine

Anthracene -9- carboxaldehyde -L- phenyl alanine and their transition metal chelates have been synthesized and then examined in the context of the structural aspect of the ligand moiety in the metal chelates.

Preparation of complexes

Metal complexes were prepared by refluxing methanolic solutions of the ligand with appropriate amount of metal salts (metal acetate/chloride) in methanol. The procedure adopted for the preparation of complexes is the same as that of the complexes of ACA. In all these cases, the complex separated was filtered, washed with 1:1 methanol water mixture and dried in a vacuum desiccator over anhydrous calcium chloride. Approximately 90% yield for all the ten complexes were obtained

Results and discussion

Metal percentage was determined by atomic absorption method, pyrolysis method and other standard methods. The percentage of carbon, hydrogen and nitrogen were determined by micro analytical method. The results are summarized in Table 1. 7. 1. The metal to ligand ratio was found to be 1 : 2 in all the complexes except Ag (I) where the metal to ligand ratio was 1 : 1.

Molar conductance

The conductivity of all the complexes at a concentration of 10^{-4} M at room temperature was measured in methanol. All the complexes possess molar conductance in the range 1 – 11 $\text{ohm}^{-1}\ \text{cm}^{2}\ \text{mol}^{-1}$ in agreement with their non electrolytic nature.

Magnetic measurements

The magnetic moment value (1.64 BM) of Cu(II) complex is suggestive of $t_{2g}^{6}\ e_{g}^{3}$ electronic configuration in an octahedral ligand field. The observed magnetic moment of the Co(II) complex confirms the high spin octahedral geometry where there is orbital contribution (5.18 BM) The magnetic moment value of Mn(II) complex (5.6 BM) was in agreement with their octahedral geometry. Octahedral structure can be assigned to Fe(III) complex (6.07 BM) based on magnetic moment value. Ni(II) complex exhibited the magnetic moment value (3.32 BM) assignable to high spin octahedral geometry. For Cr(III) complex a magnetic moment value of 3.96 BM was obtained. This value of Cr(III) complex is suggestive of high spin octahedral geometry. Remaining complexes are diamagnetic. The magnetic susceptibility values are given in Table 1 . 7. 1.

Infrared spectra

A strong intense band due to γ C = N stretch (azo methine) in the ligand appear around 1619 cm $^{-1}$ which upon coordination shifts towards lower wave number region by $\approx$ 20 - 70 cm^{-1} indicating the participation of azo methine nitrogen in coordination with metal ion. However the spectra of the chelates displayed two new bands in the range of 410 – 435 and 435 - 510 cm $^{-1}$ which were assigned to γ M – O and γ M – N respectively.

In all the complexes, the asymmetric and symmetric stretching vibrations of the carboxylate groups occur at $\approx$1630 and 1470 cm $^{-1}$ respectively showing a difference of about 230 cm $^{-1}$. This indicates the monodentate behaviour of the carboxylate group. All these complexes show broad absorption bands between 3400 – 3500 cm $^{-1}$ due to the presence of coordinated water molecules, which is further supported by the appearance of rocking mode of medium intensity bands at $\approx$ 860 cm $^{-1}$.

Electronic spectra

The ligand ACPA exhibited bands around 33898 cm $^{-1}$and 24038 cm $^{-1.}$ These bands are red shifted in complexes indicating coordination of Schiff bases to Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Ag(I) metal ions. Cr(III) shows two bands, one at 16320 cm $^{-1}$ and other at 22000 cm $^{-1}$. Based on these, the structure of Cr(III) complex can be confirmed to be octahedral. The band appearing at

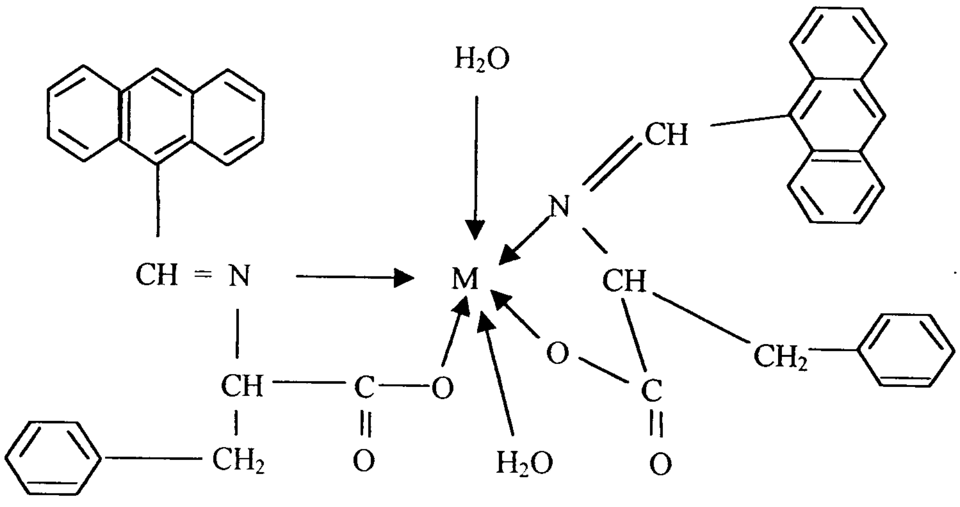
≈23000 cm^{-1} in Mn(II) complex is a support for the assigned octahedral geometry. In Fe(III) complex, weak transitions are masked by strong band seen at 15600 cm $^{-1.}$ Two bands are present in electronic spectra of Co(II) at ≈10520 cm $^{-1}$ and 23260 cm $^{-1}$. The band at ≈13037 cm $^{-1}$ and the other at 25000cm $^{-1}$ for Ni(II) complex is assignable to octahedral geometry. The octahedral geometry of Cu(II) complex is indicated by the band at 15873cm $^{-1}$

X Ray data

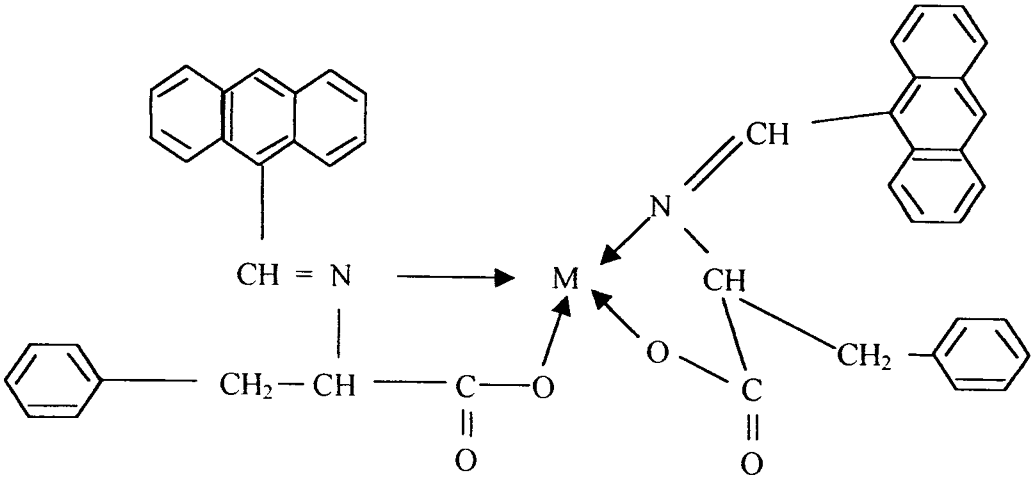
The Cu (II) complex of anthracene carboxaldehyde L phenylalanine was studied extensively, based on its powder crystallographic pattern. The complex was orthorhombic; the calculation of cell characteristic confirmed 1:2 nature of complex.

Thermal study

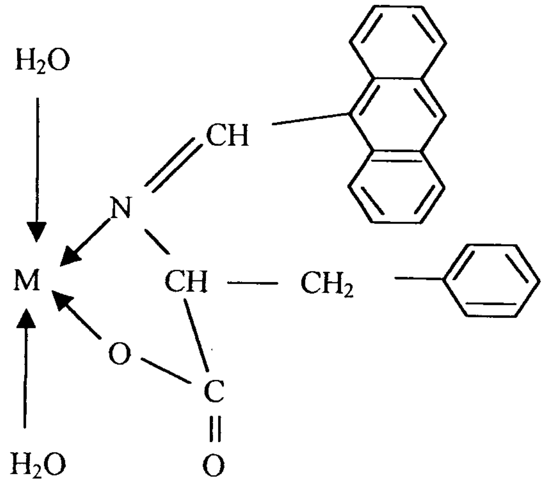
Co (II), Ni(II) and Cu(II) complexes of the title ligand were investigated for their thermal behavior during non isothermal heating. The mass loss consideration of the decomposition stages were confirmative to their structure proposed as $[ML^{V}_2(H_2O)_2.]$ Based on above studies it is seen that these three complexes possess octahedral geometry. Cr(III), Mn(II) and Fe(III) complexes also possess octahedral geometry. Remaining complexes possess tetrahedral geometry. The probable structure of complexes is given below.



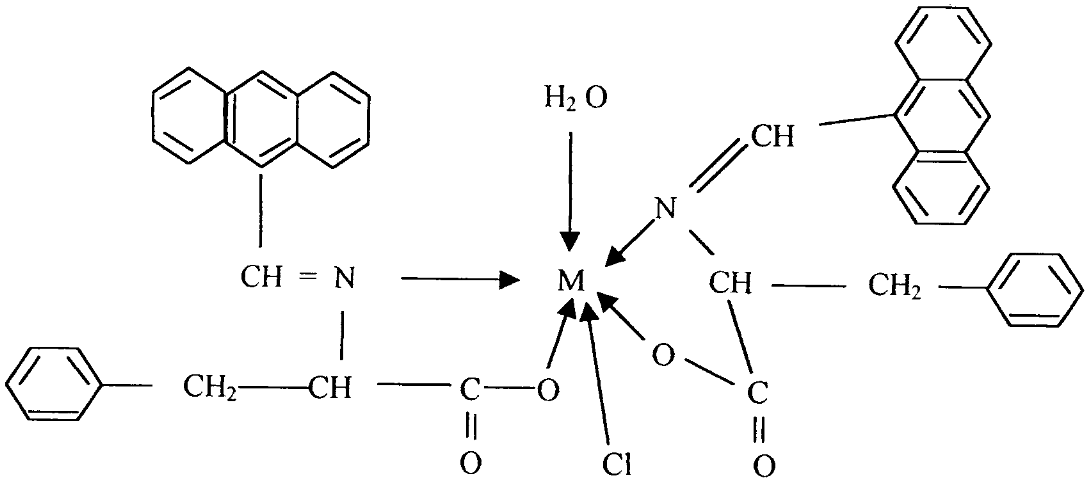
M = Mn (II), Co (II), Ni (II), Cu (II)



M = Zn (II) , Cd (II) and Hg(II)



M = Ag (I)



M = Cr (III), Fe (III)

TABLE 1.7.1

Micro analytical, magnetic moment and conductance data of transition metal chelates of Anthracene-9-carboxadehyde-L phenyl alanine

Metal Complexes	Colour	Melting point	M%	C%	H%	N%	μ_{eff} B.M.	Ω_m^{-1}
$[CrL^V_2(H_2O)Cl]$	Greenish Yellow	125	5.75 (6.4)	71.67 (71.1)	4.94 (4.69)	3.53 (3.46)	3.96	4.1
$[MnL^V_2(H_2O)_2]$	Brown	90	7.33 (6.92)	72.98 (72.40)	5.12 (5.02)	3.62 (3.52)	5.6	5.96
$[FeL^V_2(H_2O)Cl]$	Reddish Brown	110	7.01 (6.86)	71.32 (70.77)	5.01 (4.67)	3.51 (3.45)	6.07	6.5
$[CoL^V_2(H_2O)_2]$	Yellow	98	6.97 (7.3)	72.25 (72.04)	4.95 (5)	3.64 (3.5)	5.18	7.78
$[NiL^V_2(H_2O)_2]$	Greenish Yellow	198	7.99 (7.36)	72.25 (72.07)	5.09 (5.01)	3.49 (3.5)	3.32	5.2
$[CuL^V_2(H_2O)_2]$	Bluish Green	121	8.2 (7.92)	71.91 (71.63)	5.01 (4.97)	3.41 (3.48)	1.64	10.7
$[ZnL^V_2]$	Yellow	92	7.83 (8.49)	74.46 (74.8)	4.72 (4.67)	3.57 (3.63)	D	1.98
$[CdL^V_2]$	Pale Yellow	152	13.87 (13.73)	71.1 (70.5)	4.4 (4.46)	3.39 (3.42)	D	3.92
$[HgL^V_2]$	Yellow	156	21.63 (22.16)	62.28 (63.63)	4.02 (3.76)	3.97 (3.09)	D	5.1
$[AgL^V(H_2O)_2]$	Dark Green	85	21.59 (21.75)	58.12 (58.04)	4.42 (4.43)	2.69 (2.82)	D	9.2

The calculated values are given in parentheses; D dia magnetic; M metal; Ω_m^{-1} molar conductance in ohm^{-1} cm^2 mol^{-1}

TABLE 1. 7. 2

Selected absorption frequencies (cm $^{-1}$)of transition metal chelates of Anthracene carboxaldehyde L – Pheylalanine (ACPA)

Complex	γ H_2O	γ asyCOO^-	γ syCOO^-	γ C = N	In Plane deform	Out of Plane deform	γ M - N	γ M - O
Ligand	---	1655	1490	1619	870	777 731	---	---
$[Cr L^{V}_{2}Cl(H_2O)]$	3421	1632	1470	1554	872	779 740	500	412
$[Mn L^{V}_{2} (H_2O)_2]$	3429	1626	1401	1590	870	777 731	499	426
$[Fe L^{V}_{2} ClH_2O)]$	3423	1626	1434	1580	879	778 731	506	426
$[Co L^{V}_{2} (H_2O)_2]$	3429	1627	1442	1548	872	786 736	503	431
$[Ni L^{V}_{2} (H_2O)_2]$	3423	1626	1487	1590	877	786 731	503	419
$[Cu L^{V}_{2} (H_2O)_2]$	3429	1613	1434	1546	877	777 731	506	426
$[Zn L^{V}_{2}]$		1629	1407	1580	879	779 734	496	424
$[Cd L^{V}_{2}]$		1626	1400	1548	870	771 732	502	415
$[Hg L^{V}_{2}]$		1620	1420	1557	869	782 728	488	420
$[Ag L^{V} (H_2O)_2]$	3427	1627	1434	1585	879	776 733	505	426

PART II

INTRODUCTION

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

PART II

THERMOGRAVIMETRIC ANALYSIS

CHAPTER I

INTRODUCTION

Thermal analysis is a group of techniques in which a physical property of a substance or its reaction products is measured as a function of temperature, whilst the substance is subjected to a controlled temperature program [1]. Depending upon the properties measured and the temperature programs, [2 - 6] more than a dozen thermal methods can be recognized. Heating can produce different types of changes in solids .For solid-state reaction the value of the fraction decomposed depends on the nature of nucleus formation and nucleus growth. When we consider the integrated form of solid state reactions it was found that its value is decided by the model describing the solid state under consideration[7,8] .Thermal analysis techniques were prevalent in 1907 and 1912.The first thermo balance was developed by Honda[9] in 1915.Later workers like Guichard and Chevanard improved the design of the apparatus. Duval[10] has summarized early development on this technique These thermal methods find wide spread use for both quality control and research applications. We shall confine our discussion to thermo gravimetric method, which provide primarily chemical rather than physical information about samples. This technique can be used to study the kinetics of a chemical reaction and determine basic kinetic constants such as the rate constant, activation energy, order of the reaction, frequency factor and so on. In a thermo gravimetric analysis, the mass of the sample in a controlled atmosphere is recorded continuously as a function of temperature or time, as the temperature of the sample is increased linearly with time. A plot of mass or mass percent as a function of time or temperature is called a thermogram or a thermal decomposition curve. These curves provide information about the thermal stability and initial composition of the sample, intermediate compounds formed, and residue. The books by Duval[10], Smoothes and YaoChiang[11], Mackenzic[1], Schulze[12], Garn[13] give fruitful ideas about the instruments, principles and techniques of thermal analysis.

A study of thermal decomposition of Schiff base complexes of Co(II) and Cu(II) has been reported by Bhaskare and More[14]. Wendlandt and co workers[15-18] and Hill and coworkers[19,20] have studied the thermal properties of metal chelates with different types of complexing agents. Aravindakshan and Muraleedharan[21] have studied thermal stabilities of metal chelates with azomethine group. Considerable work has been done on the thermal decomposition kinetics of transition metal complexes of Schiff bases and related ligands.[22-25]

Thermo gravimetric method can be applied for the study of various reactions such as

1. Decomposition reaction of the type

$$A\,(\text{solid}) \longrightarrow B\,(\text{solid}) + C\,(\text{gas})$$

2. Reaction between two solid phases

$$A\,(\text{solid}) + B\,(\text{solid}) \longrightarrow AB\,(\text{solid}) + C\,(\text{gas})$$

3. Reaction confined exclusively to the solid phase

$$A\,(\text{solid}) + B\,(\text{solid}) \longrightarrow C\,(\text{solid}) + D\,(\text{solid})$$

4. Reaction involving participation of liquid phase at some stage

$$A\,(\text{solid}) \longrightarrow B\,(\text{solid}) + C\,(\text{liquid})$$

5. Reaction involving a solid and a gas such as from a controlled atmosphere

$$\text{A (solid)} + \text{B (gas)} \longrightarrow \text{C (solid)}$$

Studying the weight changes of a body when it is getting heated up, since the heating of the solid will produce chemical reaction between the lattice constituent units, can do the kinetic study of a substance. This study can be done either by isothermal or by non-isothermal methods. The non-isothermal methods[26 - 28] are easier, since a thermo gravimetric curve will represent the degree of transformation as a function of temperature. In these chemical processes, the reaction rate is directly proportional to the concentration of reacting molecules in the homogeneous systems, where as in heterogeneous systems they will be more complicated. In homogeneous systems, the rate of the reaction

$$k = \frac{-1}{V}\frac{dni}{dt}\ C^n \qquad (1)$$

Where C = ni / V, the concentration of the initial substance at time t and n is the reaction order.

In the heterogeneous case, this equation will be

$$k = \frac{1}{V}\frac{dVt}{dt} \qquad (2)$$

Where dVt / dt is the rate of change of volume of the product with respect to the time t. The ratio Vt / Vα where Vα is the volume of the product at the end of the reaction, give α, the fraction decomposed.

The general kinetic equation can be written as

$$\frac{-dx}{dt} = kX^{n} \qquad (3)$$

Where X is the amount of sample undergoing reaction, n is the order of the reaction and k is the specific rate constant. This equation is obtained on the basis of the assumption that the non-isothermal reactions proceed isothermally for very small time intervals. The value of X in the above equation is directly related with the mass loss using the equation

$$-dx = \frac{Wi}{W\alpha}\, dw \qquad (4)$$

Where Wi is the initial mass of the sample and Wα is the maximum mass loss. By integrating the above equation we will get,

$$\int_{Wi}^{X} X = \int_{0}^{W} \frac{Wi}{W\alpha}\,(W\alpha - W) \qquad (5)$$

In this equation the value of X varies from Wi to X , where as the value of dW varies from 0 to W

By combining the above three equations, we get

$$\frac{Wi}{W\alpha}^{1-n} \int_{0}^{W} (W\alpha - W)^{-n}\, dW = \frac{A}{\phi} \int_{T_1}^{T_2} e^{-E/RT}\, dt \qquad (6)$$

Coats - Redfern Equation[29, 30]

This equation uses the integral method of calculation for the reactions of the type

$$a A_{(S)} \longrightarrow b B_{(S)} + c C_{(g)}$$

The decomposition of the reactant A depends on the rate constant of the reaction given by

$$k = A \exp(-E/RT)$$

Here E is the activation energy of the reaction, T is the absolute temperature of the reaction, R is the gas constant and A is the Arrhenius factor. This rate constant is related with rate of decomposition of the reactant by the equation

$$d\alpha / dt = k(1 - \alpha)^n$$

Where $d\alpha / dt$ is the rate of fractional decomposition with time t, n is the order of the reaction and $\alpha = w / Wi$ where w is the mass loss at time t. On combining all these equations and making integrations we get

$$\int_0^\alpha d\alpha / (1-\alpha)^n = [A / \phi] \int_0^T e^{-E/RT} dT$$

Where ϕ is the constant rate of heating given by $\phi = dT / dt$. If $n = 1$, then the equation will become

$$-\log(1-\alpha) = (ART^2 / \phi E)[1-(2RT/E)]\exp(-E/RT)$$

And for all other values of n, the solution is,

$$[1-(1-\alpha)^{1-n}]/(1-n) = (ART^2 / \phi E)[1-(2RT/E)]\exp(-E/RT)$$

When we are taking logarithms on both sides of the equations, we get

$$\log[1-(1-\alpha)^{1-n}/(1-n)T^2] = \log[(AR/\phi E)(1-2RT/E)] - E/2.303\,RT$$

And,

$$\log[-\log(1-\alpha)/T^2] = \log[(AR/\phi E)(1-2RT/E)] - E/2.303\,RT$$

In both these equations, the right hand side contains a term $\log[(AR/\phi E)(1-2RT/E)]$, which is practically a constant. The second term of the right hand side contains only one variable, the absolute temperature of the reaction. Hence the graphs with the left hand side values on one axis and $1/T$ on the other, will produce straight lines with a slope of $-E/2.303\,R$. That is

$\log[1-(1-\alpha)^{1-n}/(1-n)T^2]$ Vs $1/T$ for $n \neq 1$ and,

$\log[-\log(1-\alpha)/T^2$ Vs $1/T$ for $n = 1$, gives straight lines with a slope of $-E/2.303\,R$

The value of n can be determined using the best-fit method of a computer. The kinetic parameters can be calculated from the equation,

$$\ln\left[1-(1-\alpha)^{1-n}/(1-n)T^2\right] = \ln\left[(AR/\phi E)(1-2RT/E)\right]-E/RT$$

A is the intercept of the graph and E can be calculated from the graph. Entropy changes can be calculated from the values of A using the equation,

$$A = \frac{k\,T_S}{h} \exp \frac{\Delta S}{R}$$

Where h is the Plank's constant , k is the Boltzmann constant.

Approximation method using Horowitz Metzger equation [31]

The kinetic parameters were calculated based on the non-mechanistic approximation method using the value of n.

$$\ln\left[1-(1-\alpha)^{1-n}/(1-n)\right] = \ln\left[A\,R\,Ts^2/\phi E\right] - E/RTs + \theta E/RTs^2$$

Where $\theta = T - Ts$.

When n = 1, the above equation would be

$$\ln[-\ln(1-\alpha)] = \ln \frac{A\,R\,Ts^2}{\phi E} - \frac{E}{RTs} + \frac{\theta E}{RTs^2}$$

E , A, and ΔS were calculated from slope and intercept as shown above.

Kinetics of phase transformation

Several studies were made on phase transformations.[32] Different theories were also proposed for the different types of process. These processes are divided for solid products and for fluid products. In the fluid products, the sublimation or melting happened without nucleation. In some cases the nucleation may happen but it will be very fast, hence negligible. The solid may also have a chance of making products without nucleation. But most of the process will be nucleated.

During the transformation of a reactant A in to a product B, an unstable phase of A and B will be formed together. But in some cases within the unstable phase of A, a stable phase of the product B domains. Hence a subsequent growth is formed. Since the lattice parameters of A and B are different, this growth will appear as lattice imperfections. The future of these growths depends on its size. If that growth attains a critical size, it can grow and that process is called nucleus growth.

This nucleation may occur either on the surface of the particle or inside the volume. This depends on the rate of nucleation. When the nucleation rate is low, a single domain on each particle is formed. If it is fast, a thin layer of products will cover the growth. The rate of surface nucleation and the rate of nuclei growth will decide the thickness of the overlapping layer. The shape of the nuclei growth depends on the structure of the crystal, the nature of the interface etc.

Different theories are available to explain the formation of growth of nuclei. The study of solid decomposition depends on the model, which we are selecting. If the model actually characterizes the real situation, the derived kinetic parameters will have real meaning.

Nucleation theories

Several theories are available to discuss the formation of nuclei, discussing the nucleus forming sites and coordination of the nuclei in such cases.

1. Exponential law

When the single surface chemical reaction is come in to act, the rate of nucleation is directly proportional to the number of reaction sites. Hence the rate of nucleation is

$$dn / dt \quad \propto \quad N_0 - N \quad = \; k_n \; (N_0 - N)$$

Where, N_0 is the number of possible sites, N is the number of the nuclei present and k_n is the rate constant of the nucleation. On integration we get

$$dN \; / \; dt \quad = \quad k_n \, N_0 \, e^{-kn\,t}$$

2. Linear law

In the case of very low rate constant, the number of nuclei present in this sites will be negligible and then the exponential law became $dN / dt = k_n N_0$, Or $N = k_n N_0 t$, and here the rate of nucleation will always be a constant.

3. Power law

This is a special case in which the number of nuclei is increases as the higher power of time [33 - 35]. Here a stable nucleus is formed by successive decomposition and the number of nuclei formed, $N = N_0 k_n t / \beta I$, where β is the number of successive events required at a time t.

4. Instantaneous nucleation

If the nucleation is complete within no time it is called instantaneous nucleation. A very large number of points called gem nuclei are produced at the regions of disorders, such as the point of emergence of dislocations, at vacancies or the impurity clusters in the crystalline specimen. This was occurred at low temperature, before the proper decomposition or due to the rapid heating to the proposed decomposition temperature. In instantaneous nucleation, the rate of nucleation dN / dt is zero or negligible.

Nuclear growth

By the term nuclear growth, we are mentioning the movement of the reactant, product interface in a direction perpendicular to the surface due to the thermal decomposition reaction. The studies of these movements show that the movement of the reaction interface is at a constant rate. Topley et al [36] had discussed the release of the gaseous product, by the different layers of the solid product. Jacobs and Tompkins [37] and young [38] had proposed the nuclear growth theories in detail.

The theories of growth of nuclei can be approached in two ways. The volume of the nuclear growth depends on shape factor and the dimension of the growth. Hence the growing nuclei may overlap with the neighboring growth. In the first approach, we neglect all these. Also we neglect the possibility of activating a gem nucleus to grow. But in the second approach, we consider all these factors in detail. The derivations of most commonly used expressions called nine equations are shown in the Table 2. 1. 1. These equations are generally separated as declaratory equations and sigmoid alpha temperature curves. The declaratory equation can be further divided on the basis, they are using such as geometrical order, order of reaction, and diffusion mechanism. Sigmoid temperature curves depends on Avrami Erofeev equations

Avrami diffusion equation

It deals with the growth of gem nuclei. According to this theory Avrami suggested that the growth of the nuclei from the stage of gem nuclei happened in single activation step. [39,40] During growth, the nearby gem nuclei may incorporate each other and overlap during the growth. Hence the overall rate of reaction reduced due to the removal of potential nucleus forming sites due to incorporation and the cessation of reactions are the areas of contact of adjoining nuclei. This complicated form can be expressed as $-\ln(1-\alpha) = kt^n$ where n = 2, 3, or 4

Decelaratory equations

In certain decomposition, initial acceleratory condition is not observed. In these cases the reactions are deceleratory, since the reaction interface progressively decreases. Examples of such equations are contracting cube, contracting area and first order equation.

The nucleation occurs very rapidly, all over the surface of a single cube of the reactant and the progress is happening in the direction of the center of the crystal. The equation of the same is given as $[1-(1-\alpha)]^{1/3} = kt$

If that progressive decrease is in the contact area , it is called contracting area equation, which is expressed as $[1 - (1 - \alpha)^{1/2}] = kt$

The first order kinetic equation is applicable in the nucleation mechanism in which the rate of appearance of the product is limited by the rate of growth of the nuclei. This process is given as $- \ln (1 - \alpha) = kt$. This model supposes a random nucleation of the product, with only one nucleus formed on each particle.

The results of the studies on thermal decomposition of Co(II), Ni(II) and Cu(II) complexes of anthracene carboxaldehyde L histidine, anthracene carboxaldehyde L tyrosine, anthracene carboxaldehyde glycine, anthracene carboxaldehyde DL alanine, and anthracene carboxaldehyde L phenyl alanine are presented in this Part, using TG technique.

The temperature regions of stability have been noted from the TG traces. The temperature of inception and decomposition and the temperature of maximum rate of decomposition have also been noted. The thermal stability and decomposition stages of the complex have been discussed. The intermediate products are confirmed by chemical analysis and infrared spectral analysis. X ray diffractometry have been used for the characterization of the ultimate decomposition products.

The non-isothermal TG curves have been subjected to mathematical analysis using the integral method of Coats Redfern and the approximation method of Horowitz – Metzger methods, and the activation parameters have been evaluated for all the complexes. The mechanism of the decomposition has been established from TG data using mechanistic equations.

TABLE 2. 1. 1

KINETIC EQUATIONS

Function	Equation, $g(\alpha) = kt$	rate controlling process
D_1	$\alpha^2 = kt$	one dimensional diffusion(parabolic law)
D_2	$(1-\alpha)\ln(1-\alpha) + \alpha = kt$	Two dimensional diffusion ,cylindrical symmetry
D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Three dimensional diffusion ,spherical symmetry try (Jander equation)
D_4	$(1-2/3\,\alpha)-(1-\alpha)^{2/3} = kt$	Three dimension equation, spherical symmetry (Ginstilling – Brownshtein equation)
F_1	$-\ln(1-\alpha) = kt$	Random nucleation, one nucleus per particle (Mampel equation)
A_2	$-\ln[(1-\alpha)^{1/2}] = kt$	Random nucleation(Avrami equation I),
A_3	$-\ln[(1-\alpha)^{1/3}] = kt$	Random nucleation(Avrami equation II
R_2	$1-(1-\alpha)]^{1/2} = kt$	Phase boundary reaction; cylindrical symmetry
R_3	$1-(1-\alpha)]^{1/3} = kt$	Phase boundary reaction;spherical symmetry

PART II

MATERIALS, METHODS AND INSTRUMENTS

CHAPTER II

MATERIALS, METHODS AND INSTRUMENTS

Materials

For synthetic purpose, analar grade (B. D. H. or E. Merk or Sisco) chemicals were used, as explained in chapter II of Part 1. Commercial solvents were distilled by standard methods. Detailed description regarding the reagents are given in Part I

Methods

Co(II), Ni(II) and Cu(II) complexes of anthracene carboxaldehyde amino acid Schiff bases were prepared by the methods described in Part I.

The TG data was recorded using 2 – 5 mg of samples at a constant heating rate of 10 ^{0} C / minute in static air. The final products were subjected to X – ray powder technology to confirm the final product of decomposition. Computational work was done using Intel P III PC (Sumsung) using C^{++} language.

Instruments

1. Perkin Elmer 7 series thermal analysis system.
2. Philips X – ray powder diffractometer
3. Intel Pentium III P C (Sumsung)

PART II

THERMAL DECOMPOSITION KINETICS AND MECHANISM OF Co(II), Ni(II) AND Cu (II) COMPLEXES OF ANTRRACENE CARBOXALDEHYDE - L - HISTIDINE

CHAPTER III

THERMAL DECOMPOSITION KINETICS AND MECHANISM OF Co (II) , Ni (II) AND Cu (II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE – L – HISTIDINE

Recently, physicochemical studies and thermal decomposition kinetics of the metal chelates derived from L – Histidine have been reported [41] Similar studies on thermal decomposition and kinetics of metal chelates of the ligand citronellal anthranilic acid and its derivatives, 5 – bromo anthranilic acid were also studied [42] . Lehtinen and some others[43 - 46] have studied the thermal decomposition of azo methine complexes between the period 1980 to 1984. Even though the kinetics and mechanism of transition metal complexes of Schiff bases have been carried out extensively, no work have been reported on the metal chelates of Schiff bases derived from anthracene carboxaldehyde – L – histidine.

In this chapter Co (II) , Ni (II) and Cu (II) complexes of the ligand anthracene carboxaldehyde – L – histidine have been studied to find out the kinetics and mechanism of the thermal decomposition by T G. The energy of activation E, Arrhenius factor A, and entropy of activation ΔS were calculated using mechanistic and non-mechanistic equations.

