STUDIES ON METAL COMPLEXES WITH HETEROCYCLIC COMPOUNDS

Thesis submitted to the University of Calicut
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CERTIFICATE

This is to certify that, this thesis is an authentic record of the research work carried out by Mrs. Jayasree S., under my guidance and supervision in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry of the University of Calicut and that no part thereof has been presented earlier for any other degree.

Dr. K.K. ARAVINDAKSHAN
(Supervising teacher)

DECLARATION

I, Jayasree, S., hereby declare that this thesis entitled "Studies on Metal Complexes with Heterocyclic Compounds", submitted to the University of Calicut in partial fulfilment of the requirements for the Doctoral degree in Chemistry, is a bonafide research work done by me under the supervision and guidance of Dr.K.K.Aravindakshan.

I further declare that no part of this thesis has previously formed the basis for the award of any degree, diploma or other similar title.

Calicut University Campus,
Date: 10 - 7 - 2002

JAYASREE S.

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Jayasree

Jayasree S.

PREFACE

Heterocyclic compounds constitute an important class of compounds because of their applications in biological, synthetic and industrial fields. These compounds act as good ligands owing to the presence of heteroatoms in their molecules, with which they can coordinate to different metal ions. Pyrazoles and imidazoles are two important groups of heterocyclic compounds. Their oxo-and thio-derivatives are biologically important and some of them are used as medicines. The coordination patterns of these derivatives are also interesting due to different donor sites present in their molecule. The antitumor activity of N_1-isonicotinoyl-3-methylpyrazolin-5-one has already been studied in our laboratory and the results were fruitful. Hence it was decided to synthesize and characterize some metal complexes of pyrazolin-5-ones and imidazoiln-2-thiones and to study their antimicrobial activities.

In the present investigation, six different ligands, *viz.* pyrazolin-5-ones and imidazolin-2-thiones were synthesized and characterized. Their coordination behaviours with different metals of the first transition series have been studied and about 67 new solid complexes were synthesized. Using various physico-chemical techniques, geometries have been assigned to them. Thermal analysis of some of these complexes were undertaken and kinetic parameters for the different steps were calculated. An attempt had been made to investigate the antimicrobial activities of some of these compounds against four fungal-and three bacterial strains.

The thesis is divided into three parts and ten chapters. Part I entitled "Synthesis and Characterization" has been further subdivided into six chapters. The first chapter starts with a general introduction. It gives a brief description of the structure of pyrazolin-5-ones and imidazolin-2-thiones and a review of research carried out on coordination compounds of these ligands. Chapter II describes the reagents used, the methods of preparation and the physico-chemical techniques employed for the characterization of the ligands and complexes. The synthesis and characterization of cobalt(II) , nickel (II) and copper (II) complexes of N_1-salicylyl-3-methylpyrazolin-5-one (SMP) are discussed in Chapter III. In Chapters IV to VI, the synthesis and characterization of metal complexes of five different 4,5-disubstituted imidazolin-2-thiones are discussed.

In the second part of the thesis, the thermal studies of ten metal complexes synthesized during the present investigation are presented. There are two chapters in this part and in the first chapter an introduction , explanation of the methods used and a brief review of thermal studies of metal complexes of pyrazolin-5-ones and imidazolin-2-thiones are included. The second chapter deals with the results of thermal analyses, including the calculation of kinetic parameters.

The third part of the thesis comprises the antimicrobial studies of some of the metal complexes synthesized here. There are 2 chapters ,of which the first forms an introductory one which explains the significance of the investigation and the methods used. A brief review of the research carried out in this field is also given. The results of antimicrobial studies undertaken are explained in the second chapter.

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PART 1
INTRODUCTION

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Part I

Synthesis and Characterisation

CHAPTER I

INTRODUCTION

Investigations on coordination compounds comprise a large body of current inorganic research. Coordination compounds have been a challenge to inorganic chemists since they were identified. They play an essential role in the chemical industry and in life itself. In 1963 Nobel prize was awarded jointly to Dr.K.Ziegler and to Prof.G.Natta for their discovery of Ziegler-Natta catalyst, a complex of the metals aluminium and titanium. This discovery was responsible for the development of the low-pressure polymerization of ethylene which now makes thousands of polyethylene articles[1]. The importance of metal complexes become evident when one realizes that chlorophyll, which is vital to photosynthesis in plants, is a Mg complex and haemoglobin which carries oxygen to animal cells is an iron complex.

It is difficult to state exactly when the first metal complex was discovered. Perhaps the earliest one as per record is Prussian blue. The discovery of hexamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$ by Tassaert[1] marks the real beginning of coordination chemistry. Coordination compounds were used long before they are recognized as such.

In almost all branches of chemistry, coordination compounds play certain prominent role. Coordination compounds have special properties by virtue of their nature. Chlorophyll present in green plants is capable of using solar energy to convert carbon dioxide and water into starch and oxygen. Myoglobin and Haemoglobin found in human body help to store, transfer and release oxygen.

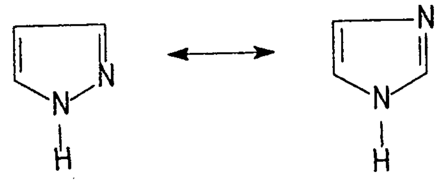
The wide applications of coordination compounds make their study interesting. The invention of powerful physico-chemical tools and the development of refined theoretical approaches based on quantum theory have catalyzed the progress of research in this field. Chemotherapy and chelation therapy using metals have now drawn attention as an additional outlet for coordination chemistry.

A. HETEROCYCLICS AS LIGANDS

A coordination compound contains a central metal atom to which the other atoms or groups are attached. The atoms or groups directly attached to the central metal atom are called coordinating groups or ligands. Most of the properties of the coordination compounds are due to the ligands- the nature and number of donor atoms and the charge on the ligands. The ligand must contain some atom capable of electron donation. The common donor atoms are nitrogen, oxygen and sulphur.

Heterocyclic compounds are cyclic compounds containing at least one heteroatom. Nitrogen, oxygen and sulphur are the most common heteroatoms of heterocyclic compounds, which are the main donor atoms for coordination compounds. Hence heterocyclic compounds act as good ligands. They can function as monodentate, bidentate and multidentate or chelate ligands.

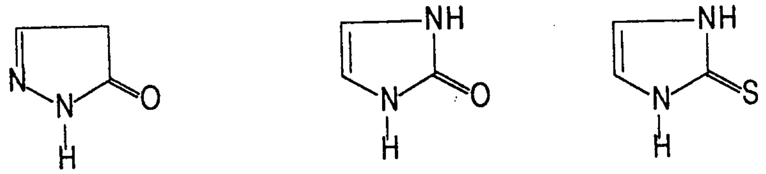
Heterocyclic compounds are widely distributed in nature and are essential to man in various ways. They represent one of the most active class of compounds having a wide spectrum of biological activities[52,53]. Among the heterocyclic compounds, five membered ones with two nitrogen atoms are of special interest. They are pyrazoles and imidazoles (**I** a and b) which are isomers.



a b

I

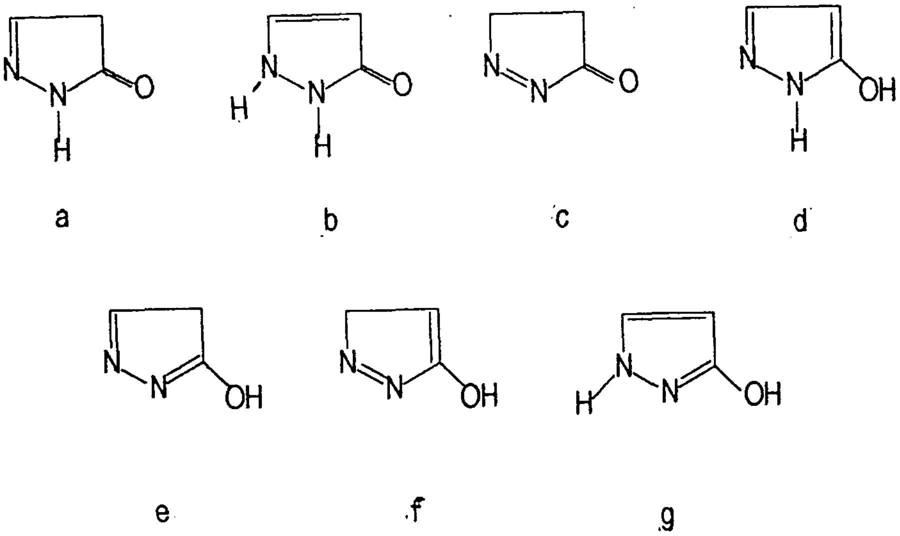
The oxo-and thio-derivatives of pyrazoles and imidazoles are very important due to their interesting coordination patterns. Among them pyrazolin-5-one, imidazolin-2-one and imidazolin-2-thione (**II** a,b and c) show enhanced biological activities and interesting coordination behaviors. They have wide ranging applications in industry [2] and medicine[3].


a b c

II

B. METAL COMPLEXES OF PYRAZOLIN–5-ONES – A REVIEW

Pyrazolinones are oxo-derivatives of pyrazolins. Pyrazolin-5-one is a pyrazolinone in which the oxo- group is in the fifth position. Knorr[4] proposed different tautomeric structures for pyrazolin-5-ones based on their methods of preparation, reactions and analyses. The following structures (**III** a to g) are possible for unsubstituted pyrazolin-5-ones.



a b c d

e f g

III

In addition, a large number of ionic tautomeric structures are also possible for pyrazolin-5-ones. Among the above structures, only a, b and d have major contributions. The effect of substitution on the structure of pyrazolin-5-one is very important. Certain tautomeric forms became impossible on substitution. For example, substitution at N_1 allows only structures a, b and d. For substitution at N_1 and disubstitution at C_4, the only structure possible is a.

Substituted pyrazolones are useful in various fields of life. The characteristic colours of pyrazolones would indicate their possible use as dyes. Metal chelates of several multidentate pyrazolones have been used for purification of metals because of their high volatility and solubility in non-polar solvents [5,6]. Pyrazolones have been reported to possess antimicrobial[7], antidiuretic[8], antipyretic[9], antirheumatic[10], antibacterial[11], antifungal[12], antituberculosis[13] and anticancer[14] activities.

Commercially, one of the most important 5-pyrazolinone is N_1-phenyl-3-methyl-5-pyrazolone (MPP) which is known as "Developer Z". Complexes of MPP, $[Cu(MPP)_2]$, $[Fe(MPP)_3]$, $[Co(MPP)_2]$, $[Co(MPP)_2OH]$, $[Ag(MPP)]$ and $[Ag(MPP)_2]$ were reported[15]. In these complexes MPP showed monodenticity through the carbonyl oxygen.

Six-coordinate lanthanide perchlorate complexes having a general composition $[Ln(MPP)_6](ClO_4)_3]$and nine coordinate lanthanide nitrate complexes with a general formula $[Ln(MPP)_3(NO_3)_3]$ were reported [16]. The IR spectra of these complexes showed the monodenticity of MPP, the ionic nature of perchlorate-and the presence of bidentately coordinated nitrate groups.

Kuncheria and Indrasenan[17] synthesized a thorium(IV) complex of MPP. Conductance-and spectral measurements showed that this complex was seven-coordinate in which MPP acted as a monodentate ligand , coordinating through the ring carbonyl oxygen atom. Pt(II) and Pd(II) complexes of MPP were also reported[18]. The general formula of these complexes was $[M(H\text{-}MPP)_2Cl_2\ 2H_2O]$. Spectral investigations showed that in these cases the coordination was through the unsubstituted nitrogen atom.

The N_1-methyl derivative of MPP, known as antipyrine (AP), which is used as an antipyretic agent, was discovered by Knorr. A large number of drugs containing AP are known. Reports of coordination compounds of AP are also available.

Patel *et al*[19] synthesized octahedral complexes of AP with perchlorates of Mn(II), Co(II), Ni(II), Cr(III) and Fe(III). From the physico-chemical studies, they have proved that AP coordinated more strongly to the trivalent metal ions than to the divalent ones. The halocomplexes of Cu(II) having a general formula $[M(AP)_2X_2]$, where X = Cl or Br, were known[20]. Spectral studies showed that they were tetrahedral. Halocomplexes of Co (II) having a general formula, $[M(AP)_2X_2]$, where X = Cl, Br or I, were also reported[20]. They also had a tetrahedral geometry. Square-planar complexes of AP with Cu(II) nitrate were also reported[21].

Mourya and Mishra[22] prepared another complex $[Cr(NO)(CN)_2AP(H_2O)]$ which was octahedral in geometry with chromium in the +1 oxidation state. Complexes of AP with lanthanide perchlorates[23], iodides[24,25] and isothiocyanate [26,27] were known. Spectral studies showed that the thiocyanate was coordinated to the metal ion in these complexes. But perchlorate and iodide remained ionic in their respective complexes.

Complex of Co(II), Ni(II) and Cu(II) with N_1-isonicotinoyl-3-methyl-2-pyrazolin-5-ones (IMP) were studied in our laboratory[14]. They were characterized on the basis of elemental analyses, conductance- and magnetic measurements, IR,-UV-Vis- and ESR spectral studies and thermo gravimetric analyses. The Cu(II) complexes of IMP showed a solitary composition [Cu(IMP)X_2], where X = Cl, Br, NO_3, OAc, SCN , ClO_4 or ½SO_4. In all these complexes IMP acted as a neutral, bidentate ligand coordinating through C=O of the amide group and the carbonyl at position-5. Based on magnetic- and electronic spectral data, a square-planar geometry was assigned to these complexes.

The Co(II) and Ni(II) complexes of IMP were suggested to have an octahedral geometry. They had different compositions as the anion changes. Depending on the nature of the anions present in them, they were formulated differently as [M$(IMP)_2X_2$], where X = Br, I, NO_3, SCN or ClO_4; [M(IMP)$X_2(H_2O)_2$], where X= Cl or ½SO_4 and [M(IMP)$(OAc)_2$]. Presence of coordinated water molecules in the chloro- and sulphato complexes were established from IR spectral- and independent pyrolytic studies. IR spectra also indicated asymmetric, bidentate coordination of acetate groups in [Co(IMP)$(OAc)_2$] and [Ni(IMP)$(OAc)_2$]. IMP showed bidenticity through the amido-and carbonyl oxygen atoms.

In IMP, there is an active methylene group on which a desired group can be introduced. Co(II), Ni(II) and Cu(II) complexes of N_1-isonicotinoyl-3-methyl-4-(p-hydroxybenzilidene)-2-pyrazolin-5-one (IMHBP) were reported[14]. The molar conductance values of all these complexes showed their non-electrolytic nature.

The Cu(II) complexes were 4-coordinate having a general formula [Cu(IMHBP)X_2], where X= Cl, Br, NO_3, OAc, ClO_4 or ½SO_4 .The magnetic moment values and electronic spectral data indicated a square-planar geometry. The Co(II) and Ni(II) complexes showed three different compositions. The halo- and sulphato complexes had a general formula [M(IMHBP)X_2(H_2O)$_2$], where X = Cl, Br, I or ½SO_4. The nitrato- and acetato complexes appeared as [M(IMHBP)X_2], whereas the thiocyanato-and perchlorato complexes were formulated as [M(IMHBP)$_2$$X_2$] . In all these complexes,IMHBP acted as a neutral, bidentate ligand coordinating through the oxygen atoms of the amide group and carbonyl group at position-5.

Five different arylazopyrazolones viz. N_1-isonicotinoyl-3-methyl-4-phenyl azopyrazolone (IMPP), N_1-isonicotinoyl–3–methyl-4-(2-chlorophenylazo)-pyrazolone (IMCPP), N_1-isonicotinoyl-3-methyl-4-(2-methylphenylazo)-pyrazolone (IMMPP), N_1-isonicotinoyl-3-methyl-4-(3-nitrophenylazo)-pyrazolone (IMMNPP) and N_1-isonicotinoyl-3-methyl-4-(4-nitrophenylazo)-pyrazolone (IMPNPP)and their metal complexes were synthesized in our laboratory[14]. The analytical data showed that all chloro complexes of these ligands were 6-coordinate and bromo complexes appeared as 4-coordiante. Analytical-magnetic-and electronic spectral data showed an octahedral geometry for the chloro - and tetrahedral geometry for the bromo complexes of Cu(II). The Co(II) complexes of these ligands were tetrahedral, irrespective of the anion. All these complexes were non-electrolytes, showing coordinated nature of anions. The ligands were neutral and bidentate, coordinating through their azo nitrogen - and hydroxyl oxygen atoms.

4-Benzoyl-3-methyl-1-phenylpyrazolin-5-one (BMPP) is another important pyrazolone derivative, which was widely studied. Nine complexes of lanthanide nitrates with BMPP having the general formula $[Ln(BMPP)_2(NO_3)_3]$, where Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) or Y(III) were synthesized and their IR spectra studied[28]. In these complexes BMPP acted as a bidentate ligand coordinating through the oxygen atoms of both carbonyl groups and the nitrate radical acted as a monodentate ligand coordinating through one of the oxygen atoms with the lanthanide ion.

Okafor[29] reported some rare- earth chelates of BMPP. IR, UV and NMR spectra of the ligand and the chelates had been recorded to establish their structures. The complexes were reported to be six- coordinate.

Mirza and Bailey[30] studied the extraction of Pb(II) with BMPP. A quantitative extraction was possible at a pH of 3.2-6.0. The IR and NMR spectra of the complex formed during the extraction showed the coordination through two oxygen atoms.

The Ni(II) complexes of 1-phenyl-3-methyl-4-benzoyl-pyrazolin-5-one (HPMBP) had been isolated and characterized by microanalyses, UV- and IR spectral studies[54]. The complexes were shown to be dihydrated bis-chelates conforming to a general molecular formula of $[Ni(PMBP)_2(H_2O)_2]$,where PMBP is the anion of the ligand. UV- and IR spectral data confirmed that π bonding interaction was not present in any of these complexes, but suggested the σ bond formation between Ni(II) and the oxygen atom of the deprotonated hydroxyl group and by acceptance of an electron pair from the oxygen atom of the carbonyl group of the ligand's keto-enol tautomer. Lanthanide complexes of HPMBP of the type $Ln(PMBP)_3nH_2O$, for La(III) to Sm(III) and for Eu(III) to Yb(III) and Y(III) were also reported [55].

Indrasenan and Sarojini[56] synthesized nine complexes of lanthanide(III) nitrates with N-4-benzoylidene-3-methyl-1-phenylpyrazolin-5-one)isonicotinyl-hydrazine (BMPIH). All these complexes had a general formula $(Ln(BMPIH)_2(NO_3)_3]$, where Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) or Y(III). In all these complexes BMPIH acted as a neutral, bidentate ligand utilising the azomethine nitrogen- and the ring carbonyl oxygen atoms for coordination. The nitrate radicals coordinated in a unidentate fashion and, hence, a coordination number of 7 was assigned to the lanthanide ions.

Lanathanide chelates of 3-methyl-1-phenyl-4-trifluoroacetylpyrazolin-5-one (HPMTFP) had been synthesized and investigated by Okafor[57]. Characterisation of these complexes was made by elemental analyses, conductivity measurements, IR- and PMR spectral studies and the complexes were shown to be neutral.