The complexes were prepared according to the procedure given in chapter III of Part I. Initial decomposition temperature have been used by earlier workers [47,48] to compare the thermal stability of complexes.

Treatment of data

Thermo gravimetric curves recorded in the static air atmosphere at a heating rate of 10 ^{0} C per minute were used and are shown in figures. The fraction of the substance decomposed (α) were found out from the graph and hence g (α) for substitution in Coats Redfern and Horowitz Metzger equations corresponding to the respective orders and in mechanistic equations. Sestak and Berggren and Satava [49,50] have discussed determination of the mechanism of reaction using the non-isothermal methods. By comparing the values obtained from mechanistic and non-mechanistic equations, probable mechanisms of decomposition were assigned for each decomposition step. Thermal data for the metal chelates are given in Tables 2.3.1 and 2.3.2. Data from independent pyrolytic experiments are also included in these Tables. The kinetic parameters calculated from T G data for the nine mechanistic equations are given in Table 2. 3. 3. The corresponding values of E, A and ΔS and r from non-mechanistic equations and the mechanistic equation suggested are given in Tables 2.3.2 and 2.3.3. Typical TG curves of Co (II), Ni (II) and Cu (II) were studied in detail and are presented in Figures 2.1, 2.2 and 2.3

Results and discussion

The complexes which were subjected to thermal decomposition study were found to have the formula $[ML^1{}_2(H_2O)_2]$, where M is the metal and L is the ligand anthracene carboxaldehyde – L – histidine. The TG curve of $[CoL^1{}_2(H_2O)_2]$ gives a three stage decomposition pattern. The first stage represents the loss of $2H_2O$ molecules and anthracene carboxaldehyde part of the ligand moiety. According to Nikolaev et al [51] water eliminated above 150 ^{0} C can be considered as coordinated water. The second stage represents the loss of the second ligand. The third stage represents the loss of histidine part. The overall mass loss for the case is 88 % while the theoretical loss in mass for the conversion of $[\mathrm{Co\,L^1_2\,(H_2O)_2}]$ to Co_3O_4 is 90.3 %.

$[\mathrm{Ni\ L^1_2\,(H_2O)_2}]$ gives a two stage decomposition pattern in its TG curve. The first stage represents the loss of 2 H_2O molecule, 1 ligand , ACA part(anthracene carboxaldehyde) while second stage represents the loss of histidine part.

$[\mathrm{Cu\,L^1_2\,(H_2O)_2}]$ also gives a two stage decomposition pattern in its TG curve. Two water molecules, one ligand and one ACA part are lost in the first stage, a histidine part is lost in the second stage of decomposition.

The mass loss at the end of the stage as recorded from the TG curve is 88.09 % and 89.9 % for Ni (II) and Cu (II) complex respectively. Initial decomposition temperature has been used to determine the thermal stability of metal chelates. In the present course of studies based on observation made by earlier workers, the relative stabilities of the three metal chelates are in the order $[\mathrm{CoL^1_2(H_2O)_2}] < [\mathrm{CuL^1_2(H_2O)_2}] < [\mathrm{NiL^1_2(H_2O)_2}]$.

Decomposition kinetics

Table 2.3.2 shows that more than one equation give good linear curves with high correlation coefficient, making the assignment of reaction mechanism a difficult task. In such cases the function (g alpha) which gives kinetic parameter in agreement with those obtained by non-mechanistic equation are considered.

Kinetic parameters viz activation energy E, Arrhenius factor A, entropy of activation ΔS and order parameters n for the thermal decomposition of the three complexes were evaluated. It can be seen from the thermal data that the values of E and A from these equations are nearly the same. It is also found that greater the thermal stability of a complex, the larger the activation energy for the decomposition. ΔS values in this case would be negative. The non-isothermal kinetic methods discussed by Sestak and Berggren and Satava have been used for deducing the mechanism of decomposition of these complexes. In the present case, it was observed that the values of E, A and ΔS for the second stage decomposition of $[Co L^1_2 (H_2 O)_2]$ obtained from Coats Redfern with n = 2/3 are in good agreement with the corresponding values obtained for R_3 mechanism based on phase boundary reaction, spherical symmetry.

For the first stage decomposition of $[NiL^1_2(H_2O)_2]$ and $[CuL^1_2(H_2O)_2]$, the values of kinetic parameters obtained for Coats Redfern equation with n = ½ are in good agreement with those values obtained for equation 8. R_2 mechanism based on phase boundary reaction, cylindrical symmetry gives the maximum correlation for the first stage decomposition of Ni (II) and Cu(II) complexes. Since the values of E and A computed from the mechanistic equation agree well with those from the non mechanistic equation (Coats Redfern), these mechanisms are confirmed. These values are also found to give good agreement with the values obtained from Horowitz Metzger equation of the same order.

TABLE 2.3.1

THERMAL DECOMPOSITION DATA OF Co (II), Ni (II) AND Cu (II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L - HISTIDINE

Complex	stage	temp range in TG (°C)	peak temp in TG (°C)	loss of mass percentage			probable assignment
				from TG	theoretical	pyrolysis	
$[Co L^{1}_{2} (H_2O)_2]$	I	120 - 240	235	30	29		loss of 2 H_2O + ACA part
	II	240 - 380	340	43	43.9		loss of second ligand
	III	380 - 520	390	15	17.4		loss of histidine part
				88	90.3	88.8	$Co L^{1}_{2} (H_2O)_2 \dashrightarrow Co_3 O_4$
$[Ni L^{1}_{2} (H_2O)_2]$	I	120 - 290	260	70.6	72.9		loss of 2 H_2O + 1L + ACA part
	II	290 - 420	330	17.49	17.5		loss of histidine part
				88.09	90.4	90.71	$Ni L^{1}_{2} (H_2O)_2 \dashrightarrow Ni O$
$[Cu L^{1}_{2} (H_2O)_2]$	I	90 - 270	260	76.9	72.49		loss of 2 H_2O + 1L+ ACA part
	II	270 - 460	450	13	17.36		loss of histidine part
				89.9	89.85	90.3	$Cu L^{1}_{2} (H_2O)_2 \dashrightarrow Cu O$

TABLE 2.3.2

Kinetic parameters for the decomposition of Co(II), Ni(II) and Cu (II) complexes of anthracene carboxaldehyde - L - histidine (L^1H) from TG using mechanistic equations

complex	parameter	mechanistic equations								
		1	2	3	4	5	6	7	8	9
$[Co L_2^1 (H_2O)_2]$	E	21.55	22.34	23.17	22.64	10.41	10.41	10.41	10.46	10.67
	A	1.28×10^8	1.67×10^8	1.02×10^8	5.33×10^7	$5. \times 10^3$	2.50×10^3	1.67×10^3	1.13×10^3	9.79×10^2
	ΔS	-68.78	-68.25	-69.23	-70.52	-90.57	-91.95	-92.76	-91.90	-92.19
	r	0.9930	0.9932	0.9933	0.9932	0.9892	0.9892	0.9892	0.9921	0.9921
$[Ni L_2^1 (H_2O)_2]$	E	27.85	29.48	31.36	30.14	15.98	15.98	15.98	14.18	14.75
	A	4.51×10^{10}	1.46×10^{11}	2.75×10^{11}	6.80×10^{10}	7.43×10^5	3.72×10^5	2.48×10^5	4.60×10^4	5.98×10^4
	ΔS	-56.69	-54.36	-53.10	-55.88	-78.58	-79.95	-80.76	-84.10	-83.59
	r	0.9983	0.9975	0.9958	0.9970	0.9940	0.9940	0.9940	0.9971	0.9964
$[Cu L_2^1 (H_2O)_2]$	E	30.44	31.92	34.35	32.74	17.45	17.45	17.45	15.59	15.28
	A	5.38×10^{11}	1.45×10^{12}	4.74×10^{12}	8.12×10^{11}	3.21×10^6	1.60×10^6	1.06×10^6	1.88×10^5	9.60×10^4
	ΔS	-51.77	-49.80	-47.45	-50.95	-75.67	-77.05	-77.86	-81.31	-82.64
	r	0.9951	0.9984	0.9967	0.9980	0.9931	0.9931	0.9931	0.9975	0.9923

E – k Cals mol^{-1} A – Sec^{-1} ΔS - eu

TABLE 2.3.3

Kinetic parameters for the decomposition of Co (II), Ni (II), and Cu (II) complexes of anthracene carboxaldehyde - L - histidine (L^1H) using non mechanistic equations

complex	parameter	Coats Redfern	Horowitz Metziger	mechanistic equation followed		order of reaction
[Co L_2^1 (H_2O)$_2$]	E	10.67	10.11	10.67	equation 9 phase boundary reaction spherical symmetry	2 / 3.
	A	2.937×10^3	2.206×10^3	9.79×10^2		
	ΔS	-90.01	-99.73	-92.19		
	r	0.9921	0.9832	0.9921		
[Ni L_2^1 (H_2O)$_2$]	E	14.18	19.04	14.18	equation 8 phase boundary reaction cylinderical symmetry	1/2.
	A	9.21×10^4	3.52×10^5	4.6×10^4		
	ΔS	-82.73	-80.06	-84.10		
	r	0.997121	.0.99863	0.997121		
[Cu L_2^1 (H_2O)$_2$]	E	15.59	20.72	15.59	equation 8 phase boundary reaction cylinderical symmetry	1/2.
	A.	3.76×10^5	1.84×10^6	1.88×10^5		
	ΔS	-79.93	-76.78	-81.31		
	r	0.9975	0.9995	0.9975		

E – k Cals mol^{-1} A – Sec^{-1} ΔS - eu

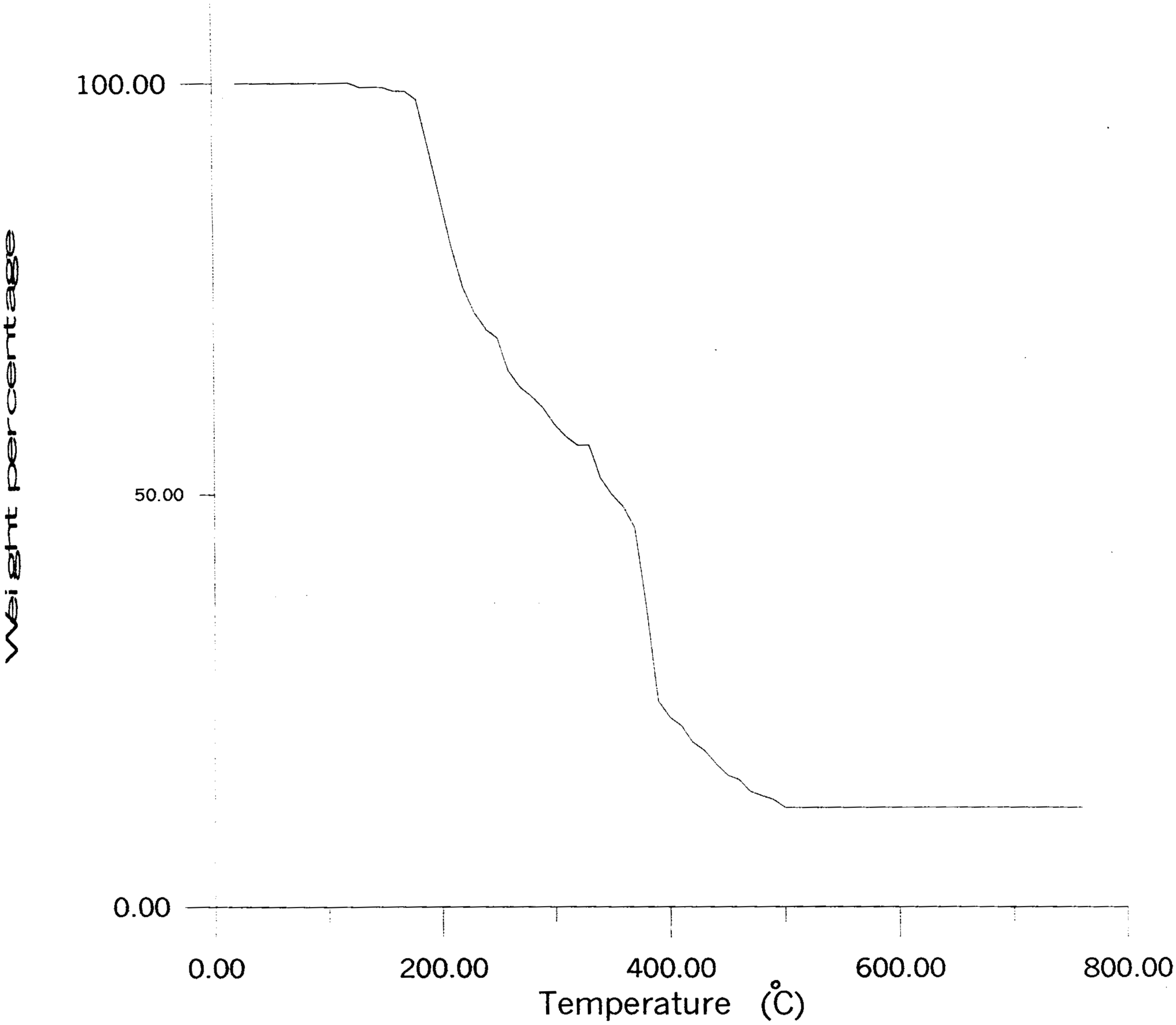


Fig. 2 . 1 TG trace of $[Co(ACH)_2(H_2O)_2]$

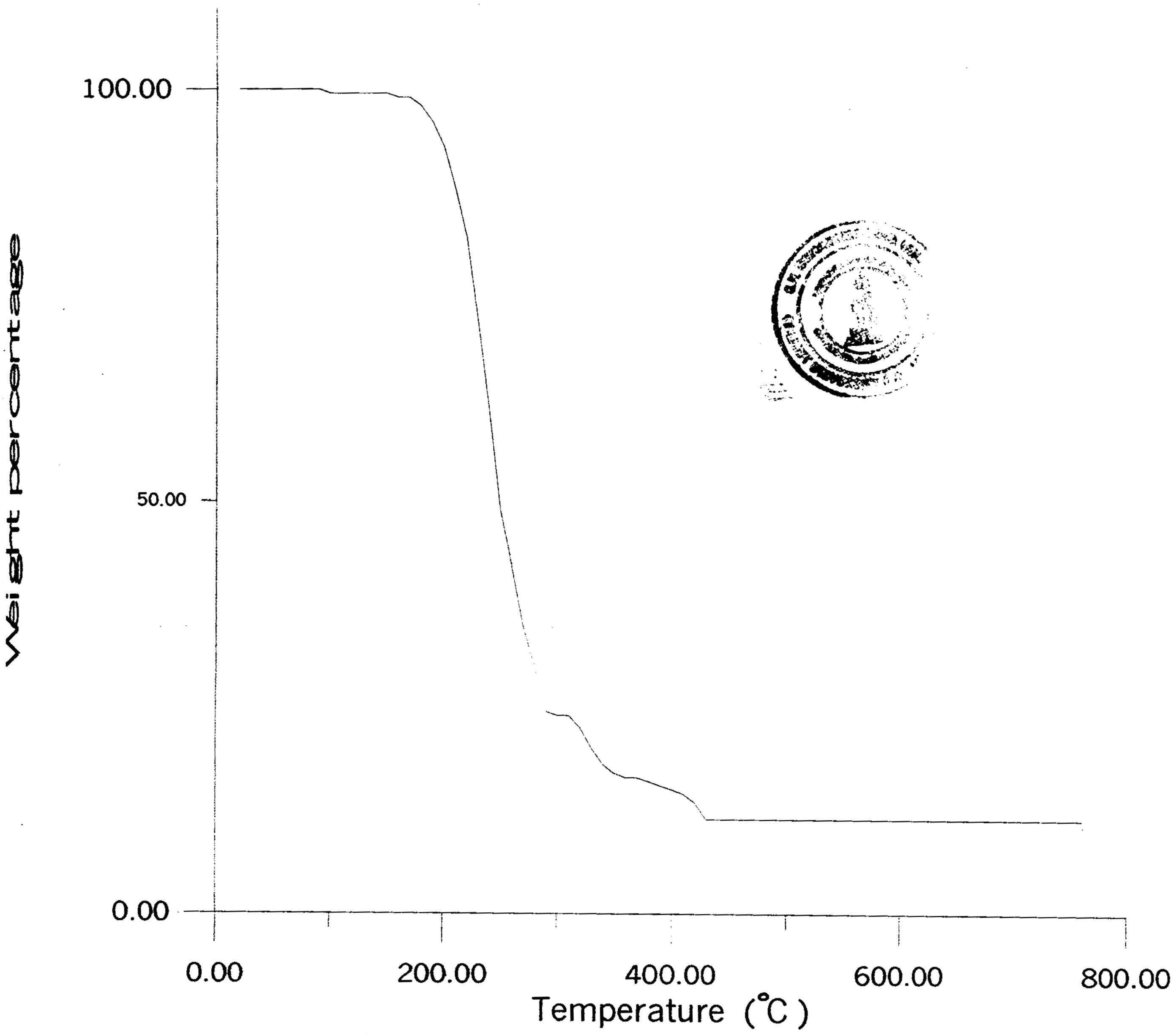


Fig : 2. 2 TG trace of [Ni $(ACH)_2(H_2O)_2$]

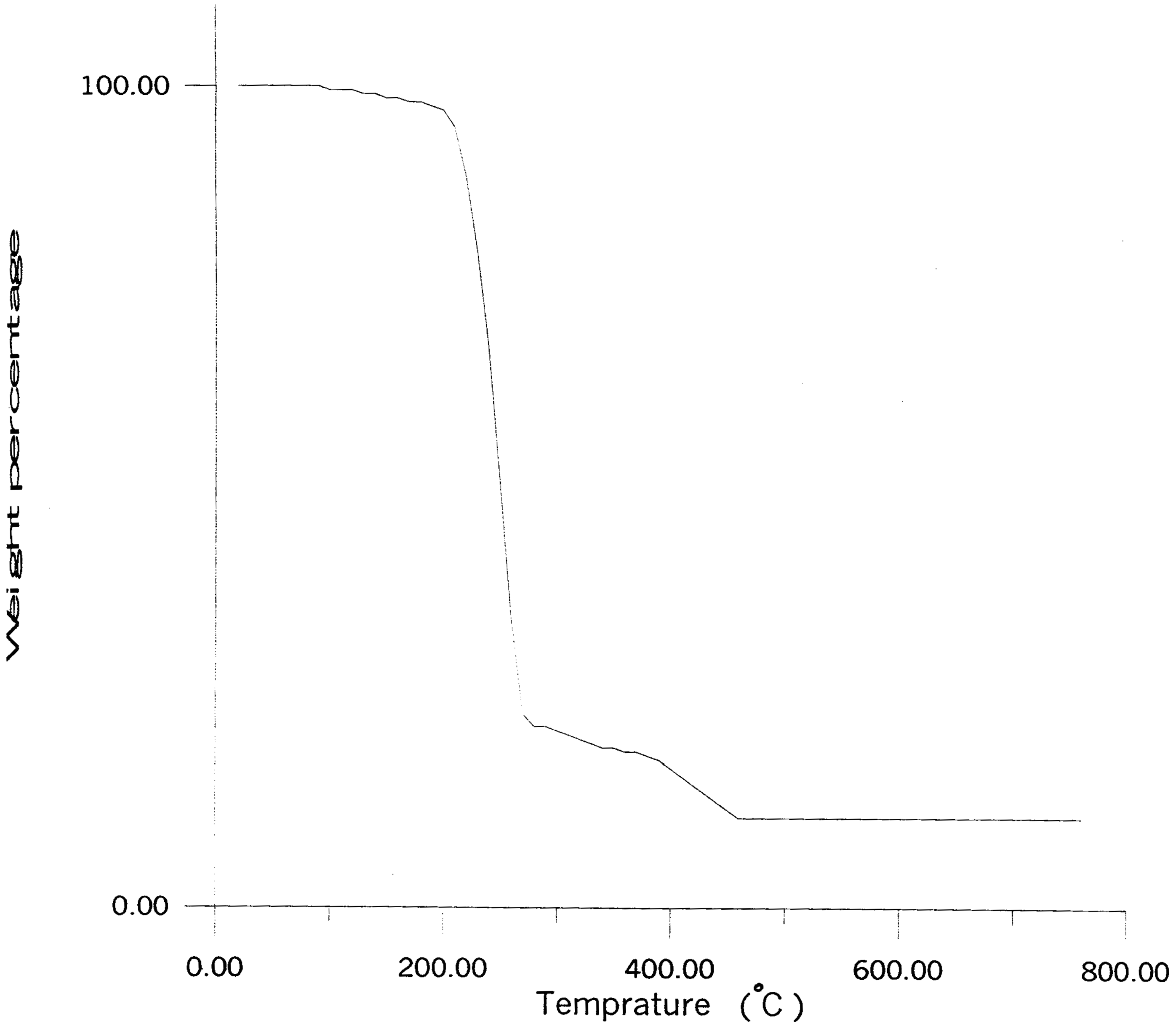


Fig: 2. 3 TG trace of [$Cu(ACH)_2(H_2O)_2$]

PART II

THERMAL DECOMPOSITION KINETICS OF Co(II), Ni(II) AND Cu(II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L - TYROSINE

G. Indira Devi “ Studies on transition metal complexes of schiff bases derived from aminoacids” Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER IV

THERMAL DECOMPOSITION KINETICS OF Co(II), Ni(II) AND Cu(II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L – TYROSINE

Thermo analytical techniques provide important information in elucidating structure and bonding in complexes. . A few workers[52,53] carried out studies on thermal decomposition and kinetics of metal chelates, with azomethine ligands. Dhar and Singh[54] have reported kinetics and thermal decomposition of some Schiff base complexes. In this chapter the thermal behavior of anthracene carboxaldehyde –L – tyrosine complexes of Co (II), Ni(II) and Cu(II) was studied by T.G. Interpretation and mathematical analysis of the thermal decomposition data and evaluation of order of reaction, entropy change, energy of activation and Arrhenius factor, based on Coats Redfern and Horowitz Metzger methods are explained. Evaluation of the reaction mechanism by non-iso thermal methods has been employed using the nine mechanistic equation.

Experimental

The method of preparation and characterization of these complexes are reported in Part I, Chapter IV. Thermal decomposition study was carried out at a heating rate of 10^0 C per minute in an atmosphere of static air .A sample mass of 2 to 5 mg was used for analysis. Mass loss considerations and X-ray diffraction data reveal the final products to be metal oxides. Calculations based on mechanistic and non mechanistic equations were performed with a computer using the programming language C^{++}

Treatment of data

The instrumental T.G. curves were redrawn as mass verses temperature (TG) curves. Typical TG curves of the Co(II), Ni(II), and Cu(II), were studied in detail and are presented in Figures 2 . 4, 2 . 5, and 2 . 6.Thermal decomposition temperature ranges are shown in Table 2. 4. 1. Nine mechanistic equations and two non-mechanistic equations were employed to evaluate kinetic data from these T.G. Curves. The thermal data for the metal chelates are given in Table 2. 4. 1, and Table 2. 4. 2. Kinetic parameters like activation energy, frequency factor and entropy of activation which are calculated using TG curves are given in Tables 2. 4 .2 , and 2. 4. 3. Data from independent pyrolytic experiments are also included in Table 2. 4. 1. The complexes of anthracene carboxaldehyde -tyrosine with Co(II) and Ni(II) having the formulae [$ML_2{}^{11}(H_2O)_2$] exhibited a one stage decomposition pattern in its TG curve. While [$CuL_2{}^{11}(H_2O)_2$] gives a two stage decomposition pattern. Two water molecules, one ligand and one anthracene carboxaldehyde part are lost in the first stage, and a tyrosine part lost in the second stage of decomposition.

Results and discussion

In all these cases the final products of decomposition are identified to be the oxides, Co_3O_4, Ni O and Cu O by X-ray diffraction study .The overall loss of mass from the TG curves are comparable to the theoretical loss in mass for the conversions.

	Loss %	
	Theoretical,	TGA value
$[CoL_2{}^{11}(H_2O)_2] \longrightarrow Co_3O_4$	90.4	91
$[NiL_2{}^{11}(H_2O)_2] \longrightarrow NiO$	91.1	91
$[CuL_2{}^{11}(H_2O)_2] \longrightarrow CuO$	90.5	90.5

The kinetic parameters namely, activation energy E, Arrhenius factor A, order parameter n and entropy of activation ΔS for these decomposition reactions calculated from the TG curves, based on the nine mechanistic equations and the two non mechanistic equations are summarized in Tables. 2 .4. 2 and 2 . 4 . 3.

Initial decomposition temperature have been used to determine the thermal stability of metal complexes .On the basis of experimental findings in the present studies the relative thermal stability of the above chelates can be given as $[CoL_2{}^{11}(H_2O)_2] > [CuL_2{}^{11}(H_2O)_2] > [NiL_2{}^{11}(H_2O)_2]$. These complexes do not show any detectable change up to 100^0 C when heated. This shows that there is no water of hydration. At around 160^0 C a loss of mass is noted in the case of Co(II), Ni(II) and Cu(II) complexes which can be assigned to the loss of coordinated water molecules.

Decomposition Kinetics

The kinetic parameters for the thermal decomposition of the three complexes were evaluated .It can be seen from the thermal data that the values of E and A from these equations are nearly the same. It is also found that the greater the thermal stability of a complex the larger the activation energy for decomposition.

The non isothermal kinetic methods discussed by Sestak and Berggren and Satava have been used for deducing the mechanism of decomposition of these complexes .In the present case it is observed that R_2 mechanism based on phase boundary reaction, cylindrical symmetry gives the maximum correlation for single stage thermal decomposition of $[CoL_2^{11}(H_2O)_2]$ and $[NiL_2^{11}(H_2O)_2\ ]$ obtained from Coats –Redfern with $n = ½$. R_3 mechanism based on phase boundary reaction, spherical symmetry gives the maximum correlation for the two stage decomposition pattern of $[CuL_2^{11}(H_2O)_2\ ]$ with $n = 2/3$ which is obtained from Coats–Redfern equation. Since the values of E and A computed from the mechanistic equation agree well with those from the non-mechanistic equation, these mechanisms are confirmed.

TABLE 2.4.1

THERMAL DECOMPOSITION DATA OF Co (II), Ni (II) AND Cu (II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L - TYROSINE

Complex	stage	temp rang in TG (°C)	peak temp in TG (°C)	loss of mass percentage			probable assignment
				from TG	theoretica	pyrolysis	
$[Co\,L_2''\,(H_2O)_2]$	I	120 - 320	280	91	90.4	91	loss of 2 H_2O + 2L" $[Co\,L''_2\,(H_2O)_2]$ ---> $Co_3\,O_4$
$[Ni\,L_2''\,(H_2O)_2]$	I	170 - 320	240	91	91.1	91.29	loss of 2 H_2O + 2L" $[Ni\,L''_2\,(H_2O)_2]$ ----> Ni O
$[Cu\,L_2''\,(H_2O)_2]$	I	150 - 300	260	71	71		loss of 2 H_2O + 1L"+1ACA PART
	II	300 - 530	500	19.5	19.5		loss of tyrosine part
				90.5	90.5	88.97	$[Cu\,L''_2\,(H_2O)_2]$ ----> Cu O

TABLE 2. 4. 2

Kinetic parameters for the decomposition of Co(II) , Ni(II) and Cu (II) complexes of anthracene carboxaldehyde - L - tyrosine ($L''H$) from TG using mechanistic equations

complex	para meter	mechanistic equations								
		1	2	3	4	5	6	7	8	9
$[CoL_2''(H2O\ )_2]$	E	34.22	35.93	37.95	36.66	19.07	19.07	19.07	17.50	17.71
	A	$1.60\mathrm{x}10^{13}$	$5.43\ \mathrm{x}10^{13}$	$1.15\ \mathrm{x}10^{14}$	$2.70\ \mathrm{x}10^{13}$	$1.30\ \mathrm{x}10^{7}$	$6.50\ \mathrm{x}10^{6}$	$4.30\ \mathrm{x}10^{6}$	$1.00\ \mathrm{x}10^{6}$	$9.70\ \mathrm{x}10^{5}$
	ΔS	-45.07	-42.64	-41.14	-44.02	-72.92	-74.30	-75.10	-77.85	-78.08
	r	0.9998	0.9996	0.9982	0.9993	0.9952	0.9952	0.9952	0.9990	0.9967
$[NiL_2''(H2O\ )_2]$	E	30.61	32.49	34.72	33.26	17.56	17.56	17.56	15.85	16.73
	A	$8.81\ \mathrm{x}10^{11}$	$3.75\ \mathrm{x}10^{12}$	$1.03\ \mathrm{x}10^{13}$	$1.98\ \mathrm{x}10^{12}$	$4.30\ \mathrm{x}10^{6}$	$2.20\ \mathrm{x}10^{6}$	$1.40\ \mathrm{x}10^{6}$	$2.90\ \mathrm{x}10^{5}$	$5.30\ \mathrm{x}10^{5}$
	ΔS	-50.79	-47.91	-45.91	-49.18	-75.09	-76.46	-77.27	-80.42	-79.24
	r	0.9989	0.9990	0.9980	0.9989	0.9954	0.9954	0.9954	0.9986	0.9980
$[CuL_2''(H2O\ )_2]$	E	37.23	37.61	39.16	38.21	19.05	18.96	19.41	18.03	18.61
	A	$2.93\ \mathrm{x}10^{14}$	$2.31\ \mathrm{x}10^{14}$	$2.92\ \mathrm{x}10^{13}$	$9.94\ \mathrm{x}10^{13}$	$1.08\ \mathrm{x}10^{7}$	$4.74\ \mathrm{x}10^{6}$	$5.24\ \mathrm{x}10^{6}$	$1.64\ \mathrm{x}10^{6}$	$2.093\ \mathrm{x}10^{6}$
	ΔS	-39.25	-39.72	-39.25	-41.40	-73.26	-74.90	-74.70	-77.00	-76.52
	r	0.9992	0.9990	0.9996	0.9992	0.9993	0.9986	0.9987	0.9993	0.9995

E --- k Cals / mol, A --- Sec^{-1} ΔS ---- eu

TABLE 2. 4. 3

Kinetic parameters for the decomposition of Co (II), Ni (II), and Cu (II) complexes of anthracene carboxaldehyde - L - tyrosine ($L^{''}H$) using non mechanistic equations

complex	parameter	Coats Redfern	Horowitz Metziger	mechanistic equation followed		order of reaction
$[CoL_2''(H_2O)_2]$	E	17.50	23.41	17.50	equation 8 phase boundary	1/2.
	A	2.18×10^{6}	4.80×10^{7}	1.06×10^{6}	reaction cylinderical symmetry	
	ΔS	-76.47	-70.33	-77.85		
	r	0.9990	0.9995	0.9990		
$[NiL_2''(H_2O)_2]$	E	15.85	21.37	15.85	equation 8 phase boundary	1/2.
	A	5.87×10^{5}	4.42×10^{6}	2.93×10^{5}	reaction cylinderical symmetry	
	ΔS	-79.04	-75.03	-80.42		
	r	0.9986	0.9990	0.9986		
$[CuL_2''(H_2O)_2]$	E	18.61	24.42	18.61	equation 9 phase boundary	2/3.
	A	6.28×10^{6}	5.90×10^{7}	2.09×10^{6}	reaction spherical symmetry	
	ΔS	-74.34	-69.88	-76.52		
	r	0.9995	0.9980	0.9995		

E —— k $\overset{C}{\text{c}}$als mol^{-1} A —— Sec^{-1} Δ S —— eu

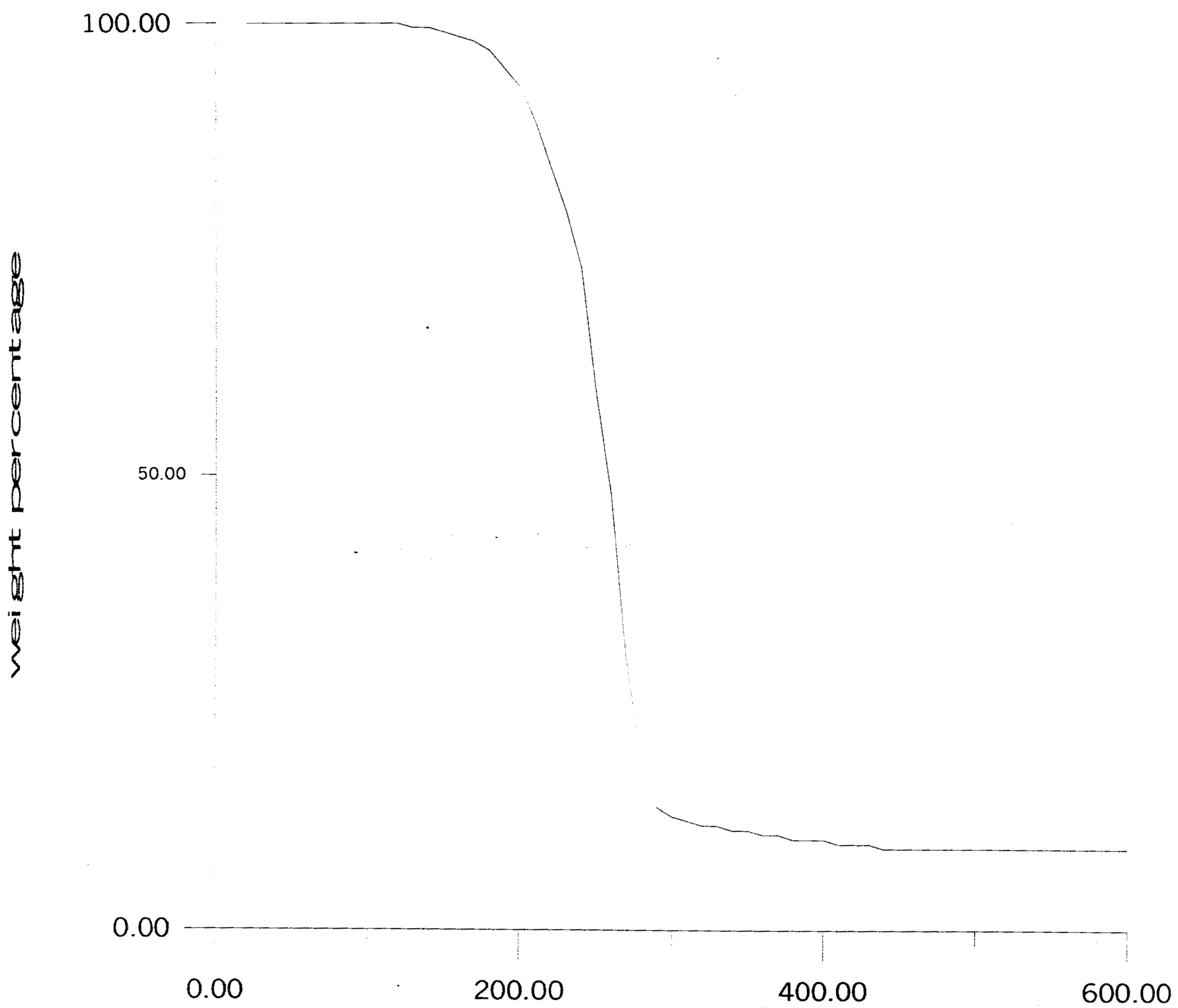


fig 2 .4 [Co (ACT)$_2$ (H$_2$O)$_2$]

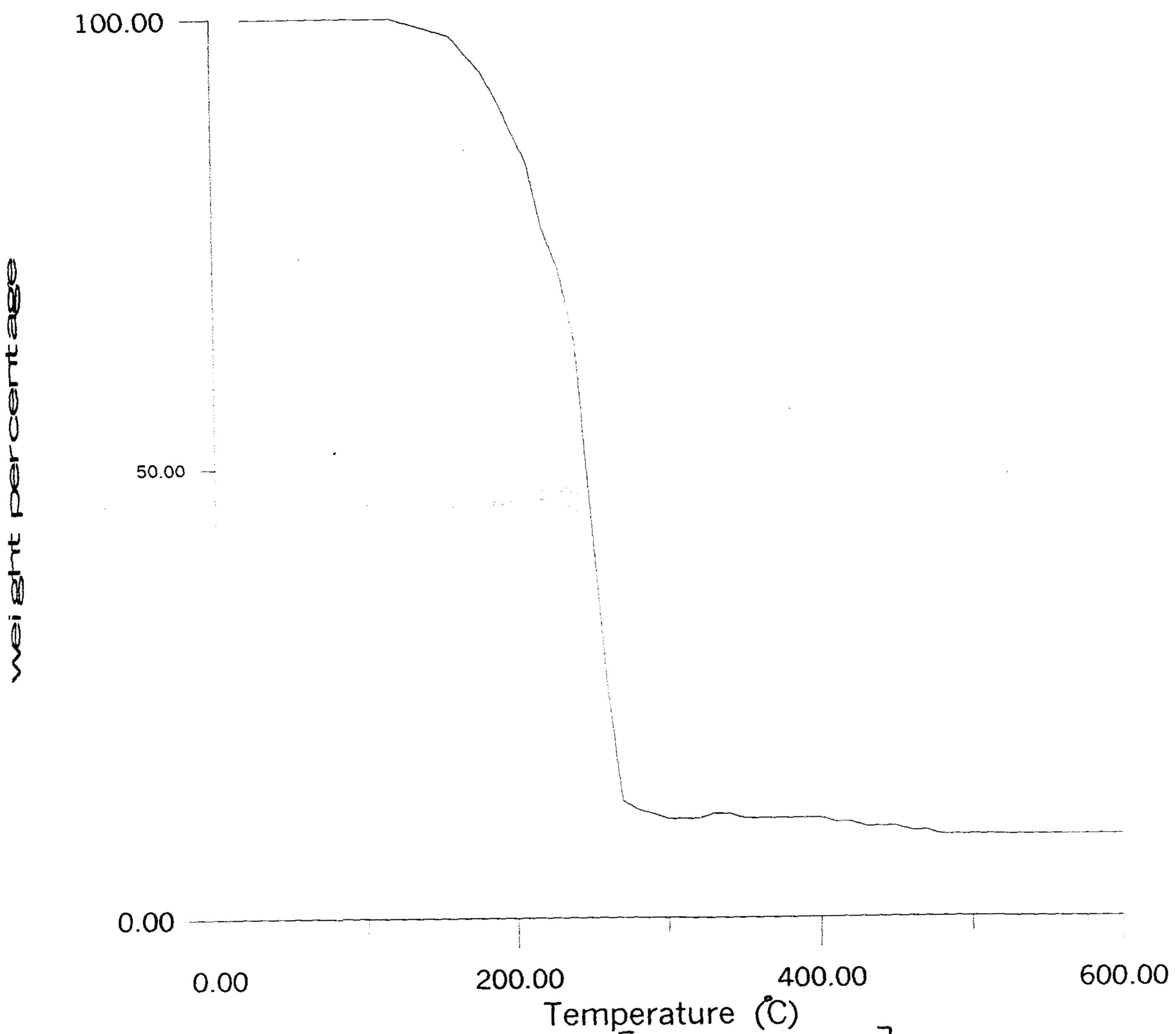


Fig. 2. 5 [Ni (ACT)$_2$ (H$_2$O)$_2$]

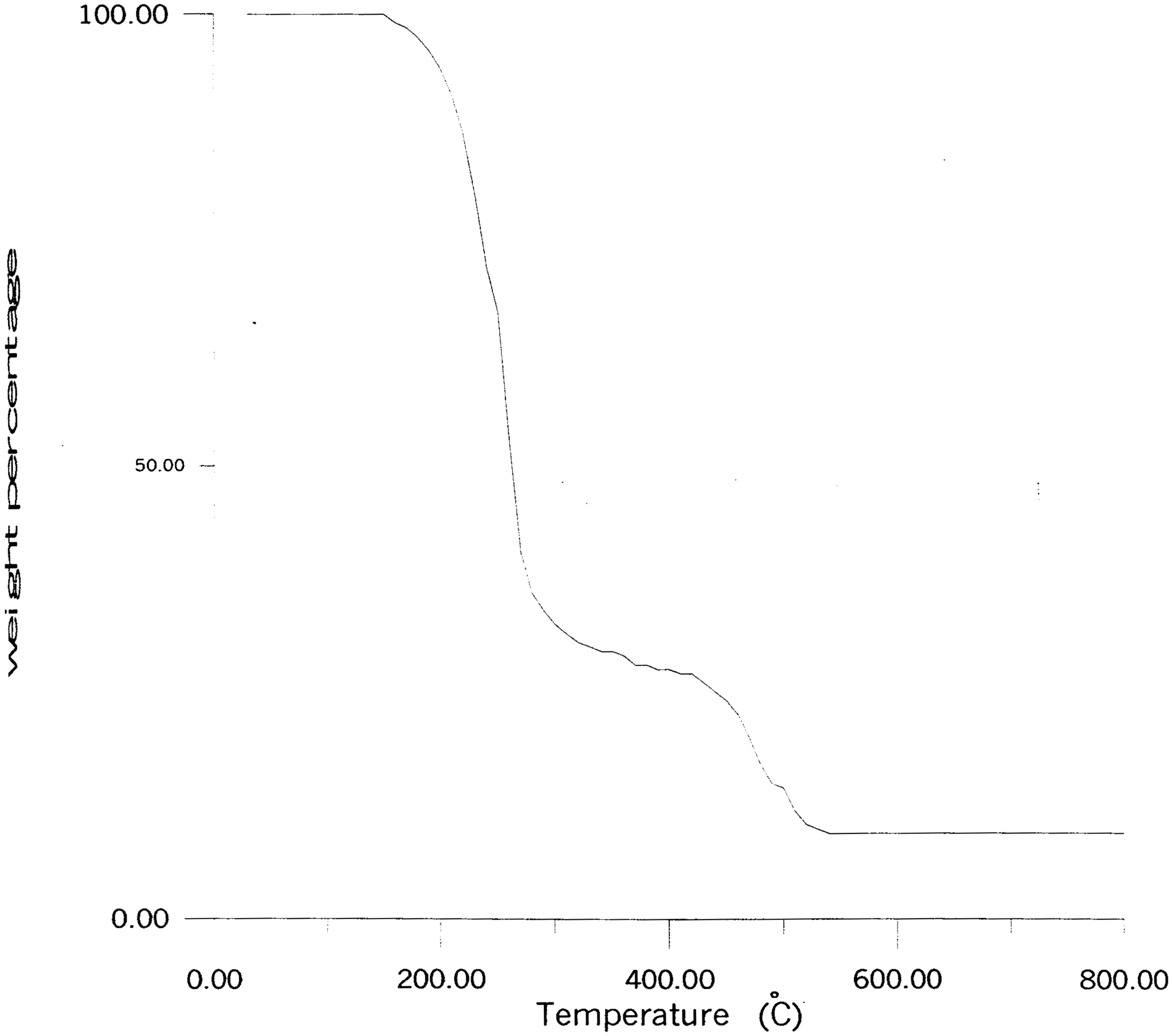


Fig. 2 . 6 [Cu (ACT)$_2$ (H$_2$O)$_2$]

PART II

THERMAL DECOMPOSITION KINETICS OF Co(II), Ni(II) AND Cu(II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L - TYROSINE

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			Theoretical,	TGA value
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$[Ni L_2{}^{11}(H_2O)_2]$	$\longrightarrow$	NiO	91.1	91
$[CuL_2{}^{11}(H_2O)_2]$	$\longrightarrow$	CuO	90.5	90.5

The kinetic parameters namely, activation energy E, Arrhenius factor A, order parameter n and entropy of activation ΔS for these decomposition reactions calculated from the TG curves, based on the nine mechanistic equations and the two non mechanistic equations are summarized in Tables. 2 .4. 2 and 2 . 4 . 3.

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Complex	stage	temp rang in TG ($^\circ$C)	peak temp in TG ($^\circ$C)	loss of mass percentage			probable assignment
				from TG	theoretica	pyrolysis	
$[Co\,L_2''(H_2O)_2]$	I	120 - 320	280	91	90.4	91	loss of 2 H_2O + 2L" $[Co\,L''_2(H_2O)_2]$ ---> Co_3O_4
$[Ni\,L_2''(H_2O)_2]$	I	170 - 320	240	91	91.1	91.29	loss of 2 H_2O + 2L" $[Ni\,L''_2(H_2O)_2]$ ----> Ni O
$[Cu\,L_2''(H_2O)_2]$	I	150 - 300	260	71	71		loss of 2 H_2O + 1L"+1ACA PART
	II	300 - 530	500	19.5	19.5		loss of tyrosine part
				90.5	90.5	88.97	$[Cu\,L''_2(H_2O)_2]$ ----> Cu O

TABLE 2. 4. 2

Kinetic parameters for the decomposition of Co(II) , Ni(II) and Cu (II) complexes of anthracene carboxaldehyde - L - tyrosine ($L''H$) from TG using mechanistic equations

complex	para meter	mechanistic equations								
		1	2	3	4	5	6	7	8	9
$[\mathrm{CoL_2}''(\mathrm{H2O})_2]$	E	34.22	35.93	37.95	36.66	19.07	19.07	19.07	17.50	17.71
	A	$1.60\mathrm{x}10^{13}$	$5.43\mathrm{x}10^{13}$	$1.15\mathrm{x}10^{14}$	$2.70\mathrm{x}10^{13}$	$1.30\mathrm{x}10^{7}$	$6.50\mathrm{x}10^{6}$	$4.30\mathrm{x}10^{6}$	$1.00\mathrm{x}10^{6}$	$9.70\mathrm{x}10^{5}$
	ΔS	-45.07	-42.64	-41.14	-44.02	-72.92	-74.30	-75.10	-77.85	-78.08
	r	0.9998	0.9996	0.9982	0.9993	0.9952	0.9952	0.9952	0.9990	0.9967
$[\mathrm{NiL_2}''(\mathrm{H2O})_2]$	E	30.61	32.49	34.72	33.26	17.56	17.56	17.56	15.85	16.73
	A	$8.81\mathrm{x}10^{11}$	$3.75\mathrm{x}10^{12}$	$1.03\mathrm{x}10^{13}$	$1.98\mathrm{x}10^{12}$	$4.30\mathrm{x}10^{6}$	$2.20\mathrm{x}10^{6}$	$1.40\mathrm{x}10^{6}$	$2.90\mathrm{x}10^{5}$	$5.30\mathrm{x}10^{5}$
	ΔS	-50.79	-47.91	-45.91	-49.18	-75.09	-76.46	-77.27	-80.42	-79.24
	r	0.9989	0.9990	0.9980	0.9989	0.9954	0.9954	0.9954	0.9986	0.9980
$[\mathrm{CuL_2}''(\mathrm{H2O})_2]$	E	37.23	37.61	39.16	38.21	19.05	18.96	19.41	18.03	18.61
	A	$2.93\mathrm{x}10^{14}$	$2.31\mathrm{x}10^{14}$	$2.92\mathrm{x}10^{13}$	$9.94\mathrm{x}10^{13}$	$1.08\mathrm{x}10^{7}$	$4.74\mathrm{x}10^{6}$	$5.24\mathrm{x}10^{6}$	$1.64\mathrm{x}10^{6}$	$2.093\mathrm{x}10^{6}$
	ΔS	-39.25	-39.72	-39.25	-41.40	-73.26	-74.90	-74.70	-77.00	-76.52
	r	0.9992	0.9990	0.9996	0.9992	0.9993	0.9986	0.9987	0.9993	0.9995

E --- k cals / mol, A --- Sec^{-1} ΔS ---- eu

TABLE 2. 4. 3

Kinetic parameters for the decomposition of Co (II), Ni (II), and Cu (II) complexes of anthracene carboxaldehyde - L - tyrosine ($L''H$) using non mechanistic equations

complex	parameter	Coats Redfern	Horowitz Metziger	mechanistic equation followed		order of reaction
$[CoL_2''(H_2O)_2]$	E	17.50	23.41	17.50	equation 8 phase boundary reaction cylinderical symmetry	1/2.
	A	2.18×10^6	4.80×10^7	1.06×10^6		
	ΔS	-76.47	-70.33	-77.85		
	r	0.9990	0.9995	0.9990		
$[NiL_2''(H_2O)_2]$	E	15.85	21.37	15.85	equation 8 phase boundary reaction cylinderical symmetry	1/2.
	A	5.87×10^5	4.42×10^6	2.93×10^5		
	ΔS	-79.04	-75.03	-80.42		
	r	0.9986	0.9990	0.9986		
$[CuL_2''(H_2O)_2]$	E	18.61	24.42	18.61	equation 9 phase boundary reaction spherical symmetry	2/3.
	A	6.28×10^6	5.90×10^7	2.09×10^6		
	ΔS	-74.34	-69.88	-76.52		
	r	0.9995	0.9980	0.9995		

E —— k cals mol^{-1} A —— Sec^{-1} Δ S —— eu

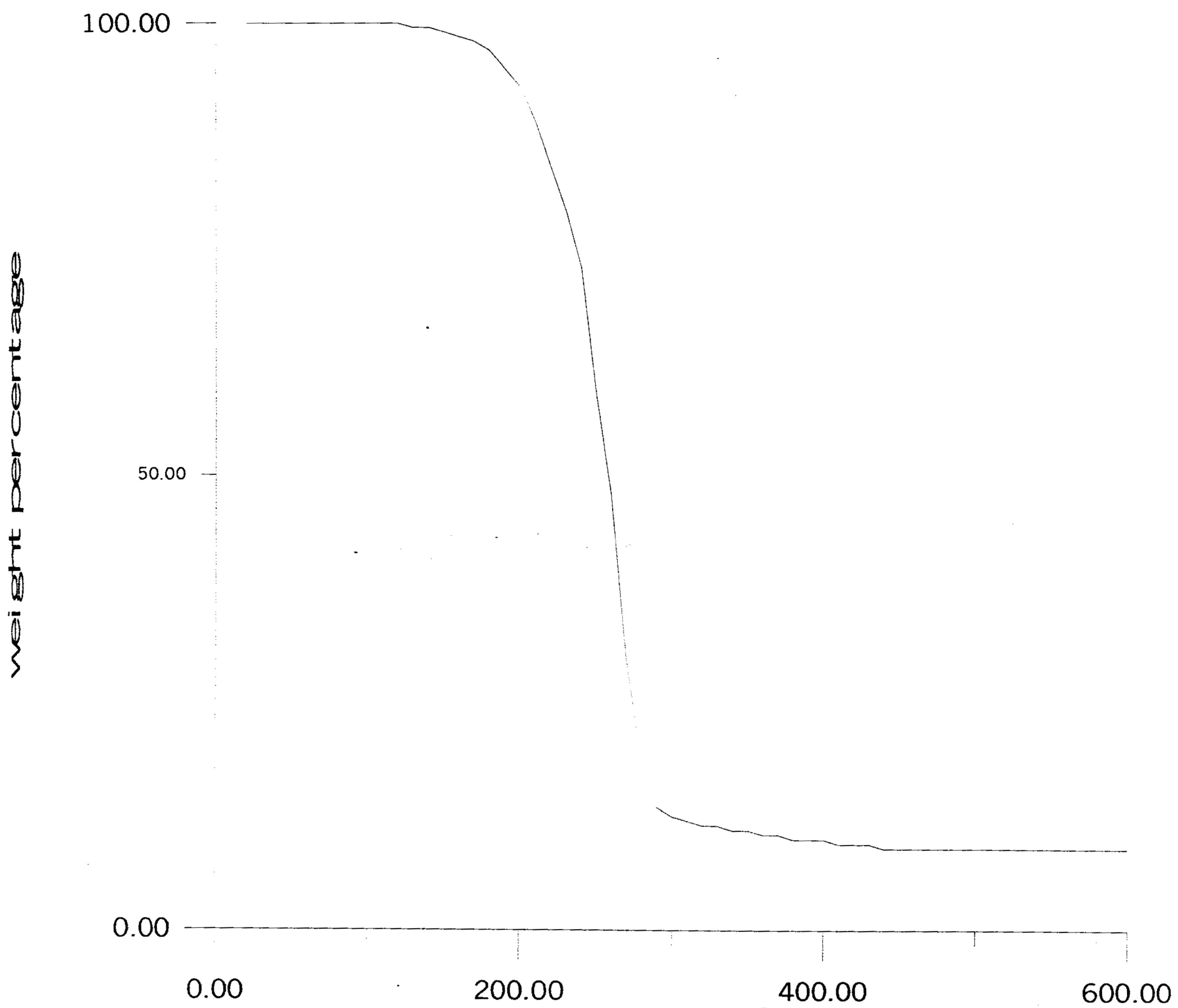

fig 2 .4 [Co (ACT)$_2$ (H$_2$O)$_2$]

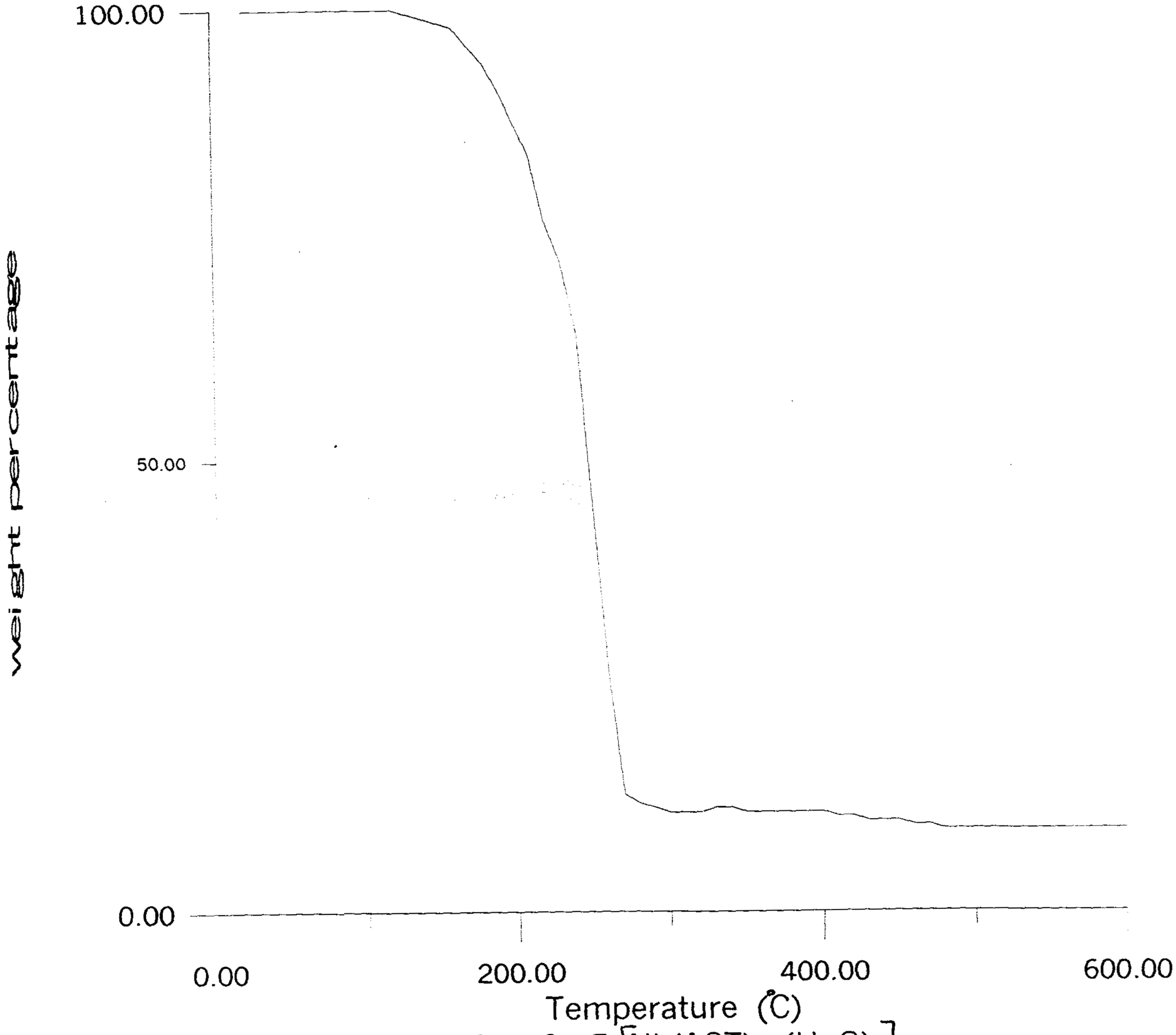

Fig . 2 . 5 $[Ni(ACT)_2(H_2O)_2]$

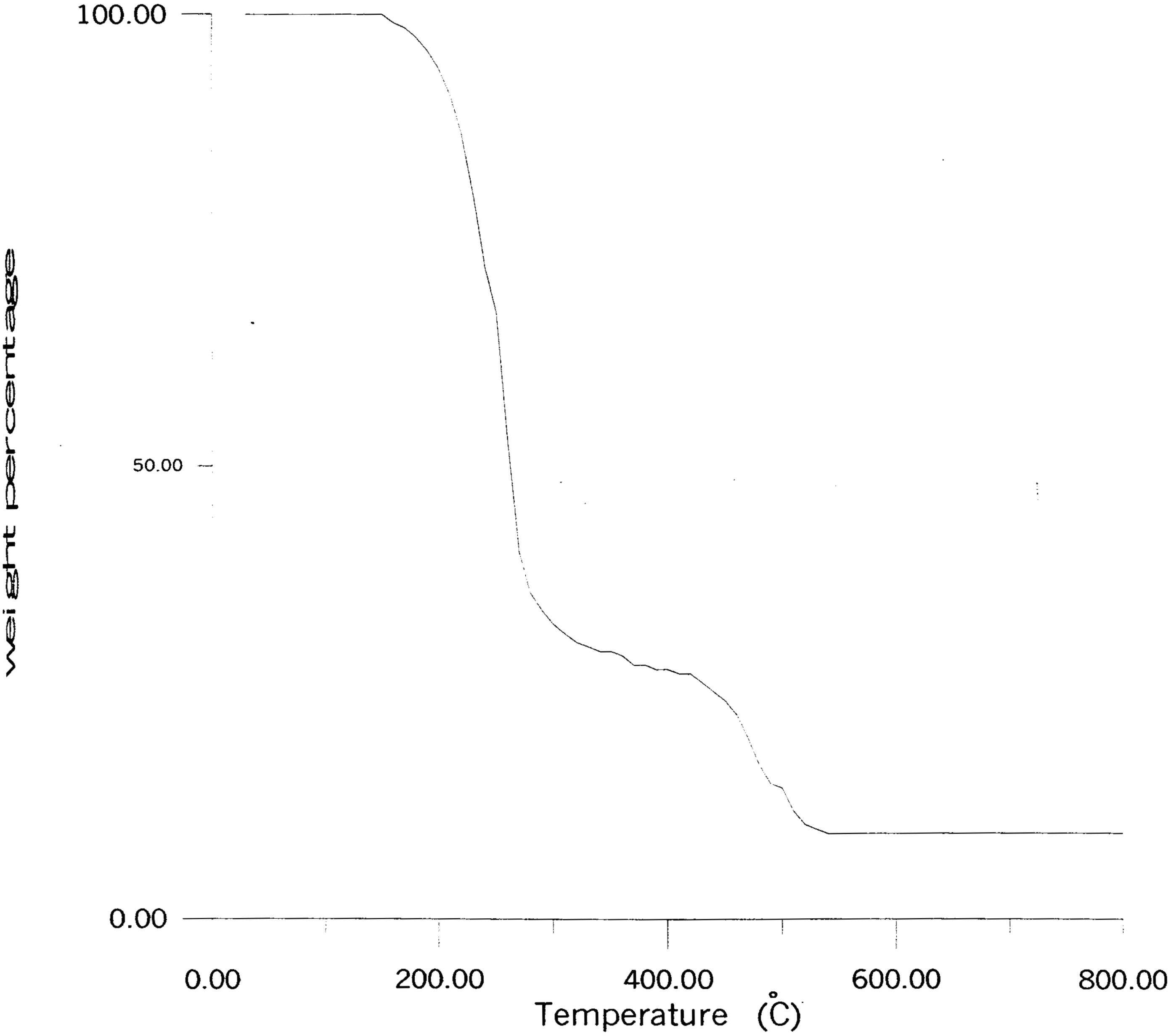

Fig. 2 . 6 [Cu (ACT)$_2$ (H$_2$O)$_2$]

PART II

THERMAL DECOMPOSITION KINETICS OF Co(II), Ni(II) AND Cu(II) COMPLEXES WITH ANTHRACENE CARBOXALDEHYDE -DL ALANINE

G. Indira Devi “ Studies on transition metal complexes of schiff bases derived from aminoacids” Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER VI

THERMAL DECOMPOSITION KINETICS OF Co(II), Ni(II) AND Cu(II) COMPLEXES WITH ANTHRACENE CARBOXALDEHYDE –DL ALANINE

In this chapter, results of thermal decomposition studies on Co(II) , Ni(II) and Cu(II) chelates of anthracene –9- carboxaldehyde –DL Alanine are presented. Li, Shu-Lan and coworkers have carried out the thermal analysis of Cu(II), Zn(II) and Ni(II) complexes derived from o-vanillin and alanine[60].Only very few works have been reported about the thermal decomposition kinetics of transition metal complex of anthracene carboxaldehyde Schiff bases [61,62]. The kinetic parameters like energy of activation E, Arrhenius factor A and entropy of activation ΔS, of the decomposition reactions were calculated, based on various mechanistic and non-mechanistic kinetic equations. The order of reaction and mechanism of decomposition are also interpreted.

Experimental

The metal complexes concerned were prepared and characterized according to the procedure described in Part 1. The TG curves were recorded in static air atmosphere at a heating rate of 10°C per minute. Calculations of kinetic parameters were carried out using a computer using C^{++} language. Thermograms are reproduced using a computer.

Treatment of data

The instrumental TG curves were redrawn as mass verses temperature and are given in figure 2. 10, 2. 11, and 2. 12. The temperature ranges, peak temperature, probable assignments and total mass loss from TG along with the independent pyrolytic experimental data are presented in Table 2. 6. 1 . The kinetic parameters calculated using nine mechanistic equations are summarized in Table 2. 6. 2. Table 2. 6. 3 include the suggested mechanism of decomposition, order of reaction and the kinetic parameters evaluated by applying different non-mechanistic methods such as Coats Redfern, and Horowitz – Metzger methods.

Results and discussion

These complexes do not show any detectable change up to 100 ^{0} C when heated, which suggest that there is no water of hydration. At around 150 ^{0} C, a loss of mass is noted in the case of Co(II), Ni(II) and Cu(II) complexes which can be attributed to the loss of two coordinated water molecules.

Co(II) complexes having the formula $[CoL_2^{IV}(H_2O)_2]$, exhibit single stage decomposition pattern, which can be assigned to the loss of two molecules of water and the two ligand part.

The Ni(II) complex having the formula $[NiL_2^{IV} (H_2O)_2]$exhibits a double stage pattern of decomposition. The first stage shows the loss of two-coordinated water molecules, one ligand and an anthracene carboxaldehyde part. The second stage in the TG curve shows the removal of alanine part.

The TG curve of the Cu(II) complex exhibits a clear well defined three stage decomposition pattern. The first stage may be attributed to the loss of two molecules of water and two anthracene carboxaldehyde part of the ligand. The second stage contributes to the loss of alanine part of the first ligand, where as the third stage indicate the removal of alanine part of the second ligand.

The final mass loss observed agrees with the values calculated for the conversion of complexes to their oxides. (Co_3O_4, NiO and CuO).

The initial decomposition temperature is frequently used to define the thermal stability of metal chelates. Based on experimental results the relative thermal stability of these chelates can be given as [Co L_2^{IV} $(H_2O)_2$] >[Cu L_2^{IV} $(H_2O)_2$] >[Ni L_2^{IV} $(H_2O)_2$]

The values of kinetic parameters obtained using the various non-mechanistic equations and the equation corresponding to the suggested mechanism of decomposition are reasonable and are in good agreement. The satisfactory value of correlation coefficient, ($r \approx 1$), indicates good agreement with experimental data. The negative ΔS values of these complexes show that the complexes are more ordered in the activated state than the reactants and the reactions are slower than normal.