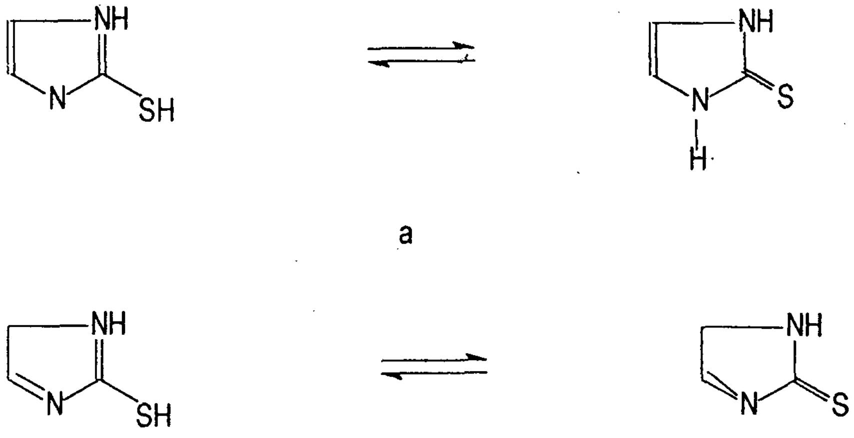
Nagar *et al* [58] reported complexes of uranyl ion with 1-phenyl-3-methyl-4-acetylpyrazolin-5-one (PMAP) and various oxo-donors. Analytical data established that they had the stoichiometry [$UO_2(PMAP)_2X$], where X is the oxo-donor.

A series of N_1-substituted–3-methylpyrazolin-5-ones were synthesized and their antibacterial activity had been studied[31]. All compounds were tested against *S. aureus* and *E. coli* and were found active. Singh and Singh[59] reported the synthesis and antitumor activity of N_1-(3pyridoyl)-3-methyl-4-(substituted azo)pyrazolin-5-ones. All compounds were tested against lymphoid leukemia L-1210 tumour system in mice and some of them showed significant antitumour activity.

The antitumour activity of N_1-isonicotinoyl-3-methylpyrazolin-5-one (IMP), N_1-isonicotinoyl–3-methyl-4-(p-hydroxybenzilidene)-2-pyrazolin-5-one (IMHBP) and their coordination compounds were studied in our laboratory[14]. The IMHPP and their complexes showed higher activity compared to the IMP analogues. The complexes with chloro anions were reported to possess appreciably high activity.

C. METAL COMPLEXES OF IMIDAZOLIN-2-THIONES - A REVIEW

Imidazolin-2-thiones are thio-derivatives of imidazoles. Due to the existence of a number of tautomeric forms, a complex system of nomenclature was adopted for these compounds. Two classes of imidazolin-2-thiones have to be differentiated. They are the 2(3H)- and 2(5H)- imidazolin-2 thiones. They tautomerize in the following manner[32] (**IV** a and b). **IV**(a) are the tautomeric forms of 2(3H)-imidazolinthione and **IV**(b) are those of 2(5H)–imidazolinthione.

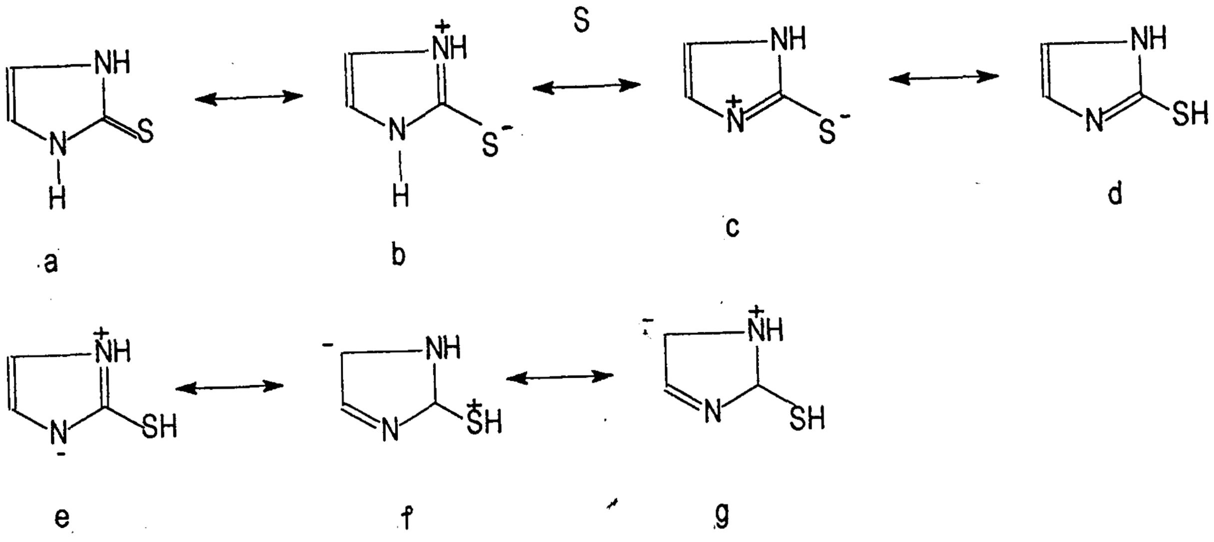


a

b

IV

The electronic structures of the 2(3H)- imidazolinthiones present a highly complex problem. The following structures (V a to g) are possible for the unsubstituted 2(3H)-imidazolinthione [32].



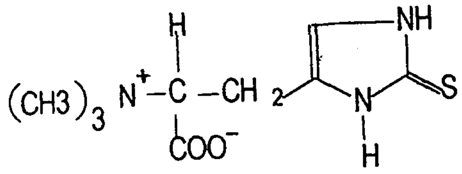
V

In solution, there exists a tautomeric equilibrium between the keto- and enol forms and in solids the keto form predominates.

The coordinating behavior of imidazolin-2-thiones are interesting due to the presence of exocyclic S-and the ring nitrogen atoms. This review covers the important aspects of the structural chemistry of metal complexes of imidazolin -2-thiones.

A number of imidazolin-2-thiones, by virtue of their pronounced antithyroid activity have found applications in clinical medicine. Stanley and Astwood[32] recognized the high antithyroid activity of imidazolin-2-thione and observed that in man, this compound is ten times more active than thiouracil.

A substituted imidazolin-2-thione, ergothioneine (**VI**) is recognized as a constituent of plant - and animal tissues[32].



VI

The antithyroid drugs, which have clinical activity, belong to the family of thioamides. Methimazole and carbimazole (**VII** a and b) are examples of such drugs[34].

a b

VII

The abilities of many heterocyclic thiones to reduce copper(II) and unpredictability of both the stoichiometry- and the structure of the reaction products have stimulated a large amount of research work in this field[35,36]. The biological importance of copper-sulphur interactions[37] and their applications in corrosion protection [37] also activated investigations in this field.

Complexes of imidazolin-2-thiones with copper were known very early[37]. Copper(I) halides form complexes with imidazolin-2-thione (imtH_2),1- methyl-imidazolin-2-thione(mimtH) and 1,3-dimethylimidazolin-2-thione (dmimt). They had general formulae $[\text{Cu (imtH}_2\text{) X}]$, where X= Cl, Br or I and $[\text{CuL}_2\text{X}]$, where L = (mimtH) or (dmimt) and X= Cl, Br or I. These complexes were characterized by physico-chemical-and spectroscopic techniques. Crystallographic studies of the above complexes had established the presence of trigonal-and tetrahedral environments for the metal, as well as terminal- and bridging sulphur donations for the ligands. In $[\text{Cu(imtH}_2\text{) X}]$, the Cu(I) was in a trigonal environment, but $[\text{Cu(mimt H)}_2\text{X}]$ had a dimeric formula with a tetrahedral geometry. However, $[\text{Cu(dmimt}_2\text{) X}]$ was trigonal in geometry.

With copper(II) nitrate (mimtH) produced $[\text{Cu(mimtH)}_3](\text{NO}_3)$[38]. The reduction of copper(II) to copper(I) by the ligand took place during complex formation. The diamagnetic character of this complex and the absence of any recognizable d-d spectra, strongly suggested the +1 state of the metal. The spectral- and single crystal X-ray studies had established the presence of copper (I) in distorted trigonal-planar $[Cu(mimtH)_3]^+$ cations and ionic nitrate. Thermal analysis in flowing air showed the complex to be anhydrous and it decomposed in the temperature range 140-745°C to copper(II) oxide.

A binuclear complex, $[Cu_2(mimtH)_5(SO_4)(H_2O)_3]$ had been reported to be synthesized by reaction between (mimtH) and copper(II) sulphate penta-hydrate[39]. The formula had been established by a combination of chemical- and thermal analyses. The binuclear cation $Cu_2(mimtH)_5^{2+}$ consisted of two trigonal copper(I) atoms, four terminal monodentate, S-bonded (mimtH) molecules and one S-bridged (mimtH) molecule.

Butler *et al*[40] reported the preparation of a complex of (mimtH) with palladium(II) chloride in acid solution. The stoichiometry, $Pd(mimtH)_4Cl_22H_2O$ had been established by chemical- and thermal analyses. Single crystal X-ray study and IR spectrum had confirmed the presence of uncoordinated water molecules, ionic chloride and square- planar $[PdS_4]^{2+}$ units bridged by H-bonds.

Raper *et al*[45] reported a coordination compound of (mimtH) which was prepared by the reaction between copper(II) tetrafluoroborate and (mimtH) in acetone-acetonitrile mixture. The empirical formula of the complex had been established as $Cu(mimtH)_3BF_3$ with the help of a variety of physico-chemical techniques. Thermal decomposition of the complex in air involved the evolution of (mimtH), desulpherisation of (mimtH) and copper(I,II) sulphide production, followed by conversion of the mixed sulphides to copper(II) oxide.

Colorless, crystalline solid complex having an empirical formula Cu(mimtH)CN was reported[46] The compound crystallized in a monoclinic unit cell. The coordination was through the sulphur atom. Thermal studies showed a three-stage decomposition for the complex.

Complexes of ($imtH_2$) and (mimtH) with halides of Cu(II), Zn(II), Cd(II) and Hg(II) were reported by Shanmugam and Satyanarayana[41]. The general formula of the complexes was [ML_2X)] for Cu(I) complexes, where, X = Cl or Br in which the ligand reduced the copper(II) to copper(I). For Zn(II), Cd(II) and Hg(II), the general formula was [ML_2X_2], where X = Cl or Br. The complexes were characterized by means of IR- and ^{13}C-NMR spectroscopic studies. By comparison with analogous complexes, the Zn(II), Cd(II) and Hg(II) complexes were assigned a tetrahedral geometry, while the Cu(I) complexes had a dimeric structure.

Crystal structures of two nickel(II) complexes of monodentate, S-donating (mimtH) had been established[44]. The paramagnetic, trans-octahedral complex, [$Ni(mimtH)_4Cl_2$] crystallized in an orthorhombic unit cell. The diamagnetic complex [$Ni(mimtH)_4](BF_4)_2$, contained a distorted square-planar cation which was H-bonded to the BF_4^- anions. The behavior of (mimtH) towards divalent nickel was particularly interesting in view of formation of both paramagnetic

$[Ni(mimtH)_4Cl_2]$ and $[Ni(mimtH)_2(NCS)_2]$ as well as diamagnetic $[Ni(mimtH)_4X_2]$, where X = Br, I, NO_3, BF_4 or ClO_4[60].

Raper and Crackett prepared complexes of ($imtH_2$) with Co(II) and Zn(II) salts[42]. Stoichiometries of the complexes, $M(imtH_2)_2X_2$ for the halides and $M(imtH_2)_4X_2$ for the nitrates and perchlorates had been established by chemical analyses. Thermal analyses had revealed the extent of hydration among cobalt complexes. The complexes were characterized by means of magnetic susceptibility data, infrared- and visible spectral measurements. The ligand coordinated by means of its exocyclic sulphur atom and one of its ring nitrogen atoms in the solid complexes. For the soluble complexes, coordination involved the sulphur atom alone. Thermal analyses showed a two-stage decomposition for these complexes. The magnetic moments of the bromo- and nitrato complexes were in the range associated with octahedral Co(II), whereas the remaining values were associated with tetrahedral Co(II).

Complexes of (mimtH) with Co(II)- and Zn(II) halides and perchlorates had been prepared[43]. Through Chemical analyses, their formulae had been suggested as $M(mimtH)_2X_2$,where X = Cl^-, Br^-or I^- and $[M(mimtH)_4(ClO_4)_2]$. On the basis of electrolytic conductivities in nitromethane, room temperature magnetic moments, solid-state IR-and visible spectra, the complexes had been shown to be tetrahedral in geometry. The ligand was monodentate and S-bonded in all cases.

Raper[61] studied the thermal decomposition of the Co(II) complexes of (mimtH) in air and argon by means of TG and DTG as well as in nitrogen by DTA. The reaction enthalpies from melting- and decomposition endotherms in nitrogen using DTA were calculated.

Complexes of, dimethylimidazolin-2-thione (dmimt) with Co(II)- and Ni(II) halides were reported[62]. The general stoichiometry was $[M(dmimt)_2X_2]$, where M = Co(II) or Ni(II) and X = Cl, Br or I. The pseudo-tetrahedral structures of these complexes and the S-bonding character of the ligand had been established by a combination of spectrochemical- and X-ray methods. The thermo chemistry of these complexes were also studied in detail[63]. The thermal decomposition of Ni(II) and Co(II) complexes of (dmimt) had been studied in air and argon by means of TG and DTG as well as in nitrogen by DTA. The reaction products in air had been identified by X-ray powder diffraction. Both sets of complexes degraded to the respective oxides in air over the temperature range 155-800° C.

Complexes with a general formula $[Fe(LH)_2Cl_2]$ were reported for $(imtH_2)$ and (mimtH)[64]. They were formed by the reaction between the ligand and $FeCl_24H_2O$ in rigorously anhydrous media. Infrared- and electronic spectra, as well as room temperature magnetic moment values showed the mononuclear, pseudo-tetrahedral geometry for the complexes. The ligands coordinated through the sulphur atom. Thermal decompositon studies of the complexes were carried out in flowing air. The complexes degraded to α-Fe_2O_3 in the temperature range 200-725°C.

Complexes of Cu(I) and Ag(I) were prepared with 4,5-diphenylimidazolin-2-thione in our laboratory[47]. They were characterized by chemical analyses, electrical conductance-and magnetic moment measurements and IR spectral data. The ligand, in this case also reduced Cu(II) to Cu(I) in the complexes. The copper complexes showed a general formula CuLX, where X = Cl^-, Br^-, NO_3^- or 0.5 SO_4^{2-}. The ligand acted as neutral and monodentate, coordinating through the thione slulphur. In the silver(I) complexes, [$AgLNO_3$] and [$AgL(0.5SO_4)$], the ligand behaved in a similar way. In nitrato-and sulphato complexes of Cu(I),an additional M-N interaction was noted.

4,5-diphenylimidazolin-2-thione acted as an anionic, bidentate ligand in a few complexes of copper and silver. These complexes had a general formula ML, where M = Cu(I) or Ag(I). Coordination of the ligand in these complexes was through the sulphur-and one of the ring nitrogen atoms[47].

The coordination properties of pyridine-2-thione (HPyS) and 1-hydroxy-pyridine-2-thione (HPyOS) with tertiary phosphines as co-ligands were reported by Lobana[65]. The metal ions used were Fe(II), Ru(II), Ni(II), Pd(II), Pt(II), Cu(II), Ag (I)and Hg(II). Reactions of anhydrous $FeCl_3$ with(HpyS) in ethanol, followed by the addition of tertiary phosphine (PPh_3), resulted in the formation of

$FeCl_2(HPyS)_2$. The X-ray analysis of this compound established a tetrahedral structure with HPyS binding to Fe(II) through the S atom and the free NH group forming an intermolecular H-bond with chlorine atoms of the adjacent molecules.

Palladium(II) acetate[65] with (HpyS) formed N,S bridged dimer which on reaction with PPh_3 in 1:2 mol ratio formed $Pd(PyS\text{-}S)_2(PPh_3)_2$. ^1H-and ^{13}C-NMR data and X-ray structure of these complexes showed a *trans*-square–planar geometry[66]. The analogous reaction of Pt(II), resulted in $Pt(PyS\text{-}S)_2$- $(PPh_3)_2$ having S-bonded HPyS.

With $CuCl_22H_2O$ and PPh_3, HPyS formed a complex $[CuCl(HPyS\text{-}S)(PPh_3)_2]$. X-ray analysis of this complex established tetrahedral structure with NH···Cl intra-molecular hydrogen bonding[67].

Very recently two new cavitand-based imidazoyl ligands and their Cu(I) complexes were reported[48]. The ligands were pre-organized to provide biologically representative imidazolyl donor for metal ion coordination. The ligands reported were 1,3,5-tris-(3-methyl-1-imidazolyl-2-thione)-2,4,6-triethyl-benzene (TriMIm) and 1,3-bis-(3-methyl-1-imidazolyl-2-thione)-2,4,6-triethylbenzene (BiMIm). Reaction of $[Cu(CH_3CN)_4]BF_4$ with TriMIm yielded $[(TriMIm)Cu]BF_4$ as a white solid. X-ray diffraction showed that TriMIm bound to the copper(I) ion in a trigonal- planar geometry. Reaction of $[Cu(CH_3CN)_4]BF_4$ with BiMIm in ethylene chloride afforded $[(BiMIm)Cu(CH_3CN)]BF_4$ as a white solid. This was characterized by X-ray diffraction studies and its structure revealed that Cu(I) ion in a trigonal geometry. The acetonitrile ligand in this complex was sufficiently labile to permit access to three -coordinate derivatives with CO, PMe_3 , N_3^- and SCN^- coordination.

D. CONCLUSIONS AND SIGNIFICANCE OF THE PRESENT INVESTIGATION

In this literature survey, the chelating properties of pyrazolin-5-ones and imidazolin-2-thiones have been reviewed. It has been found that even though a large quantum of work has been done on the coordination behaviors of pyrazolones, not much systematic study on the synthesis and characterization of N_1-substituted-3-methylpyrazolin-5-one has been made so far. Similarly, the coordination behaviors of alkyl substituted-and unsubstituted imidazolin-2-thiones have been investigated in detail. However, reports on the complexes of aryl substituted imidazolin-2-thiones are scanty.

Synthesis and characterization of biologically active compounds are being carried out in our laboratory for the last ten years. The changes in the biological activity upon coordination are also being subjected to study. The anticancer activity of substituted pyrazolin-5-ones and their metal chelates were studied in detail. These studies revealed the inhibitory power of these complexes on the growth of tumour in mice. Our earlier works pertaining to the anticancer activity of metal chelates of acetoacetanilide semicarbazone were also proved highly useful. Recently, the antifungal activity of metal chelates of semicarbazones, thiosemicarbazones and hydrazones were conducted in our laboratory. All these compounds showed a high degree of activity against different strains of fungi.

In earlier studies on anticancer activities of pyrazolin-5-ones, it has been observed that the OH substituent on pyrazolin-5-one derivatives increases the liposolubility of the compounds, which in turn enhances their cytotoxicity and tumour reducing power. Therefore, in the present investigation we have introduced a salicylyl group at the N_1 position of the pyrazolin-5-one. The coordination behavior of this compound, N_1 salicylyl-3-methylpyrazolin-5-one (SMP), may be interesting due to the presence of different coordination sites.