Decomposition kinetics

The order parameter n, and the kinetic parameters such as activation energy E, pre exponential factor A and entropy of activation ΔS for the thermal decomposition of these three complexes were evaluated and summarized in Table 2. 6. 2 and 2. 6. 3. It can be seen from these data that more than one equation gives a good linear curve with a high value of correlation coefficient. It is also found that the greater the thermal stability of the complex, the larger the activation energy for decomposition.

In the present course of studies based on these mathematical evaluations, it is observed that the kinetic parameters calculated for the decomposition of Co(II) complex from the Coats Redfern equation with n = ½ is in good agreement with those obtained for the R_2 mechanism. R_2 mechanism based on phase boundary reaction cylinderical symmetry gives maximum correlation for $[CoL_2^{IV}(H_2O)_2]$. For the decomposition of Ni(II) complex, kinetic parameters obtained from Coats Redfern equation with n = 2/3 are in good agreement with those obtained for the R_3 mechanism based on phase boundary reaction spherical symmetry. Maximum correlation was obtained between the kinetic parameters computed using Coats Redfern method with n = 1/3 and R_2 mechanism based on phase boundary reaction cylindrical symmetry for the decomposition of Cu(II) complex.

TABLE 2. 6. 1

THERMAL DECOMPOSITION DATA OF Co (II), Ni (II) AND Cu (II) COMPLEX OF ANTHRACENE CARBOXALDEHYDE - DL - ALANINE

Complex	stage	temp range in TG (°C)	peak temp in TG (°C)	loss of mass percentage			probable assignment
				from TG	theoretica	pyrolysis	
$[CoL_2^{IV}(H_2O)_2]$	I	110 - 390	280	89.1	88.42		loss of 2 H_2O + $2L^{IV}$
				89.1	88.42	87.16	$Co\,L^{IV}_2\,(H_2O)_2$ ---> $Co_3\,O_4$
$[NiL_2^{IV}(H_2O)_2]$	I	120 - 440	250	77.1	77.63		loss of 2 H_2O + L^{IV} + ACA part
	II	440 - 590	510	11.5	10.82		loss of alanine part
				88.6	88.45	88.24	$Ni\,L^{IV}_2\,(H_2O)_2$ ----> Ni O
$[CuL_2^{IV}(H_2O)_2]$	I	130 - 310	260	61.17	63.84		loss of 2 H_2O + 2 ACA
	II	310 - 490	470	13.39	13.19		loss of alanine part
	III	490 - 620	600	12.37	10.75		loss of alanine part
				87.79	86.93	87.8	$Cu\,L^{IV}_2\,(H_2O)_2$ ----> Cu O

TABLE 2. 6. 2

KINETIC PARAMETERS FOR THE DECOMPOSITION OF Co(II) , Ni(II) AND Cu (II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - DL ALANINE(L^{IV} H) FROM TG USING MECHANISTIC EQUATIONS

complex	para meter	mechanistic equations								
		1	2	3	4	5	6	7	8	9
$[CoL_2^{IV}(H_2O)_2]$	E	31.73	34.48	38.51	35.82	18.61	18.61	18.61	17.31	17.93
	A	1.22×10^{12}	1.19×10^{13}	1.99×10^{14}	1.13×10^{13}	7.84×10^{6}	3.92×10^{6}	2.61×10^{6}	8.81×10^{5}	1.19×10^{6}
	ΔS	-50.21	-45.68	-40.09	-45.79	-73.97	-75.35	-76.15	-78.31	-77.70
	r	0.9968	0.9985	0.9989	0.9991	0.9981	0.9981	0.9981	0.9985	0.9984
$[NiL_2^{IV}(H_2O)_2]$	E	23.55	27.62	27.33	26.00	13.74	13.74	13.74	12.19	12.69
	A	5.77×10^{6}	2.28×10^{10}	4.70×10^{9}	1.03×10^{9}	7.03×10^{4}	3.52×10^{4}	2.35×10^{4}	5.71×10^{3}	6.84×10^{4}
	ΔS	-65.32	-58.01	-61.15	-64.16	-83.22	-84.60	-85.41	-88.22	-87.85
	r	0.9976	0.9980	0.9930	0.9950	0.9884	0.9884	0.9884	0.9937	0.9921
$[CuL_2^{IV}(H_2O)_2]$	E	33.54	37.22	38.36	39.16	14.58	16.21	18.06	17.07	15.30
	A	1.15×10^{13}	3.22×10^{14}	2.59×10^{14}	6.08×10^{14}	1.04×10^{5}	3.20×10^{5}	1.69×10^{6}	8.07×10^{5}	8.20×10^{4}
	ΔS	-45.69	-39.06	-39.49	-37.80	-82.48	-80.21	-76.94	-78.41	-82.95
	r	0.9951	0.9968	0.9971	0.9977	0.9923	0.9926	0.9959	0.9945	0.9947

E – k Cals mol^{-1} A – Sec^{-1} Δs = eu

TABLE 2.6.3

KINETIC PARAMETERS FOR THE DECOMPOSITION OF Co (II), Ni (II), AND Cu (II) COMPLEX OF ANTHRACENE CARBOXALDEHYDE -D L ALANINE ($L^{IV}H$) USING NON MECHANISTIC EQUATIONS

complex	parameter	Coats Redfern	Horowitz Metziger	mechanistic equation followed		order of reaction
$[CoL_2^{IV}(H_2O)_2]$	E	17.31	23.00	17.31	equation 8 phase boundary reaction cylindrical symmetry	1/2.
	A	1.76×10^{6}	1.26×10^{7}	8.81×10^{5}		
	ΔS	-76.94	-73.02	-78.31		
	r	0.9985	0.9979	0.9985		
$[NiL_2^{IV}(H_2O)_2]$	E	12.69	16.64	12.69	equation 9 phase boundary reaction spherical symmetry	2 / 3.
	A	2.05×10^{4}	3.42×10^{4}	6.84×10^{3}		
	ΔS	-85.69	-84.66	-87.85		
	r	0.9921	0.9978	0.9921		
$[CuL_2^{IV}(H2O)_2]$	E	17.07	21.02	17.07	equation 8 phase boundary reaction cylindrical symmetry	1/3.
	A	1.61×10^{6}	$2.11- \times 10^{6}$	8.07×10^{5}		
	ΔS	-77.04	-76.50	-78.41		
	r	0.9945	0.9902	0.9945		

E ------- kCals mol^{-1} , A ------ Sec^{-1} , ΔS ---eu

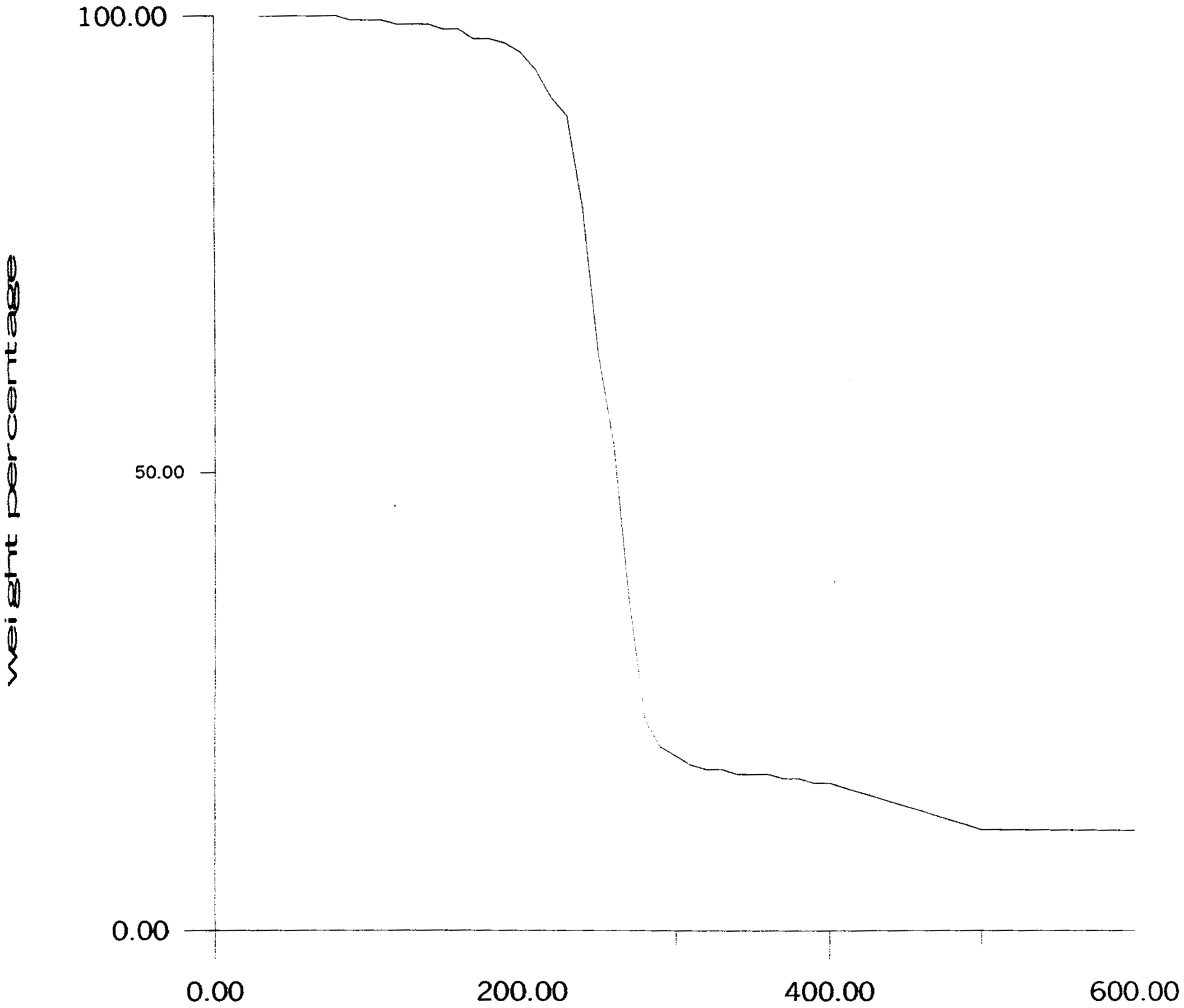

Fig . 2. 10 [Co (ACA)$_2$ (H$_2$O)$_2$]

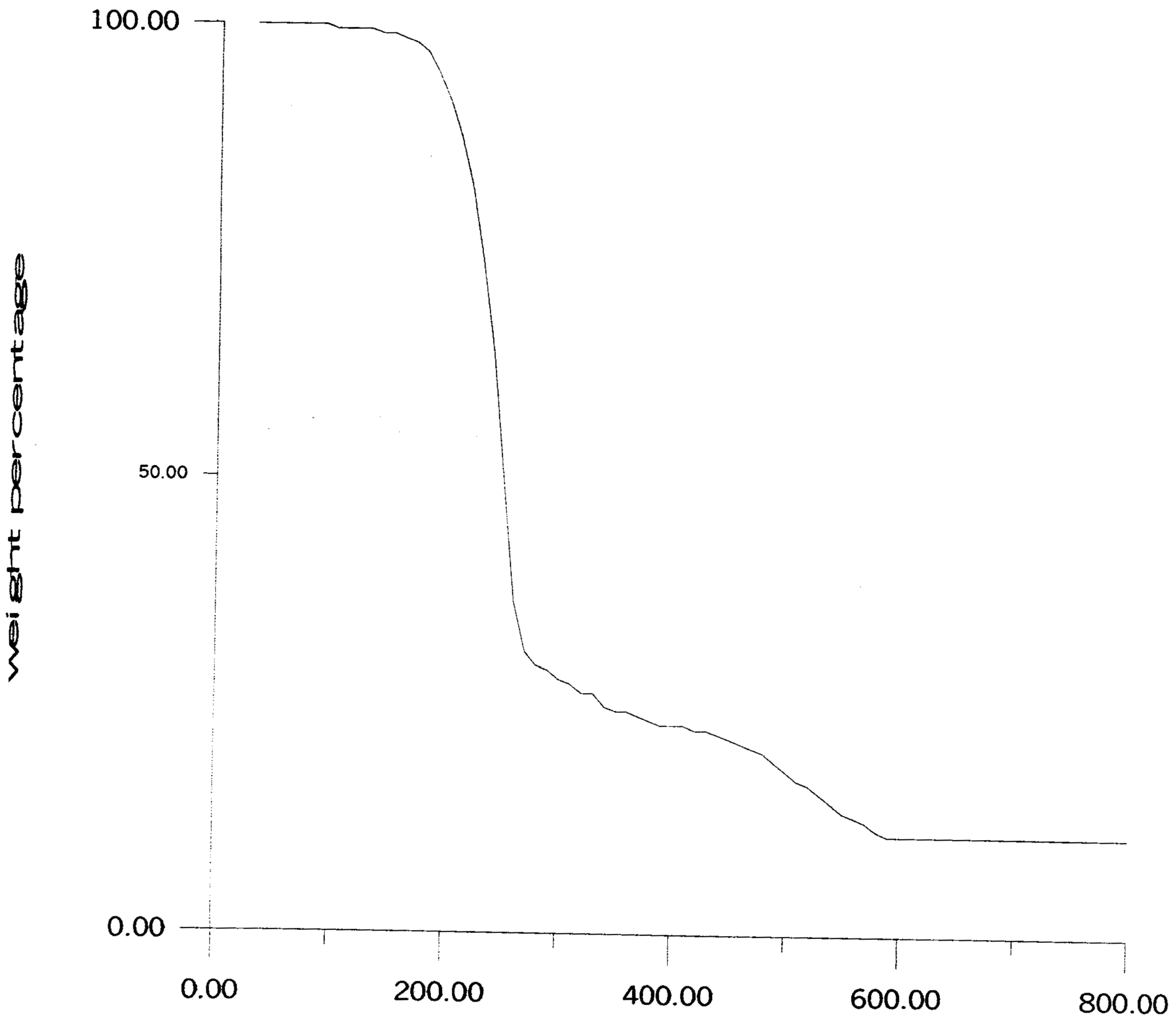

Fig. 2. 11 $[Ni(ACA)_2(H_2O)_2]$

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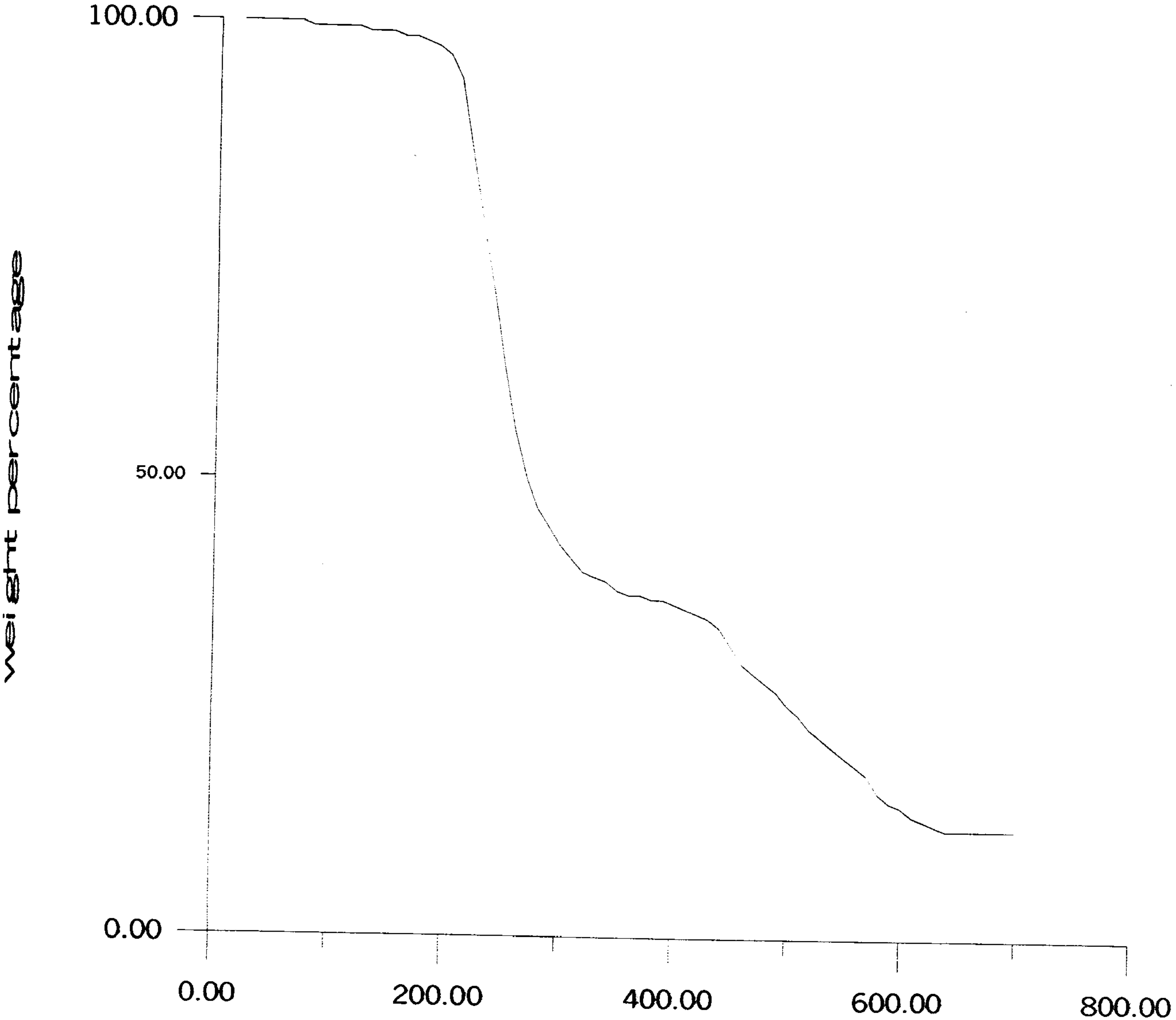

Fig. 2.12. [Cu (ACA)$_2$ (H$_2$O)$_2$]

PART II

THERMAL DECOMPOSITION KINETICS AND MECHANISM OF Co(II), Ni(II) AND Cu(II) COMPLEXES DERIVED FROM ANTHRACENE CARBOXALDEHYDE - L - PHENYL ALANINE

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER VII

THERMAL DECOMPOSITION KINETICS AND MECHANISM OF Co(II), Ni(II) AND Cu(II) COMPLEXES DERIVED FROM ANTHRACENE CARBOXALDEHYDE – L – PHENYL ALANINE

Thermal behavior of complexes of Schiff bases derived from amino acid and its derivatives were studied extensively using TG by non isothermal method [63-69]. Some new Cu (II) and Zn(II) complexes of Schiff bases derived from o-vanillin and glycine, DL-alanine, L-leucine, and L-phenyl alanine were synthesized and their studies were carried out by Wang [70] et al. The thermal degradation of the complexes of Co (II), Ni (II), Zn(II) and Cd (II) with phenyl alanine and aldehyde or ketone were studied in air by dynamic TG from ambient temperature to 900^0 C [71]. Non-isothermal methods have been widely used to study the kinetics and thermal decomposition of solids. This study therefore attempts to establish the mechanism of decomposition of Co (II), Ni(II) and Cu(II) complexes derived from anthracene carboxaldehyde L-phenyl alanine.

Interpretation and mathematical analysis of the thermal decomposition data and evaluation of order of reaction, entropy change, energy of activation and Arrhenius factor based on Coats –Redfern and Horowitz-Metzger methods are described. Evaluation of the reaction mechanism by non-isothermal methods has been discussed using the nine mechanistic equations.

Experimental

The ligand was prepared by refluxing a methanolic mixture (1 : 1) of anthracene carboxaldehyde and L phenyl alanine for two hours. Yellow crystals separated on cooling were purified by re crystallization from methanol and characterized. Samples of Co (II), Ni (II) and Cu (II) chelates of anthracene carboxaldehyde – L – Phenyl alanine were prepared by refluxing methanolic solution of the ligand and methanolic solution of metal salt in 2:1 ratio. The mixture was refluxed and the precipitated complex collected, and dried .The complexes having general formula $[ML^V{}_2(H_2O)_2]$were characterized and thermal analysis was carried out in static air atmosphere. A constant heating rate of 10degree per minute and a sample mass of 2-5mg were used for the entire studies. Computational work was performed with a computer using the programming language C^{++}.

Treatment of data

The instrumental TG curves are presented in Fig 2.13, 2.14, and 2.15. Decomposition temperature ranges for the metal chelates are given in Table 2. 7. 1. Data from pyrolytic experiments are also included in this table. Table 2. 7. 1 also summarizes the probable assignments for the various stages of decomposition of these complexes. Nine mechanistic equations and two non-mechanistic equations were employed to evaluate kinetic data from these TG traces. The kinetic parameters calculated from TG data for the nine mechanistic equations are given in Table 2. 7. 2. The corresponding values of E, A, ΔS and r from non-mechanistic equations (Coats Redfern, and Horowitz - Metzger) and the mechanistic equation suggested are given in Table 2. 7. 3.

Results and discussion

Based on analytical, magnetic, and spectral studies, these complexes are represented as $[CoL_2^V(H_2O)_2]$, $[NiL_2^V(H_2O)_2]$, and $[CuL_2^V(H_2O)_2]$. The TG curve of the Co(II) complex exhibits a clear well defined double stage decomposition pattern, while the complex of Ni(II) shows a three stage decomposition pattern. In the case of Co(II) complex, the first stage may be attributed to the loss of two coordinated water molecules, one ligand and one phenylalanine part of the second ligand. The second stage contributes to the loss of anthracene carboxaldehyde part of the ligand. TG curve of the Ni(II) complex having the formula $[NiL_2^V(H_2O)_2]$ shows a three stage decomposition pattern. Mass loss considerations from TG curve indicate that the first step of decomposition consists of the removal of two molecules of water and one ligand. The loss of anthracene carboxaldehyde part takes place in the second step, where as the third stage indicates the removal of phenylalanine part. TG curve of Cu(II) complex shows a two stage decomposition pattern. The first stage may be attributed to the loss of two molecules of water, one ligand and phenyl alanine part of the second ligand. The loss of anthracene carboxaldehyde part takes place in the second step. The overall mass loss from TG trace also correlates with the total theoretical mass loss for the conversion of these complexes to their corresponding oxides such as Co_3O_4, NiO and CuO.

The kinetic parameters such as activation energy E, pre-exponential factor A and entropy of activation ΔS were calculated for the decomposition of the above chelates using mechanistic and non-mechanistic equations, and the results are summarized in Tables

2. 7. 2 and 2. 7. 3. It is also noticed that the greater the thermal stability of a compound, the larger the activation energy for decomposition. The relative thermal stabilities of these complexes can be given as[Co $L_2{}^V$ $(H_2O)_2$] > [Cu $L_2{}^V$ $(H_2O)_2$] > [Ni $L_2{}^V$ $(H_2O)_2$]

Decomposition kinetics

It is very difficult to assign a reaction mechanism unequivocally because more than one equation gives good linear correlation with a higher correlation coefficient. In such cases the function g (α), which gives kinetic parameters in agreement with those obtained by the numerical method was chosen. Since E, A and ΔS values obtained from Coats Redfern method with n = ½ are in good agreement with those obtained from the equation 8. R_2 mechanism based on phase boundary reaction cylinderical symmetry, for [$CoL_2{}^V(H_2O)_2$.] In the case of Ni(II) and Cu(II) complexes it is observed that kinetic parameters calculated for R_3 mechanism based on phase boundary spherical symmetry gives good agreement with those obtained for Coats Redfern with n = 2/3. The E, A and ΔS values calculated by the different non-mechanistic equation such as Horowitz – Metzger also show good agreement.

TABLE 2.7.1

THERMAL DECOMPOSITION DATA OF Co (II), Ni (II) AND Cu (II)

COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L - PHENYL ALANINE

Complex	stage	temp range in TG (°C)	peak temp in TG (°C)	loss of mass percentage			probable assignment
				from TG	theoretica	pyrolysis	
[$CoL_2^V(H_2O)_2$]	I	110 - 285	270	66.93	66.86	90.6	loss of $2H_2O+L^V+$ phenyl alanine
	II	285 - 540	500	23.77	23.78		loss of ACA part
				90.7	90.64	90.6	$Co L_2^V (H_2O)_2$ ---> $Co_3 O_4$
[$NiL_2^V(H_2O)_2$]	I	110 - 285	220	49.62	48.58		Loss of 2 $H_2O+ L^V$
	II	285 - 500	310	21.94	23.79		Loss of ACA part
	III	500 - 610	570	19	18.3		Loss of phenyl alanine
				90.56	90.67	89.83	$Ni L_2^V (H_2O)_2$ ----> Ni O
	I	110 - 395	270	63.4	66.46		loss of $2H_2O+L^V+$ phenyl alanine
[$CuL_2^V(H_2O)_2$]	II	395 -565	500	25.66	23.64		loss of ACA part
				89.06	90.1	89.68	$Cu L_2^V (H_2O)_2$ ----> Cu O

E ------- kCals/ mol , A ------ 1/S , S ----- eu

TABLE 2.7.2

KINETIC PARAMETERS FOR THE DECOMPOSITION OF Co(II), Ni(II) AND Cu (II) COMPLEXES OF ANTHRACENE CARBOXALDEHYDE - L - PHENYL ALANINE(L^VH) FROM TG USING MECHANISTIC EQUATIONS

complex	para meter	mechanistic equations								
		1	2	3	4	5	6	7	8	9
$[CoL_2^V(H_2O)_2]$	E	27.66	28.55	29.13	28.42	14.04	13.66	14.19	13.32	13.35
	A	2.27×10^{10}	3.22×10^{10}	1.43×10^{10}	6.22×10^{9}	6.39×10^{4}	2.14×10^{4}	2.53×10^{4}	1.34×10^{4}	9.39×10^{3}
	ΔS	-58.10	-57.40	-59.01	-60.67	-83.49	-85.67	-85.33	-86.59	-87.30
	r	0.9946	0.9958	0.9971	0.9962	0.9978	0.9985	0.9977	0.9958	0.9963
$[NiL_2^V(H_2O)_2]$	E	2.30	2.97	3.79	3.24	1.24	1.46	1.27	0.61	0.81
	A	5.7×10^{-2}	8.55×10^{-2}	6.61×10^{-2}	2.89×10^{-2}	3.08×10^{-2}	2.20×10^{-2}	1.08×10^{-2}	3.5×10^{-3}	3.95×10^{-3}
	ΔS	-110.32	-109.51	-110.02	-111.66	-111.54	-112.20	-113.62	-115.86	-115.62
	r	0.9918	0.9918	0.9912	0.9916	0.9711	0.9580	0.9621	0.9273	0.9599
$[CuL_2^V(H_2O)_2]$	E	20.47	20.08	20.96	21.52	9.37	9.74	9.42	9.02	9.25
	A	1.38×10^{7}	5.08×10^{6}	3.20×10^{6}	5.32×10^{6}	4.03×10^{2}	3.12×10^{2}	1.42×10^{2}	1.27×10^{2}	1.14×10^{2}
	ΔS	-72.74	-74.72	-75.64	-74.63	-93.48	-93.99	-95.55	-95.78	-96.00
	r	0.9924	0.9959	0.9968	0.9942	0.9940	0.9965	0.9947	0.9945	0.9953

E ------- kCals mol^{-1}, A ------ S^{-1}, ΔS ----- eu

TABLE 2. 7. 3

KINETIC PARAMETERS FOR THE DECOMPOSITION OF Co (II), Ni (II), AND Cu (II) COM ANTHRACENE CARBOXALDEHYDE - L – PHENYLALANINE ($L^V H$) USING NON MECHANISTIC EQUATIONS

complex	parameter	Coats Redfern	Horowitz Metziger	mechanistic equation followed		order of reaction
$[CoL_2^V(H_2O)_2]$	E	13.32	17.30	13.32	equation 8 phase boundary	1/2.
	A	2.68×10^{4}	3.75×10^{4}	1.34×10^{4}	reaction cylindrical symmetry	
	ΔS	-85.21	-84.55	-86.59		
	r	0.9958	0.9923	0.9958		
$[NiL_2^V(H_2O)_2]$	E	0.81	1.25	0.81		
	A	1.19×10^{-2}	1.28×10^{-3}	3.95×10^{-3}	equation 9 phase boundary	2 / 3.
	ΔS	-113.43	-117.85	-115.61	reaction spherical symmetry	
	r	0.9599	0.9980	0.9599		
$[CuL_2^V(H_2O)_2]$	E	9.25	12.66	9.25		
	A	3.41×10^{2}	3.40×10^{2}	1.14×10^{2}	equation 9 phase boundary	2 / 3.
	ΔS	-93.81	-93.82	-96.00	reaction spherical symmetry	
	r	0.9953	0.9921	0.9953		

E —— kCals mol^{-1} , A —— Sec^{-1} , ΔS —— eu

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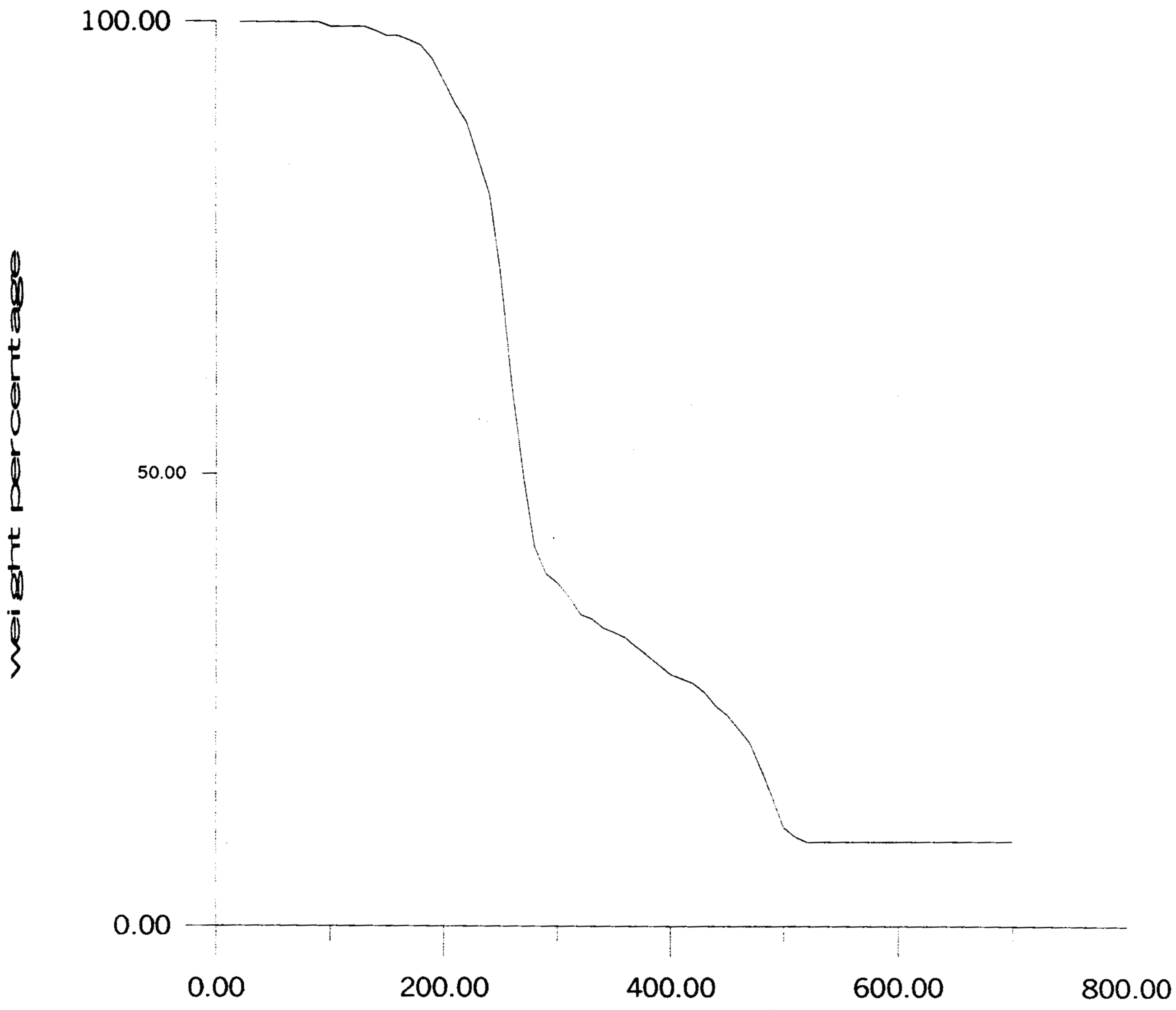