The coordination chemistry of heterocyclic thiones containing –NH–C=S group is of immense interest because such compounds mimic sulphur coordination in metal enzymes and comprise purine–and pyramidine bases. Therefore, we have synthesized some imidazolin-2-thiones and their metal chelates.

Thus, in the present investigation, one substituted pyrazolin-5-one and five different 4,5-disubstituted imidazolin-2-thiones as ligands were synthesized and used. The metal chelates of these ligands with several transition metal ions were also prepared. Structural characterization, thermal decomposition studies and investigations on antimicrobial activities of these compounds were undertaken. The kinetic parameters for the different stages of thermal decomposition of some of these complexes were calculated. Preliminary investigations on the antifungal activities of some of these complexes against four different fungal strains, namely *Aspergillus niger*, *Aspergillus paraciticus, Rhizopus orysea* and *Candida albicans* were conducted. Antibacterial activities of these complexes against three different bacterial strains, namely, *Psuedomonas aeruginosa, Staphylococcus aureus* and *E.coli* were also studied.

PART I

REAGENTS, APPARATUS AND GENERAL PROCEDURAL DETAILS

Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER II

REAGENTS, APPARATUS AND GENERAL PROCEDURAL DETAILS

This chapter deals with the details regarding the reagents and apparatus used and the methods adopted for the preparation and characterization of the compounds. The details of the instruments used for the physico-chemical investigations and their operational characteristics are also explained here. However, all specific synthetic procedures are explained in the relevant chapters.

A. METAL SALTS

The acetates, chlorides, nitrates and sulphates of Cu(II), Ni(II), Co(II), Mn(II), Ag(I), Fe(III) and Cd(II) were of BDH Analar grade. The hydrated salts were used as such for the preparation of the complexes. The bromides and perchlorates of the above metals were prepared by treating the respective metal carbonates with hydrobromic- and perchloric acids respectively. The products obtained were then dried over P_4O_{10}.

B. SOLVENTS

Solvents like ethanol, methanol, amyl alcohol, dimethylsulphoxide, dimethylformamide, diethyl ether etc, were used for the synthesis, extraction and recrystallisation of ligands and complexes. Ethanol was used after distillation. Others were of E.Merk, German reagents and were used as such. Dimethylsulphoxide and dimethylformamide used were of BDH spectroscopic grade.

C. LIGANDS

In the present investigation six different heterocyclic compounds have been synthesized and used as ligands. They include one, pyrazolin-5-one and five, imidazolin-2-thiones. They were prepared as follows.

1. N_1-salicylyl-3-methyl pyrazolin-5-one(SMP)

SMP was prepared by refluxing ethyl butyrate-2-salicylylhydrazone in orthodichlorobenzene for 5 h. The solution on keeping overnight, SMP separated out as a red solid. The SMP thus formed is filtered and washed with a small quantity of ethanol, and recrystallised from ethanol. Yield = 70%, m.p. 270°C.

2. 4,5-Disubstituted imidazolin-2-thione

4,5-Disubstituted imidazolin-2-thiones were synthesized by refluxing a mixture of respective benzoin and ammonium thiocyanate in isoamyl alcohol for about one hour. The crystalline products formed were filtered off, washed with ether and recrystallised from methanol.

In the present investigation five, different imidazolin-2-thiones were prepared.

a) 4,5-difuranyl-2H-imidazolin-2-thione (DFIT), yield = 50%, m.p . = > 330^0C.

b) 4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione (MDPIT), yield = 65%, m.p. = 245^0C.

c) 4,5-di(2-hydroxyphenyl)-2H-imidazolin-2-thione (HDPIT), yield = 45%, m.p. = 230^0C.

d) 4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione (CPDMPIT), yield = 60%, m.p. = 255^0C.

e) 4-(2-chlorophenyl)-5-(3,4-dichloromethylenedioxyphenyl)-2H-imidazolin-2-thione (CPDOMPIT), yield = 65%, m.p. = 220^0C.

The ethyl butyrate-2-salicylylhydrazone was synthesized as per reported methods[31]. Furoin, anisoin, salicyloin and mixed benzoins were synthesized by reported methods[49] and purified.

The details regarding the preparation of the ligands are given in the respective chapters.

D. ANALYTICAL METHODS

The purity of the compounds were checked by standard methods of semi microanalyses . The metal content of the complexes were estimated by standard methods[3]. Copper, cobalt, zinc and cadmium were estimated volumetrically after decomposing a known amount of their complexes with a mixture of nitric, hydrochloric- and perchloric acids. The digestion process was repeated for 3 or 4 times by adding fresh nitric acid. Finally the digestion was carried out with fresh hydrochloric acid. The residue was cooled, dissolved in distilled water and used for estimation. Copper present was estimated iodometrically using standard sodium thiosulphate solution. Cobalt, Zinc and Cadmium were determined by EDTA titrimetric method. Other metals were estimated by gravimetric methods. The metal content of all perchlorate samples were estimated by atomic absorption spectral method.

The anions present in the complexes were estimated by standard methods. Sulphate present in the complexes was determined gravimetrically as barium sulphate. The complexes were decomposed and the sulphate present in them was precipitated as barium sulphate using barium chloride solution. Chloride and bromide were estimated by Volhard's method after sodium carbonate fusion and dissolution in nitric acid. Thiocyanate was determined gravimetrically as silver thiocyanate. For the estimation of perchlorate, Kurz's[68] method was followed.

Carbon, Hydrogen and Nitrogen were estimated by microanalysis using Hitachi CHN-O rapid analyzer.

E. EXPERIMENTAL TECHNIQUES

Physico-chemical techniques such as electrical conductance- and magnetic susceptibility measurements along with spectral studies like UV-Vis, IR and ^{1}H-NMR have been used for the characterization of the complexes. Thermogravimetric studies have been carried out wherever possible.

1. Electrical conductance

The electrical conductances of the complexes were measured using their 10^{-3} molar solutions in dimethyl formamide and the molar conductance values were measured. The measurements were carried out using Systronic Conductivity Bridge 305 and dip-type cell calibrated with a solution of A.R. Potassium chloride. Corrections were applied on the basis

$$L_{solution} = L_{solute} + L_{solvent}.$$

2. Magnetic measurements

Magnetic susceptibilities of the complexes were determined by a Gouy-type magnetic balance. $Hg[Co(NCS)_4]$ was used as a calibrant. Diamagnetic corrections using Pascal's constants [50] were applied to get the corrected molar susceptibilities. From these, the effective magnetic moments were calculated. The measurements were made at room temperature.

3. Electronic spectra

The solutions of the complexes (10^{-3} M) solutions were prepared in dimethylformamide and the UV-Vis. spectra were recorded on UV-1601, Shimadzu spectrophotometer. For the insoluble complexes, the UV spectra were recorded using a mull technique[51].

4. Infrared spectra

The infrared spectra of the ligands and the complexes were recorded using KBr discs on FTIR-8101Shimadzu spectrophotometer. The measurements were taken in the range of 4000-400 cm^{-1}.

5. ^{1}H-NMR spectra

The ^{1}H-NMR spectra of the ligands and some of the diamagnetic complexes were recorded in $CDCl_3$ or DMSO-d_6 on a Varian 300 NMR spectrometer.

6. Thermogravimetry (TG)

The thermogravimetric curves of the complexes were recorded on a Mettler TA 4000 Thermal analysis system with following operational characteristics; heating rate, 20°/min; atmosphere-static air; sample size, 2-10 mg; crucible, platinum.

7. Independent pyrolytic studies

Independent pyrolytic studies of the complexes were carried out in order to check the mass-loss data obtained from TG experiments. A known amount of the complex was heated to 800° C in a silica crucible still a constant weight was obtained. The observed mass-losses were compared with those from TG data. The chemical identification of the final residue were also done.

8. Antimicrobial studies

The details of the materials used and procedures adopted are described in Part III of this thesis.

PART 1

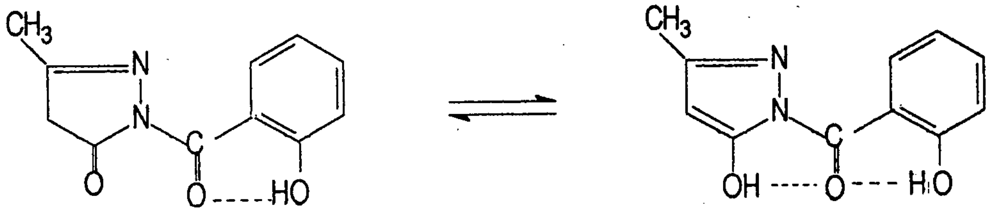
COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II) WITH N_1-SALICYLYL-3-METHYLPYRAZOLIN-5-ONE

Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER III

COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II) WITH N_1-SALICYLYL-3-METHYLPYRAZOLIN-5-ONE

Derivatives of pyrazolin-5-ones are extensively being used as dyes and pharmaceuticals. Reports on antitumour,[14] antifungal and antibacterial[31] activities of these compounds are also available. They act as chelating ligands towards transition metals and their coordination features are interesting because of the presence of different donor sites in these molecules. However, detailed investigations on the synthetic, structural and biological aspects of metal complexes of substituted pyrazolin-5-ones are scanty[14]. In substituted pyrazolin-5-ones, additional donor sites in close proximity of the carbonyl group on the heterocyclic ring, influence the ligational behaviour. Hence, it seems to be worthwhile and interesting to synthesize N_1-salicylyl-3-methyl-2-pyrazolin-5-one (SMP) (**I**) and its metal complexes and to conduct detailed investigations on their structure, magnetic- and spectral properties, stereochemistry, thermal decomposition patterns and biological activities.



I

A. EXPERIMENTAL

1. Materials and methods

The details regarding the chemicals used and the methods adopted for the characterization of the compounds involved in the present investigation are described in Chapter II.

2. Synthesis of ligand

Synthesis of N_1-salicylyl-3-methyl-2-pyrazolin-5-one involves the following three steps.

a) Preparation of salicylylhydrazine[71]

Methylsalicylate and hydrazine hydrate (99.9%) were mixed together in 1:1 molar ratio in the presence of a little dry ethanol (2 ml) and refluxed on a water bath for about 2 h. The reaction mixture was then cooled to room temperature and the solid separated out was filtered off, washed with ethanol and dried. The product thus obtained was recrystallised from ethanol.

b) Preparation of ethyl acetoacetate salicylylhydrazone

Ethyl acetoacetate (0.005 mol) was added to a solution of salicylylhydrazine (0.01 mol) in 1,4-dioxane (20 ml) and refluxed for about 4 h. The solvent was then removed by distillation under reduced pressure. The residue left behind was added to ice-cold water and the yellow solid thus separated out was recrystallised from ethanol.

c) Synthesis of SMP[31]

A solution of ethylacetoacetatesalicylylhydrazone (0.01 mol) in o-dichlorobenzene (20 ml) was refluxed for about 5 h and the contents were left overnight. The solid compound formed was filtered and recrystallised from ethanol (yield = 65%).

3. Synthesis of complexes

a) Complexes of cobalt(II)

An ethanolic solution (10 ml) of cobalt(II) acetate (0.001 mol) was added to an ethanolic solution (20 ml) of SMP and the mixture was refluxed for 15 min. The reaction mixture was cooled to room temperature. The solid product thus formed was filtered and washed with ethanol . It was dried under reduced pressure over anhydrous calcium chloride. In the case of the other cobalt(II) salts (chloride, bromide, nitrate and sulphate), solid complexes were formed at a higher pH. The pH of the reaction mixture was maintained between 8 and 9 by adding dilute ammonia solution. The thiocyanate complex of cobalt(II) with SMP was prepared in a different way. The cobalt(II) acetate (0.001 mol) solution in ethanol (10 ml) was added to an ethanolic solution (20 ml) of SMP (0.001 mol) containing stoichiometric quantity of ammonium thiocyanate.

b) Complexes of nickel(II)

The nickel(II) complexes were prepared in a method similar to that of cobalt(II) complexes.

c) Complexes of copper(II)

All the copper(II) complexes, except the thiocyanate complex, were formed in neutral medium. The thiocyanate complex of copper(II) with SMP was prepared in a same way as that of the thiocyanate complexes of cobalt(II) and nickel(II).

B. RESULTS AND DISCUSSION

The structures and properties of the ligand and the complexes had been elucidated with the help of analytical-, physico-chemical- and spectral data.

1. Characterisation of SMP

The SMP is red, non-hygroscopic solid with a melting point of 270°C. The purity of the compound was established by TLC and elemental analyses. The percentages of carbon, nitrogen and hydrogen were in close agreement with the suggested formula of $C_{11}H_{10}N_2O_3$ (Table 1). It was further characterised by IR spectral study (Table 10).

2. Formulae and general properties of the complexes

The analytical data of the ligand and the complexes are presented in Tables 1-3. All the complexes are non-hygroscopic and stable in air. They are insoluble in common solvents like water, methanol, ethanol, etc., but are soluble in DMF and DMSO.

TABLE 1

Analytical data of cobalt(II) complexes of N_1 –salicylyl-3-methylpyrazolin-5-one (SMP) (L)

Compound	Molecular Formula	Molecular weight	Colour	Melting point (°C)	Found (calculated) %				
					Metal	C	H	N	Anion
SMP (L)	$C_{11}H_{10}N_2O_3$	218	Red	270	--	59.66 (60.55)	4.60 (4.58)	12.64 (12.84)	--
$[CoL(OAc)_2]$	$CoC_{15}H_{16}N_2O_7$	395	Brown	> 300	14.77 (14.91)	46.02 (45.56)	4.15 (4.05)	7.18 (7.08)	--
$[CoLCl_2]$	$CoC_{11}H_{10}N_2O_3Cl_2$	347	Dark Brown	> 300	17.10 (16.71)	39.43 (38.04)	2.90 (2.88)	8.76 (8.06)	20.24 (20.46)
$[CoLBr_2]$	$CoC_{11}H_{10}N_2O_3Br_2$	436	Brown	> 300	13.80 (13.30)	30.19 (30.27)	2.30 (2.29)	6.89 (6.42)	37.01 (36.69)
$[CoL(NO_3)_2]$	$CoC_{11}H_{10}N_4O_9$	400	Brown	> 300	14.07 (14.50)	34.18 (33.00)	2.78 (2.50)	14.01 (14.00)	--
$[CoL(SO_4)]$	$CoC_{11}H_{10}N_2SO_7$	374	Light Brown	> 300	15.80 (15.50)	35.30 (35.29)	2.78 (2.67)	7.62 (7.48)	26.38 (26.20)
$[CoL(CNS)_2]$	$CoC_{13}H_{10}N_4S_2O_3$	393	Brown	> 300	15.37 (14.99)	40.80 (39.70)	2.70 (2.54)	14.30 (14.25)	30.28 (29.52)

TABLE 2

Analytical data of nickel(II) complexes of N_1 –salicylyl-3-methylpyrazolin-5-one (SMP)(L)

Compound	Molecular formula	Molecula-r weight	Colour	Melting point (°C)	Found (calculated) %				
					Metal	C	H	N	Anion
$[NiL(OAc)_2]$	$NiC_{15}H_{16}N_2O_7$	395	Red	> 340	14.14 (14.87)	46.08 (45.60)	4.12 (4.05)	7.12 (7.09)	--
$[NiLCl_2]$	$NiC_{11}H_{10}N_2O_3Cl_2$	348	Brick-red	> 340	16.20 (16.88)	37.57 (37.96)	2.90 (2.87)	8.00 (8.05)	20.18 (20.41)
$[NiLBr_2]$	$NiC_{11}H_{10}N_2O_3Br_2$	437	Brick-red	290	13.86 (13.44)	30.18 (30.22)	2.25 (2.28)	6.30 (6.40)	35.93 (36.63)
$[NiL(NO_3)_2]$	$NiC_{11}H_{10}N_4O_9$	400	Brownish-red	> 340	14.55 (14.64)	32.02 (32.94)	2.70 (2.49)	14.08 (13.97)	--
$[NiL(SO_4)]$	$NiC_{11}H_{10}N_2SO_7$	375	Brick-red	> 330	15.82 (15.66)	34.92 (35.22)	2.70 (2.66)	7.50 (7.47)	25.93 (26.15)
$[NiL(CNS)_2]$	$NiC_{13}H_{10}N_4S_2O_3$	393	Red	> 300	18.79 (19.04)	34.02 (33.61)	2.04 (2.54)	14.12 (14.26)	29.38 (29.53)

TABLE 3

Analytical data of copper(II) complexes of N_1 –salicylyl-3-methylpyrazolin-5-one (SMP) (L)

Compound	Molecular formula	Molecular weight	Colour	Melting point (°C)	Found (calculated) %				
					M	C	H	N	Anion
$[CuL(OAc)_2]$	$CuC_{15}H_{16}N_2O_7$	400	Brown	> 340	16.19 (15.89)	46.92 (45.05)	4.12 (4.05)	7.42 (7.08)	---
$[CuLCl_2]$	$CuC_{11}H_{10}N_2O_3Cl_2$	353	Brown	> 340	17.52 (18.01)	37.40 (37.44)	2.79 (2.83)	7.85 (7.94)	20.18 (20.14)
$[CuL(NO_3)_2]$	$CuC_{11}H_{10}N_4O_9$	406	Brown	> 340	15.81 (15.65)	32.09 (32.55)	2.85 (2.46)	14.08 (13.81)	---
$[CuL(SO_4)]$	$CuC_{11}H_{10}N_2SO_7$	380	Brown	> 340	17.05 (16.73)	34.52 (34.78)	2.70 (2.63)	7.40 (7.37)	25.85 (25.82)
$[CuL(ClO_4)_2]$	$CuC_{11}H_{10}N_2O_{11}Cl_2$	481	Brown	> 340	12.28 (13.21)	27.50 (27.47)	2.81 (2.08)	5.02 (5.82)	41.50 (41.40)
$[CuL(CNS)_2]$	$CuC_{13}H_{10}N_4S_2O_3$	398	Brown	> 340	15.25 (15.97)	39.24 (39.24)	2.49 (2.51)	14.02 (14.08)	29.08 (29.18)

The molar conductance of the complexes were determined in DMF. The values were compared with standard values[72] and found that the complexes act as non-electrolytes. The coordination of anions to the metal ions is hence confirmed.

The analytical- and molar conductance data of the complexes agree to a general formula $[MLX_2]$, where M = Co(II), Ni(II) or Cu(II), L = SMP and X = OAc, Cl, Br, NO_3, $\frac{1}{2}SO_4$, ClO_4 or CNS.

3. Magnetic behaviour

The magnetic susceptibility values of the complexes were determined using Gouy balance. The measurements were made at room temperature. The Gouy balance was standardized using $Hg[Co(NCS)_4]$ as calibrant.[77] The molar susceptibilities,together with the diamagnetic corrections and magnetic moment values of the complexes calculated from corrected magnetic susceptibilities are presented in Tables 4-6.