Fig . 2.13 [Co (ACPA)$_2$ (H$_2$O)$_2$]

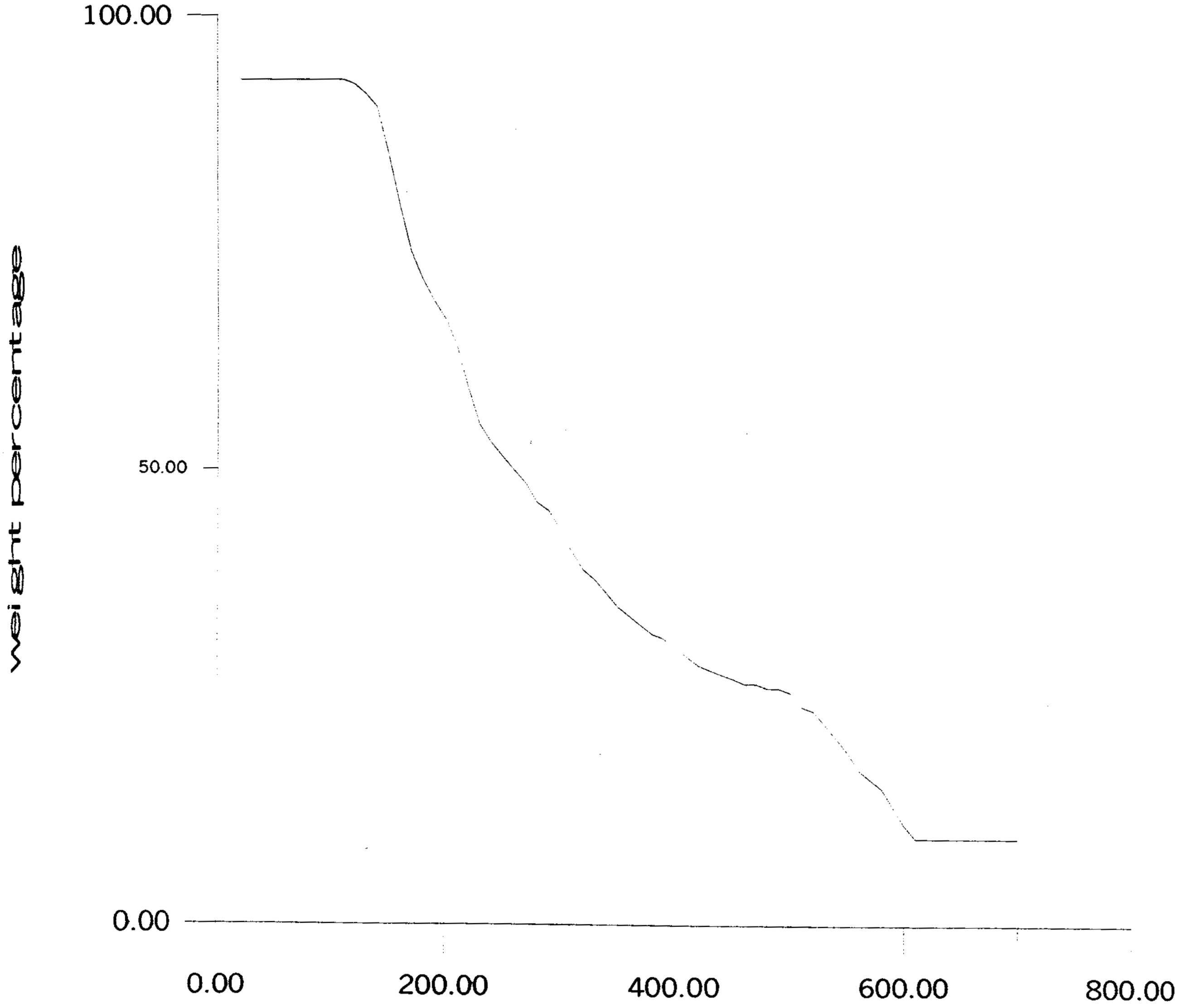


Fig 2. 14 [Ni (ACPA)$_2$ (H$_2$O)$_2$]

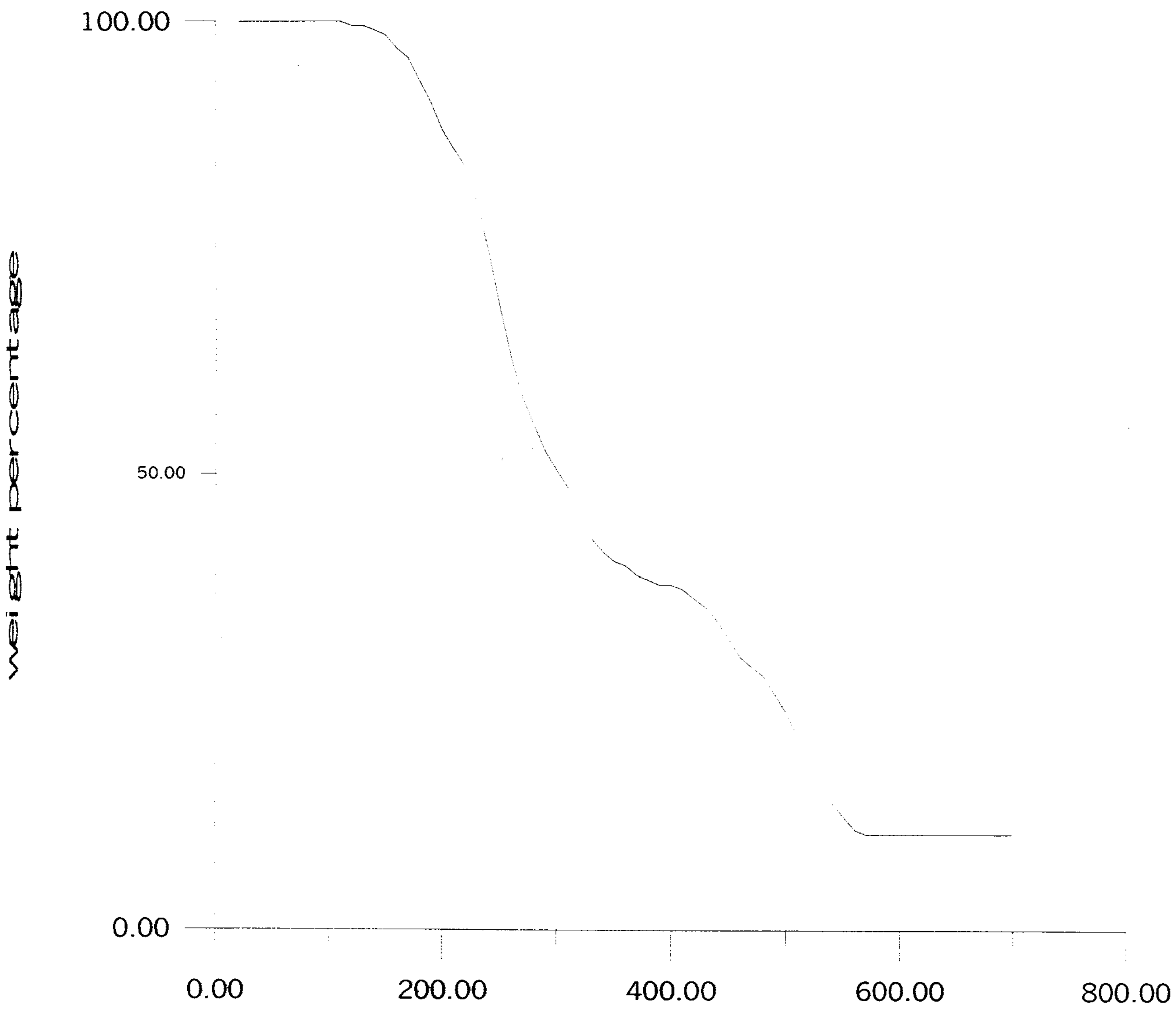


Fig 2. 15 [Cu (ACPA)$_2$ [H$_2$O]$_2$]

PART III

INTRODUCTION

G. Indira Devi “ Studies on transition metal complexes of schiff bases derived from aminoacids” Thesis. Department of Chemistry , University of Calicut, 2002

PART III

X – RAY DIFFRACTION STUDIES

CHAPTER I

INTRODUCTION

X-Ray diffraction has provided a wealth of important information to science and industry .It was discovered by Von Laue in 1912 and first used by Debye and Scherrer.

This method is adapted due to its simplicity and versatility. Using this technique, a clear-cut idea can be obtained about the arrangement and spacing of atoms in crystalline materials.

X-ray diffraction currently plays an important role in elucidating the structure of metal complexes .The materials, which cannot be obtained in single crystalline form, can be studied by powder methods. X-ray powder methods are based upon the fact that an X - ray diffraction is unique for each crystalline substance. It is the only analytical method that is providing qualitative and quantitative information about the compounds present in a solid sample. For analytical diffraction studies the sample is ground to a fine homogeneous powder. When an X-ray beam traverses the material a significant number of the particles can be oriented in such a way to fulfill Bragg condition for reflection. Diffraction patterns are obtained by automatic scanning. The identification of a species from its diffraction pattern is based upon position of lines and their relative intensities. The X-ray powder diffraction method is used nowadays to determine the lattice type of complexes.

X ray method used in the determination of the structure of coordination compounds has increased immensely during the last decade. The work on coordination compounds has confirmed the basis of Werner's theory concerning structure of such compounds. In X-ray crystallographic studies graphical methods have been used by Hull and Davey[1], Bjurstrom[2] and Bunn[3] for indexing powder photographs. Hesse[4] and Lipson[5] introduced easier methods for studying crystallographic pattern. Henry, Lipson and Wooster[6] introduced equations for studying powder crystallographs.

X-ray diffraction is the only convenient and hence widely used physical procedure for the complete determination of molecular structure. Crystallographic study of materials depends on the nature of crystals. Studies of crystal faces and their intercepts on crystal axes show that all known crystals can be classified into seven systems. Particular axial lengths and axial angles characterize each system. Depending on these values the crystals are classified as cubic, tetragonal, orthorhombic, trigonal, hexagonal, monoclinic and triclinic. Bhagavantam[7], Hearmon[8], Krishnan[9] and Suryanarayana[10] already report a number of studies on elastic constants of such compounds. By the X-ray crystallographic studies the determination of unit cell dimensions, lattice type of the crystal, the inter planar spacing of lattice planes and miller indices of the reflection planes are possible. This is obtained by allowing the X-rays of required wavelengths to fall on the crystal The interference pattern will be created because of the scattering of these rays from neighboring atoms produces diffraction. Since this diffraction obeys Bragg's law

$$n\lambda = 2d \sin\theta$$

Where, n is an integer, λ is the wave length of the incident light , d is the inter planar distance and θ is the angle of diffraction. The X-ray crystallographic pattern between twice the angle of diffraction (2θ) against intensity of diffraction is very useful for the analysis.

Determination of crystal system

In the study of crystal systems, the relationship between the inter planar space d and Miller indices h, k, l are used. Crystals belonging to regular or cubic system are built up on three equal axes at right angles. In this case axial lengths $a = b = c$ and, axial angles $\alpha = \beta = \gamma = 90^0$. In this case the relation d and Miller indices (h, k ,l) is given as

$$1 / d^2 = (h^2 + k^2 + l^2) / a^2 \qquad \text{and}$$

$$d^2 = \lambda^2 / 4 \sin^2\theta$$

$$\sin^2\theta = \lambda^2 (h^2 + k^2 + l^2) / 4a^2 \quad \text{---------------} (1)$$

$h^2 + k^2 + l^2$ will be constant and other than 7,15,23 etc

On measuring Bragg angles , the values of $\sin^2\theta$ will be obtained . It is found to be an integral multiple of $\lambda^2/4a^2$ which is a constant.

For a tetragonal system all axial angles are 90^0 whereas $a = b \neq c$. Because of the change in values of c the above equation (1) will become,

$$\mathrm{Sin}^2\theta = [\lambda^2(h^2 + k^2) / 4a^2] + \lambda^2 l^2 / 4c^2 \quad \text{---------------} (2)$$

If all the axial lengths are different in each other for the same axial angles, such a crystal system is called orthorhombic and for this, the equation is

$$\mathrm{Sin}^2\theta = [\lambda^2 h^2 / 4a^2] + \lambda^2 k^2 / 4b^2 + \lambda^2 l^2 / 4c^2 \qquad \text{--------------(3)}$$

d (h k l) represent distance between adjacent planes .For an orthorhombic lattice the inter planar distance is given by the equation,

$$1 / d^2 (h k l) = (h / a)^2 + (k / b)^2 + (l / c)^2 \qquad \text{---------------(4)}$$

For a cubic lattice,

$a = b = c$

Hence, $1 / d^2 (h k l) = (h / a)^2 + (k / a)^2 + (l / a)^2$

$$= (h^2 + k^2 + l^2) / a^2 \qquad \text{-------------(5)}$$

$$d(h k l) = a / (h^2 + k^2 + l^2)^{1/2} \qquad \text{------------------- (6)}$$

For a hexagonal system $a = b \neq c$ and $\alpha = \beta = 90^0$, $\gamma = 120^0$, $\mathrm{Sin}^2\theta$ in this case is,

$$\mathrm{Sin}^2\theta = \lambda^2 / 3 a^2 (h^2 + h k + k^2) + \lambda^2 l^2 / 4 c^2 \qquad \text{------------(7)}$$

For rhombohedral or trigonal system $a = b = c$, $\alpha = \beta = \gamma \neq 90^0$, for monoclinic system, $a = b \neq c$, $\alpha = \gamma = 90^0$, and $\beta \neq 90^0$, and for triclinic system, $a \neq b \neq c$, , $\alpha \neq \beta \neq \gamma \neq 90^0$.

Density and number of molecules per unit cell of the complex have been calculated by using the formula

$$D = n M / V N \qquad \text{--------------------------------(8)}$$

Where, D is the density of the complex, n the number of molecules in the unit cell, N the Avogadro number, V volume of unit cell and M is the molecular mass of the complex.

The relative intensity of each peak can be calculated using the equation, 100 I / I_0, where I is the intensity of diffracted beam and I_0 is the intensity of the incident beam.

The synthesis and crystal structure of the Schiff base complex of Cu (II) complexes have been reported by Doman [11]et al. X-ray powder analysis of complex of Ni (II) with Schiff bases derived from *o*.vanillin and diamines have been reported.[12] X-ray analysis of Cu(II) complexes of Schiff base derived from salicylaldehyde and glycine was carried out by Nathmala[13]. Mononuclear and binuclear Cu(II) complexes with Schiff base were prepared and studied by X-ray powder method[14]. X-ray diffraction structure of two N-salicyclidene tryptophanato diaquo Cu(II) complexes (erythro and threo isomers) have been reported by Garcia – Raso[15] et al. The structure of salicylaldehyde valine copper was studied[16] by this method. Synthesis and X-ray crystal structure of Schiff bases prepared from salicylaldehyde and diamino acids have been reported by Mahmood Saleem[17] et al. The structure of N – salicylidene amino acidate complexes of oxovanadium (IV) dissolved in pyridine complexes (glycine,alanine) were detected by X –ray diffraction analysis[18]. In both the tridentate Schiff base ligands occupy equatorial positions and an octahedral geometry was suggested.

The application of X-ray diffraction technique to the determination of structure of co-ordination compounds has increased immensely during the last few years. There are reports on study of different types of crystalline systems of coordination compounds [19 - 23]

X-ray diffraction studies of Cd (II) complexes of anthranilic acid and 5- bromoanthranilic acid derived Schiff bases have been reported[24]. X-ray diffraction studies of Fe(II), Ni(II) and Cu(II) complexes of o-vanillin L - histidine were carried out [25] . The crystal and molecular structure of neutral Cu(II)complexes of Schiff bases from 2 aminopyridine and substituted salicylaldehydes were detected by X-ray diffraction method by Castineiras et al[26] .The structure of β alanine Schiff base complexes was detected by X-ray crystallography[27].

Scope of present investigation

In this dissertation attempt has been made to determine the crystalline systems of Cr(III), Fe(III), Ni(II), Cu(II), Zn(II) and Ag(I) complexes of anthracence carboxaldehyde amino acids.

The unit cell dimensions a, b, c number of molecules per unit cell n, and density D has been found out from crystallographic data. The densities of the above complexes have been measured by making pellets under 7-ton pressure[20].

PART III

MATERIALS, METHODS AND INSTRUMENTS

CHAPTER II

MATERIALS, METHODS AND INSTRUMENTS

Reagents

Analar grade chemicals supplied by Sigma, Sisco, BDH, or E . Merck were used for synthetic purpose. Commercial solvents were purified by distillation.

Preparation of ligands and complexes

The ligand anthracene carboxaldehyde - L - histidine (ACH), anthracene carboxaldehyde –L-tyrosine (ACT) , anthracene carboxaldehyde – glycine (ACG), anthracene carboxaldehyde DL alanine (ACA) and anthracene carboxaldehyde L phenyl alanine were synthesized by the procedures described in Part I. The detailed methods of preparation of complexes were also discussed in the same Part.

Instruments

Instruments used for studying crystalline nature are

1. Bruker D 5005 AXS X ray diffractometer.
2. Pellitiser
3. Densitometer
4. Vernier Calipers
5. Screw gauge
6. Computer

PART III

X-RAY DIFFRACTION STUDIES OF SOME TRANSITION METAL COMPLEXES OF AMINO ACID SCHIFF BASES OF ANTHRACENE CARBOXALDEHYDE

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER III

X-RAY DIFFRACTION STUDIES OF SOME TRANSITION METAL COMPLEXES OF AMINO ACID SCHIFF BASES OF ANTHRACENE CARBOXALDEHYDE

X ray powder method is found to be applicable in determining the structure of complexes in solid state, when are obtained in the single crystal form. Lipson et al [6] have proposed useful equations for studying the X ray powder pattern of each type of crystalline systems. The application to seven complexes of anthracene carboxaldehyde - amino acids shows that all are orthorhombic

Experimental

The reagents used for the preparation of complexes were of analar grade and the detailed methods of preparation are explained in Part I. The diffraction pattern was obtained using Bruker D 5005 AXS X ray diffractometer. The powder lines were recorded for 2θ values from 4^0 to 60^0 at a chart speed of 20 mm / min and a scan speed of 2^0 mm^{-1} with Cu kα (λ - 1. 54184 A^0) radiation. The density of each complex was found out by making pellets at a pressure of 6.5 Ton

Treatment of data

Even though powder diffraction pattern between 2θ values of 4^0 and 60^0 is recorded for simplicity first few peaks are considered using Lipsons equations [6] The nature of crystalline systems and constants A, B, C (where $A = \lambda^2 / 4 a^2$, $B = \lambda^2 / 4 b^2$ and

$C = \lambda^2 / 4 c^2$) were found out from which the lattice constants a, b, c and hence the volume were obtained.. The complexes were made into pellets by applying the 6.5 Ton pressure and density was calculated. The density and number of molecules per unit cell were also found out by using the equation (8) in Chapter 1.

Results and discussion

The X-ray diffraction pattern of Ni(II) and Cu(II) complexes of ACH, Ag(I),Fe(III) complexes of ACG ,Zn(II) complex of ACT, Cr(III) complex of ACA and Cu(II) complex of ACP were recorded.15 peaks between 4-51^0 were used. All the reflections have been indexed for h, k, l values using methods reported in literature[6]. The X-ray crystallographic pattern of Ag(I) complex of ACG and Cu(II) complex of ACP, Cu(II) complex of ACPA, Cu(II) complex of ACH, Cr(III) complex of ACA have been shown in figure 3. 3. 1, 3. 3. 2, 3. 3. 3, 3. 3. 4 and 3. 3. 5. All the seven complexes have been found to be orthorhombic. The values of $\sin^2\theta$ for each peak have been calculated with the help of the cell parameters and the corresponding h, k, l in all cases are in good agreement with observed values as in Table 3.3.1 to 3.3.7.The lattice constants a, b, and c for each unit cell have been found out and are tabulated in Tables along with density and number of molecules per unit cell. The calculated density of each complex was in good agreement with that of experimental value found out. This confirms the molecular structure. Except Ag(I) complex there occur 1:2 stochiometry between metal ion and ligand. In the case of Ag(I)complex metal : ligand ratio was 1:1.

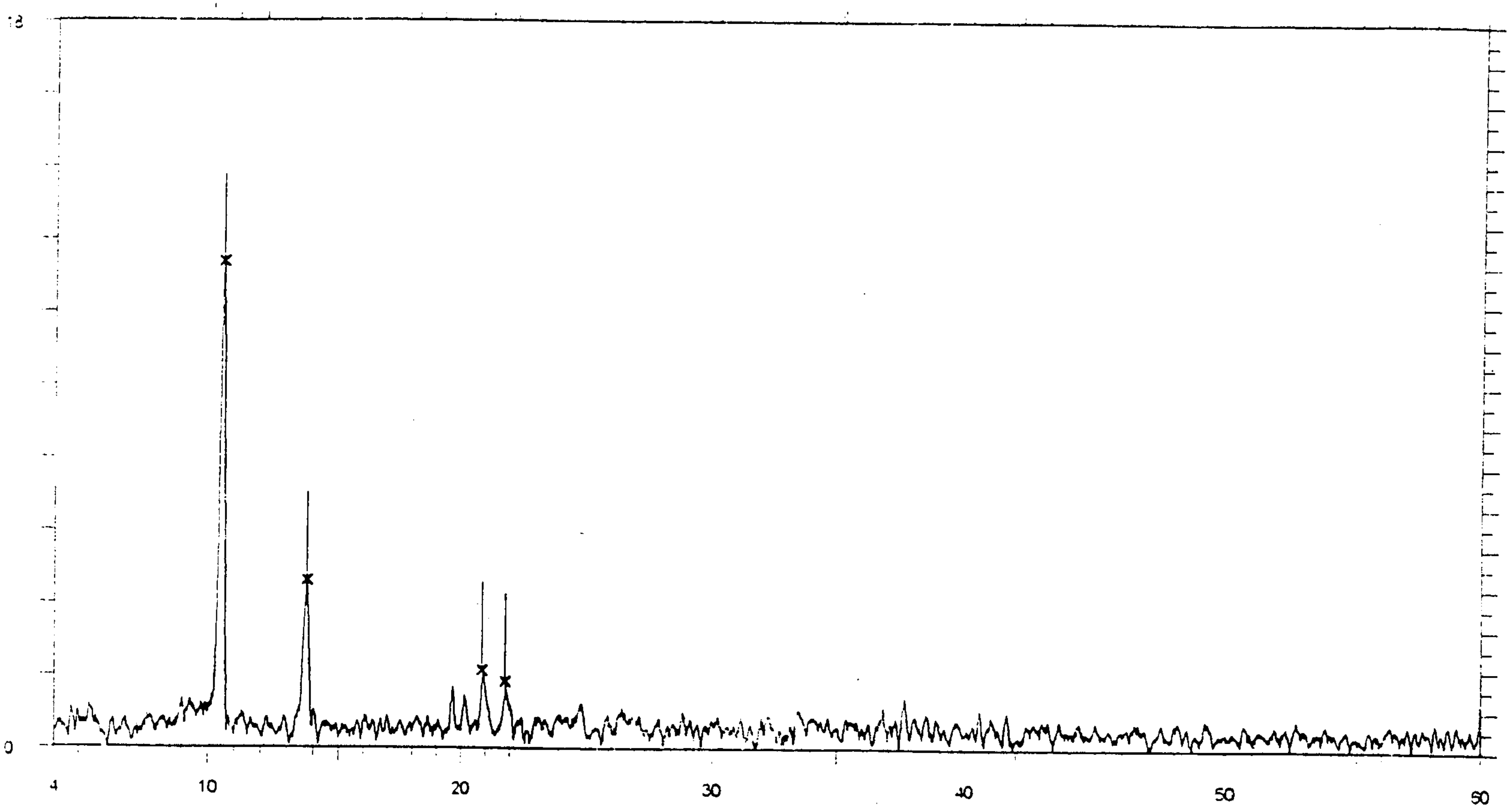


FIG 3 . 3. 1 ; CRYSTALLOGRAPHIC PATTERN OF [Ni $(ACH)_2(H_2O)_2$]

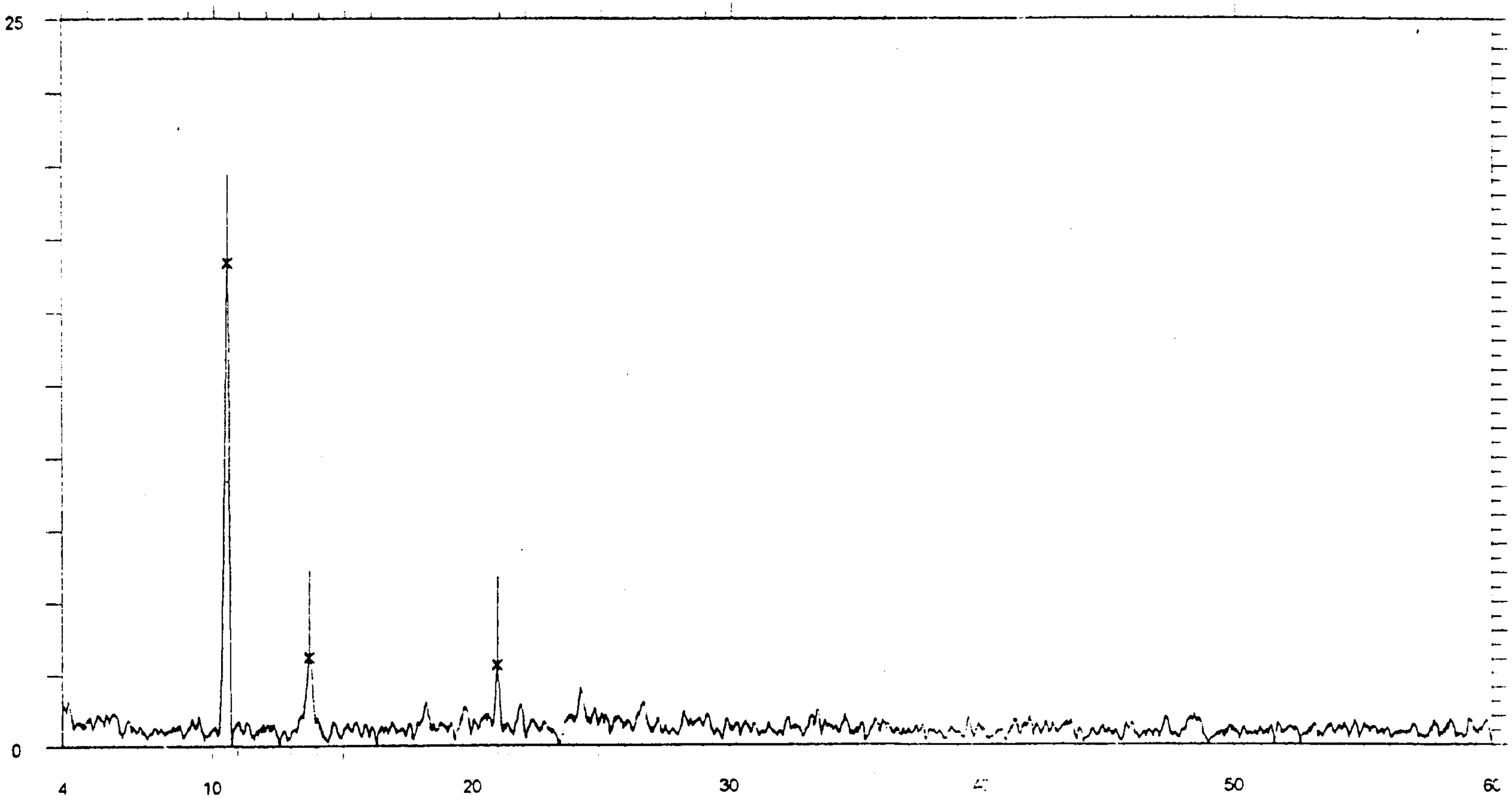


FIG 3 . 3. 2 ; CRYSTALLOGRAPHIC PATTERN OF [Zn (ACT)$_2$]

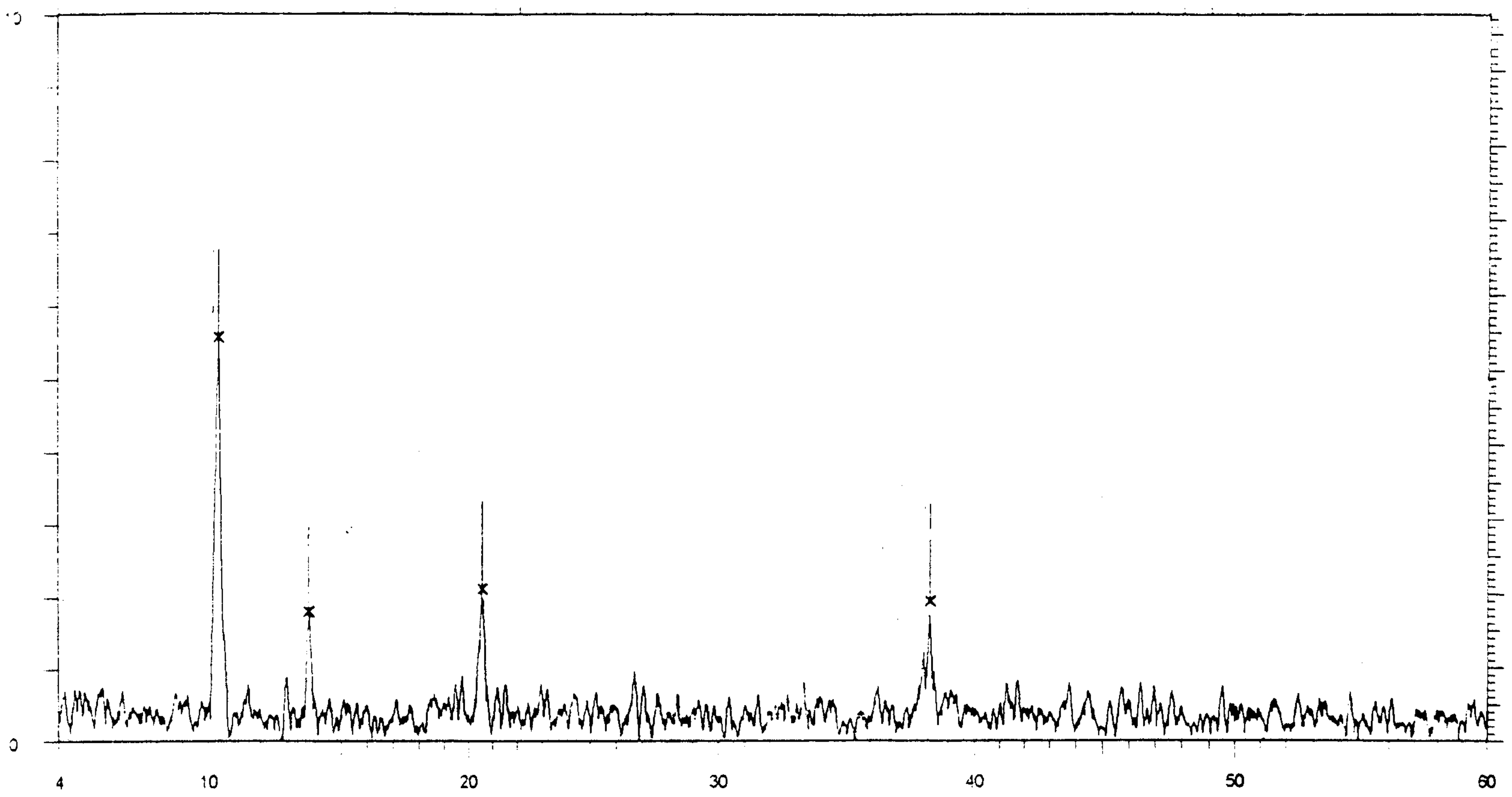


FIG 3 . 3. 3 ; CRYSTALLOGRAPHIC PATTERN OF [Ag (ACG) $(H_2O)_2$]