When a sample is weighed in the presence - and in the absence of a magnetic field, a weight change is observed. Diamagnetic materials having no unpaired electrons show a slight decrease in weight. Paramagnetic materials have unpaired electrons and they show an increase in weight in presence of magnetic field. From this change in weight, the paramagnetic susceptibility and effective magnetic moment can be calculated[77]. The magnetic moment values provide informations regarding the number of unpaired electrons present in a molecule and the orbitals in which they are situated. Some indications of the structures and geometries of the complexes are also obtained from the magnetic moment values [78]

The magnetic properties of transition metal complexes are discussed in detail by Figgis and Lewis[78]. Octahedral- and tetrahedral Co(II) complexes differ in their magnetic properties. In high-spin octahedral complexes of Co(II), the ground term is $^4T_{1g}$ which results in a considerable orbital contribution. Hence the observed magnetic moment value (5.20 B.M.) is higher than the spin-only value for three unpaired electrons (3.87 B.M.)[78]. The low-spin octahedral Co(II) complex has a ground term ^2E_g, hence no orbital contribution is expected. Therefore, the observed magnetic moment value of low-spin octahedral complex of Co(II) is very close to the spin-only value for one unpaired electron (1.73 B.M.). In tetrahedral high-spin complex of Co(II), the ground term is $^4A_2$ and has no orbital contribution. The expected magnetic moment is the spin-only value for three unpaired electrons (3.87 B.M.). However, the actual value lies between 4.40 and 4.80 B.M. This high value is due to the spin-orbit coupling perturbation. In the case of four-coordinate low-spin complexes, which are square-planar, it is not possible to predict accurately the magnetic properties. A magnetic moment rather above the spin-only value for one unpaired electron (1.73 B.M.) is expected[78]. The Co(II) complexes of SMP register magnetic moment values near 2.20 B.M. These values indicate the square-planar stereochemistry of the complexes. The dark colours of the complexes support this observation.

From the magnetic point of view, the complexes of Ni(II) may be divided into three categories[78]. (1) Six-coordinate octahedral, paramagnetic complexes with $^3A_{2g}$ ground term (both high-spin and low-spin) (2) four-coordinate, square-planar, diamagnetic complexes with a spin-singlet ground term and (3) four-coordinate, paramagnetic complexes with a triplet ground term. Of the two paramagnetic types, the octahedral complexes show magnetic moments in the range of 2.90-3.30 B.M. As per the ground term is $^3A_{2g}$, no orbital contribution is expected. A slightly higher value of the moment than the spin-only value for two electrons, is due to spin-orbit coupling or higher state mixing with the ground state. For tetrahedral complexes the magnetic moment values fall between 3.60 and 4.00 B.M. The higher value than the expected spin-only value for two electrons, is due to appreciable orbital contribution of the T ground state. Large distortions and inequalities in the field of the coordinated ligands are found to produce magnetic moments with small orbital contributions and the observed values are as low as 3.20 B.M. Square-planar Ni(II) complexes have a spin-singlet ground state and hence are diamagnetic. The Ni(II) complexes of SMP register magnetic moment values around 3.50 B.M. The complexes are intensely coloured. These observations indicate their tetrahedral geometry.

The copper(II) complexes usually have a distorted octahedral stereochemistry. A few are known with square-planar- or approximate tetrahedral stereochemistry. But the stereochemistry has little effect on the magnetic moment

TABLE 4

Magnetic susceptibilities and magnetic moments of cobalt(II) complexes of N_1 –salicylyl-3-methylpyrazolin-5-one (SMP)(L)

Complex	$\chi_M \times 10^{-6}$ cgs units	$-\chi_D \times 10^{-6}$ cgs units	$\chi_C \times 10^{-6}$ cgs units	μ_{eff} (B.M.)
$[CoL(OAc)_2]$	1915	118	2033	2.20
$[CoLCl_2]$	1926	132	2058	2.22
$[CoLBr_2]$	2026	114	2140	2.26
$[CoL\,(NO_3)_2]$	2082	123	2205	2.30
$[CoL(SO_4)]$	1866	138	2004	2.19
$[CoL(CNS)_2]$	2091	140	2231	2.31

χ_M = Molar susceptibility
χ_D = Diamagnetic correction
χ_C = Corrected molar susceptibility

TABLE 5

Magnetic susceptibilities and magnetic moments of nickel(II) complexes of N_1-salicylyl-3-methylpyrazolin-5-one (SMP)(L)

Complex	$\chi_M \times 10^{-6}$ cgs units	$-\chi_D \times 10^{-6}$ cgs units	$\chi_C \times 10^{-6}$ cgs units	μ_{eff} (B.M.)
$[NiL(OAc)_2]$	5123	158	5282	3.56
$[NiLCl_2]$	4636	181	4818	3.40
$[NiLBr_2]$	5257	204	5461	3.62
$[NiL(NO_3)_2]$	4476	172	4649	3.34
$[NiL(SO_4)]$	5167	174	5342	3.58
$[NiL(CNS)_2]$	5356	165	5522	3.64

χ_M = Molar susceptibility

χ_D = Diamagnetic correction

χ_C = Corrected molar susceptibility

TABLE 6

Magnetic susceptibilities and magnetic moments of copper(II) complexes of N_1–salicylyl-3-methylpyrazolin-5-one (SMP)(L)

Complex	$\chi_M \times 10^{-6}$ cgs units	$-\chi_D \times 10^{-6}$ cgs units	$\chi_C \times 10^{-6}$ cgs units	μ_{eff} (B.M.)
$[CuL(OAc)_2]$	1335	154	1490	1.89
$[CuLCl_2]$	1456	178	1635	1.98
$[CuL(NO_3)_2]$	1177	202	1380	1.82
$[CuL(SO_4)]$	1432	178	1611	1.96
$[CuL(ClO_4)_2]$	1312	175	1488	1.89
$[CuL(CNS)_2]$	1262	163	1426	1.85

χ_M = Molar susceptibility
χ_D = Diamagnetic correction
χ_C = Corrected molar susceptibility

of Cu(II) ion, which should be about 1.90 B.M. A regular octahedral Cu(II) complex has a ground term ^2E_g and hence no orbital contribution is expected. A magnetic moment value corresponding to one unpaired electron (1.73 B.M.) is expected. But the observed values fall in the range 1.80 to 2.10 B.M. A slightly higher value is due to the spin-orbit coupling. In regular tetrahedral Cu(II) complex, the ground term being a triplet state, orbital contribution is expected and the theoretically predicted value of magnetic moment is 2.20 B.M.[79]. But the observed value is near 1.95-2.00 B.M.[80]. Square-planar complexes of Cu(II) are reported to exhibit magnetic moments near 2.20 B.M.[81] The observed magnetic moment values of Cu(II) complexes of SMP are near 1.90 B.M. From these values, a four-coordinate tetrahedral geometry can be assigned to them. The brown colour of the complexes supports this observation.

4. Electronic spectra

The electronic spectra of all the complexes of SMP were recorded in DMF. The main electronic spectral bands of the complexes and their probable assignments are given in Tables 7-9.

The electronic spectrum exhibited by a coordination compound depends upon the energy of the metal d-orbitals, their degeneracy and the number of electrons distributed in them. These features in turn are controlled by the oxidation state of the metal, the number- and kind of ligands and the geometry of the complexes.[94]

Octahedral geometry is most commonly met with Co(II) complexes. Such complexes are pink in colour. The expected d-d transitions are:

$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) \simeq 1250 - 1100$ nm

$^4T_{1g}(F) \rightarrow {}^2E_g(F) \simeq 880$ nm

$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) \simeq 625 - 550$ nm

$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) \simeq 500 - 475$ nm

But the spectrum will be complicated by the poor resolution of several of these bands. This makes the assignment of the spectrum difficult, and only limited confidence on the calculated Δo and β values.

For tetrahedral Co(II) complexes, which are generally deep blue in colour, the expected transitions are:

$^4A_2(F) \rightarrow {}^4T_1(F) \simeq$ 1600 nm

$^4A_2(F) \rightarrow {}^4T_2(F) \simeq$ 660 nm

$^4A_2(F) \rightarrow {}^4T_1(P) \simeq$ 510 nm

For square-planar Co(II) complexes[95], which are generally dark-brown in colour, weak and broad bands are present in the region 1200-1000 nm.

In the present investigation, all the Co(II) complexes register broad bands around 1100 nm. The positions of these bands, together with the dark-brown colour of the complexes suggest a square-planar geometry for the Co(II) complexes of SMP.

For octahedral Ni(II) complexes the expected transitions are

$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \simeq$ 1170 nm

$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) \simeq$ 700 nm

$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) \simeq$ 395 nm

The ratio of the wave numbers of the first two bands lie in the range 1.6-1.8 which is one of the distinguishing features of octahedral nickel(II) complexes.[99]

The two readily accessible bands in the spectrum of tetrahedral Ni(II) complexes are:

$^3T_1(F) \rightarrow {}^3A_2(F) \simeq$ 1500 nm

$^3T_1(F) \rightarrow {}^3T_1(P) \simeq$ 700-595 nm

Along with this, another band due to $^3T_2(F) \rightarrow {}^3T_1(F)$ transition is observed at 3300-2000 nm. But this is usually marked by absorption of organic parts in the molecule or the solvent. Most of the tetrahedral complexes have intense blue colour due to the presence of an absorption band in the red part of the visible region. The occasional appearance of a green- or red colour in tetrahedral complexes is due to the charge-transfer absorption tailing into the visible region from the ultraviolet region.

The square-planar Ni(II) complexes are generally red, yellow or brown. This is due to the presence of absorption bands of medium intensities in the 600-580 nm range. However, other colours do occur when additional absorption bands are present.[97] All the Ni(II) complexes under the present investigation, show two bands near 1280 and 650 nm. These may be respectively, due to $^3A_2(F) \rightarrow {}^3T_1(F)$ and $^3T_1(F) \rightarrow {}^3T_1(P)$ transitions of tetrahedral complexes. The complexes are red in colour which may be due to charge-transfer absorptions.

A greenish-blue colour is associated with penta-or hexa-coordinated Cu(II) and brown-and violet colours indicate four-coordinate Cu(II)[83,84]. For octahedral Cu(II) complexes, only a single band due to the transition $^2E_g \rightarrow {}^2T_{2g}$ would result. But the observed band is very broad and clearly contains several components which is a result of tetragonal distortion due to Jahn-Teller effect[94].

In tetrahedral Cu(II) complexes the d-d transitions occur in the range 1430-1000 nm. If the region 1000-500 nm , where square- or distorted-octahedral Cu(II) complexes absorb is blank, it can be inferred that the complexes have a tetrahedral geometry. Also the energy of the bands of tetrahedral Cu(II) complexes are low compared to those of square-planar- or tetragonal complexes.

TABLE 7

Electronic spectral bands of Co(II) complexes of N_1-salicylyl-3-methylpyrazolin-5-one(SMP) (L) and their assignments

Complex	Band (nm)	Assignment	Geometry
$[CoL(OAc)_2]$	1058	d-d transitions	Square planar
$[CoLCl_2]$	1085	"	"
$[CoLBr_2]$	1050	"	"
$[CoL(NO_3)_2]$	1030	"	"
$[CoL(SO_4)$	1080	"	"
$[CoL\ (CNS)_2]$	1090	"	"

TABLE 8

Electronic spectral bands of Ni(II) complexes of N_1–salicylyl-3-methylpyrazolin-5-one (SMP)(L) and their assignments

Complex	Band (cm^{-1})	Assignment	Geometry
$[NiL(OAc)_2]$	1300 640	$^3T_1(F) \rightarrow {}^3A_2(F)$ $^3T_1(F) \rightarrow {}^3T_1(P)$	Tetrahedral
$[NiLCl_2]$	1298 650	$^3T_1(F) \rightarrow {}^3A_2(F)$ $^3T_1(F) \rightarrow {}^3T_1(P)$	Tetrahedral
$[NiLBr_2]$	1360 665	$^3T_1(F) \rightarrow {}^3A_2(F)$ $^3T_1(P) \rightarrow {}^3T_1(F)$	Tetrahedral
$[NiL(NO_3)_2]$	1285 660	$^3T_1(F) \rightarrow {}^3A_2(F)$ $^3T_1(F) \rightarrow {}^3T_1(P)$	Tetrahedral
$[NiL(SO_4)]$	1300 668	$^3T_1(F) \rightarrow {}^3A_2(F)$ $^3T_1(F) \rightarrow {}^3T_1(P)$	Tetrahedral
$[NiL(CNS)_2]$	1300 650	$^3T_1(F) \rightarrow {}^3A_2(F)$ $^3T_1(F) \rightarrow {}^3T_1(P)$	Tetrahedral

TABLE 9

Electronic spectral bands of Cu(II) complexes of N_1–salicylyl-3-methylpyrazolin-5-one (SMP)(L) and their assignments

Complex	Band (cm^{-1})	Assignment	Geometry
$[CuL(OAc)_2]$	1050	$^2T_2 \rightarrow E^2$	Tetrahedral
$[CuLCl_2]$	1030	$^2T_2 \rightarrow E^2$	Tetrahedral
$[CuL(NO_3)_2]$	1020	$^2T_2 \rightarrow E^2$	Tetrahedral
$[CuL(SO_4)]$	1045	$^2T_2 \rightarrow E^2$	Tetrahedral
$[CuL(ClO_4)_2]$	1015	$^2T_2 \rightarrow E^2$	Tetrahedral
$[CuL(CNS)_2]$	1028	$^2T_2 \rightarrow E^2$	Tetrahedral

In the present investigation, all the Cu(II) complexes of SMP register a band above 1000 nm and there are no bands in the region 1000-500 nm. Therefore, a tetrahedral geometry can be assigned to these complexes. The brown colour of the complexes supports this observation.

5. Infrared spectra

Infrared spectroscopy is one of the powerful- and versatile physical methods for structural- and analytical investigations. It is extremely useful in the identification and characterization of compounds and in assigning structures and geometries to them. The significant vibrational bands and their assignments of the ligand and the complexes are given in Tables 10-12. The assignments are made on the basis of comparisons with other pyrazolone system[73-78].

The IR spectra of SMP shows bands at 3168 and 2598 cm^{-1} which are due to the OH of enol and $\nu_{OH...O}$, respectively. A strong band at 1611 cm^{-1} is due to the stretching vibration of the intra-molecular hydrogen bonded amide carbonyl group. The absence of stretching band due to the ring carbonyl group in the ligand spectrum indicates the stabilisation of the enol form. The other bands of importance are 1555 (pyrazole ring stretch), 1484 $\beta_{as(CH_3)}$, 1365 $\beta_{s(CH_3)}$ and 740 cm^{-1} ν_{CH}. The structure of SMP is thus confirmed (**I**).

a) Cobalt(II) complexes

The Co(II) complexes of SMP are of two types. In [Co(SMP)$(OAc)_2$] and [Co(SMP)$(CNS)_2$] the two bands present in the ligand spectrum at 3168 and 2598 cm^{-1}, which are due to ν_{OH} of enol and $\nu_{OH....O}$, respectively, are absent. This shows that the ligand, when coordinated to the metal ion is in the keto form. In both complexes new bands appear near 3300 cm^{-1} which can be assigned to ν_{OH} of the salicylyl group. Due to coordination, the electron density of the amide oxygen decreases and hence the possibility for hydrogen bond decreases. New vibrational bands appear at 1692 and 1630 cm^{-1} in the spectra of [Co(SMP)$(OAc)_2$] and [Co(SMP)$(CNS)_2$], respectively. These can be attributed to the stretching vibration of coordinated ring C=O bond. The amide C=O stretching band in the free ligand is at 1611 cm^{-1}. The low frequency of the band is due to the hydrogen bonding with the enolic OH-and the salicylyl OH groups. In the complexes, this band shows a small negative shift, indicating coordination through this oxygen.

In the other Co(II) complexes, [Co(SMP)X_2], where X = Cl, Br, NO_3 or ½SO_4, the coordination pattern of SMP is different. The stretching frequency of enolic OH observed at 3168 cm^{-1} in the ligand spectrum is found to be shifted to a lower frequency region, i.e., near 3060 cm^{-1}, which indicates that the enolic OH of SMP is coordinating (without deprotonation) in these cases. This is further indicated by the fact that no new bands appear near 1650 cm^{-1}corresponding to the ring C=O group in the spectra of these complexes. It is worthwhile to note here that these complexes are formed in a slightly basic medium (pH 8-9) where the enol form of SMP gets stabilized. In the spectra of these complexes, new bands arise near 3400 cm^{-1} which are due to ν_{OH} of the salicylyl group. The amide $\nu_{C=O}$, which is present at 1611 cm^{-1} in the spectrum of the free ligand suffers a small negative shift during complex formation.

The forgoing spectral discussions indicate that the Co(II) complexes of SMP are of two types. In [Co(SMP)X_2], where X = OAc or CNS, SMP is in keto form and acts as a neutral, bidentate ligand coordinating through two oxygen atoms. But in all the other complexes, the enol form of SMP is coordinating without deprotonation and here again it acts as a neutral, bidentate ligand.

b) Nickel(II) complexes

In the nickel(II) complexes, the coordination pattern of SMP is the same as that in the Co(II) complexes. In [Ni(SMP)$(OAc)_2$] and [Ni(SMP)$(CNS)_2$] the keto form of the ligand coordinates. This is clear from the fact that the band corresponding to ν_{OH} of enol form is absent in the spectra of both the complexes. At the same time new bands appear at 1672 and 1688 cm^{-1}, respectively, which are due to the stretching vibration of coordinated C=O of the ring.

In all the other complexes of Ni(II), SMP is in the enol form which is clear from the presence of ν_{OH} enol band near 3050 cm^{-1}. Also, no new bands appear in the region 1680 cm^{-1}. This is consistent with the fact that this set of Ni(II) complexes are formed at the pH range of 8-9, where the enol form of the ligand gets stabilised.

c) Copper(II) complexes

All the Cu(II) complexes of SMP are formed in the neutral medium and they have similar IR features. A band at 3168 cm^{-1} in the ligand spectrum is absent in the spectra of all the Cu(II) complexes and new bands are found near 1670 cm^{-1}, indicating the coordination of the ligand in the keto form. The vibrational band of the amide C=O, which is present at a lower wave number in the ligand spectrum due to hydrogen bonding, shows a small negative shift in the spectra of the complexes, indicating coordination through the oxygen.

Thus in all Cu(II) complexes, SMP is in keto form and acts a neutral bidentate ligand, coordinating through the two oxygen atoms.

d) IR features of coordinated anions in the complexes

(i) *Acetato complexes*

Infrared spectroscopy can be used to determine the mode of coordination of anions in the complexes. Itoh and Bernstein[85] had noticed the $\nu_{as(CO_2^-)}$ and $\nu_{s(CO_2^-)}$ of free acetate radicals around 1560 and 1416 cm^{-1}, respectively. When the carboxylate group acts as unidentate ligand, one of the C–O bonds experiences enhanced double bond character and gives rise to a high frequency $\nu_{(CO_2^-)}$ band. Hence the separation between the two bands is much larger than that in the free ion. When it acts as bidentate ligand, the trend became opposite and the separation becomes smaller than that in the free acetate radical. But in the complexes where it acts as bridging ligand ,the two ν_{CO} are close to the free ion values[86-88].

In the present case, determination of the status of the acetate group is difficult from the IR spectra alone. In the region where $\nu_{C=O}$ of acetate are expected, there are bands due to ligand vibrations. However, in [CoSMP(OAc)$_2$] two bands at 1575 and 1400 cm^{-1}, in [NiSMP(OAc)$_2$] the bands at 1526 and 1400 cm^{-1} and in [CuSMP(OAc)$_2$] those at 1570 and 1406 cm^{-1}can be attributed to the $\nu_{c=o}$ and ν_{c-o^-} of the coordinated acetate groups. The position of these bands and their wide separation ($\Delta\nu \approx 150$cm^{-1}) show that the acetate groups are acting as unidentate ligands in these complexes.

(ii) *Halo complexes*

In halo complexes, the bands due to M–X ,(where X = Cl or Br)vibrations are observed below 400 cm^{-1} which is out of the range of our instrument. But the analytical data indicate the presence of two halogen atoms per molecule of the complex. Non-conducting nature of the complexes shows that the halogen atoms are coordinated to the metal ions.

(iii) *Nitrato complexes*

The free nitrate ion has a D_{3h} symmetry and the IR spectrum is simple. The totally symmetric N–O stretching mode is IR inactive, but the doubly degenerate N–O stretching mode gives rise to a strong band at ~ 1390 cm^{-1}. There are two more IR active deformation modes, one of which is doubly degenerate, at 830 cm^{-1} and 720 cm^{-1}. When nitrate radical is coordinated, the effective symmetry is reduced to C_{2V}, the degenerous states split and all modes become IR active. Kunchandy and Indrasen[76] reported the ν_1, ν_4 and ν_2 modes of vibration of the coordinated nitrate radicals at 1430, 1300 and 1025 cm^{-1}, respectively, and that the ν_1 and ν_4 modes of the nitrate radical are the two split- components of the ν_3 mode of the free nitrate radical. In the present investigation, all the nitrato complexes show the vibrational bands of coordinated nitrate groups. In $[Co(SMP)(NO_3)_2]$, new bands appear at 1427, 1348 and at 1043 cm^{-1}, in $[Ni(SMP)(NO_3)_2]$ the new bands are at 1434, 1300 and 1020 cm^{-1} and in $[Cu(SMP)(NO_3)_2]$ these bands are at 1410, 1303 and 1010 cm^{-1}. The magnitudes of splitting of ν_1 and ν_4 are of the order of 79, 134 and 107 cm^{-1}, respectively. This type of splittings are reported in complexes where the nitrate ion coordinate unidentately to the metal ions[90]. Therefore, it can be inferred that in the nitrate complexes under present investigation, nitrate radicals act as monodentate ligands.

(iv) *Sulphato complexes*

The sulphate radical can act as unidentate, bidentate, chelate or bidentate bridging ligand[91]. The free sulphate radical has a regular tetrahedral structure with T_d symmetry. The symmetry is lowered to C_{3V} when it acts as a unidentate ligand. When two oxygen atoms are coordinated, either to the same metal ion or to different ones, the symmetry is lowered still further to C_{2V}. In free sulphate radical, of the four fundamentals, only ν_3 and ν_4 are IR active. The ν_1 appears as a weak band near 970 cm^{-1}. The ν_3 and ν_4 appear near 1135 and 617 cm^{-1}, respectively.

When sulphate radical acts as unidentate ligand, ν_3 splits into two bands near 1130 and 1038 cm^{-1} and ν_4 splits into another set of two bands near 645 and 604 cm^{-1}. The ν_1 and ν_2 appear near 980 and 438 cm^{-1}, respectively. When sulphate radical acts as a bidentate ligand, ν_1 and ν_2 are observed around 995 and 462 cm^{-1}, respectively, and ν_3 and ν_4 split into three bands each[92]. The three components of ν_3 are seen at 1170, 1105 and 1055 cm^{-1} and those of ν_4 at 641, 610 and 571 cm^{-1}. Bidentate bridging sulphate groups show the same splitting pattern.

In the sulphato complexes of SMP with Co(II), Ni(II) and Cu(II), the sulphate radicals act as bidentate ligands. It is clear from the IR data of the sulphato complexes (Tables 10-12).

(v) *Perchlorato complexes*

The perchlorate radical has a T_d symmetry with a characteristic triply degenerate Cl-O stretching modes around 1110 cm^{-1}. A weak band due to IR-forbidden symmetric stretching vibration, at about 980 cm^{-1} is also present[91]. When perchlorate acts as a unidentate ligand, the symmetry lowers to C_{3V} and three bands near 1120, 1040 and 920 cm^{-1} appear. In complexes containing bidentate perchlorate ligand, four Cl–O stretching bands are observed around 1200, 1100, 1000 and 900 cm^{-1}.

In $[Cu(SMP)(ClO_4)_2]$, ClO_4^- radicals act as unidentate ligands. The charactersitic vibrational bands appear at 1140, 1035 and 930 cm^{-1} in the IR spectrum of the complex.

(vi) *Thiocyanato complexes*

The thiocyanate group can cordinate to a metal through the nitrogen- or the sulphur atoms or both. Generally 'Class a' metal ions prefer M-N bonds and 'Class b' metal ions prefer M-S bonds[14]. The mode of coordination is influenced by other factors, such as the oxidation state of the metal, the nature of the other ligands in the complex and steric consideration.

The CN stretching frequency of thiocyanate (ν_1) is generally lower in N-bonded complexes (near 2050 cm^{-1}) than in S-bonded ones (near 2100 cm^{-1}).

TABLE 10

Significant IR spectral bands (cm^{-1}) of N$_1$–salicylyl-3-methylpyrazolin-5-one (SMP)(L), its cobalt(II) complexes and their assignments

SMP (L)	[CoL(OAc)$_2$]	[CoLCl$_2$]	[CoLBr$_2$]	[CoL(NO$_3$)$_2$]	[CoL(SO$_4$)]	[CoL(CNS)$_2$]	Assignments
	3325	3404	3409	3410	3323	3396	ν_{OH}
3168		3084	3058	3065	3056		ν_{OH} of enol
2598							$\nu_{OH..O}$
						2050	ν_{CN} of CNS
	1692					1630	$\nu_{C=O}$ of ring
1611	1606	1600	1606	1600	1600	1593	$\nu_{C=O}$ of amide
	1575						$\nu_{C=O}$ of acetate
1555	1555	1560	1553	1566	1573	1560	Pyrazole ring stretch
1484	1475	1467	1474	1474	1474	1460	β_{as} of CH$_3$
				1427			ν_1 of NO$_3^-$
	1400						$\nu_{C=O}$ of acetate
1365	1361	1379	1387	1381	1378	1389	β_s CH$_3$
				1348			ν_4 of NO$_3^-$
				1043			ν_2 of NO$_3^-$
						839	ν_3 of CNS$^-$
					1142 1082 976 758 625 459		SO$_4^{--}$

TABLE 11

Significant IR spectral bands (cm^{-1}) of N_1 ~salicylyl-3-methylpyrazolin-5-one (SMP)(L), its nickel(II) complexes and their assignments

SMP (L)	$[NiL(OAc)_2]$	$[NiLCl_2]$	$[NiLBr_2]$	$[NiL(NO_3)_2]$	$[NiL(SO_4)]$	$[NiL(CNS)_2]$	Assignments
	3423	3409	3416	3350	3350	3426	ν_{OH}
3168		3058	3071	3060	3058		ν_{OH} of enol
2598							$\nu_{OH...O}$
						2040	ν_{CN} of CNS^-
	1672					1688	$\nu_{C=O}$ of ring
1611	1610	1600	1606	1606	1606	1615	$\nu_{C=O}$ of amide
1555	1555	1566	1573	1573	1573	1579	Pyrazole ring freq.
	1526						$\nu_{C=O}$ of acetate
1484	1482	1474	1480	1474	1474	1460	β_{as} of CH_3
				1434			ν_1 of NO_3
	1400						$\nu_{C=O}$ of acetate
1385	1381	1394	1374	1387	1394	1369	β_s of CH_3
				1300 (w)			ν_4 of NO_3^-
					1248		SO_4^{--}
					1142		SO_4^{--}
				1020			ν_2 of NO_3^-
					983	845	ν_3 of CNS^-
					744		SO_4^{--}
					618		SO_4^{--}
					559		SO_4^{--}

TABLE 12

Significant IR spectral bands (cm^{-1}) of N$_1$ –salicylyl-3-methylpyrazolin-5-one (SMP)(L), its copper(II) complexes and their assignments

SMP (L)	[CuL(OAc)$_2$]	[CuLCl$_2$]	[CuL(NO$_3$)$_2$]	[CuL(SO$_4$)]	CuL(ClO$_4$)$_2$	[CuL(CNS)$_2$]	Assignments
	3424	3427	3360	3427	3296	3290	ν_{OH}
3168							ν_{OH} of enol
2598							$\nu_{OH...O}$
						2109	ν_{CN} of CNS
	1720	1722	1720	1700	1732	1710	
	1680	1680	1680	1673	1684	1670	$\nu_{C=O}$ ring
1611	1610	1608	1608	1607	1610	1607	$\nu_{C=O}$ amide
	1570						C=O of acetate
1555	1560	1565	1569	1562	1565	1563	Pyrazole ring stretching
1484	1473	1476	1486	1478	1481	1483	β_{as} of CH$_3$
	1406						C-O of acetate
			1410				ν_1 of NO$_3^-$
1365	1361	1379	1387	1381	1378	1389	ν_s of C=O
			1303				ν_4 of NO$_3^-$
					1140		perchlorate
					1035		perchlorate
			1010				ν_2 of NO$_3^-$
					930		perchlorate
						845	ν_3 of CNS
				1225			SO$_4^-$
				1140			
				970			
				710			
				630			
				570			
				455			

The value is well above 2100 cm^{-1}, when thiocyanate acts as a bridging ligand[98]. The N-bonded complexes show additional bands in the region 860-780 cm^{-1} and a single sharp band around 480 cm^{-1} which are due to ν_3 and ν_2 modes of vibration, respectively. In the S-bonded complexes, these bands occur, respectively, around 720-690 and 420 cm^{-1}.

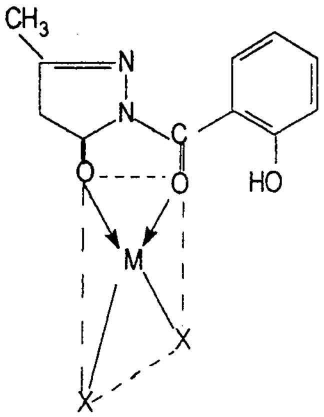
The thiocyanate complexes under present investigation show a strong band near 2050 cm^{-1} (ν_1) suggesting N-coordination in them. The bands near 845 and 480 cm^{-1} can be assigned to ν_2 and ν_3 modes of vibrations. Hence in all these complexes the thiocyanate radicals act as monodentate ligands, coordinating through N-atom.

6. Thermal analysis

The thermograms of five copper complexes of SMP were recorded in oxygen atmosphere. All these complexes decompose in a single step. The decomposition starts around 300°C and ends at about 500°C. The end products are chemically identified as CuO. The thermal decomposition data are in good agreement with the proposed structures of the complexes. Independent pyrolytic studies of the complexes were also carried out. The details are given in Part II of this thesis.

C. CONCLUSIONS

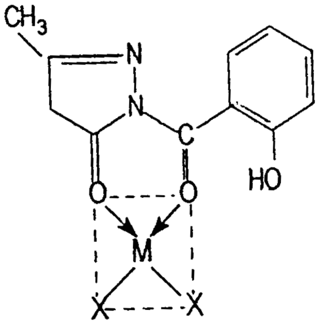
Coordination compounds of Co(II), Ni(II) and Cu(II) with N_1-salicylyl-3-methyl-2-pyrazolin-5-one (SMP) (L) were prepared and their physico-chemical properties were studied. The complexes had a general formula [M(SMP)X_2], where M = Co(II), Ni(II) or Cu(II) and X = OAc, Cl, Br, NO_3, ½SO_4, ClO_4 or CNS. Conductance-and IR spectral studies revealed the coordinated nature of counter anions in all the complexes. Based on magnetic measurements and electronic spectral studies, geometries were assigned to them. All the Cu(II) and Ni(II) complexes were found to be tetrahedral-, whereas the Co(II) complexes were square- planar in geometry. In all the complexes, SMP acted as bidentate ligand coordinating through two oxygen atoms. In all the Cu(II) complexes and in [Co(SMP)X_2] and [Ni(SMP)X_2], where X = OAc or CNS, the keto form of the ligand coordinated while in all the other complexes the enol form of the ligand coordinated without deprotonation. The structures of the complexes are given below (**II-V**).



when M = Cu(II), X = OAc, Cl, NO_3, ½SO_4 ClO_4 or CNS

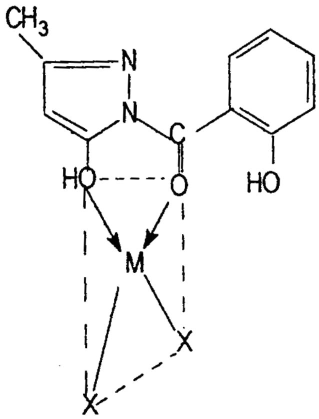
M = Ni(II), X = OAc or CNS

II



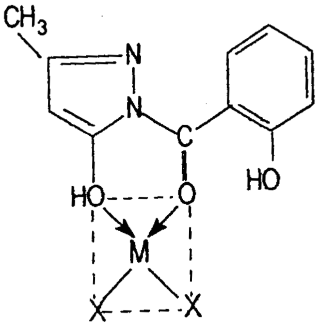
When M = Co(II) and
X = OAc or CNS

III



When M = Ni(II) and
X = Cl, Br, NO_3 or ½SO_4

IV



When M = Co(II) and
X = Cl, Br, NO_3 or ½SO_4

V

PART 1

COMPLEXES OF COPPER(I) WITH SYMMETRICALLY 4,5-DISUBSTITUTED IMIDAZOLIN-2-THIONES

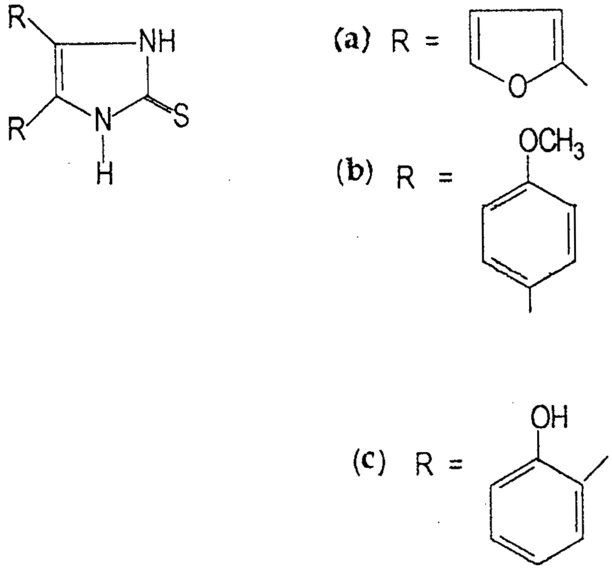
Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER IV

COMPLEXES OF COPPER(I) WITH SYMMETRICALLY 4,5-DISUBSTITUTED IMIDAZOLIN-2-THIONES

The coordination chemistry of heterocyclic thiones containing –NH–CS ↔ N=CSH tautomeric linkage is of immense interest because such compounds (a) mimic cystine sulphur coordination in metalloenzymes, (b) show electronic- and structural properties of the active sites in copper blue proteins involving SN coordination and (c) comprise purine and pyrimidine bases.[65]

Heterocyclic thiones exhibit diverse donor characteristics due to the presence of exocyclic sulphur- and two ring nitrogen atoms. Many reviews, devoted to the donor characteristics of such compounds, indicate that most of the works undertaken are on the donor properties of unsubstituted imidazolin-2-thione and their simple derivatives[100,111]. But systematic works on 4,5-disubstituted imidazolin-2-thiones are rare[47]. Therefore, as a part of the present investigation, several new 4,5-disubstituted imidazolin-2-thiones have been synthesised. Among them, three are symmetrically 4,5-di substituted ones. They are represented in (**I**).



I

Their chemical abstract names are (a) 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione (DFIT) (L), (b) 1,3-dihydro-4,5di(4-methoxyphenyl)2H-imidazolin-2-thione (MDPIT)(L') and (c) 1,3-dihydro-4,5di(2-hydroxyphenyl)2H-imidazolin-2-thione (HDPIT) (L"), respectively.

A. EXPERIMENTAL

1. Materials and methods

The details regarding the materials and methods used are given in Chapter II.

2. Synthesis of ligands

4,5-disubstituted imidazolin-2-thiones were synthesized from benzoins according to a general method[115]. Benzoins were synthesized by refluxing a solution of the respective aldehyde (0.05 mol) in 50% ethanol (5 ml) with 50% aqueous solution of NaCN (10 ml) for 2.5 h. The respective benzoin - furoin, anisoin or salicyloin, (0.05 mol) and ammonium thiocyanate (0.12 mol) were refluxed in isoamyl alcohol (250 ml) for about 1 h. The solid that separated out was filtered off after cooling the reaction mixture to room temperature , washed thoroughly with ether and dried over P_4O_{10}. The yields of the products were about 60%. The products were dried and recrystallised from ethanol.

3. Synthesis of complexes

The reactions of the three ligands with several copper(II) salts were carried out so as to isolate the solid complexes. A methanolic solution (25 ml) of the ligand (0.001 mol) was kept at refluxing temperature and to this, a methanolic solution (20 ml) of the copper(II) salt (0.001 mol) was added slowly. Certain complexes precipitated out instantly, while the others formed only after refluxing for 1 h. The complexes were filtered off, washed thoroughly with methanol and dried under reduced pressure over P_4O_{10}. The thiocyanate complexes were prepared by a different method. A methanolic solution of Cu(II) acetate was added to a methanolic solution (20 ml) of the ligand containing stoichiometric quantity of ammonium thiocyanate. The solid complexes that formed were filtered off, washed with methanol and dried under reduced pressure over P_4O_{10}.

B. RESULTS AND DISCUSSION

The properties, structures and geometries of the complexes had been elucidated with the help of analytical data and various other physico-chemical investigations.

1. Characterisation of ligands

The three ligands synthesized are non-hygroscopic solids. The purities of the compounds were established by TLC technique. The elemental analyses data (Table 1) are in accordance with the formulae of the ligands. Further confirmation of their structures had been made using IR spectral studies (Tables 8-10).