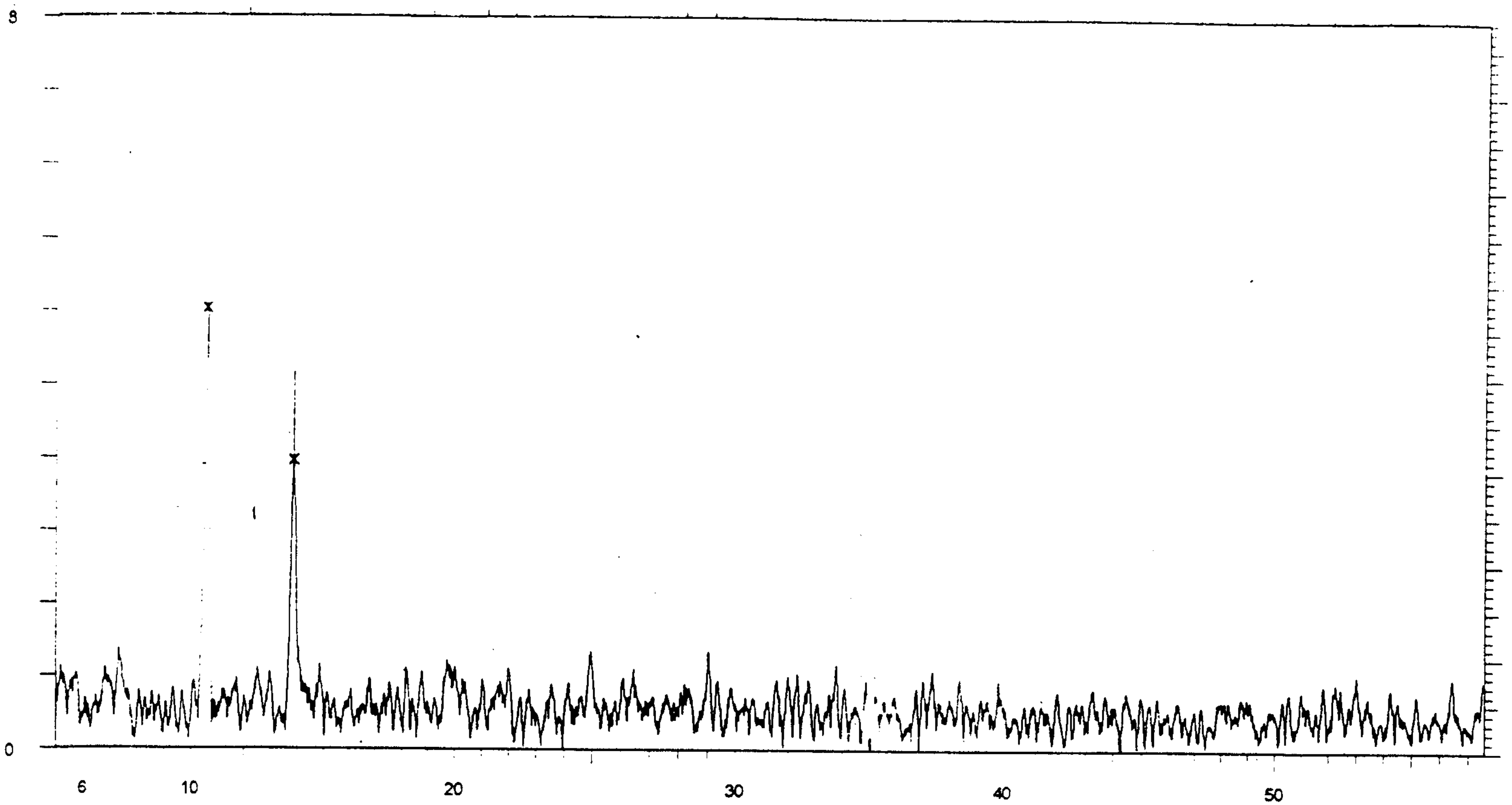


FIG 3 . 3. 4 ; CRYSTALLOGRAPHIC PATTERN OF [Cr (ACA)$_2$ H$_2$O Cl]

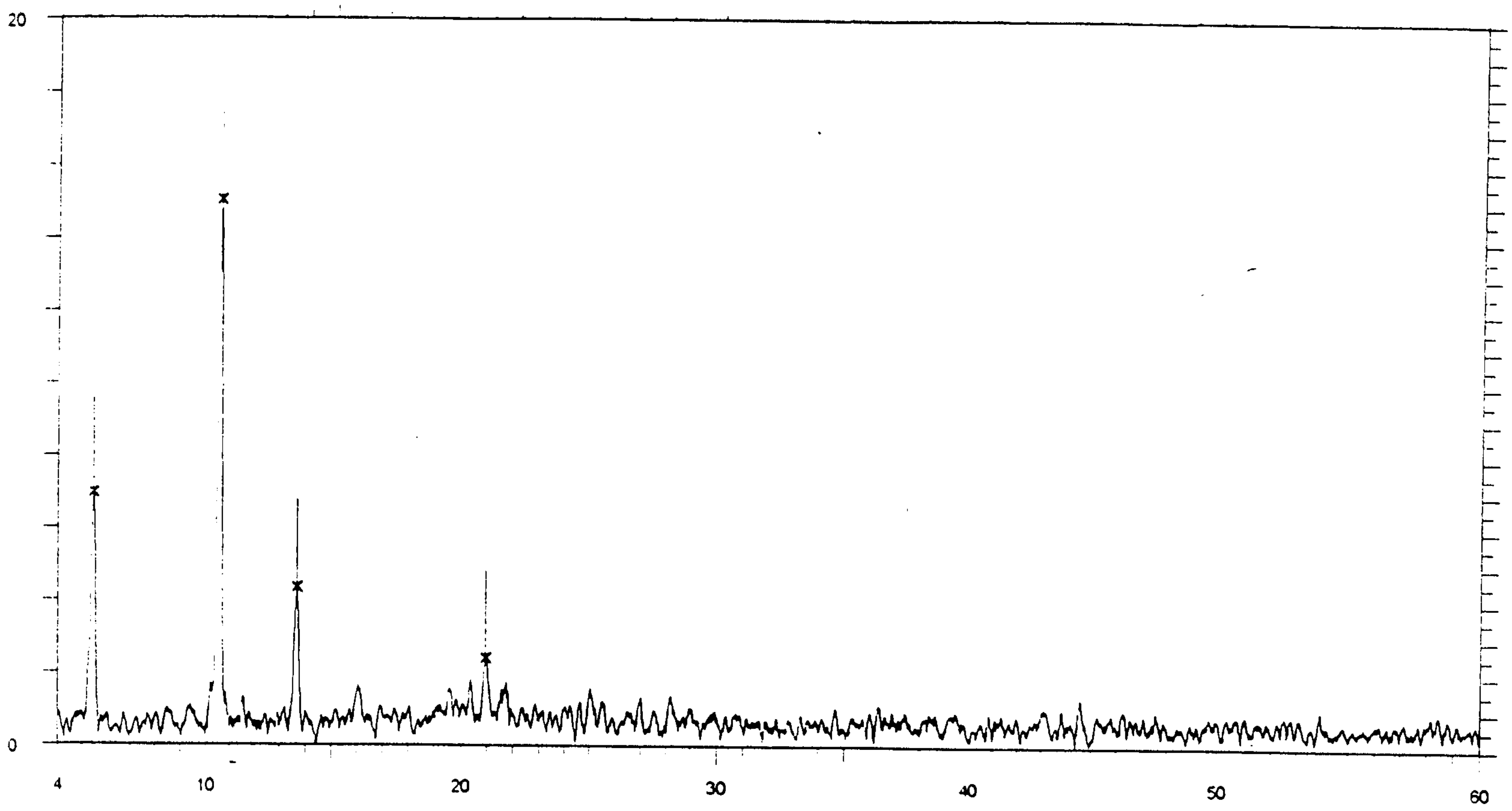


FIG 3 . 3. 5 ; CRYSTALLOGRAPHIC PATTERN OF [Cu (ACPA)$_2$ (H$_2$O)$_2$]

TABLE 3--3--1

X - RAY DATA OF $[Ni(ACH)_2(H_2O)_2]$

Crystal system : orthorhombic

A = 0.008372 B = 0.004186 C = 0.002093

a = 8.425481 A^0 b = 11.91543 A^0 c = 16.85096 A^0

Cell volume : 1691.72 $[A^0]^3$

Density : 1.435 g / cm ^{3}

No of molecules per unit cell : 2

Peak no	d spacing A^0	relative intensity	$Sin^2\theta$		h k l
			observed	calculated	
1	8.4255	100	0.008372	0.008372	1 0 0
2	6.3691	39	0.014851	0.014851	1 1 1
3	4.6736	12	0.028678	0.027209	1 2 1
4	4.3509	7	0.030903	0.031395	1 1 3
5	4.2127	17	0.033208	0.033488	2 0 0
6	4.08696	14	0.035755	0.035581	2 0 1
7	3.59261	9	0.046475	0.046046	2 1 2
8	3.370192	8	0.05253	0.052325	2 2 1
9	2.97886	7	0.066113	0.066976	2 0 4
10	2.77028	7	0.077132	0.077441	3 0 1
11	2.664371	8	0.08426	0.08372	3 0 2
12	2.4322	8	0.099629	0.100464	3 2 3
13	2.4073	10	0.103317	0.102557	2 4 1
14	2.2126	8	0.121211	0.121394	3 3 3
15	2.1575	7	0.126964	0.127673	3 0 5

TABLE 3--3--2

X - RAY DATA OF [Ag (ACG) $(H_2O)_2$]

Crystal system : orthorhombic

A = 0.008372 B = 0.004186 C = 0.002093

a = 8.425481 A^0 b = 11.91543 A^0 c = 16.85096 A^0

Cell volume : 1691.72 $[A^0]^3$

Density : 1.507 g / cm ^{3}

No of molecules per unit cell : 4

Peak no	**d spacing A^0**	**relative intensity**	**$\sin^2\theta$**		**h k l**
			observed	**calculated**	
1	8.43	100	0.008372	0.008372	1 0 0
2	7.537979	14	0.010037	0.010465	1 0 1
3	6.8794	17	0.012814	0.012558	1 1 0
4	6.3691	32	0.014432	0.014651	1 1 1
5	4.6736	17	0.027524	0.027209	1 2 1
6	4.3509	38	0.031662	0.031395	1 1 3
7	4.08696	14	0.035432	0.035581	2 0 1
8	3.8659	14	0.039745	0.039767	2 1 1
9	3.51367	13	0.04777	0.048139	1 3 1
10	3.3047	17	0.054296	0.054418	1 3 2
11	2.6644	16	0.083535	0.08372	3 0 2
12	2.457965	13	0.098066	0.098371	3 1 3
13	2.336808	34	0.10869	0.108836	3 0 4
14	2.18	35	0.125515	0.12558	3 2 4
15	2.08	14	0.138509	0.138138	4 1 0

TABLE 3--3--3

X - RAY DATA OF [Fe (ACG $)_2$(H_2O)Cl]

Crystal system : orthorhombic

A = 0.008372 B = 0.003987 C = 0.002042
a = 8.425481 A^0 b = 12.20968 A^0 c = 17.0603 A^0

Cell volume : 1755.03 [A^0]^3
Density : 1.5566 g / cm^3
No of molecules per unit cell : 3

Peak no	**d spacing A^0**	**relative intensity**	**Sin$^2\theta$**		**h k l**
			observed	**calculated**	
1	8.4255	100	0.008372	0.008372	1 0 0
2	6.99264	9	0.011384	0.011215	0 1 2
3	6.4242	27	0.014432	0.014401	1 1 1
4	4.39728	8	0.029795	0.030736	1 1 3
5	4.21274	14	0.033208	0.033488	2 0 0
6	4.02648	13	0.036406	0.036658	0 1 4
7	3.26204	8	0.055688	0.055852	2 1 3
8	3.00405	8	0.064818	0.065829	0 4 1
9	2.80813	8	0.075972	0.075367	1 2 5
10	2.39	8	0.103317	0.104042	0 1 7
11	2.1414	7	0.12842	0.129606	3 3 3
12	2.1127	9	0.132831	0.133155	2 5 0
13	2.04494	8	0.141841	0.14212	4 0 2
14	1.91597	8	0.161425	0.161898	0 6 3
15	1.81647	10	0.180271	0.18012	2 2 8

TABLE 3--3--4

X - RAY DATA OF [Zn (ACT $)_2$]

Crystal system : orthorhombic

A = 0.008372 B = 0.003805 C = 0.002262

a = 8.425481 A^0 b = 12.49701 A^0 c = 16.20674 A^0

Cell volume : 1706.46 [A^0 $]^3$

Density : 1.313 g / cm ^{3}

No of molecules per unit cell 2

Peak no	**d spacing A^0**	**relative intensity**	**$\sin^2\theta$**		**h k l**
			observed	**calculated**	
1	8.4255	100	0.008372	0.008372	1 0 0
2	6.415394	18	0.014432	0.0144	1 1 1
3	4.948241	9	0.024741	0.024273	0 2 2
4	4.547719	7	0.029116	0.028736	1 0 3
5	4.21274	16	0.033208	0.033488	2 0 0
6	4.034528	8	0.036406	0.036512	0 3 1
7	3.651425	11	0.044116	0.044575	1 0 4
8	3.399553	9	0.051561	0.051425	0 2 4
9	3.152604	7	0.059551	0.059797	1 2 4
10	3.071774	6	0.062687	0.062985	1 3 3
11	2.767251	5	0.077132	0.077611	3 0 1
12	2.653635	7	0.084264	0.084379	3 0 2
13	2.597275	6	0.087932	0.088101	2 3 3
14	2.509459	5	0.094208	0.094375	2 4 0
15	2.276507	5	0.114181	0.114678	0 1 7

TABLE 3--3--5

X - RAY DATA OF $[Cr(ACH)_2(H_2O)Cl]$

Crystal system : orthorhombic

A = 0.008372 B = 0.004186 C = 0.002093

a = 8.425481 A^0 b = 11.91543 A^0 c = 16.85096 A^0

Cell volume : 1691.72 $[A^0]^3$

Density : 1.275 g / cm ^{3}

No of molecules per unit cell : 2

Peak no	d spacing A^0	relative intensity	$Sin^2\theta$		h k l
			observed	calculated	
1	8.4255	100	0.008372	0.008372	1 0 0
2	6.879376	18	0.011851	0.012558	1 1 0
3	6.36907	66	0.014432	0.014651	1 1 1
4	5.957715	19	0.017036	0.016744	1 0 2
5	4.864453	18	0.025013	0.025116	0 2 2
6	4.67362	17	0.026674	0.027209	1 0 3
7	4.3509	21	0.030152	0.013395	1 1 3
8	4.21274	16	0.0332	0.033488	2 0 0
9	3.97181	19	0.036406	0.037674	2 1 0
10	3.592637	22	0.046846	0.046046	2 1 2
11	3.4396	16	0.0506	0.050232	2 2 0
12	3.37019	20	0.052141	0.052325	2 0 3
13	3.129145	22	0.062687	0.060697	1 0 5
14	2.664371	20	0.084264	0.08373	3 0 2
15	2.40728	18	0.101993	0.102557	2 4 1

TABLE 3--3--6

X - RAY DATA OF [Cu (ACH $)_2$ $(H_2O)_2$]

Crystal system : orthorhombic

A = 0.008372 B = 0.004186 C = 0.001395

a = 8.425481 A^0 b = 11.91543 A^0 c = 20.63813 A^0

Cell volume : 2071.93 $[A^0]^3$

Density : 1.461 g / cm^3

No of molecules per unit cell : 2

Peak no	d spacing A^0	relative intensity	$\sin^2\theta$		h k l
			observed	calculated	
1	8.4255	100	0.008372	0.008372	1 0 0
2	6.5263	32	0.013814	0.013953	1 1 1
3	5.723987	9	0.019368	0.018139	0 2 1
4	5.328742	9	0.021592	0.02093	1 0 3
5	4.503609	9	0.028678	0.029372	0 2 3
6	4.40006	11	0.030152	0.030697	1 0 4
7	4.2127	17	0.03243	0.033488	2 0 0
8	4.0869	16	0.03608	0.03488	2 0 1
9	3.5926	12	0.045017	0.046046	1 3 0
10	3.3929	14	0.05253	0.051627	2 2 1
11	3.1473	14	0.060588	0.059999	2 1 4
12	2.9788	7	0.066983	0.066976	0 4 0
13	2.8085	7	0.075972	0.075348	3 0 0
14	2.7099	7	0.08066	0.080929	3 1 1
15	2.521349	7	0.092937	0.093487	3 2 1

TABLE 3--3--7

X - RAY DATA OF [Cu (ACP)$_2$ (H$_2$O)$_2$]

Crystal system : orthorhombic

A = 0.001311 B = 0.001192 C = 0.000436

a = 21.2924 A^0 b = 22.33165 A^0 c = 36.87951 A^0

Cell volume : 17536[A^0]^3

Density : 1.472 g / cm ^{3}

No of molecules per unit cell : 19

Peak no	d spacing A^0	relative intensity	Sin ^{2} θ		h k l
			observed	calculated	
1	21.292	39.74	0.001311	0.001311	1 1 0
2	8.4607	100	0.008372	0.008372	1 0 4
3	7.70515	9	0.010037	0.01001	1 2 3
4	6.5662	29	0.013814	0.013784	1 3 2
5	5.52	11	0.019368	0.019505	0 4 1
6	4.548962	10	0.028678	0.028721	3 1 6
7	4.329922	12	0.031662	0.0317	4 3 0
8	4.23	17	0.033208	0.033209	5 0 1
9	4.132658	11	0.034789	0.034798	3 4 3
10	3.5324	10	0.04777	0.047629	6 0 1
11	3.3034	9	0.054494	0.054462	0 4 9
12	3.1281	10	0.060588	0.060738	5 0 8
13	3.0772	7	0.062687	0.062764	5 4 5
14	2.9762	10	0.066983	0.067094	4 3 9
15	2.033514	9	0.143367	0.143722	3 9 9

PART IV
INTRODUCTION

G. Indira Devi “ Studies on transition metal complexes of schiff bases derived from aminoacids” Thesis. Department of Chemistry , University of Calicut, 2002

PART IV

ANTI FUNGAL STUDIES

CHAPTER I

INTRODUCTION

Anti fungal agents are widely used to prevent or control diseases of plants and animals. It is to reduce damage to materials caused by fungal attack. According to Somers[1] earlier protective fungicides used in agriculture were non-specific poisons which acted by selective accumulation. Newer systemic compounds are considered as highly active with specific modes of action (Kaars [2] and Fehrmann [3]), Siegel [4], Byrde and Richmond [5] suggested that anti fungal agents possess considerable selectivity. The morphological (Richmond[6]) and bio chemical effect (Corbett [7]) explaining the effect of fungicides on fungi have been reviewed.

The use of fungicide started with Millardet's discovery of Bordeux mixture [8, 9]. The use of Bordeaux mixture as a contact fungicide against foot rot of black pepper have been reported by many workers [10-16] . Phenyl amides introduced during seventies and its derivatives like acyl alanines, butyrolactones etc play important role in this field[17,18]. Metalaxyl is used as a systemic fungicide to control the *PHYTOPHTHORA CAPSICI* infections in various crops[19-23]. Metalaxyl is reported to inhibit both protein and nucleic acid synthesis (Fisher and Hayes 1982 [24]). Hegde 1987 [25] reported that spray with metalaxyl give good control on black pepper due to *PHYTOPHTHORA CAPSICI.*

Recent studies have demonstrated that phosphorous compounds have powerful and selective anti fungal characteristics [26 - 29] . Phenolic compounds have been implicated a variety of resistant reactions of plants to attack by fungal parasites. Onion varieties with colored outer scale leaves are resistant to attack by fungus due to the presence of phenolic compounds, catechol and protocatechuic acid[30]. Chlorogenic acid, the major phenolic compound in potato tubers[31] acts as anti fungal agent. In this work the anti fungal activity of transition metal complexes of Schiff bases are carried out. Emphasis is given to *PHYTOPHTHORA CAPSICI* causing foot rot of black pepper. Fungi were included in the plant kingdom and were classified as eukaryotes. *PHYTOPHTHORA* is considered to be a typical fungus.

Black pepper (*Piper nigrum* L) the "king of spices" is an important commercial crop. It is the native of Western Ghats of India. It belongs to the family piperaceae. India is the leading producer and exporter of black pepper. Black pepper is a perennial woody climber with adventitious roots. Kerala ranked first both in area and production of pepper in India. India had an exclusive procession in pepper production in the world. But now this status diminishes gradually because of low productivity. Foot rot caused by *PHYTOPHTHORA CAPSICI* is a major production constraint in black pepper[32]. Among various diseases affecting black pepper in India, foot rot known as Quick Wilt caused by *PHYTOPHTHORA CAPSICI* [33 - 37] is the most serious one (Sarma et al 1994)[38] . On a global scale an annual crop loss of approximately 4.7 to 7.5 million due to foot rot have been reported by Deward [39].

The disease was first reported in India as early as in 1902, (Barber 1902,1903, Butler 1906)[40–42]. Even though isolation of *PHYTOPHTHORA* in black pepper was reported in Karnataka[43], as early as in, an authentic report that it is caused by *PHYTOPHTHORA* came from Samraj and Jose[44]. Tsao et al now resolved that

PHYTOPHTHORA of black pepper is *PHYTOPHTHORA CAPSICI*. Sarma et al [45] have reported that *PHYTOPHTHORA CAPSICI* is soil born and the disease has two important phases, namely aerial phase and soil phase. All the parts of black pepper are affected by *PHYTOPHTHORA CAPSICI*, the disease spread from the feeder roots to thicker roots leading to the death of the vine (Anandaraj et al 1991,1994)[46,47]. *PHYTOPHTHORA CAPSICI* is a wet weather pathogen. It is precise in its requirement for growth and sporulation.

The name of the genus *PHYTOPHTHORA* is derived from the Greek, that literarily mean *PHYTO* (plant) and *PHTHORA* (destroyer) .The life history of *PHYTOPHTHORA CAPSICI*, a term that recommended by Dick 1987 [48] rather than life cycle is illustrated in fig 1. The detailed morphology of the organism have drawn from the classic paper by Black well [49]. The thallus of the fungus is called mycelium. It consists of large number of tubular structures. When mycelium is cultured in suitable media or when it grows out of infected tissue under moist condition, it is un pigmented. When viewed with a microscope (100 X), the young mycelium is nearly transparent. In several days culture occasional cross walls can be seen. Ho [50] reported that the variation of branching pattern is associated with environmental effect.

The most common and characteristic asexual spore is called sporangium. It is a vessel containing zoospores. The number of zoospores produced within a sporangium varies among species. Sporangia vary in size and shape. It may have spherical, ovoid, lemon shape etc. sporangium germinates in aqueous solutions or an agar media. According to Gisi et al [51,52] zoospore emerge from the sporangium in a membranous vesicle that soon breaks, allowing zoospore to swim away. The zoospores are reni form (like a kidney) in shape. Bimpong and Clerk,[53] reported that zoospores swim for hours. Bartnicki – Garcia[54] have reported that within minutes, the swimming zoospore round up and cell wall development is carried out. At this stage the spore is called cyst. Encystment is induced by agitation produced artificially by shaking zoospore in a flask. Cysts germinate by producing germ tubes and mycelia. Occasionally another zoospore may form within the cyst and be released. According to Drechsler [55], and Black well [49] it is termed repeated emergence. The chlamydospore is spherical to oval.

Sporulation is a complex process that depends on water potential, light, temperature, presence of cations etc. Neutrients like sucrose – aspargine media stimulated the production of sporangia. Nitrogen sources like L alanine, L aspartic acid, glycine etc have stimulatory effect on sporangium production, where as phenyl alanine, leucine etc are inhibitory on sporangium production. Carbon to nitrogen ratio gently influenced sporangium formation. Allen and Nandra [56], Halsall [57] have reported that Mg^{2+}, and Fe^{3+} have stimulatory effect on sporangium production, while Cu^{2+} ions in very low concentration inhibited sporangium formation. Alizadeh and Tsao [58] have reported that light plays an important role in the production of sporangia in *PHYTOPHTHORA CAPSICI* . Hendrix [59] reported that sporangia were produced abundantly by *PHYTOPHTHORA CAPSICI* in the light when cholesterol was added to the medium. Sporangia production is enhanced in UV region.

The anti fungal study of *PHYTOPHTHORA CAPSICI* is gaining momentum in the field of agricultural research. Fry[60](1977 b) predicts that chemicals probably always be needed for the control of disease like foot rot of pepper. Of several fungicides tested Bordeaux mixture has given a measure of control. Bordeaux mixture and other copper containing fungicides are still used today. Bordeaux mixture (1 %) once as a pre monsoon during May, June and again during July, August as a post monsoon treatment were found effective (Sasikumaran et al 1981)[61]. The pesticides manual of Worthing and Walker [62] updated and issued periodically is a valuable source of the properties of fungicides. Metalaxyl found significant effect on disease control (Malebennur et al) [63]. Smith[64] reported that dilute solution of sodium hypochlorite would kill most pathogens. Pegg [65] have reported the use of chlorine in 2 ppm concentration to kill zoospores of *PHYTOPHTHORA* in nurseries. Klotz [66] suggested the use of copper sulphate as fungicide. Matheron and Matejka [67] have reported that sodium tetra thio carbonate can reduce sporangium production by *PHYTOPHTHORA CAPSICI*.

Baker et al (1957) [68] reported that 2 % copper naphthenate, a wood protective can be used to prevent carry over of *PHYTOPHTHORA* and pathogens in a glass house. This can be applied by painting the benches once or twice a year with 2 % copper naphthenate. Rodrijuez, Kabana et al [69] and Munnecke [70] have given general reviews of control by use of methyl bromide and other soil fungicides. Methyl bromide mixed with 50:50 with chloropicrin effectively eradicates *PHYTOPHTHORA* . Metham sodium is an alkaline water soluble carbamate that breaks down in soil to methyl iso thiocyanate (Munnecke et al [71], Munnecke [72]) can be used as fungicide. Organic tin compounds like fentin acetate or fentin hydroxide are particularly effective anti sporulant fungicides. Dithio carbamates have been used as broad-spectrum fungicides[73]. Phthalimides (captan, captafol and folpet) have been used to control foot rot.

Recent studies indicated the efficiency of potassium phosphonate both as a foliar spray and soil drench in checking *PHYTOPHTHORA* infections.[74 - 78]. Cynoacetamide oximes , phenyl amide formerly called aceyl alanine are all fungicides. Young and Slawecki [79] have investigated the anti fungal mechanism of zoxamide and its effects on cellular micro tubules. In vivo control and in vitro anti fungal activity of rhamnolipids B and glycolipids against *PHYTOPHTHORA CAPSICI* have been reported by Kim – Beomseok et al [80]. In the glass houses the efficiency of rhamnolipids B against *PHYTOPHTHORA* blight was similar to that of metalaxyl on pepper plants. Isolation and identification of anti fungal agent N – butyl benzene sulphonamide was reported by Kim – Keunki et al [81]. Isolation, identification and anti fungal activity of oligomycin have been reported by Kim – Beomseok et al [82] . Purification, N terminal amino acid sequencing and anti fungal activity of chitinases from pepper treated with mercuric chloride have been reported by Kim – Youngin et al [83] . Sarma et al [84] have reported the use of potassium phosphonate as anti fungal agent. Thomas Barberan [85] et al reported the anti fungal activity of phloro glucinol and aceto phenone derivatives. The development of systemic fungicidal control of *PHYTOPHTHORA* and other related fungi stimulated the field of research.

In this study emphasis is given to the development of modern effective fungicides derived from Schiff base complexes of transition metals. Though the work in this area is very few, Schiff base complexes are long been used for the anti fungal activities.

Complexes derived from transition metal complexes are effective in anti fungal treatment. Some of the complexes have been studied for their mechanism of action. The increases in the inhibition of Cu 2+ by the addition of KEDTA to the medium have already been reported. In Vitro anti microbial activity of new organo tin (IV) complexes of Schiff bases derived from amino acids have been reported by Nath mala and Yadav Rakesh[86] . Phenyl tin (IV) complexes of Schiff bases derived from the condensation of 2 hydroxy – 1 naphthaldehyde and benzaldehyde with glycine , DL alanine, L Methionine , D phenyl alanine, 2 amino butyric acid and N lecuine have been synthesized for the above work. Goyal and Lal [87] reported the fungicidal activity of Schiff bases of 5 – nitro and 5 – chloro salicylaldehyde with sulfa furazole, sulfa phenazole, sulfa diazine, sulfa dimidine, sulfa di methoxine and sulfa methoxi pyridine and their complexes with Mn (II) . The fungicidal activity of the ligand and the complexes were detected using the growth method. All samples showed fungicidal activity but the effect was reduced upon chelation.

Fungicidal studies were also done on Mn (II), Fe (III) ,Co (II) , Ni (II) and Cu(II) complexes of Schiff bases derived from some sulfa drugs.[88] . Transition metal (II) complexes of 1 – (α - hydroxy naphthyl) – 2 – (3^{1} methyl – 5^{1}mercapto – 1^{1}, 2^{1}, 4^{1}, triazole) = 2 aza ethane have been screened as possible fungicides[89] . Ahmed et al [90] studied the anti fungal activities of the salicylaldehyde ethylene diamine Schiff base complexes of Mn (II) Fe (II) ,Co (II), Ni (II) and Cu (II). Anti microbial activity of Zn (II) and Cd (II) complexes of Schiff bases have been reported by Varshney et al [91]. The anti fungal and anti bacterial efficiency of Cu(II) carboxalate were studied [92] . Dwyer and Albert have shown that metal complexes are very effective against certain microbial infections. [93,94] Anti microbial activity of several aromatic azo methines were reported [95 - 97]. Anti fungal activity of aromatic Schiff bases like salicylaldehyde ortho amino phenol were also studied [98]. Many Schiff bases have been used as fungicides [99] and herbicides[100] A series of Schiff bases having the general formula 3,5 – X2 – 2 – HO C6 H5 CH = N R OH were X is a halogen and R is a bivalent radical with 2 to 4 carbon atom are claimed to be good fungicides [101]. Recently a number of Schiff bases [102]have been synthesized and were found to be useful fungicide against wheat odium, tomato alternaria etc.

There are only few reports of anti fungal activity of Schiff base complexes, no notable work has been reported on the anti fungal studies of transition metal complexes on Schiff bases derived from anthracene carboxaldehyde – amino acids. Hence this work seems to be worthwhile in this field.

Fig : 1

LIFE HISTORY OF *PHYTOPHTHORA*

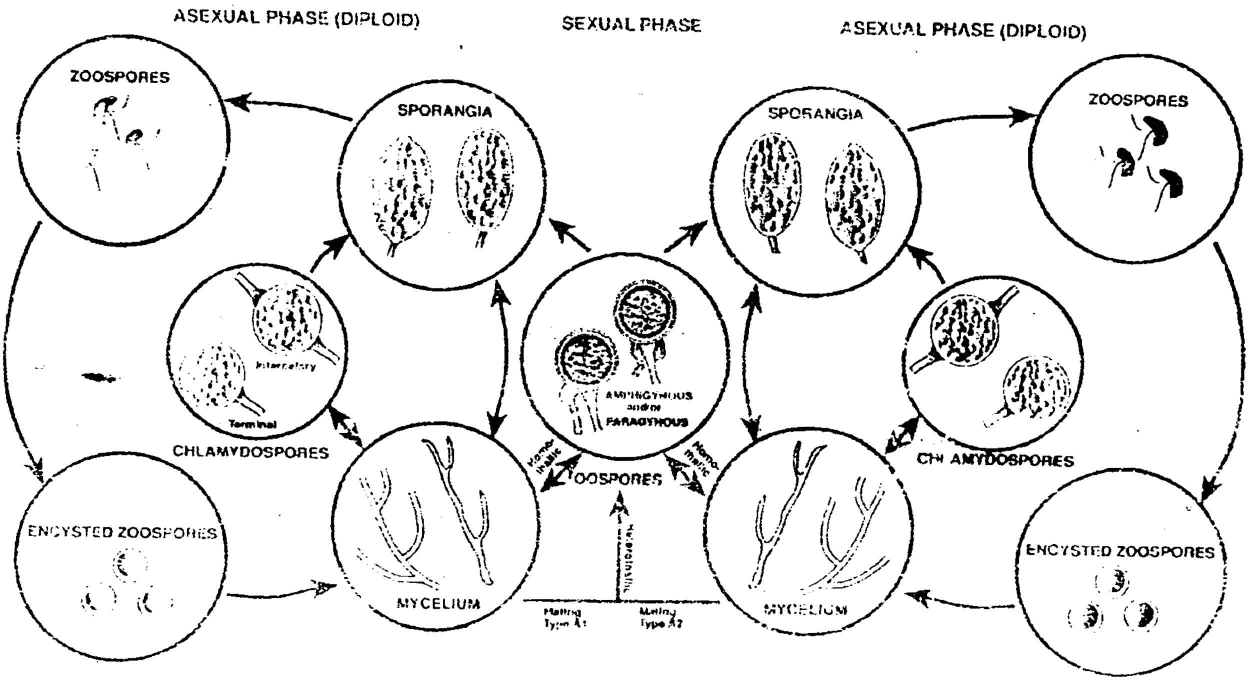


Figure 1.1. Life history of *Phytophthora*

PART IV

MATERIALS, METHODS AND INSTRUMENTS

G. Indira Devi “ Studies on transition metal complexes of schiff bases derived from aminoacids” Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER II

MATERIALS, METHODS AND INSTRUMENTS

For the study of the anti fungal activity of the transition metal complexes [Co (II), Cu (II). Ni (II), and Mn (II)] of Schiff base anthracene carboxaldehyde aminoacid to the causal organism of foot rot of black pepper, *PHYTOPHTHORA CAPSICI* , the facilities of Indian Institute of Spices Research, Calicut, Kerala, India, were used

MATERIALS

The materials used for the preparation of complexes were of analar quality. Amino acids were obtained from Loba and Sisco research laboratory, Bombay. The preparation of ligands and complexes were described in Part 1.The solvents used were purified by standard methods. 3:1 methanol water mixture was used as solvent. The pathogen *PHYTOPHTHORA CAPSICI* used was isolated from infected plant parts using the selective medium P V P H, and culture were maintained in carrot agar for the studies.

METHODS

Test solution of complexes have been prepared by dissolving appropriate amounts of complexes in 3:1 methanol water mixture. In this work the pathogen *PHYTOPHTHORA CAPSICI* isolated from infected pepper plant and the culture already maintained in National Repository of *PHYTOPHTHORA*, I I S R , Calicut, was used. The effect of complexes on growth of *CAPSICI* , sporulation, sporangial germination and zoospore germination , the four critical stages of the life cycle of *PHYTOPHTHORA* were studied.

For growth studies carrot agar medium was used.(Griffin 1977) [103]. Carrot agar medium was prepared as follows:

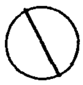
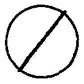
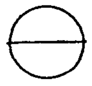
Carrot - 200mg
Agar - 18g
Distilled water- 1 Lit

Carrot after pealing was weighed and then washed thoroughly with water. It was then cut in to pieces. Later it was mixed with 150 ml distilled water and blended well in a mixer grinder. The extract was squeezed through muslin cloth and was made up to 1litre with distilled water. It was warmed and to this18g agar was added, stirred well, boiled and filtered for 20 minutes. It was then poured into 250ml flask (150 ml / flask),closed with non-absorbent cotton and sterilized in an autoclave at a pressure 15lb and temperature 120^{0}C for 15 minutes .This was used for all growth studies. For growth study the test solution in concentrated form ranging from 0.25 to 2 % were taken and for the other three stages 200 ppm, 400 ppm , 500 ppm and 1000 ppm were used .Test solutions were prepared in 3:1 methanol water solution .

1. MYCELIUM GROWTH

For the studies on growth of mycelium poisoned food technique[104] was used. The test solution in the definite concentration form was taken and appropriate volume mixed with molten 2% carrot agar to obtain final concentrations ranging from 0.2 –2 %. This chemical amended medium was transferred in to 9cm perti plates. *PHYTOPHTHORA*

CAPSICI from black pepper was cultured on carrot agar; 1cm diameter mycelial discs of actively growing culture were cut with cork borer and placed in the center of petri plate containing carrot agar and test solution mixture. In control sets appropriate quantities of methanol water solution was incorporated in place of test solution. Three plates were kept for each concentration. The plates were incubated at 25 ±1 ^{0}C, growth of colony (fungal growth) measured in every 24 hours, at three points along the diameter of the plate and the mean of these three readings taken as the diameter of the colony.

The growth of the colony in control sets was compared with that of various treatments and the percent inhibition was calculated.

2. SPORULATION

Different test concentration of complexes is prepared in 3 : 1 methanol water mixture. For testing the effect of complexes on sporulation, *PHYTOPHTHORA CAPSICI* was grown on carrot agar in dark for 48 h at 20 ^{0} C and 1 cm diameter discs of mycelium were cut and placed in petri plates (5 disc per plate). Methanolic solutions of different concentrations of complexes were placed on these discs and incubated under continuous light for 48 hours. In control, the discs were covered with aqueous methanol. Numbers of sporangia produced per microscopic field were counted under 10 X magnification. The average of 5 fields for each replication was counted and compared with that of control.

3. ZOOSPORE RELEASE

To study the effect of complexes on zoospore release (indirect germination of sporangium) *PHYTOPHTHORA CAPSICI* culture grown on carrot agar medium for 48 hours were taken. 1 cm diameter discs were cut and put in sterile distilled water and allowed to sporulate by incubating in fluorescent light as described above. Such sporulating disc were taken in petri plates, test solution of desired concentrations ranging from 200 – 1000 ppm placed over them and incubated at 4 ^{0}C for 10 minutes (keep in the freezer of a refrigerator for 10 minutes.). These plates were taken out and kept at laboratory temperature for 30 minutes before observation. For control set 3 : 1 methanol water mixture was used in place of complex solution. Due to cold shock, zoospores formed inside the sporangia were released. The number of sporangia, which released zoospores, were counted. Six microscopic fields were observed for each replication and percent inhibition was calculated by comparing with control plates.

4. GERMINATION OF ZOOSPORE

To evaluate the effect of complexes on germination of zoospore, sporulating discs were subjected to cold shock at 4 ^{0} C for 10 minutes as described above to get release of zoospores. Zoospores were collected in test tubes and vortexed. The zoospores which settle at the bottom and 50 μl of the water containing zoospore were placed in the cavities slides and 50μl test solution were poured and mixed to form the final concentration of 200 to 1000 ppm . In control 3 : 1 methanol water mixture was used. All slides were incubated at room temperature inside petri plates lined with moist filter paper for 12 hour. The treatment was replicated three times. In each slide, the microscopic fields were observed for number of zoospores present and the number germinated were counted. Inhibition percentage was calculated in comparison with control.

INSTRUMENTS

1. Laminar flow chamber
2. Microscope (Nikon)
3. Mixer
4. Micro pipettes
5. Auto clave
6. Hot air oven
7. Refrigerator

PART IV

ANTIFUNGAL STUDIES ON COMPLEXES OF SCHIFF BASES DERIVED FROM ANTHRACENE CARBOXALDEHYDE - L -HISTIDINE AND ANTHRACENE CARBOXALDEHYDE -L - TYROSINE

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER III

ANTIFUNGAL STUDIES ON COMPLEXES OF SCHIFF BASES DERIVED FROM ANTHRACENE CARBOXALDEHYDE – L –HISTIDINE AND ANTHRACENE CARBOXALDEHYDE -L – TYROSINE

In view of the season bound nature of the diseases in plants, and lack of early detection method for root infections, fixed schedules of fungicide application is the recommended strategy. Copper fungicides because of their high toxicity were found to be highly effective in reducing the disease. Based on field trial, application of Bordeaux mixture treatment was found very effective. Copper oxychloride drenching and Bordeuax spray has been adopted in Kerala. The efficiency of metalaxyl and Fosetyl Al both in vitro and in vivo in reducing *PHYTOPHTHORA* infection was established and were found to be superior to bordeux mixture (Ramachandran and Sarma 1990)[105].

Twenty-seven metal complexes synthesized from transition metals and Anthracene carboxaldehyde –Aminoacids were tested for their antifungal action. The active complexes were subjected to four phases of study. Based on this, the studies of two ligands Anthracene carboxaldehyde –L – histidine (ACH), Anthracene carboxaldehyde-L - tyrosine (ACT) and their Mn(II) ,Co(II), Ni(II), and Cu(II) complexes were tried on *PHYTOPHTHORA CAPSICI* and the results are presented in this chapter.

Experimental

Schiff bases were prepared by refluxing ethanolic / methanolic solutions of Anthracene carboxaldehyde with potassium salt of L-histidine and L-tyrosine respectively.

The metal complexes of the Schiff bases ACH, and ACT were synthesized and characterized as explained in Part 1.The metal ions used for the preparation of complexes include Mn (II) ,Co (II), Ni (II) and Cu(II). The methods employed for the experiment are explained in chapter II in a detailed manner.

Result and discussion

The results of mycelial growth studies, sporulation study, zoospore release studies and zoospore germination studies are discussed here. The effect of these ligands and complexes on different growth phases of *PHYTOPHTHORA CAPSICI* is presented in table 4. 3. 1 to 4. 3. 6.

a) Mycelial growth

The test solutions, with two concentrations, ranging from 0.5 and 1 % were used for mycelial growth studies. Among the ligand, potassium salt of anthracene carboxaldehyde L histidine and its complexes with Cu (II) , Co (II), Mn (II), and Ni (II) , whose solutions were tried on *PHYTOPHTHORA CAPSICI* on its mycelium growth phase, Cu (II) complex had the maximum percentage of inhibition at 1 % concentration, where as in the lower concentration it was not very effective. In the lower concentration, Co (II) and Mn (II) complexes possess almost same percentage inhibition on mycelial growth (61.8 % and 61.3 %) . In both concentrations the ligand posses lower percentage inhibition when compared with the complex. At lower concentration, the percentage inhibition of the ligand ACH and its complexes are in the order Co (II) ≅ Mn(II) > Cu(II)

> Ni (II) > ligand ACH. At the higher concentration, they are in the order Cu (II) > Mn (II) > Co (II) > Ni (II) > ligand ACH . The diameter of mycelial growth was measured and percentage inhibition calculated based on methanol control is given in Table 4.3.1. The ligand is least resistant to this fungus when compared to the complexes. Among the complexes Ni(II) complex inhibited mycelial growth by 53.85 %and found not to have a significant action at both lower and higher concentration.

Comparison of potassium salt of anthracene carboxaldehyde – L – tyrosine and its complexes showed that all the metal complexes are active, compared to the ligand. Among these, Ni (II) complex is more active against *PHYTOPHTHORA CAPSICI* having a percentage inhibition of 69 % at higher concentration. The comparative study of all the result given in Table 4.3.1, shows that at lower concentration, the ligand and the complexes were found to be inactive. In the case of Co(II) complex of anthracene carboxaldehyde – L – tyrosine(ACT), the activity increased with increase in concentration. At higher concentration, the ligand ACT and the complexes affected the mycelial growth of *PHYTOPHTHORA CAPSICI* in the order Ni(II) > Mn (II) > Cu (II) >Co (II) >ACT, the corresponding values being in the order 69 %, 68 %, 59 %, 56% and 46 % (shown in table).

b) Sporulation

Cu(II) complexes of ACH and ACT were found to be active at all concentrations. It possess 100 % inhibition on sporulation phase, where as Mn(II) complexes of ACH and ACT were not so effective at lower concentration (200 ppm). At higher concentration

(1000 ppm) both were very effective. The sporulation inhibitory activity of ACH and its complexes were found to be in the order Cu(II) > Mn (II) ≅ Co (II) > Ni (II) > ligand ACH. ACT and its complexes exhibited the percentage inhibition of 100 % for ACT, [Cu (ACT) $_2$ $(H_2O)_2$] , [Mn (ACT) $_2$ $(H_2O)_2$], [Ni (ACT) $_2$ $(H_2O)_2$] and 98.75 % for [Co (ACT) $_2$ $(H_2O)_2$] at 1000 ppm concentration . In both cases, percentage inhibition increases as concentration increases. In the case of ACT, it possess, 100 % inhibition at high concentration. The results of sporulation study on *PHYTOPHTHORA CAPSICI* with different concentrations of ligands and complexes are given in Tables 4.3.2 and 4.3.3. Co(II) complex of ACT and the ligand ACH were found to be less active at low concentration (200 ppm) ,whereas at 500ppm and 1000 ppm, the two ligands and their complexes were very active with percentage inhibition equal to or nearly equal to 100 %.

c) Zoospore release

The effect of these ligands and complexes on zoospore release of *PHYTOPHTHORA CAPSICI* is presented in Tables 4. 3. 4 and 4.3.5. Zoospore release were completely inhibited by Mn (II) complex of ACT and Co (II) complex of ACH at higher concentration (1000 ppm) . Cu (II) and Mn(II) complexes inhibited zoospore germination by nearly 100 % at 500 ppm and 1000 ppm . The ligand (ACH) and (ACT) had inhibitory effect on zoospore release at all concentration . At 1000 ppm , the two ligands and the eight complexes had inhibitory effect on zoospore release.

d) Zoospore germination

The percentage inhibition in zoospore germination of *PHYTOPHTHORA CAPSICI* is given in Table 4. 3. 6 .The Mn (II) complex of ACT, $[Mn(ACT)_2(H_2O)_2]$, $[Ni(ACT)_2(H_2O)_2]$ and $[Mn(ACH)_2(H_2O)_2]$, shows the maximum percentage inhibition of 100 % at all concentration whereas Co $(ACH)_2(H_2O)_2$ exhibits the percentage inhibition as 100 %, 100 %, 62.5 % and 100 % at 200 ppm, 400 ppm, 500 ppm, and 1000 ppm concentration. The two ligands exhibited percentage inhibition in the order ACT > ACH. The four complexes of ACH exhibited percentage inhibition in the order Mn (II) > Co (II) > Ni (II) > Cu (II) and the four complexes of ACT had percentage inhibition in the order Ni (II) $\cong$ Mn (II) > Co (II) > Cu (II) . Ligands are active at high concentration, than at lower concentration. Complexes possess more percentage inhibition , when compared to the ligand. From this it is clear that due to chelation, percentage inhibition of these complexes on zoospore germination of *PHYTOPHTHORA CAPSICI* increases.

TABLE 4.3.1

EFFECT OF ACH , ACT AND THEIR COMPLEXESON MYCELIAL GROWTH OF PHYTOPHTHORA CAPSICI

Control for 1% concentration 50 51 51

Control for .5% concentration 60 61 60

Complex	Concentration 0.5 % Mycelial growth in mm			Concentration 1 % Mycelial growth in mm			inhibition percent .5	inhibition percent 1
ACH	48	54	43	30	28	30	19.8895	41.9908
	52	48	48	26	28	26		
	50	52	52	26	26	28		
[Mn L^1_2 $(H_2O)_2$]	22	24	24	13	15	15	61.3260	71.6546
	22	31	22	22	20	20		
	26	22	24	15	20	18		
[Co L^1_2 $(H_2O)_2$]	26	21	22	16	15	15	61.8784	69.6770
	27	20	26	14	12	12		
	27	25	25	14	12	12		
[Ni L^1_2 $(H_2O)_2$]	33	33	33	22	24	24	45.3038	53.8563
	35	33	35	26	24	22		
	33	33	33	22	24	24		
[Cu L^1_2 $(H_2O)_2$]	35	30	30	7	7	7	47.5138	86.1569
	22	30	33	7	7	7		
	33	33	33	7	7	7		
ACT	44	42	42	31	24	26	29.2817	46.6052
	46	44	46	22	31	30		
	44	44	42	0	0	0		
[Mn L^{II}_2 $(H_2O)_2$]	37	36	37	17	15	16	39.2265	68.3586
	37	38	37	18	19	19		
	35	35	34	15	16	15		
[Co L^{II}_2 $(H_2O)_2$]	39	39	39	25	24	22	34.9900	57.4589
	38	38	42	23	21	22		
	38	37	43	19	20	18		
[Ni L^2_2 $(H_2O)_2$]	39	35	35	17	15	15	39.7790	69.0178
	30	37	39	22	20	17		
	37	39	35	15	13	15		
[Cu L^2_2 $(H_2O)_2$]	35	35	37	22	20	20	40.8840	59.1299
	30	30	33	22	20	20		
	33	30	30	22	17	20		

TABLE 4.3.2

Effect of ACH and its complexes on sporulation of PHYTOPHTHORA CAPSICI

Chemical concentration	field	sporangia per field of ACH	percentage inhibition	sporangia per field Mn $L^1_2(H_2O)_2$	percentage inhibition	sporangia per field Co $L^1_2(H_2O)_2$	percentage inhibition	sporangia per field Ni $L^1_2(H_2O)_2$	percentage inhibition	sporangia per field Cu $L^1_2(H_2O)_2$	percentage inhibition
200 ppm	field 1	48	43.2624	27	68.0851	24	49.7908	17	64.4351	0	100
	field 2	41	51.5366	38	55.0827	25	47.6987	13	72.8033	0	100
	field 3	44	47.9905	32	62.1749	16	66.5272	23	51.8828	0	100
	field 4	40	52.7187	33	60.9929	20	58.1590	21	56.0669	0	100
	field 5	47	44.4444	24	71.6312	22	53.9749	11	76.9874	0	100
	average	44	47.9905	30.8	63.5934	21.4	55.2301	17	64.4351	0	100
400 ppm	field 1	25	70.4492	17	79.9054	4	91.6318	10	79.0795	0	100
	field 2	32	62.1749	12	85.8156	10	79.0795	8	83.2636	0	100
	field 3	36	57.4468	12	85.8156	12	74.8954	6	87.4477	0	100
	field 4	24	71.6312	9	89.3617	4	91.6318	9	81.1715	0	100
	field 5	44	47.9905	9	89.3617	2	95.8159	11	76.9874	0	100
	average	32.2	61.9385	11.8	86.0520	6.4	86.6109	8.8	81.5900	0	100
500 ppm	field 1	23	72.8132	0	100	0	100	0	100	0	100
	field 2	20	76.3593	0	100	0	100	0	100	0	100
	field 3	23	72.8132	0	100	0	100	3	93.72385	0	100
	field 4	25	70.4492	0	100	0	100	6	87.4477	0	100
	field 5	21	75.1773	0	100	0	100	1	97.90795	0	100
	average	22.4	73.5225	0	100	0	100	2	95.8159	0	100
1000 ppm	field 1	4	95.2719	0	100	0	100	0	100	0	100
	field 2	8	90.5437	0	100	0	100	0	100	0	100
	field 3	7	91.7258	0	100	0	100	0	100	0	100
	field 4	3	96.4539	0	100	0	100	0	100	0	100
	field 5	7	91.7258	0	100	0	100	0	100	0	100
	average	5.8	93.1442	0	100	0	100	0	100	0	100
control		84.6		84.6		47.8		47.8		27.4	

TABLE 4 . 3 . 3

Effect of ACT and its complexes on sporulation of PHYTOPHTHORA CAPSICI

Chemical concentration	field	sporangia per field of ACT	percentage inhibition	sporangia per field Mn $L^{II}_2(H_2O)_2$	percentage inhibition	sporangia per field Co $L^{II}_2(H_2O)_2$	percentage inhibition	sporangia per field Ni $L^{II}_2(H_2O)_2$	percentage inhibition	sporangia per field of Cu $L^{II}_2(H_2O)_2$	percentage inhibition
200 ppm	field1	5	89.5397	3	93.7238	31	35.1464	0	100	0	100
	field2	7	85.3556	10	79.0795	27	43.5146	0	100	0	100
	field3	6	87.4477	6	87.4477	19	60.2510	0	100	0	100
	field4	4	91.6318	3	93.7238	23	51.8828	0	100	0	100
	field5	8	83.2636	11	76.9874	29	39.3305	0	100	0	100
	average	6	87.4477	6.6	86.1925	25.8	46.0251	0	100	0	100
400 ppm	field1	0	100	0	100	27	43.5146	0	100	0	100
	field2	0	100	0	100	28	41.4226	0	100	0	100
	field3	0	100	0	100	14	70.7113	0	100	0	100
	field4	0	100	0	100	19	60.2510	0	100	0	100
	field5	0	100	0	100	17	64.4351	0	100	0	100
	average	0	100	0	100	21	56.0669	0	100	0	100
500 ppm	field1	0	100	0	100	6	87.4477	0	100	0	100
	field2	0	100	0	100	7	85.3556	0	100	0	100
	field3	0	100	0	100	4	91.6318	0	100	0	100
	field4	0	100	0	100	6	87.4477	0	100	0	100
	field5	0	100	0	100	9	81.1715	0	100	0	100
	average	0	100	0	100	6.4	86.6109	0	100	0	100
1000 ppm	field1	0	100	0	100	0	100.0000	0	100	0	100
	field2	0	100	0	100	0	100.0000	0	100	0	100
	field3	0	100	0	100	1	97.9079	0	100	0	100
	field4	0	100	0	100	0	100.0000	0	100	0	100
	field5	0	100	0	100	2	95.8159	0	100	0	100
	average	0	100	0	100	0.6	98.7448	0	100	0	100
control		47.8		47.8		47.8		47.8		27.4	

TABLE 4.3.4

Effect of ACH , ACT , and their complexes on zoospore release of PHYTOPHTHORA CAPSICI

CONCENTRATION 200 ppm							CONCENTRATION 400 ppm				
complex	field	total no sporang	zoospore released	% of release	% of inhibition	average % of inhibiti	total no sporang	number released	% of release	% of inhibition	average% of inhibiti
ACH	1	182	6	3.2967	73.5022	84.8743	169	4	2.3669	85.2710	85.5701
	2	153	2	1.3072	89.4933		182	3	1.6484	89.7423	
	3	192	2	1.0417	91.6274		102	3	2.9412	81.6970	
[Mn L_2' $(H_2O)_2$]	1	188	6	3.1915	74.3479	66.7065	86	0	0.0000	100.0000	97.7933
	2	134	4	2.9851	76.0070		94	1	1.0638	93.3798	
	3	112	7	6.2500	49.7646		73	0	0.0000	100.0000	
[Co L_2' $(H_2O)_2$]	1	193	2	1.0363	91.6708	93.0617	149	0	0.0000	100.0000	100.0000
	2	256	1	0.3906	96.8603		102	0	0.0000	100.0000	
	3	172	2	1.1628	90.6539		158	0	0.0000	100.0000	
[Ni L_2' $(H_2O)_2$]	1	151	1	0.6623	94.6770	89.2352	126	5	3.9683	75.3055	83.2992
	2	163	3	1.8405	85.2068		115	2	1.7391	89.1774	
	3	132	2	1.5152	87.8217		128	3	2.3438	85.4148	
[Cu L_2' $(H_2O)_2$]	1	203	8	3.9409	68.3245	78.0130	196	0	0.0000	100.0000	98.9025
	2	142	2	1.4085	88.6794		124	0	0.0000	100.0000	
	3	210	6	2.8571	77.0353		189	1	0.5291	96.7074	
ACT	1	216	7	3.2407	73.9520	79.0495	282	9	3.1915	80.1393	80.6883
	2	107	3	2.8037	77.4645		154	6	3.8961	75.7545	
	3	169	3	1.7751	85.7320		135	3	2.2222	86.1711	
[Mn L" $(H_2O)_2$]	1	176	2	1.1364	90.8663	83.5281	174	12	6.8966	57.0826	75.3461
	2	132	2	1.5152	87.8217		216	5	2.3148	85.5949	
	3	143	5	3.4965	71.8963		187	5	2.6738	83.3609	
[Co L" $(H_2O)_2$]	1	184	3	1.6304	86.8951	67.4226	215	6	2.7907	82.6334	81.6619
	2	128	12	9.3750	24.6470		301	14	4.6512	71.0557	
	3	260	3	1.1538	90.7258		143	2	1.3986	91.2965	
[Ni L" $(H_2O)_2$]	1	146	10	6.8493	44.9475	52.1366	146	2	1.3699	91.4753	88.1904
	2	94	5	5.3191	57.2465		112	4	3.5714	77.7749	
	3	158	9	5.6962	54.2159		133	1	0.7519	95.3210	
[Cu L" $(H_2O)_2$]	1	200	3	1.5000	87.9435	89.4484	118	5	4.2373	65.9421	80.2938
	2	148	2	1.3514	89.1383		196	3	1.5306	87.6975	
	3	184	2	1.0870	91.2634		126	2	1.5873	87.2418	
Control				12.4414					16.0694		

TABLE 4 . 3 . 5

Effect of ACH , ACT , and their complexes on zoospore release of PHYTOPHTHORA CAPSICI

complex	field	CONCENTRATION 500 ppm total no sporang	number released	% of release	% of inhibition	average % of inhibitic	CONCENTRATION 1000 ppm total no sporang	number released	% of release	% of inhibition	average% of inhibiti
ACH	1	408	7	1.7157	91.3178	92.8538	213	4	1.8779	90.0620	91.1311
	2	482	9	1.8672	90.5510		192	3	1.5625	91.7313	
	3	306	2	0.6536	96.6925		126	2	1.5873	91.6000	
[Mn L_2' $(H_2O)_2$]	1	98	0	0	100	97.3011	536	13	2.4254	87.1650	77.5309
	2	84	0	0	100		182	11	6.0440	68.0155	
	3	125	2	1.6	91.9032		492	21	4.2683	77.4123	
[Co L_2' $(H_2O)_2$]	1	503	0	0	100	100	486	0	0	100	100
	2	357	0	0	100		580	0	0	100	
	3	256	0	0	100		512	0	0	100	
[Ni L_2' $(H_2O)_2$]	1	410	2	0.4878	97.5315	98.6259	126	2	1.5873	91.6000	96.0240
	2	380	0	0	100		150	1	0.6667	96.4720	
	3	612	2	0.3268	98.3462		98	0	0	100	
[Cu L_2' $(H_2O)_2$]	1	224	1	0.4464	97.7409	98.2547	342	0	0	100	98.7077
	2	510	3	0.5882	97.0232		546	4	0.7326	96.1231	
	3	122	0	0	100		136	0	0	100	
ACT	1	520	8	1.5385	92.2146	92.2047	486	7	1.4403	92.3778	91.7908
	2	608	9	1.4803	92.5092		424	7	1.6509	91.2632	
	3	624	10	1.6026	91.8903		512	8	1.5625	91.7313	
[Mn L_2" $(H_2O)_2$]	1	482	3	0.6224	96.8503	94.3358	115	0	0	100	100
	2	508	9	1.7717	91.0346		123	0	0	100	
	3	415	4	0.9639	95.1224		256	0	0	100	
[Co L_2" $(H_2O)_2$]	1	197	5	2.5381	87.1561	87.4084	326	2	0.6135	96.7534	97.6767
	2	201	5	2.4876	87.4117		412	1	0.2427	98.7155	
	3	123	3	2.4390	87.6574		434	2	0.4608	97.5613	
[Ni L_2" $(H_2O)_2$]	1	506	22	4.3478	77.9979	76.4975	536	9	1.6791	91.1142	86.1689
	2	493	24	4.8682	75.3648		318	7	2.2013	88.3510	
	3	318	15	4.7170	76.1298		101	4	3.9604	79.0416	
[Cu L_2" $(H_2O)_2$]	1	109	1	0.9174	94.2908	94.7360	294	0	0	100	97.4954
	2	226	2	0.8850	94.4929		132	1	0.7576	95.9909	
	3	408	3	0.7353	95.4243		302	2	0.6623	96.4954	
Control				19.7610					18.8965		

TAB LE 4.3.6

EFFECT OF (ACH), (ACT) AND THEIR COMPLEXES ON ZOOSPORE GERMINATION OF P - CAPSICI

CONCENTRATION 200 PPM					CONCENTRATION 400 PPM				CONCENTRATION 500 PPM				CONCENTRATION 1000 PPM			
sample	total n zoosp	zoosp germin	% of germination	% of inhib	total n zoosp	zoosp germin	% of germination	% of inhib	total zoos	zoos germi	% of germination	% of inhib	total zoos	zoos germ	% of germination	% of inhi
control	**27**	**9**	**33.3333**		**27**	**9**	**33.3333**		**27**	**9**	**33.3333**		**27**	**9**	**33.3333**	
ACH	16	5	31.2500	6.2500	19	4	21.0526	36.8421	11	2	18.1818	45.4545	18	2	11.1111	66.6667
$MnL_2^1(H_2O)_2$	9	0	0.0000	100.0000	14	0	0.0000	100.0000	27	0	0.0000	100.0000	12	0	0.0000	100.0000
$Co\ L_2^1(H_2O)_2$	4	0	0.0000	100.0000	7	0	0.0000	100.0000	8	1	12.5000	62.5000	6	0	0.0000	100.0000
ACT	25	7	28.0000	16.0000	21	6	28.5714	14.2857	19	3	15.7895	52.6316	15	1	6.6667	80.0000
$Mn\ L_2^{11}(H_2O)_2$	8	0	0.0000	100.0000	12	0	0.0000	100.0000	15	0	0.0000	100.0000	17	0	0.0000	100.0000
$Cu\ L_2^{11}(H_2O)_2$	11	3	27.2727	18.1818	14	4	28.5714	14.2857	9	1	11.1111	66.6667	7	1	14.2857	57.1429
control	**21**	**9**	**42.8571**		**21**	**9**	**42.8571**		**21**	**9**	**42.8571**		**21**	**9**	**42.8571**	
$Co\ L_2^{11}(H_2O)_2$	14	5	35.7143	16.6667	9	2	22.2222	48.1481	16	0	0.0000	100.0000	11	0	0.0000	100.0000
$Ni\ L_2^{11}(H_2O)_2$	28	0	0.0000	100.0000	11	0	0.0000	100.0000	18	0	0.0000	100.0000	9	0	0.0000	100.0000
$Ni\ L_2^1(H_2O)_2$	15	1	6.6667	84.4440	18	2	11.1111	74.0741	18	2	11.1111	74.0741	11	0	0.0000	100.0000
$Cu\ L_2^1(H_2O)_2$	32	9	28.1250	34.3750	22	4	18.1818	57.5758	27	2	7.4074	82.7160	24	0	0.0000	100.0000

PART IV

ANTIFUNGAL STUDIES OF COMPLEXES OF ANTHRACENE CARBOXALDEHYDE AMINO ACIDS

G. Indira Devi " Studies on transition metal complexes of schiff bases derived from aminoacids" Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER IV

ANTIFUNGAL STUDIES OF COMPLEXES OF ANTHRACENE CARBOXALDEHYDE AMINO ACIDS

Schiff base complexes like Cu (II) complexes of K E D T A are long been used for the antifungal activity. Anthracene carboxaldehyde – amino acids form stable chelates with transition metals. In continuation of the work carried out, the antifungal activity of the complexes of Co(II) , Cu(II) , Ni(II) and Mn (II) with Schiff bases anthracene carboxaldehyde glycine (ACG), anthracene carboxaldehyde DL alanine (ACA), and anthracene carboxaldehyde – L – phenyl alanine (ACPA) were carried out at I I S R , Calicut. The details of the study are given below.