2. Formulae and general properties of complexes

The solid complexes of three ligands were synthesized using different copper(II) salts, CuX_2, where X = OAc, Cl, Br, NO_3, $\frac{1}{2}SO_4$, ClO_4 or CNS. All

TABLE 1

Analytical data of the ligands

Name of the ligand[@]	Molecular formula	Molecular weight	Colour	M.P. (°C)	Yield (%)	Found (calculated) %		
						C	H	N
DFIT(L)	$C_{11}H_8N_2SO_2$	232	Brown	> 330	70	56.32 (56.89)	3.44 (3.48)	13.15 (12.06)
MDPIT(L')	$C_{17}H_{16}N_2SO_2$	313	Light-yellow	245	60	65.23 (65.17)	5.10 (5.30)	8.59 (8.94)
HDPIT(L")	$C_{15}H_{12}N_2SO_2$	284	Yellow	230	55	64.28 (63.38)	4.22 (4.40)	9.05 (10.02)

[@]DFIT = 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione
MDPIT = 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
HDPIT = 1,3-dihydro-4,5-di(2-hydroxyphenyl)-2H-imidazolin-2-thione

TABLE 2

Analytical data of copper(I) complexes of 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione(DFIT) (L)

Complex	Molecular formula	Molecular weight	Colour	Found (calculated) %				
				Metal	C	H	N	Anion
$[CuL(OAc)(H_2O)]$	$CuC_{13}H_{12}N_2SO_5$	372	Light- green	16.18 (17.09)	31.34 (31.99)	2.80 (3.20)	7.56 (7.50)	--
$[CuLCl(H_2O)]$	$CuC_{11}H_{10}N_2SO_3Cl$	348	Light-green	18.55 (18.24)	37.28 (37.93)	2.50 (2.87)	8.92 (8.04)	11.08 (10.18)
$[CuLBr(H_2O)]$	$CuC_{11}H_{10}N_2SO_3Br$	393	Yellowish-green	16.19 (16.17)	33.88 (33.63)	2.50 (2.54)	7.02 (7.13)	20.25 (20.38)
$[CuL(NO_3)(H_2O)]$	$CuC_{11}H_{10}N_3SO_6$	375	Pale-green	17.68 (16.95)	35.49 (35.24)	2.70 (2.67)	10.28 (11.21)	--
$[Cu_2L_2(SO_4)(H_2O)_2]$	$Cu_2C_{22}H_{20}N_4S_3O_{10}$	723	Light- green	17.88 (17.56)	37.24 (36.51)	2.30 (2.76)	7.38 (7.74)	14.50 (13.55)
$[CuL(ClO_4)(H_2O)]$	$CuC_{11}H_{10}N_2SO_7Cl$	412	Bluish-green	15.02 (15.41)	33.02 (32.03)	2.38 (2.42)	6.29 (6.79)	25.00 (24.13)
$[CuL(CNS)(H_2O)]$	$CuC_{12}H_{10}N_3S_2O_3$	371	Yellowish-green	18.09 (17.13)	39.02 (38.86)	2.30 (2.69)	12.08 (11.33)	16.45 (15.65)

TABLE 3

Analytical data of copper(I) complexes of 1,3 dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione (MDPIT) (L')

Complex	Molecular formula	Molecular weight	Colour	Found (calculated) %				
				Metal	C	H	N	Anion
[CuL'(OAc)(H_2O)]	$CuC_{19}H_{20}N_2SO_5$	453	Yellow	15.17 (14.03)	50.76 (50.38)	4.70 (4.41)	7.02 (6.18)	--
[CuL'Cl(H_2O)]	$CuC_{17}H_{17}N_2SO_3Cl$	429	Bluish-violet	15.16 (14.80)	47.84 (47.55)	3.70 (3.96)	7.21 (6.52)	8.24 (8.26)
[CuL'Br(H_2O)]	$CuC_{17}H_{17}N_2SO_3Br$	474	Light-blue	12.84 (13.41)	43.04 (43.08)	3.50 (3.59)	6.80 (5.91)	15.08 (15.89)
[CuL'(NO_3)(H_2O)]	$CuC_{17}H_{17}N_3SO_6$	456	Yellow	12.43 (13.94)	44.52 (44.78)	3.60 (3.73)	8.16 (9.22)	--
[$Cu_2L'_2$(SO_4)(H_2O)$_2$]	$Cu_2C_{34}H_{34}N_4S_3O_{10}$	885	Yellow	13.3 (14.35)	47.08 (46.10)	3.99 (3.84)	6.48 (6.32)	10.98 (11.07)
[CuL'(ClO_4)(H_2O)]	$CuC_{17}H_{17}N_2SO_6Cl$	493	Yellow	13.38 (12.88)	41.02 (41.37)	3.40 (3.44)	6.02 (5.67)	20.02 (20.08)
[CuL'(CNS)(H_2O)]	$CuC_{18}H_{17}N_3S_2O_3$	452	Yellow	13.51 (14.06)	47.03 (47.84)	3.98 (3.76)	8.92 (9.30)	12.86 (12.84)

TABLE 4

Analytical data of copper(I) complexes of 1,3-dihydro-4,5-di(2-hydroxyphenyl)-2H-imidazolin-2-thione (HDPIT)(L")

Complex	Molecular formula	Molecular weight	Colour	Found (calculated) %				
				Metal	C	H	N	Anion
$[CuL''Cl(H_2O)]$	$CuC_{15}H_{14}N_2SO_3Cl$	401	Greenish-yellow	15.67 (15.83)	45.08 (44.89)	3.50 (3.49)	6.99 (6.98)	8.90 (8.84)
$[CuL''Br(H_2O)]$	$CuC_{15}H_{14}N_2SO_3Br$	446	Yellow	14.99 (14.25)	40.12 (40.4)	3.29 (3.14)	6.29 (6.28)	17.83 (17.95)
$[CuL''(NO_3)(H_2O)]$	$CuC_{15}H_{14}N_3SO_6$	428	Reddish-yellow	14.96 (14.85)	41.50 (42.10)	3.37 (3.27)	9.89 (9.82)	--
$[Cu_2L''_2(SO_4)(H_2O)_2]$	$Cu_2C_{30}H_{28}N_4S_3O_{10}$	829	Yellow	14.90 (15.31)	42.98 (43.42)	3.48 (3.37)	6.89 (6.75)	11.79 (11.82)
$[CuL''(ClO_4)(H_2O)]$	$CuC_{15}H_{14}N_2SO_7Cl$	465	Light-yellow	13.02 (13.67)	37.92 (38.75)	3.48 (3.01)	6.12 (6.02)	21.83 (21.31)

these complexes are non-hygroscopic and stable in air. They are insoluble in common organic solvents like methanol, ethanol, etc., but are freely soluble in DMF and DMSO.

The analytical data of the complexes are given in Tables 2-4. They generally agree to the stoichiometry [CuLX(H_2O)], where L = DFIT, MDPIT or HDPIT and X = OAc, Cl, Br, NO_3, ClO_4 or CNS. The sulphato complexes are found to be of the type [Cu_2L_2(SO4)(H_2O)$_2$].

3. Molar conductance

Molar conductances of 10^{-3} molar solutions of the complexes in DMF were determined at room temperature (Tables 5-7).

TABLE 5

Molar conductances of copper(I) complexes of 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione (DFIT) (L)

Complex	Molar conductance in DMF (ohm^{-1} cm^2 mol^{-1})
[CuL(OAc)(H_2O)]	3.61
[CuLCl(H_2O)]	21.85
[CuLBr(H_2O)]	34.57
[CuL(NO_3)(H_2O)]	29.73
[Cu_2 L_2(SO_4)(H_2O)$_2$]	13.84
[CuL(ClO_4)(H_2O)]	54.68
[CuL(CNS)(H_2O)]	41.42

TABLE 6

Molar conductances of copper(I) complexes of 1,3-dihydro-4,5-di(4-methoxyphenyl) 2H-imidazolin-2-thione (MDPIT) (L')

Complex	Molar conductance in DMF ($ohm^{-1}\ cm^2\ mol^{-1}$)
$[CuL'(OAc)(H_2O)]$	6.30
$[CuL'Cl(H_2O)]$	42.27
$[CuL'Br(H_2O)]$	45.43
$[CuL'(NO_3)(H_2O)]$	55.72
$[CuL'_2(SO_4)(H_2O)_2]$	39.5
$[CuL'(ClO_4)(H_2O)]$	39.7
$[CuL'(CNS)(H_2O)]$	22.5

TABLE 7

Molar conductances of copper(I) complexes of 1,3-dihydro-4,5 di(2-hydroxyphenyl) 2H-imidazolin-2-thione (HDPIT) (L")

Complex	Molar conductance in DMF ($ohm^{-1}\ cm^2\ mol^{-1}$)
$[CuL''Cl(H_2O)]$	31.46
$[CuL''Br(H_2O)]$	39.13
$[CuL''(NO_3)(H_2O)]$	50.48
$[Cu_2L''_2(SO_4)(H_2O)_2]$	51.32
$[CuL''(ClO_4)(H_2O)]$	56.42

The range of molar conductance for 1:1 electrolytes in DMF is 65-90[118]. For most of the complexes, the molar conductance values are lower than that expected for a 1:1 electrolyte, indicating that they are non-electrolytes. The behaviour of some other complexes are different. The high value of molar conductance for some of the complexes may be due to their dissociation in DMF. Molar conductance measurements of the complexes could not be carried out in nitrobenzene, because of their insolubility in it.

4. Magnetic behaviour

The magnetic susceptibility values of solid complexes were determined using a Gouy-type magnetic balance at room temperature. The magnetic measurements indicate that the complexes under investigation are diamagnetic in nature. Therefore, the copper present in the complexes may be in (+1) oxidation state. The complete reduction of Cu(II) takes place during complex formation. In copper complexes of heterocyclic thiones, this type of behaviour is common.[106,107] The oxidation of thiourea class compounds by Cu(II) salts is well documented[106].

5. Electronic Spectra

The electronic spectra of the complexes were recorded in DMSO. They do not register any characteristic bands in the visible region. This supplements the magnetic susceptibility data and confirms that the metal ions in the complexes are in the (+1) oxidation state. In Cu(I), the 3d orbitals are completely filled and hence no d-d transition occurs. This is again confirmed by the colour of the complexes. All the complexes are pale-yellow or colourless.

6. Infrared spectra

The significant IR spectral bands of the three ligands and their copper(I) complexes along with the probable assignments are given in Tables (8-10). The assignments were made by comparing the spectra of these compounds with those of related ones[108,109].

The IR spectra of thioamides have been extensively studied[102,119]. They are characterised by broad bands of strong intensities, near 3000 cm^{-1} due to ν_{NH} and four bands in the region between 1600 and 700 cm^{-1} which are represented as thioamide bands I to IV . The IR spectra of the three ligands investigated here show broad bands of strong intensities at about 3000 cm^{-1} which are attributed to $\nu_{NH.}$ The dominance of thione form of the ligand in the solid state is indicated by the absence of ν_{SH} band near 2500 cm^{-1} in the spectra of the three ligands[100, 41, 103]. Shamugam and Sathynarayana[41] had proved this by comparing the IR spectra of imidazolin-2-thione and its N-methyl derivative in solid state and in solution. The position of ν_{NH} band at a lower frequency region and its broad nature show the existence of NH….S hydrogen bonding in the solid state.

In the IR spectrum of DFIT,ν_{NH} is at 3126 cm^{-1}. The band at 1645 cm^{-1} is assigned to $\nu_{C=C} + \nu_{C\text{-}N}$. Two bands at 1548 and 1480 cm^{-1} (with shoulders at 1508 and 1394 cm^{-1}) are the thioamide band I.[47] These are the coupled bands arising from $\nu_{C\text{-}N}$ and $\delta_{C\text{-}H}$. This has been split because of the presence of two thioamide groups in DFIT. A band at 1222 cm^{-1} in the spectrum of the ligand is the thioamide band II. It has major contributions from $\nu_{C=S}$, $\nu_{C\text{-}N}$ and $\delta_{N\text{-}H}$. The thioamide band III at 1020 cm^{-1} has contributions from$\nu_{C\text{-}N}$ and $\nu_{C=S}$. The bands of varying intensities present in the range 900 to 600 cm^{-1} have been assigned as thioamide band IV in a variety of similar compounds containing thioamide groups[103-105] . In the IR spectrum of DFIT, there are a number of bands in this region. However, a band of medium intensity at 815 cm^{-1} has been assigned as thioamide band IV. It has contributions from $\nu_s(C=S)$, $\nu_{as}(C=S)$, ring deformation, $\nu_{C\text{-}N}$, etc. The $\nu_{C=S}$ vibration in DFIT is assigned at 592 cm^{-1} by comparing with the IR spectrum of imidazolin-2-thione[41] where it occurs at 507cm^{-1}.

In MDPIT the ν_{NH} is at 3045 cm^{-1}. The band at 1610 cm^{-1} is assigned to $\nu_{C=C} + \nu_{C=N}$. The thioamide bands I are at 1570 and 1458 cm^{-1} (with shoulders at 1514 and 1373 cm^{-1}). Medium intensity band at 1249 is assigned to thioamide band II. The thioamide band III is at 1090 cm^{-1} and a band at 792 cm^{-1} is assigned as thioamide band IV. The $\nu_{C=S}$ is assigned at 536 cm^{-1}.

In HDPIT the ν_{NH} and $\nu_{C=C} + \nu_{C=N}$ are at 3045 and 1632 cm^{-1}, respectively. Two bands at 1578 and 1450 cm^{-1} are assigned to thioamide band I and those at 1248 and 1202 cm^{-1} are due to thioamide band II. The thioamide band III is observed at 1080 cm^{-1} and thioamide band IV at 825 cm^{-1}. The band due to $\nu_{C=S}$ is observed at 750 cm^{-1}.

Thus, the IR spectra of the three ligands contain all the four characteristic thioamide bands and hence they exist in thione form in the solid state.

In the spectra of all the complexes of DFIT, MDPIT and HDPIT, the ν_{NH} band is shifted to higher frequency by about 20-50 cm^{-1}. The coordination of these ligands through the nitrogen atom would result a shift of this band to lower frequency region by 200-300 cm^{-1}.[41] But here the situation is complicated due to the fact that the imido groups of the coordinated ligands can form hydrogen bonds with the anions in the complexes. Therefore, we are of the argument that the changes in position and nature of the NH band during complexation cannot be used for detecting the N-coordination. This band in the spectra of all the complexes is very broad which indicates the existence of hydrogen bonding as proposed above. Therefore, we are of the opinion that the upward shift in ν_{NH} by 20-50 cm^{-1} results from a combination of factors including electronic changes within the molecule upon coordination as well as hydrogen bonding effects.

According to Raper and Crackett[110], the bands which show significant changes upon coordination are the thioamide bands I and IV. It has been reported by several workers that the thioamide band IV alone can be used as diagnostic for metal-ligand bonding[111]. Some are of the opinion that a clear idea of the nature of bonding between metal and this type of ligands can be derived only from a thorough study of the nature of changes in positions, intensities and other characters of all the four thioamide bands[115]. We are also of the same opinion. The spectra of the copper(I) complexes of the three ligands under investigation show well defined changes in all the four thioamide bands upon coordination (Tables 8-10).

Of the four thioamide bands, II, III and IV have contributions from $\nu_{C=S}$. Therefore, coordination through sulphur atom of the ligands should affect the positions and intensities of these bands. In the complexes of DFIT, no characteristic changes are observed in thioamide band I upon coordination. But the thioamide band II splits into two weak- and broad bands. The thioamide band III shifts to a lower frequency region during complexation. The thioamide band IV has the greatest contribution from $\nu_{C=S}$ and hence coordination of the ligand through C=S brings the most significant changes for this band. In the complexes of DFIT, the thioamide band IV shows a downward shift by 15 cm^{-1}. Thus ,from these changes in the thioamide bands upon complex formation, it can be inferred that the coordination is through the sulphur atom.

The changes in the four thioamide bands are more distinct in the spectra of the complexes of MDPIT than in those of DFIT. As in the case of complexes of DFIT, there are not much changes in thioamide band I. Significant changes are observed in thioamide bands II. A band at 1211 cm^{-1} in the spectra of the ligand is absent in the spectra of the complexes. The thioamide band III shows a negative shift of 60-70 cm^{-1}. Similarly, the thioamide band IV also shows a negative shift of 20 cm^{-1}. These changes indicate the coordination of MDPIT through the sulphur atom.

In the IR spectra of the complexes of HDPIT, there are not much changes observed in the thioamide bands I and II. The thioamide band III shows a shift to lower wave number by 70 cm^{-1} and the thioamide band IV also shifts to a lower region indicating the coordination through the sulphur atom of the ligand.

The IR spectra of all the complexes show broad bands due to intense absorptions near 3400 cm^{-1}, which are due to stretching vibrations of OH groups of coordinated water. The bending frequency of coordinated water molecule, which is expected near 1600 cm^{-1} [119] is not clear in the spectra of the complexes because of the presence of ligand vibrations in the same region. However, comparing the nature of the bands near 1600 cm^{-1} in the spectra of the ligands and the complexes, the coordinated nature of water can be confirmed.

(a) IR features of coordinated anions in the complexes

(i) Acetato complexes

The separation between two $\nu_{C\text{-}O}$ bands of the acetate group indicates the mode of coordination as explained in the previous chapter. In the acetato complexes of DFIT and MDPIT, this separation is wide which shows the unidentate coordination of the acetate group to Cu(I)[117].

(ii) Halo complexes

The M-Cl and M-Br vibrations are observed below 400 cm^{-1}, which is out of the range of our instrument. Halogens tend to form bridges between two metal atoms. But in the present study, the halo complexes are monomeric which is clear from the elemental analyses data.

(iii) Nitrato complexes

The separation between ν_1 and ν_4, i.e., $\Delta\nu$, is used as a criterion to find out the denticity of nitrate groups in complexes. If nitrate is bidentate, $\Delta\nu$ is in the range of 190-250 cm^{-1} and for unidentate, the value is below 130 cm^{-1}[120,121]. In the present study, the $\Delta\nu$ values are around 100 cm^{-1}, which suggest that the nitrate groups act as unidentate ligands in these complexes.

(iv) Sulphato complexes

For bidentate-and bidentate bridging sulphate groups, ν_1 and ν_2 are observed near 950 and 440 cm^{-1}, respectively[65]. At the same time ν_3 and ν_4 split into three bands each.

In the sulphato complexes of the three ligands discussed in this chapter, sulphate radicals act as bidentate bridging ligands. This is clear from the position and nature of ν_1, ν_2, ν_3 and ν_4 bands (Tables 8-10).

(v) Perchlorato complexes

The perchlorato complexes of the three ligands show bands around 1110 and 1075 cm^{-1}. These bands can be assigned to ν_3 vibration of perchlorate group. The split nature of these bands indicates the monodentate behaviour of the perchlorate groups[117]. The ν_1 appears as weak band near 920 cm^{-1},while ν_4 is observed as a strong band near 620 cm^{-1}. These bands are characteristic of complexes containing monodentate perchlorate groups[117].

(f) Thiocyanato complexes

The thiocyanato complexes of Cu(I) with DFIT and MDPIT were prepared. In both these complexes ν_1 is present near 2100 cm^{-1}, indicating that the thiocyanate ligand is S-bonded to the metal ion[122]. This is the expected mode of coordination in these complexes, as Cu^{+} ion is a soft acid. The ν_3 and ν_2 modes of

TABLE 8

Significant IR bands(cm^{-1}) of 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione (DFIT)(L), its copper (I) complexes and their assignments

DFIT (L)	[CuL(OAc)(H_2O)]	[CuLCl(H_2O)]	[CuLBr(H_2O)]	[CuL(NO_3)(H_2O)]	[Cu_2L_2 (SO_4)(H_2O)$_2$]	[CuL(ClO_4)(H_2O)]	[CuL(CNS)(H_2O)]	Assignments[@]
	3390	3400	3420	3413	3458	3372	3413	ν_{OH} of coord. water
3126	3141	3150	3136	3138	3140	3128	3122	ν_{NH}
1645	1643	1645	1645	1643	1643	1643	1643	$\nu_{C=C} + \nu_{C\text{-}N}$
1548		1542	1550	1550	1580	1546	1546	
1508	1528	1502	1502		1505	1498	1506	TA I
1480	1469	1467	1465	1450	1462	1465	1471	
1394	1390	1380	1384	1382	1380	1386	1392	
1222	1215	1200	1206	1215	1203	1206	1210	TA II
	1157	1161	1159	1161		1161	1159	
1020	1076	1074	1083	1076	1070	1070	1076	TA III
	1012	1012	1016	1016	1006	1016	1014	
815	802	800	805	802	802	802	800	TA IV
690	670	665	671	675	670	669	672	δ_{NH}
592	590	584	590	590	588	590	590	$\nu_{C=S}$
	1599							$\nu_{C\text{-}O}$ of acetate
	1410							$\nu_{C=O}$ of acetate
				1414				ν_4 of NO_3^-
				1336				ν_1 of NO_3^-
				1010				ν_2 of NO_3^-
					1250			SO_4^{--}
					1120			
					940			
					620(s)			
						1109		ν_3 of ClO_4^-
						1070		
						921 (w)		ν_1 of ClO_4^-
						620 (s)		ν_4 of ClO_4^-
							2085	ν_1 of CNS^-
							736	ν_3 of CNS^-

[@] TA = Thioamide band

TABLE 9

Significant IR bands(cm^{-1}) of 1,3-dihydro-4,5-di (4-methoxyphenyl)-2H-imidazolin-2-thione (MDPIT)(L'), its copper(I) complexes and their assignments

MDPIT (L')	[CuL'(OAc)(H_2O)]	[CuL'Cl(H_2O)]	[CuL'Br(H_2O)]	[CuL'NO_3(H_2O)]	[Cu_2L_2(SO_4)(H_2O)$_2$]	[CuL'(ClO4)(H_2O)]	[CuL'(CNS)(H_2O)]	Assignments[@]
	3242	3136	3251	3420	3327	3421	3246	ν_{OH} of coord. water
3045	3040	3053	3143	3009	3049	3145	3040	ν_{NH}
1610	1614	1614	1616	1614	1620	1612	1610	$\nu_{C=C} + \nu_{C=N}$
1570	1528	1550	1558	1571	1571	1575	1570	
1514	1506	1514	1508	1515	1519	1512	1506	TA I
1458	1458	1458	1458	1458	1460	1460	1458	
1373	1373	1370	1398	1384		1388	1373	
1249	1247	1253	1253	1251	1251	1253	1247	
1211								TA II
1174	1174	1176	1176	1178	1176	1178	1174	
1090	1029	1028	1026	1076	1093	1083	1028	TA III
792	773	781	773	770	770	770	771	TA IV
536	532	532	522	534	536	540	536	νC=S
	1640							νC=O of acetate
	1400							νC-O of acetate
				1408				ν_4 of NO_3^-
				1299				ν_1 of NO_3^-
				1000				ν_2 of NO_3^-
					1140			
					1030			
					990 (sh)			
					680			SO_4^{--}
					577			
					461			
						1130		ν_3 of ClO_4^-
						1081		
						920		ν_1 of ClO_4^-
						623		ν_4 of ClO_4^-
							2123	ν_1 of CNS^-
							727	ν_3 of CNS^-

[@] TA = Thioamide band

TABLE 10

Significant IR bands(cm^{-1}) of 1,3-dihydro-4,5-di(2-hydroxyphenyl)-2H-imidazolin-2-thione HDPIT(L"), its copper(I) complexes and their assignments

HDPIT (L")	[CuL"Cl(H_2O)]	[CuL"Br(H_2O)]	[CuL"(NO_3)(H_2O)]	$[Cu_2L_2(SO_4)(H_2O)_{2\,2}]$	[CuL"(ClO_4)(H_2O)]	Assignments[@]
	3372	3370	3378	3376	3375	ν_{OH} of coord. water
3145	3175	3175	3175	3175	3175	ν_{NH}
1632	1612	1610	1610	1612	1610	$\nu_{C=C} + \nu_{C=N}$
1578	1554	1554	1554	1552	1556	TA I
1481	1481	1480	1464	1408	1450	
1450	1450	1468				
1419						
1248	1259	1260	1260	1260	1259	
1202	1210	1225	1211	1215	1215	TA II
1080	1018	1018	1010	1018	1018	TA III
858	877	875	867	885	877	
825	831				831	TA IV
792					787	
750	758	742	754	745	745	$\nu_{C=S}$
			1414			ν_4 of NO_3^-
			1310			ν_1 of NO_3^-
			1050			ν_2 of NO_3^-
				1220		
				1040		
				990		
				720		SO_4^{--}
				618		
				570		
				460		
					1107	ν_3 of ClO_4^-
					1070	
					920	ν_1 of ClO_4-
					625	ν_4 of ClO_4^-

[@] TA = Thioamide band

vibrations are expected near 720 and 420 cm^{-1}, respectively. The v_3 band is observed at about 730 cm^{-1} but v_2 mode is not clear as there are a number of bands of low intensities in this region.

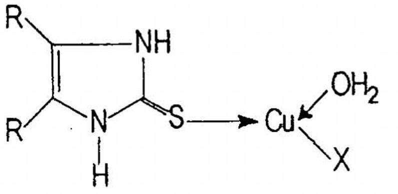
7. Thermal analysis

Thermograms of five complexes of MDPIT were recorded. The complexes decompose in 3 to 5 stages, in which the water molecule, the anion and the methoxy group of the ligand get decomposed. This is in good agreement with the proposed structures of the complexes. Finally, the metal oxide (CuO) was formed which was identified chemically. Independent pyrolytic studies were also carried out. The details of the thermogravimetric studies are given in Part II of this thesis.

C. CONCLUSIONS

The complex formation reactions of three imidazolin-2-thiones with several copper(II) salts, CuX_2, where X = OAc, Cl, Br, NO_3, $1/2SO_4$, ClO_4 or CNS were carried out. The solid complexes formed were isolated and characterised. The electronic spectral studies and magnetic moment data indicated the reduction of Cu(II) to Cu(I) during complex formation with these ligands. Analytical studies indicated that the general formula of the complexes as $[CuLX(H_2O)]$, where X = OAc, Cl, Br, NO_3, ClO_4 or CNS and L=DFIT,MDPIT or HDPIT. The sulphato complexes were found to be binuclear, $[Cu_2L_2(SO_4)(H_2O)_2]$. The IR data confirmed the presence of coordinated water and- anions in the complexes.

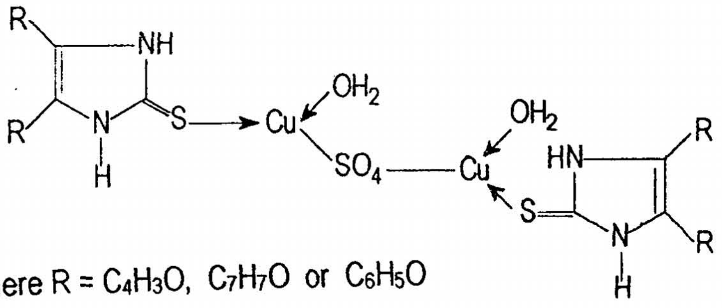
As the complexes are of Cu(I), the elucidation of their geometries from the magnetic moment values and electronic spectra is not possible. However, comparing with the geometries assigned to the complexes of similar ligands,[107,108,115] a triangular geometry can be assigned to these complexes. The imidazolin-2-thiones act as neutral, monodentate ligands, coordinating through the sulphur atom. The structures of the complexes can be represented as follows: **II**



Where X = OAc, Cl, Br, NO_3, ClO_4 or CNS and R = C_4H_3O, C_7H_7O or C_6H_5O

II

The sulphato complexes with a binuclear structure and bridging SO_4^{2-} may have the following structure: **III**



where R = C_4H_3O, C_7H_7O or C_6H_5O

III

PART 1

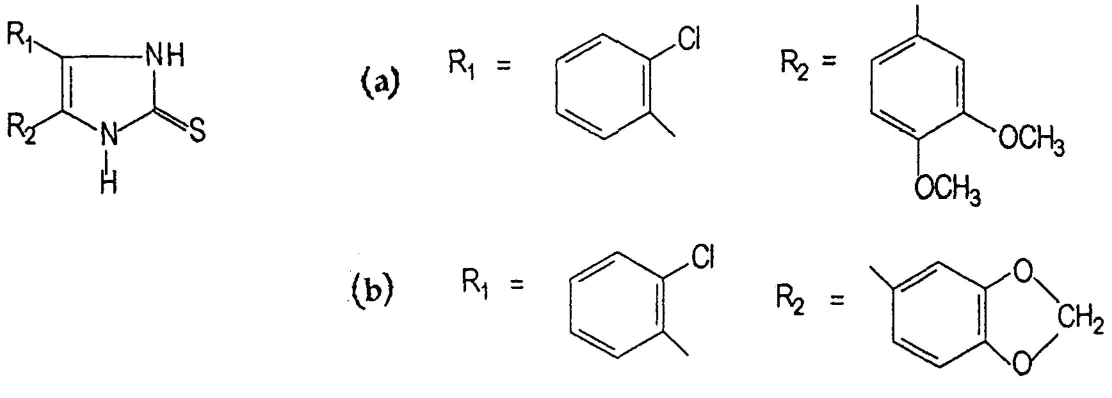
COMPLEXES OF COPPER(I) WITH UNSYMMETRICALLY 4,5-DISUBSTITUTED IMIDAZOLIN-2-THIONES

Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER V

COMPLEXES OF COPPER(I) WITH UNSYMMETRICALLY 4,5-DISUBSTITUTED IMIDAZOLIN-2-THIONES

In continuation with our investigations on the metal complexes of imidazolin-2-thiones, we report in this chapter two new imidazolin-2-thiones which are unsymmetrically substituted at 4 and 5 positions and their copper complexes . It has been reported that the antifungal activity of azoles, in general, increases when they possess two or more aromatic rings, atleast one of which is halogen substituted and the other by non-polar functional groups[34]. With this view, we have now synthesised two new imidazolin-2-thiones with halogen-, and methoxy- or methylenedioxy substituted aromatic rings. The structures of the ligands are represented in **I** a and b.



I

Their chemical abstract names are (a) 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione (CPDMPIT)(L) and (b) 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-methylenedioxyphenyl)-2H-imidazolin-2-thione (CPDOMPIT) (L').

A. EXPERIMENTAL

1. Materials and methods

The details regarding the materials and methods used are given in Chapter II.

2. Synthesis of ligands

The synthesis of the ligands involve two different steps.

a) Preparation of benzoins

A solution of 2-chlorobenzaldehyde (0.05 mol) in 50% ethanol (5 ml) was mixed with 3,4-dimethoxybenzaldehyde or 3,4-methylenedioxybenzaldehyde

(0.05 mol) and 50% aqueous solution of NaCN (10 ml). The mixture was refluxed for 2.5 h. The benzoins, crystallised on cooling the reaction mixtures, were then filtered off, washed several times with water and dried. They were recrystallised from ethanol.

b) Synthesis of CPDMPIT and CPDOMPIT

The ligands were synthesised by refluxing a mixture of the respective benzoin (0.01 mol) and ammonium thiocyanate (2 gm) in isoamyl alcohol (30 ml) for 1 h. The solid products formed were filtered off, washed several times with ether and recrystallised from ethanol.

3. Synthesis of complexes

The copper(I) complexes of the two ligands were synthesised as follows: To a refluxing solution of the ligand (.001 mol) in methanol (20 ml) copper(II) salt solution (0.001 mol) in methanol (20 ml) was added in drops. In most cases, immediate formation of the solid complexes resulted. In certain other cases, the solid complexes formed only after refluxing the reaction mixtures for 10-15 min. The mixtures were kept at the refluxing temperature for 0.5h to ensure the completion of the reaction. They were cooled to room temperature, filtered off, washed with methanol and dried over P_4O_{10}.

The copper(I) thiocyanate complexes were prepared by adding copper(II) acetate (0.001 mol) solution in methanol (20 ml) to a methanolic solution (20ml)of the ligand (0.001 mol), containing stoichiometric quantity of ammonium thiocyanate.

B. RESULTS AND DISCUSSION

The properties, structures and geometries of the complexes had been established with the help of analytical-, physico-chemical- and spectral investigations.

1. Characterisation of ligands

Both the ligands prepared are non-hygroscopic solids. The purity of the compounds were established by TLC technique.

The analytical data of the ligands are given in Table 1. The values show good agreement with the proposed formulae. Further confirmation of their structures had been made by IR-and ^{1}H-NMR spectral studies.

2. Formulae and general properties of the complexes

Complexes of CPDMPIT and CPDOMPIT with CuX_2, where X=OAc, Cl, Br, NO_3, ½SO_4, ClO_4 or CNS, were prepared. All the complexes are non-hygroscopic and stable in air. They are insoluble in common organic solvents like

TABLE 1

Analytical data of the ligands

Name of the Ligand[@]	Molecular Formula	Molecular weight	Colour	M.P. (°C)	Yield (%)	Found (calculated %)		
						C	H	N
CPDMPIT (L)	$C_{17}H_{15}N_2SO_2Cl$	346	White	255	60	58.57 (58.57)	4.50 (4.33)	7.95 (8.08)
CPDOMPIT (L")	$C_{16}H_{11}N_2SO_2Cl$	330	Pale-yellow	225	70	58.30 (58.10)	3.50 (3.32)	8.42 (8.47)

[@] CPDMPIT - 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione
CPDOMPIT - 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-methylenedioxyphenyl)-2H-imidazolin-2-thione

TABLE 2

Analytical data of copper(I) complexes of 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione (CPDMPIT) (L)

Complex	Molecular formula	Molecular weight	Colour	Found (calculated) %				
				Metal	C	H	N	Anion
$[CuL(OAc)(H_2O)]$	$CuC_{19}H_{20}N_2SO_5Cl$	487	Pale-yellow	12.36 (13.03)	46.50 (46.80)	4.02 (4.10)	6.02 (5.74)	----
$[CuLCl(H_2O)]$	$CuC_{17}H_{17}N_2SO_3Cl_2$	463	Ivory	13.85 (13.70)	44.80 (44.01)	3.89 (3.66)	6.01 (6.04)	14.90 (15.31)
$[CuLBr(H_2O)]$	$CuC_{17}H_{17}N_2SO_3ClBr$	508	Greenish-yellow	12.44 (12.5)	40.63 (40.15)	3.06 (3.34)	5.70 (5.51)	---
$[CuL(NO_3)(H_2O)]$	$CuC_{17}H_{17}N_3SO_6Cl$	490	Pale-yellow	11.04 (12.95)	40.84 (41.16)	3.40 (3.40)	8.60 (8.57)	---
$[Cu_2L_2(SO_4)(H_2O)_2]$	$Cu_2C_{34}H_{34}N_4S_3O_{10}Cl_2$	952	Pale-yellow	13.69 (13.34)	43.02 (42.85)	3.30 (3.57)	6.02 (5.88)	10.80 (10.29)
$[CuL(ClO_4)(H_2O)]$	$CuC_{17}H_{17}N_2SO_7Cl_2$	598	Pale-yellow	9.32 (10.60)	34.04 (34.08)	2.68 (2.84)	4.02 (4.67)	--
$[CuL(CNS)(H_2O)]$	$CuC_{18}H_{17}N_3S_2O_3Cl$	482	White	13.80 (13.17)	45.02 (44.81)	3.62 (3.52)	8.34 (8.71)	--

TABLE 3

Analytical data of copper(I) complexes of 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-methylene dihydroxyphenyl)-2H-imidazolin-2-thione (CPDOMPIT) (L')

Complex	Molecular formula	Molecular weight.	Colour	Found (calculated) %				
				Metal	C	H	N	Anion
Cu[L'(OAc)(H_2O)]	$CuC_{18}H_{16}N_2SO_5Cl$	471	White	14.01 (13.48)	45.63 (45.86)	3.40 (3.39)	5.85 (5.90)	----
[CuL'Cl(H_2O)]	$CuC_{16}H_{13}N_2SO_2Cl_2$	447	Pale-yellow	15.42 (14.19)	41.02 (42.91)	3.02 (2.90)	6.01 (6.25)	8.01 (7.92)
[CuL'Br(H_2O)]	$CuC_{16}H_{13}N_2SO_2ClBr$	491	Pale-yellow	13.20 (12.90)	40.50 (39.02)	2.70 (2.64)	5.78 (5.69)	---
[CuL'(NO_3)(H_2O)]	$CuC_{16}H_{13}N_3SO_5Cl$	473	White	13.42 (13.39)	40.94 (40.51)	2.80 (2.74)	8.34 (8.86)	---
[$Cu_2L'_2$ (SO_4)(H_2O)$_2$]	$Cu_2C_{32}H_{22}N_4S_2O_{10}Cl_2$	795	Pale-yellow	15.21 (15.97)	49.02 (49.30)	2.92 (2.76)	7.14 (7.04)	13.04 (12.32)
[CuL'(ClO_4)(H_2O)]	$CuC_{16}H_{13}N_2SO_7Cl_2$	511	Pale-yellow	12.61 (12.41)	38.83 (37.54)	2.58 (2.54)	5.49 (5.47)	--
[CuL'(CNS)(H_2O)]	$CuC_{17}H_{13}N_3S_2O_3Cl$	469	Pale-yellow	14.12 (13.51)	43.46 (43.40)	2.82 (2.76)	8.83 (8.93)	--

methanol, ethanol, etc. They are freely soluble in DMF and DMSO. All the complexes are pale- green in colour.

Analytical data of the complexes are given in Tables 2 and 3. They generally agree to the stoichiometry $[CuLX(H_2O)]$, where L = CPDMPIT or CPDOMPIT and X = OAc, Cl, Br, NO_3, ClO_4 or CNS. The sulphato complexes are found to be binuclear of the type $[Cu_2L_2(SO_4)(H_2O)_2]$.

3. Molar conductance

Molar conductances of all the complexes (10^{-3} M solution) were determined in DMF. The complexes were insoluble in nitrobenzene and hence conductance measurements could not be carried out in it.

TABLE 4

Molar conductance of copper(I) complexes of 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione (CPDMPIT) (L)

Complex	Molar conductance in DMF ($Ohm^{-1}cm^2mol^{-1}$)
$[CuL(Oac)(H_2O)]$	2.81
$[CuLCl(H_2O)]$	43.43
$[CuL Br(H_2O)]$	49.52
$[CuL(NO_3)(H_2O)]$	51.36
$[Cu_2L_2(SO_4) (H_2O)_2]$	48.32
$[CuL(ClO_4) (H_2O)]$	51.13
$[CuL (CNS)(H_2O)]$	24.38

TABLE 5

Molar conductance of copper(I) complexes of 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-methylenedioxyphenyl)-2H-imidazolin-2-thione (CPDOMPIT) (L')

Complex	Molar conductance in DMF ($Ohm^{-1}cm^{2}mol^{-1}$)
[CuL'(OAc)(H_2O)]	20.36
[CuL'Cl(H_2O)]	44.3
[CuL'Br(H_2O)]	33.38
[CuL'(NO_3)(H_2O)]	33.73
[$Cu_2L'_2$(SO_4) (H_2O)$_2$]	48.92
[CuL'(ClO_4) (H_2O)]	39.08
[CuL'(CNS)(H_2O)]	18.37

For most of the complexes, the molar conductance values are lower than that expected for 1:1 electrolytes in DMF[118]. This shows that the complexes act as non-electrolytes, ie., the anions are coordinated to the metal ions. In a few cases the values are higher, which may be due to their dissociation to a certain extent, in DMF.