The anti fungal activity of the complexes was studied against *PHYTOPHTHORA CAPSICI*, the activity on casual organism of foot rot of black pepper, four phases of study namely mycelial growth , sporulation study, zoospore release and zoospore germination were carried out. For mycelial growth, two different concentrations, and for the other three phases, four different concentrations (200ppm, 400ppm, 500ppm, 1000ppm) of test solutions were used. The complexes were prepared as explained in Part I . They (2mg – 10mg) were dissolved in 3 : 1 methanol water mixture to prepare test solution . *PHYTOPHTHORA CAPSICI* was used for the studies . Four complexes of each ligand were studied. Methods adopted for these studies were explained in chapter II.

Results and discussion

A) Mycelial growth study

Mycelial growth of *P . capsici* were checked by Ni (II) , Co (II), Cu (II) and Mn(II) complexes. The results are shown in Table 4.4.1. Complexes of the ligand anthracene carboxaldehyde – L – phenyl alanine (ACP) gave maximum percentage inhibition. These complexes gave more than 50 % inhibition at higher concentration. Cu (II) complex of ACG had the highest percentage of inhibition at higher concentration and that of Co (II) posses least percentage of inhibition. At lower concentration except Cu (II) complexes of ACPA, all other complexes were comparatively inactive against mycelial growth. They have percentage inhibition less than 45 %, but [Cu $(ACPA)_2$ $(H_2O)_2$] inhibited mycelial growth by 50.27 %. At the higher concentration, the percentage inhibition of various complexes is in the order $[Cu(ACG)_2(H_2O)_2]$ > $[Cu(ACPA)_2(H_2O)_2]$ > $[Ni(ACPA)_2(H_2O)_2]$ > $[Co(ACP)_2(H_2O)_2]$ > $[Co(ACA)_2(H_2O)_2]$ ≅ $[Ni(ACA)_2(H_2O)_2]$ > $[Mn(ACG)_2(H_2O)_2]$ > $[Cu(ACA)_2(H_2O)_2]$ > $[Ni(ACG)_2(H_2O)_2]$ > $[Co(ACG)_2(H_2O)_2]$ > $[Mn(ACA)_2(H_2O)_2]$

Sporulation

Among these eleven complexes, Co (II) ,and Cu (II) complexes of ACP and Mn(II) complex of ACG show 100 % inhibitory effect on sporulation of *PHYTOPHTHORA CAPSICI* . Other complexes at higher concentration of 500 ppm and 1000 ppm showed higher levels of inhibitory action on sporulation . The effect of these complexes on sporulation of *PHYTOPHTHORA CAPSICI* is presented in Tables 4.4.2 and 4.4.3. The ACG complexes of Co (II), Ni(II) and Cu(II) were very effective only at 1000 ppm concentration , but these are not as effective as the complexes of anthracene carboxaldehyde – L – phenyl alanine in other concentrations. The complexes of Mn(II), Co (II), Ni (II) and Cu (II) of ACA were inhibited sporulation by 75.1% ,87.2%, 71.3%, and 100% at 1000 ppm concentration. These were not very effective in lower concentrations.

Sporangial production were completely inhibited by [Cu $(ACPA)_2$ $(H_2O)_2$] at all concentrations. Similarly [Co $(ACA)_2$ $(H_2O)_2$] inhibited sporulation completely at 400 ppm, 500 ppm, and 1000 ppm concentration. At 200 ppm the inhibition was 92.05%. Co (II), Ni (II) and Mn (II) complexes of ACA was not very effective. ACPA complexes were found to be very effective at all concentrations, but other complexes were not as effective as ACPA complexes. Co(II) and Ni(II) complexes of ACG inhibited sporulation by 100% at 1000ppm whereas on other concentrations they are not very effective .

Zoospore release study

PHYTOPHTHORA CAPSICI was used for all the complexes. Total number of sporangia present and the number sporangia, which released zoospore, were counted. Three microscopic fields were observed for each replication and percent of inhibition was calculated by comparing with control plates containing methanol water mixture. It was calculated using the formulae (C – T x100) / C where T is the % of zoospore release from test solution, C is the percentage of release from control .

Among these eleven complexes Ni(II) complex did not show any adverse effect on zoospore release even at higher concentration as 1000ppm.The effect of these complexes on zoospore release phase of *PHYTOPHTHORA CAPSICI* is presented in Tables 4.4.4 and 4.4.5. Zoospore production and release were inhibited by the complexes of ACG , ACA, and ACP at 1000ppm concentration .Co(II) complex of ACP had inhibitory effect on zoospore release at all concentrations. Complexes of the ligand ACPA, ACG gave maximum inhibitory action .These complexes gave more than 50% at all concentrations expect Ni(II) of ACG .This complex of Nickel having the formulae $[Ni(ACG)_2(H_2O)_2]$ possess very low percentage of inhibition (24.9 %,29.9%) at low concentrations of 200ppm and 400ppm.As concentration increases percentage inhibition on zoospore release of *PHYTOPHTHORA* CAPSICI also increases in the case of Ni(II) complex of anthracene carboxaldehyde – glycine. At 500ppm, and 1000ppm all these complexes possess maximum percentage inhibition on zoospore release and are found to be very effective at higher concentration.

Zoospore germination

To evaluate the effect of complex on zoospore germination sporulating discs were subjected to cold shock in the freezer of a fridge for 10 minutes as described in Chapter II . 50µl zoospore solution is treated with 50µl of test solution. The results are shown in Table 4.4.6. Even at lower concentration as 200ppm, the complex of Mn(II) of anthracene carboxaldehyde inhibited zoospore germination .Except Mn(II) and Cu(II) complex ACG the other complexes showed only 16 - 45% inhibition at the low concentration (200ppm). At 400ppm the complexes of ACG, having the formula $[Cu(ACG)_2 (H_2O)_2]$, $[Mn(ACG)_2(H_2O)_2]$, and the Ni(II) complexes with formula $[Ni(ACA)_2(H_2O)_2]$and $[Ni(ACP)_2(H_2O)_2]$are highly active (100% inhibition). Mn(II) complex of ACA is least active at this concentration on zoospore germination. At 500ppm the complexes $[Cu(ACG)_2(H_2O)_2]$, $[Co(ACG)_2(H_2O)_2]$, $[Mn(ACG)_2(H_2O)_2]$, $[Cu(ACP)_2(H_2O)_2]$and $[Ni(ACP)_2(H_2O)_2]$inhibited zoospore germination completely. At 1000ppm concentration all complexes are active. Concentrated solutions of these complexes gave more than 50% inhibition on zoospore germination.

TABLE 4.4.1

Effect of complexes of ACG, ACA, and ACP on mycelial growth of PHYTOPTHORA CAPSICI

Control for 1% concentration	**50**	**51**	**51**
Control for 0.5% concentration	**60**	**61**	**60**

complex	concentration 0.5 % Mycelial growth in mm			concentration 1 % Mycelial growth in mm			inhibition percent .5	inhibition percent 1
Mn L^{III}_2 $(H_2O)_2$	37	39	37	31	26	31	37.5690	41.9908
	42	42	42	33	33	31		
	0	0	0	26	28	28		
Co L^{III}_2 $(H_2O)_2$	57	59	61	35	42	42	2.2099	21.5558
	50	55	53	42	37	37		
	0	0	0	39	39	37		
Ni L^{III}_2 $(H_2O)_2$	42	43	46	35	35	36	27.6243	30.1253
	45	42	41	37	36	39		
	40	43	44	39	39	39		
Cu L^{III}_2 $(H_2O)_2$	33	33	35	13	11	11	44.1989	76.9282
	33	35	33	13	13	15		
	33	33	33	15	13	15		
Mn L^{IV}_2 $(H_2O)_2$	46	48	48	39	42	41	21.5469	19.5782
	49	46	44	40	42	41		
	45	46	46	41	38	40		
CoL^{IV}_2 $(H_2O)_2$	37	39	39	31	26	26	36.4641	45.2868
	44	42	42	31	22	24		
	42	37	42	24	20	26		
Ni L^{IV}_2 $(H_2O)_2$	50	46	50	28	28	26	19.3370	45.9460
	48	53	50	26	24	26		
	0	0	0	26	28	27		
CuL^{IV}_2 $(H_2O)_2$	55	55	57	31	31	31	7.7348	38.6948
	57	55	57	31	33	31		
	55	53	55	22	31	31		
Co L^{V}_2 $(H_2O)_2$	45	36	40	20	21	20	33.1491	59.7891
	40	40	41	18	17	17		
	36	36	35	19	20	20		
Ni L^{V}_2 $(H_2O)_2$	36	37	39	26	16	16	38.1215	61.7667
	35	32	32	26	26	25		
	35	39	40	25	26	24		
Cu L^{V}_2 $(H_2O)_2$	31	31	28	13	20	24	50.2762	62.4259
	31	31	26	15	22	22		
	24	26	22	24	24	22		

TABLE 4.4.2

Effect of ACG complexes on sporulation of PHYTOPHTHORA CAPSICI

Chemical concen- tration	field	sporangia per field of Mn $L^{III}_{3}(H_2O)_2$	percen- tage inhibition	sporangia per field Co $L^{III}_{2}(H_2O)_2$	percen- tage inhibition	sporangia per field of Ni $L^{III}_{2}(H_2O)_2$	percen- tage inhibition	sporangia per field Cu $L^{III}_{2}(H_2O)_2$	percen- tage inhibition
200 ppm	field1	0	100	27	43.5146	19	30.6569	6	87.4477
	field2	0	100	29	39.3305	22	19.7080	13	72.8033
	field3	0	100	21	56.0669	18	34.3066	9	81.1715
	field4	0	100	25	47.6987	22	19.7080	11	76.9874
	field5	0	100	29	39.3305	21	23.3577	5	89.5397
	average	0	100	26.2	45.1883	20.4	25.5474	8.8	81.5900
400 ppm	field1	0	100	16	66.5272	17	37.9562	0	100
	field2	0	100	23	51.8828	13	52.5547	0	100
	field3	0	100	27	43.5146	11	59.8540	0	100
	field4	0	100	19	60.2510	12	56.2044	0	100
	field5	0	100	23	51.8828	14	48.9051	0	100
	average	0	100	21.6	54.8117	13.4	51.0949	0	100
500 ppm	field1	0	100	14	70.7113	10	63.5036	0	100
	field2	0	100	16	66.5272	4	85.4015	0	100
	field3	0	100	17	64.4351	4	85.4015	0	100
	field4	0	100	13	72.8033	8	70.8029	0	100
	field5	0	100	19	60.2510	7	74.4526	0	100
	average	0	100	15.8	66.9456	6.6	75.9124	0	100
1000 ppm	field1	0	100	0	100	0	100	0	100
	field2	0	100	0	100	0	100	0	100
	field3	0	100	0	100	0	100	0	100
	field4	0	100	0	100	0	100	0	100
	field5	0	100	0	100	0	100	0	100
	average	0	100	0	100	0	100	0	100
control		27.4		47.8		27.4		47.8	

TABLE 4.4.3

Effect of ACA and ACP complexes on sporulation of PHYTOPHTHORA CAPSICI

Chemi conce-ntration	field	sporangia per field of Mn $L^{IV}_2(H_2O)_2$	percentage inhibition	sporangia per field of Co $L^{IV}_2(H_2O)_2$	percentage inhibition	sporangia per field of Ni $L^{IV}_2(H_2O)_2$	percentage inhibition	sporangia per field of Cu $L^{IV}_2(H_2O)_2$	percentage inhibition	sporangia per field of Co $L^{V}_2(H_2O)_2$	% of inhibition	sporangia per field of Ni $L^{V}_2(H_2O)_2$	percentage inhibition	sporangia per field of Cu $L^{V}_2(H_2O)_2$	% of inhibition
200 ppm	field1	57	32.6241	46	45.6265	61	27.8960	0	100	0	100	41	51.5366	0	100
	field2	63	25.5319	51	39.7163	56	33.8061	4	91.6318	0	100	39	53.9007	0	100
	field3	59	30.2600	52	38.5343	51	39.7163	3	93.7238	0	100	48	43.2624	0	100
	field4	71	16.0757	45	46.8085	62	26.7139	7	85.3556	0	100	41	51.5366	0	100
	field5	67	20.8038	36	57.4468	69	18.4397	5	89.5397	0	100	43	49.1726	0	100
	average	63.4	25.0591	46	45.6265	59.8	29.3144	3.8	92.0502	0	100	42.4	49.8818	0	100
400 ppm	field1	45	46.8085	34	59.8109	47	44.4444	0	100	0	100	31	63.3570	0	100
	field2	32	62.1749	32	62.1749	38	55.0827	0	100	0	100	27	68.0851	0	100
	field3	37	56.2648	41	51.5366	42	50.3546	0	100	0	100	34	59.8109	0	100
	field4	41	51.5366	48	43.2624	45	46.8085	0	100	0	100	33	60.9929	0	100
	field5	52	38.5343	39	53.9007	45	46.8085	0	100	0	100	29	65.7210	0	100
	average	41.4	51.0638	38.8	54.1371	43.4	48.6998	0	100	0	100	30.8	63.5934	0	100
500 ppm	field1	30	64.5390	11	86.9976	42	50.3546	0	100	0	100	0	100.0000	0	100
	field2	32	62.1749	27	68.0851	39	53.9007	0	100	0	100	4	95.2719	0	100
	field3	39	53.9007	19	77.5414	33	60.9929	0	100	0	100	0	100	0	100
	field4	37	56.2648	26	69.2671	41	51.5366	0	100	0	100	5	94.08983	0	100
	field5	36	57.4468	30	64.5390	31	63.3570	0	100	0	100	0	100	0	100
	average	34.8	58.8652	22.6	73.2861	37.2	56.0284	0	100	0	100	1.8	97.87234	0	100
1000 ppm	field1	19	77.5414	13	84.6336	22	73.9953	0	100	0	100	0	100	0	100
	field2	24	71.6312	15	82.2695	27	68.0851	0	100	0	100	0	100	0	100
	field3	21	75.1773	7	91.7258	23	72.8132	0	100	0	100	0	100	0	100
	field4	15	82.2695	2	97.6359	18	78.7234	0	100	0	100	0	100	0	100
	field5	26	69.2671	17	79.9054	31	63.3570	0	100	0	100	0	100	0	100
	average	21	75.1773	10.8	87.2340	24.2	71.3948	0	100	0	100	0	100	0	100
control		84.6		84.6		84.6		47.8		84.6		84.6		84.6	

Table 4.4.4 **EFFECT OF COMPLEXES OF ACG, ACA AND ACP ON ZOOSPORE RELEASEOF PHYTOPHTHORA CAPSICI**

CONCENTRATION 200 ppm (Control --- 12.44143)							CONCENTRATION 400 ppm (Control ---16.06937)				
complex	field	total no of sporangia	number released	% of release	% of inhibition	aver % of inhibitic	total no sporang	number released	% of release	% of inhibition	average% of inhibiti
MnL^{III} $(H_2o)_2$	1	124	4	3.2258	74.0721	85.8481	342	3	0.8772	94.5412	91.7199
	2	132	1	0.7576	93.9109		95	1	1.0526	93.4495	
	3	154	2	1.2987	89.5615		194	4	2.0619	87.1690	
CoL^{III} $(H_2o)_2$	1	208	5	2.4038	80.6787	83.3050	126	2	1.5873	90.1222	92.2939
	2	160	4	2.5000	79.9059		282	6	2.1277	86.7595	
	3	226	3	1.3274	89.3305		107	0	0.0000	100.0000	
NiL^{III} $(H_2o)_2$	1	127	14	11.0236	11.3959	24.9847	176	14	7.9545	36.0641	29.9869
	2	132	11	8.3333	33.0195		145	16	11.0345	11.3086	
	3	162	14	8.6420	30.5388		126	9	7.1429	42.5882	
CuL^{III} $(H_2o)_2$	1	140	0	0.0000	100.0000	98.5596	258	9	3.4884	78.2918	81.8269
	2	186	1	0.5376	95.6787		125	4	3.2000	80.0863	
	3	158	0	0.0000	100.0000		193	4	2.0725	87.1026	
MnL^{IV} $(H_2o)_2$	1	268	13	4.8507	61.0114	51.8400	116	3	2.5862	79.2130	70.5384
	2	192	17	8.8542	28.8332		308	11	3.5714	71.2941	
	3	281	12	4.2705	65.6755		186	9	4.8387	61.1081	
CoL^{IV} $(H_2o)_2$	1	210	3	1.4286	88.5176	84.0181	182	3	1.6484	89.7423	96.5808
	2	183	6	3.2787	73.6470		117	0	0.0000	100.0000	
	3	159	2	1.2579	89.8897		120	0	0.0000	100.0000	
NiL^{IV} $(H_2o)_2$	1	142	11	7.7465	37.7364	49.1013	117	2	1.7094	89.3624	81.5664
	2	174	14	8.0460	35.3292		113	5	4.4248	72.4645	
	3	156	5	3.2051	74.2383		109	3	2.7523	82.8724	
CuL^{IV} $(H_2o)_2$	1	156	0	0.0000	100.0000	100.0000	182	0	0.0000	100.0000	88.6449
	2	172	0	0.0000	100.0000		152	6	3.9474	75.4355	
	3	168	0	0.0000	100.0000		131	2	1.5267	90.4992	
CoL^{V} $(H_2o)_2$	1	146	3	2.0548	83.4843	86.4200	212	5	2.3585	81.0433	80.6398
	2	168	4	2.3810	80.8627		318	11	3.4591	72.1968	
	3	158	1	0.6329	94.9129		142	2	1.4085	88.6794	
NiL^{V} $(H_2o)_2$	1	122	11	9.0164	27.5293	57.8307	232	11	4.7414	70.4943	80.2054
	2	131	6	4.5802	63.1863		358	12	3.3520	79.1407	
	3	140	3	2.1429	82.7764		276	4	1.4493	90.9811	
CuL^{V} $(H_2o)_2$	1	117	0	0.0000	100.0000	98.1132	402	8	1.9900	87.6159	92.5898
	2	184	0	0.0000	100.0000		135	0	0.0000	100.0000	
	3	142	1	0.7042	94.3397		316	5	1.5823	90.1535	

Table 4.4.5 EFFECT OF COMPLEXES OF ACG, ACA AND ACP\ON ZOOSPORE RELEASEOF PHYTOPHTHORA CAPSICI

CONCENTRATION 500 ppm (Control ---- 19.76096)							CONCENTRATION 1000 ppm (Control --- 18.8965)				
complex	field	total sporangi	number released	% of release	% of inhibition	av. % of inhibition	total sporangi	number releasd	% of release	% of inhibition	av. % of inhibition
MnL^{III} $(H_2o)_2$	1	215	0	0	100	100	620	0	0	100	99.3082
	2	89	0	0	100		510	2	0.3922	97.9247	
	3	73	0	0	100		605	0	0.0000	100.0000	
CoL^{III} $(H_2o)_2$	1	588	7	1.1905	93.9756	91.8554	182	4	2.1978	88.3693	86.8754
	2	326	6	1.8405	90.6862		156	2	1.2821	93.2154	
	3	612	11	1.7974	90.9044		101	4	3.9604	79.0416	
NiL^{III} $(H_2o)_2$	1	601	7	1.1647	92.7519	91.3598	502	14	2.7888	85.2415	70.3619
	2	414	5	1.2077	92.4843		204	11	5.3922	71.4648	
	3	502	9	1.7928	88.8432		116	10	8.6207	54.3794	
CuL^{III} $(H_2o)_2$	1	302	11	3.6424	81.5678	81.7132	382	6	1.5707	91.6880	87.6317
	2	326	12	3.6810	81.3725		487	9	1.8480	90.2201	
	3	398	14	3.5176	82.1993		501	18	3.5928	80.9869	
MnL^{IV} $(H_2o)_2$	1	221	2	0.9050	94.3683	94.8157	318	7	2.2013	88.3510	92.6118
	2	492	4	0.8130	94.9406		504	5	0.9921	94.7500	
	3	384	3	0.7813	95.1383		402	4	0.9950	94.7343	
CoL^{IV} $(H_2o)_2$	1	410	12	2.9268	85.1888	84.7974	204	3	1.4706	92.2177	96.0224
	2	432	17	3.9352	80.0861		510	4	0.7843	95.8494	
	3	186	4	2.1505	89.1172		126	0	0.0000	100.0000	
NiL^{IV} $(H_2o)_2$	1	246	13	5.2846	73.2576	86.7827	298	0	0.0000	100.0000	98.5711
	2	196	3	1.5306	92.2544		320	1	0.3125	98.3463	
	3	392	4	1.0204	94.8362		402	2	0.4975	97.3672	
CuL^{IV} $(H_2o)_2$	1	580	0	0.0000	100.0000	98.3935	136	4	2.9412	84.4353	83.1656
	2	612	0	0.0000	100.0000		116	2	1.7241	90.8759	
	3	630	6	0.9524	95.1805		123	6	4.8780	74.1854	
CoL^{V} $(H_2o)_2$	1	124	2	1.6129	89.9629	79.9322	208	1	0.4808	97.4558	99.1519
	2	396	4	1.0101	93.7141		152	0	0.0000	100.0000	
	3	156	11	7.0513	56.1197		84	0	0.0000	100.0000	
NiL^{V} $(H_2o)_2$	1	410	2	0.4878	97.5315	98.6259	582	0	0.0000	100.0000	100.0000
	2	380	0	0.0000	100.0000		126	0	0.0000	100.0000	
	3	612	2	0.3268	98.3462		125	0	0.0000	100.0000	
CuL^{V} $(H_2o)_2$	1	72	0	0	100	100	636	0	0.0000	100.0000	99.3082
	2	193	0	0	100		402	0	0.0000	100.0000	
	3	492	0	0	100		510	2	0.3922	97.9247	

TABLE 4 . 4 . 6

EFFECT OF (ACG) , (ACA) AND (ACP) COMPLEXES ON ZOOSPORE GERMINATION OF PHYTOPHTHORA - CAPSICI

	CONCENTRATION 200 PPM				CONCENTRATION 400 PPM				CONCENTRATION 500 PPM				CONCENTRATION 1000 PPM			
complex	total no of zoospo	zoospo germinated	% of germination	% of inhibition methanol	total no of zoospo	zoospo germinated	% of germination	% of inhibition methanol	total no of zoospo	zoospo germinated	% of germination	% of inhibition methanol	total no of zoospo	zoospo germinated	% of germination	% of inhibiti metha
control	**21**	**9**	**42.85714**		**21**	**9**	**42.8571**		**21**	**9**	**42.8571**		**21**	**9**	**42.8571**	
$MnL_2^{III}(H_2o)_2$	12	0	0	100	12	0	0	100	24	0	0	100	20	0	0	100
$CoL_2^{III}(H_2o)_2$	13	4	30.76923	28.2051	7	1	14.2857	66.6667	10	0	0	100	4	0	0	100
$CoL_2^{IV}(H_2o)_2$	23	6	26.08696	39.1304	25	4	16	62.6667	13	2	15.3846	64.1026	11	1	9.0909	78.788
$CuL_2^{IV}(H_2o)_2$	13	4	30.76923	28.2051	4	1	25	41.6667	4	1	25	41.6667	3	0	0	100
$NiL_2^{V}(H_2o)_2$	15	4	26.66667	37.7778	26	0	0	100	28	0	0	100	8	0	0	100
control	**27**	**9**	**33.33333**		**27**	**9**	**33.3333**		**27**	**9**	**33.3333**		**27**	**9**	**33.3333**	
$NiL_2^{III}(H_2o)_2$	19	5	26.31579	21.0526	21	4	19.0476	42.8571	24	3	12.5	62.5	12	1	8.3333	75
$CuL_2^{III}(H_2o)_2$	15	2	13.33333	60	9	0	0	100	18	0	0	100	23	0	0	100
$MnL_2^{IV}(H_2o)_2$	18	5	27.77778	16.6667	9	2	22.2222	33.3333	16	3	18.75	43.75	14	2	14.2857	57.143
$NiL_2^{IV}(H_2o)_2$	14	3	21.42857	35.7143	7	0	0	100	11	1	9.0909	72.7273	5	0	0	100
$CoL_2^{V}(H_2o)_2$	14	4	28.57143	14.2857	13	2	15.3846	53.8462	8	1	12.5	62.5	6	0	0	100
$CuL_2^{V}(H_2o)_2$	11	2	18.18182	45.4545	6	1	16.6667	50	9	0	0	100	20	0	0	100

PART IV
SUMMARY

SUMMARY

Part I comprises various methods of preparation and characterization of some Schiff base ligands and their metal complexes. Structural elucidation was carried out on the basis of elemental analysis, magnetic measurements, conductance experiments, spectral, X-ray and thermal studies.

Anthracene carboxaldehyde L-histidine(ACH), anthracene carboxaldehyde L-tyrosine(ACT), anthracene carboxaldehyde glycine(ACG), anthracene carboxaldehyde DL-alanine(ACA) and anthracene carboxaldehyde L-phenyl alanine(ACPA), five potential bidentate Schiff base ligands, form stable and solid complexes with transition metal ions. Chapter I give an introduction and a review on the work done so far in this field. The description about materials, methods and instruments is given in Chapter II.

Synthesis and characterization of the ligand anthracene carboxaldehyde L histidine and its complexes with Cr (III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Ag (I) ions are described in chapter III. Micro analytical, magnetic and conductance data reveal that there exists a 1:2 stochiometry between the metal and the ligands in all these complexes except Ag (I) where the metal to ligand ratio was 1:1. All these complexes were found to be non electrolytic in nature. Monovalent bidentate nature of the ligands was established by IR spectral studies. Based on these results an octahedral structure was assigned to all these complexes except for Zn (II), Cd (II), Hg (II), and Ag (I) complexes which have tetrahedral geometry. Chapter IV explains the similar work done on the Schiff base anthracene carboxaldehyde L tyrosine and chapter V deals with the synthesis and characterization of ten complexes of the ligand anthracene carboxaldehyde glycine. The IR spectral data reveals that the ligand acts as bidentate. Chapter VI covers the preparation and properties of the ligand anthracene carboxaldehyde DL-alanine and its complexes and chapter VII explains the preparative as well as physicochemical investigation of Cr (III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Hg (II) and Ag (I)complexes of the ligand anthracene carboxaldehyde Lphenyl alanine. These complexes also possess monovalent bidentate nature. All these 50 complexes were found to be non-electrolytes.

Thermo gravimetric investigations on fifteen newly prepared Schiff base complexes with Co (II), Ni (II) and Cu (II) were carried out using TG technique and presented in Part II. Thermo gravimetric analysis of these coordination compounds were made in static air atmosphere at a heating rate of 10 ^{0}C / minute, by using about 2 – 5 mg of the sample. The final mass loss observed agrees well with the values calculated for the conversion of the complexes to their corresponding metal oxides.

Various kinetic methods, both mechanistic and non-mechanistic have been utilized in order to analyze the decomposition curves. All the TG traces were subjected to kinetic analysis and kinetic parameters namely, energy of activation, Arrhenius frequency factor, and entropy of activation of decomposition have been calculated. Also attempts were made to suggest the mechanism and order of decomposition reactions followed during the thermal decay of these complexes. On the basis of the temperature of inflection, and initial decomposition, the relative thermal stabilities of the chelates were assigned.

Integral equations by Coats – Redfern, and approximation equation by Horowitz – Metzger, are the non-mechanistic kinetic equations employed during the present course of studies, so as to establish the kinetic parameters. Based on the correlation between the kinetic parameters obtained from mechanistic and non-mechanistic kinetic methods, reaction mechanism of the different decomposition stages was ascertained. The order of reaction was evaluated by trial and error methods. Chapter I of part II give an introduction and chapter II explains the materials, methods and instruments used for the present study.

Thermal decomposition studies on Co (II), Ni (II) and Cu (II) complexes of anthracene carboxaldehyde – L – histidine are discussed in chapter III. Ni (II) and Cu (II) complexes exhibited a two stage decomposition pattern and Co (II) complex followed a three stage decomposition pattern. Thermal decomposition data as well as the kinetic parameters calculated are presented in Tables 2. 3. 1, 2. 3. 2 and 2. 3. 3. The relative thermal stabilities of the metal chelates can be given as $[CoL^{I}_{2}(H_2O)_2]$ < $[CuL^{I}_{2}(H_2O)_2]$ < $[NiL^{I}_{2}(H_2O)_2]$.

Chapter IV includes the kinetics and mechanism of thermal decomposition of complexes of the Schiff base anthracene carboxaldehyde – L – tyrosine with Co (II) , Ni (II) and Cu (II) . Results of these studies are summarized in Tables 2. 4. 1, 2. 4. 2, and 2. 4. 3. Thermal stability of the chelates were determined relatively, which can be represented as $Co\,L^{II}_{2}(H_2O)_2 > Cu\,L^{II}_{2}(H_2O)_2 > Ni\,L^{II}_{2}(H_2O)_2$.

The thermal behavior of anthracene carboxaldehyde glycine complexes of Co (II), Ni (II) and Cu (II) was studied by TG and the results are represented in chapter V. A clear well defined three stage decomposition pattern was shown by Co (II) chelate where as a double stage pattern was exhibited by Ni (II) and Cu (II) complexes . Thermal and kinetic data of these complexes are given in Tables 2. 5.1, 2. 5. 2 and 2. 5. 3.

Chapter VI consists of an investigation on Co (II), Ni (II) and Cu (II) complexes of anthracene carboxaldehyde – DL – alanine. All these complexes have the general formula $[M L_2 (H_2O)_2]$, where M = Co (II) , Ni (II) or Cu (II) , L – ligand moiety of ACA. Co (II) followed a single stage decomposition scheme and Ni (II) followed a two-stage decomposition pattern. First stage in Ni (II) complex consists of the removal of the ligand part, anthracene carboxaldehyde part and two molecules of water. The loss of alanine part takes place in the second decomposition stage. Cu (II) complex showed a three-stage decomposition pattern. Tables 2. 6. 1, 2. 6. 2 and 2.6.3 give the detailed information regarding the kinetic parameters of decomposition of these chelates.

TG traces of Co (II), Ni (II) and Cu (II) chelates of anthracene carboxaldehyde – L – phenyl alanine were examined in detail and the kinetic parameters, order of stability , mechanism of decomposition and order of reactions have been calculated in chapter VII. The results are summarized in Tables 2. 7. 1, 2. 7. 2 and 2. 7. 3.

Part III consists of unit cell determination of seven Schiff base complexes using X – ray powder diffraction technology. Chapter II and I give the introduction, materials and methods employed respectively. In Chapter III, the X – ray diffraction studies of Ni (II) and Cu (II) complexes of anthracene carboxaldehyde – L – histidine (ACH), Ag (I) and Fe (III) complexes of anthracene carboxaldehyde glycine (ACG) , Zn (II) complex of anthracene carboxaldehyde – L – tyrosine (ACT), Cr (III) complex of anthracene carboxaldehyde - DL – alanine (ACA) and Cu (II) complex of anthracene carboxaldehyde – L – phenyl alanine (ACPA) are presented. All the seven complexes have been found to be orthorhombic. The calculated density of each complex was in good agreement with experimental value found out, which confirm the proposed molecular formula of the complexes and the existence of 1 : 2 stoichiometry between the metal ion and the ligand for all complexes, except for the Ag (I) complex, where it is 1 : 1 stoichiometry.

Part IV of this thesis consists of studies on anti fungal activity of Schiff base complexes derived from antracene carboxaldehyde and amino acids through four phases, mycelial growth, sporulation, zoospore release and zoospore germination of *PHYTOPHTHORA CAPSICI*.

Chapter II and I give the introduction to anti fungal treatment, materials, methods and instruments employed in the present study. Chapter III and IV comprise the results of the above-mentioned studies in a detailed manner. Tables 4. 3. 1 to 4. 4. 6 gives the information regarding the anti fungal activities of the compounds. All the studies confirm the fact that at higher concentration all the four phases namely mycelial growth, sporangial production, zoospore production and release and zoospore germination were completely inhibited by all complexes. ACA complexes were not very effective at the mycelial growth phase. Even at the low concentration they were very effective in the other three phases of *PHYTOPHTHORA CAPSICI*. Complexes of ACH and ACP inhibited mycelial growth and sporangial production, whereas zoospore release and zoospore germination were inhibited not as effective as the first two phases. The experimental results revealed that most of these compounds possess anti fungal activity. Some of them showed less activity at low concentration, but upon increasing the concentration, they also showed considerable activity.

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