4. Magnetic behaviour

The magnetic susceptibility values of all the solid complexes were determined using a Gouy balance at room temperature. The magnetic measurements show that the complexes are diamagnetic in nature. This reveals that copper ions in the complexes are in (+1) oxidation state. Thus, it can be concluded that during complex formation, the ligands completely reduce Cu(II) to Cu(I). This is in accordance with the reports that the heterocyclic thiones usually reduce Cu(II) to Cu(I)[106,107]. This observation is further confirmed by the fact that all these complexes are either pale coloured or colourless.

5. Electronic spectra

The electronic spectra of the complexes were recorded in DMF. But no characteristic absorption bands were observed in the visible region. Therefore, the reduction of Cu(II) to Cu(I) by the ligands is again confirmed. Cu(I) has completely filled d orbitals and hence no d-d transitions are expected.

6. Infrared spectra

The significant IR spectral bands of the ligands and their copper(I) complexes along with their probable assignments are given in Tables 6 and 7. The assignments were made by a comparison with the spectra of related compounds[38,108,109].

According to Rao and Venkataraghavan[103] the IR spectra of thiocarbonyl compounds contain four characteristic bands (thioamide bands) due to the mixed vibrations of $\text{H}-\overset{|}{\text{N}}-\overset{|}{\text{C}}=\text{S}$ tautomeric linkage. All these four bands are present in the spectra of the two ligands investigated here. Absence of bands near 2500 cm^{-1}

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shows that the ligands exist in the thione form in the solid state. This situation is similar to that observed for three imidazolin-2-thiones described in Chapter IV.

In the spectrum of CPDMPIT, a broad band at 3269 cm^{-1} is assigned to ν_{NH}. A band of medium intensity at 1633 cm^{-1} is due to the mixed vibrations, $\nu_{C=C} + \nu_{C-N}$. A band of strong intensity at 1512 cm^{-1} with a shoulder at 1438 cm^{-1} is assigned to thioamide band I. The thioamide bands II, which have major contributions from $\nu_{C=S}$, ν_{C-N} and δ_{N-H} are present at 1257 and 1213 cm^{-1}. The bands at 1141 and 1020 cm^{-1} are assigned to thioamide bands III and those at 761 and 680 cm^{-1} are thioamide bands IV.

In the spectrum of CPDOMPIT, a broad band at 3085 cm^{-1} is assigned to ν_{NH}. A medium intensity band at 1639 cm^{-1} is due to the mixed vibrations, $\nu_{C=C} + \nu_{C-N}$. A band of very strong intensity at 1498 cm^{-1} with a shoulder at 1460 cm^{-1} can be assigned as the thioamide band I, and those at 1340 and 1234 cm^{-1} are thioamide bands II. The medium intensity bands present in the range 1114-1033 cm^{-1} are thioamide bands III and thioamide bands IV are present in the range 815-754 cm^{-1}.

In the spectra of the complexes, the bands due to ν_{NH} show a shift to higher frequency. In the spectrum of the ligand, the position of this band at a lower frequency region and its nature indicate the presence of NH - - - S hydrogen bonding in the solid ligands. In the complexes, the possibility of hydrogen bonding decreases due to the reduction in electron density on the sulphur atom and the blue shift of the ν_{NH} may be due to this.

In the spectra of the complexes of CPDMPIT and CPDOMPIT, striking changes are observed in the thioamide bands. Coordination of the ligands through the sulphur atom should affect the positions and intensities of thioamide bands II, III and IV, which have contribution from $\nu_{C=S}$.

In the IR spectra of the Cu(I) complexes of these ligands, there are not much changes in the position and intensity of thioamide band I. The changes in the thioamide band II in the complexes of CPDMPIT are noticeable. One band at 1213 cm^{-1} in the ligand spectrum is absent in the spectra of the complexes. However, in the spectra of the complexes of CPDOMPIT, the changes in the thioamide band II is not striking. The thioamide bands III of the Cu(I) complexes of CPDMPIT do not show much variations in positions and intensities. But the changes are marked in the Cu(I) complexes of CPDOMPIT. The band shows a negative shift indicating the involvement C=S in complex formation[115]. The most significant changes in the IR spectra are observed for the thioamide band IV. In the complexes of both the ligands, this band is shifted to lower frequency region, indicating the participation of C=S in complex formation.

Thus, the changes in the intensities and positions of the four thioamide bands show that the coordination of the ligand is through C=S group. This is anticipated, as Cu(I) is a soft acid which forms stable compounds with soft bases (such as sulphur) according to HSAB concept.

The IR spectra of the complexes under present investigation show broad absorptions near 3400 cm^{-1} which indicate the presence of coordinated water in them. The other characteristic absorption bands of coordinated water cannot be located due to the presence of ligand vibrations in the same region.

a) ***IR features of coordinated anions in the complexes***

The IR spectra and the coordination patterns of the anions are the same as those of the complexes discussed in Chapter IV.

(i) Acetato complexes

The separation between the $\nu_{C=O}$ and ν_{C-O} is large in the spectra of both sets of complexes indicating that the acetate radicals are acting as monodentate ligands in them.

(ii) Halo complexes

The mode of coordination of halogen atoms cannot be ascertained from the IR spectra, as M-X ,(where X=Cl or Br) absorbs below the range of the instrument used. However, the analytical data indicate the monodenticity of coordinated halogen atoms in the complexes.

(iii) Nitrato complexes

The separations between the ν_1 and ν_4 in the spectra of nitrato complexes investigated here are around 100 cm^{-1}. This suggests that the nitrate radicals are unidentately coordinated to Cu(I).

(iv) Sulphato complexes

The sulphate radicals are acting as bidentate bridging ligands which is clear from the positions of ν_1 and ν_2 and the split nature of ν_3 and ν_4 into three bands each.

(v) Perchlorato complexes

In the spectra of the perchlorato complexes, ν_3 is split into two bands and are observed near 1110 and 1080 cm^{-1}, while ν_1 and ν_4 are present near 920 and 625 cm^{-1} ,respectively. The positions of these bands and the split nature of ν_3 indicate that the perchlorate radicals are monodentately coordinated in these complexes.

(vi) Thiocyanato complexes

In the spectra of the thiocyanato complexes, the ν_1, ν_3 and ν_2 of thiocyanate groups are present around 2100, 730 and 420 cm^{-1},respectively. This indicates that

TABLE 6

Significant IR bands (cm^{-1}) of 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione (CPDMPIT) (L), its copper(I) complexes and their assignments

CPDMPIT (L)	[CuL(OAC) (H_2O)]	[CuLCl (H_2O)]	[CuLBr (H_2O)]	[Cu(LNO_3)(H_2O)]	[Cu_2 L_2 (SO_4) (H_2O)$_2$	[Cu L (ClO_4) (H_2O)]	[Cu L (CNS) (H_2O)]	Assignments@
	3377	3431	3420	3458	3417	3406	3410	ν_{OH} of coor. water
3269	3180	3244	3209		3270	3276	3303	ν_{NH}
1633	1637	1639	1633	1637	1633	1635	1639	$\nu_{c=o} + \nu_{C\text{-}N}$
1587								
1512	1510	1521	1515	1517	1517	1515	1515	
1438(sh)	1463	1456	1458	1458	1460	1758	1461	TAI
	1436							
1257	1257	1263	1259	1259	1257	1259	1257	TAII
1213								
1141	1136	1143	1141	1139	1145	1116	11139	
1020	1026	1026	1022	1022	1018	1024	1026	TAIII
813	761	761	763	763	763	763	763	TAIV
680								
630	640	670	642	630	620	623	630	δ_{NH}
553	542	550	550	520	530	530	520	$\nu C = S$

	1585							$\nu_{C=O}$ of acetate
	1373							
				1428				ν_4 NO_3^-
				1323				ν_1 of NO_3^-
					1215			SO_4^{--}
					1093			
					732			
					620			
					550			
					468			
						1114		ν_3 of ClO_4^-
						1080		ν_1 of ClO_4^-
						930		
							2117	ν_1 of CNS^-
							731	ν_3 of CNS^-
							418	ν_2 of CNS^-

@ TA = Thioamide band

TABLE 7

Significant IR bands (cm^{-1}) of 1, 3-dihydro-4-(2-chlorophenyl)-5-(3,4-methylenedioxyphenyl)-2H-imidazolin-2-thione(CPDOMPIT)(L'), its copper(I) complexes and their assignments

CPDOMPIT (L')	[Cu L' (OAc) (H_2O)]	[Cu L' Cl (H_2O)]	[Cu L' Br (H_2O)]	[Cu L'(NO_3)(H_2O)]	[Cu_2 L'_2 (SO_4) (H_2O)$_2$]	[Cu L'(ClO_4)(H_2O)]	[Cu L' (CNS) (H_2O)]	Assignme-nts$^{@}$
	3450	3400	3410	3423	3470	3450	3430	ν_{OH} of coor. water
3394								
3085(br)	3286	3067	310	3193	3203	3020	3068	ν_{NH}
1639	1633	1632	1614	1637	1641	1613	1649	$\nu_{C=C} + \nu_{C=N}$
1498	1496	1524	1522	1500	1511	1534	1507	
1460(sh)	1461	1501	1489	1469	1482	1500	1473	TAI
	1472							
	1440							
1390	1371	1378	1380	1384	1380	1380	1368	TAII
1234	1240	1244	1238	1240	1242	1242	1241	
1114	1112	1114	1110	1112	1112	1122	1112	
1057	1037	1042	1041	1037	1042	1040	1039	TA III
1057	1037	1042	1041	1037	1042	1040	1039	
1033								
815	810	808	810	813	813	813	810	

754	736	730(sh)	730(sh)	730(sh)	730(sh)	730(sh)	730(sh)	TAIV
	1590 (sh) 1450							$\nu_{C=O}$ of acetate
				1410(sh)				ν_4 NO_3^-
				1329				$\nu_1$of NO_3^-
					1220 1100 933 730 620 580 46			SO_4^-
						1110		ν_3 of ClO_4^-
						1080 (sh) 931		ν_1 of ClO_4^-
							2080	ν_1 of CNS^-
							730	ν_3 of CNS^-
							418	ν_2 of CNS^-

$^{@}$ TA = Thioamide band

the thiocyanate is monodentatly coordinated to the metal ion and that the coordination is through the sulphur atom of the thiocyanate group. Since Cu(I) is a soft acid, the coordination of CNS through S (soft base) is anticipated.

7. ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of the two ligands and their Cu(I) acetate complexes were recorded in $CDCl_3$. The data are given in Table 8.

a) CPDMPIT

The ^{1}H-NMR spectrum of CPDMPIT shows two sets of multiplets at 6.69 - 6.86 and 7.31 - 7.62 ppm. These can be assigned to the two types of aromatic protons present in the ligand. The presence of chlorine atom on one of the aromatic rings desheilds the protons and results in slightly higher δ value for one set of aromatic protons .The other aromatic ring is methoxy substituted which causes a sheilding effect, and slightly lower δ value for the other set of aromatic protons may be due to this effect.

The δ value of imidazole NH is expected around 7.45 ppm[123] which cannot be identified due to presence of multiplets of aromatic protons in the same region. There are two closely spaced singlets at 3.80 and 3.64 ppm, which may be assigned to the protons of the methoxy groups which are in slightly different environments. A singlet present at 2.97 ppm may be due to the SH proton, which indicates that the ligand exists in the thiol form in solution. This has already been proved by Shanmugam and Sathyanarayana[41] in the case of similar heterocyclic thiones.

Thus, the ^{1}H-NMR spectrum of the ligand is in accordance with the suggested structure.

b) ***[Cu(CPDMPIT)(OAc)(H$_2$O)]***

In the ^{1}H-NMR spectrum of [Cu(CPDMPIT)(OAc)(H_2O)], the main changes are observed at the SH proton region. The peak corresponding to SH proton at 2.97 ppm in the NMR spectrum of the ligand is absent in the spectrum of the complex. This indicates that the thione- form of the ligand is coordinating with Cu(I). Another main change is observed in the regions of aromatic - and imidazole NH protons. When the thione- form of the ligand coordinates, there are two NH protons on the ligand and changes in the region may be due to this. The new peaks 3.34 and 1.5 ppm are assigned to the protons of coordinated water and acetate groups, respectively.

c) ***CPDOMPIT***

The peaks of the aromatic protons are observed as two sets of multiplets at 6.65 - 6.76 and 7.29 to 7.51 ppm. The peak of imidazole NH is expected in the same region and therefore, it cannot be identified. A singlet at 2.9 ppm is due to SH proton, which shows that CPDOMPIT also exists in thiol- form in solution. A

TABLE 8

Significant ^{1}H-NMR spectral assignment of CPDMPIT (L), CPDOMPIT[@] (L') and their Cu(I) acetate complexes

Compound	δ(ppm)	Proton
CPDMPIT(L)	2.97(s) 3.64(s) 3.80(s) 6.69 - 6.86 (m) 7.31 - 7.62(m)	-SH two - OCH_3 aro. protons + imidazole NH
[CuL (OAc)(H_2O)]	1.5(s) 3.34(s) 3.7(s) 3.8(s) 6.1 - 6.9 (m) 7.1 - 7.6 (m)	$-CH_3$ of acetate Coordinated water two $-OCH_3$ aromatic protons + imidazole NH
CPDOMPIT(L')	1.4 (s) 2.9(s) 6.65 - 6.76 (m) 7.29 - 7.51 (m)	$-CH_2$ –SH aro. protons + imidazole NH
[CuL'(OAc)(H_2O)]	1.25 (s) 3.37(s) 2.60(s) 5.9 - 6.7(m) 7.3 - 7.5(m)	$-CH_2$ Coordinated water $-CH_3$ of acetate aro. protons + imidazole NH

[@] CPDMPIT - 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione

CPDOMPIT - 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-methylenedioxyphenyl)-2H-imidazolin-2-thione

singlet at 1.4 ppm may be due to the CH_2 of the methylene group. Thus the ^{1}H-NMR spectrum of CPDOMPIT is in good agreement with the proposed structure.

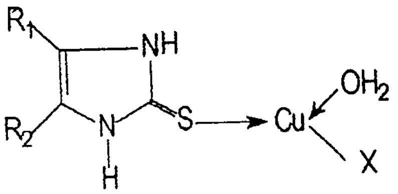
d) *[Cu(CPDOMPIT)(OAC)(H_2O)]*

The peaks observed as two sets of multiplets at 5.9 - 6.7 and 7.3 - 7.5 ppm are due to the aromatic protons present in the ligand. The peak due to imidazole NH is also expected in the same region. The singlet observed at 1.25 ppm may be due to the CH_2 protons and that at 2.60 ppm is due to protons of the coordinated acetate group.The peak due to the protons of coordinated water is observed at 3.37 ppm.

C. CONCLUSIONS

The reactions of two imidazolin-2-thiones with different copper(II) salts, CuX_2, where X = OAc, Cl, Br, NO_3, ½SO_4, ClO_4 or CNS, were carried out and the solid complexes formed were isolated. Electronic spectral studies and magnetic moment data of these complexes showed that Cu(II) had been reduced to Cu(I) during complex formation. Elemental analyses data indicated the general formula of the complexes to be [CuLX(H_2O)], where L = CPDMPIT or CPDOMPIT and X = OAc, Cl, Br, NO_3, ClO_4 or CNS. The sulphate complexes were found to be binuclear of the type [$Cu_2L_2(SO_4)(H_2O)_2$].

The IR spectra of the complexes showed that the ligands were in the thione form. The presence of coordinated water and anions in the complexes were also indicated in the IR spectra. In all the complexes, the ligands acted as neutral, monodentate ones coordinating through thione sulphur atoms. The correct geometries of the complexes could not be assigned. However, comparing with the geometries assigned to similar types of complexes[47,107,108], a triangular geometry was assigned to these complexes. The structures can be represented as follows. **II**

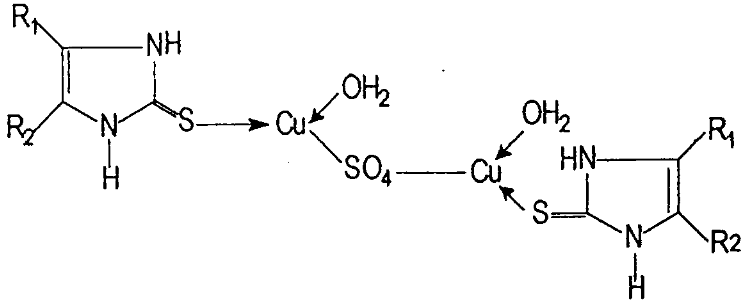


II

where X = OAc, Cl, Br, NO_3, ClO_4 or CNS

R_1 = C_6H_4Cl and R_2 = $C_8H_9O_2$ or $C_7H_5O_2$

The sulphato complexes were found to be binuclear with bridging SO_4^{2-} radicals. **III.**



III

where R_1 = C_6H_4Cl

R_2 = $C_8H_9O_2$ or $C_7H_5O_2$

PART 1

COMPLEXES OF SYMMETRICALLY 4,5-DISUBSTITUTED IMIDAZOLIN-2-THIONES

Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER VI

COMPLEXES OF SYMMETRICALLY 4,5-DISUBSTITUTED IMIDAZOLIN-2-THIONES

In the last two chapters we have been discussing about copper(I) complexes of 4,5 disubstituted imidazolin-2-thiones which are formed by the reaction between copper(II) salts and the ligands. Under similar conditions, these ligands did not form complexes with other metals. Therefore, adopting a different procedure,we have synthesised and characterized complexes of 1,3-dihyrdo-4,5-difuranyl-2H-imidazolin-2-thione(DFIT)(L) and 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione(MDPIT)(L') with other metal ions like Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Ag(I) and Cd(II) and presented in this chapter.

A. EXPERIMENTAL

1. Materials and methods

The details regarding the materials and methods used are given in Chapter II.

2. Synthesis of ligands

Complexes of the ligands DFIT and MDPIT are described in this chapter. The methods of synthesis of these ligands are discussed in detail in Chapter IV.

3. Synthesis of complexes

The silver complexes were prepared by stirring a methanolic solution (20 ml) of the ligand (0.001 mol) with an aqueous solution (10 ml) of the silver salt (0.001 mol) for about 1h. The solid complexes formed were filtered off, washed with methanol and dried over P_4O_{10}. The whole synthetic processes were carried out in the absence of direct sunlight and the dried complexes were stored in amber coloured bottles.

The cadmium complexes were synthesised in a different method. A methanolic solution (10 ml) of the metal salt (0.001 mol) was added in drops to a refluxing solution of the ligand (0.001 mol) in (20 ml) DMF, and the solution mixture was refluxed for 1 h. On cooling to room temperature brown solids separated out which were filtered off, washed with methanol and dried over P_4O_{10}.

The metal nitrate complexes were synthesised by the following procedure[110]. To a solution of the ligand (0.001 mol) in hot ethyl acetate (20 ml), added a solution of the metal nitrate (0.001 mol) in hot ethyl acetate (10 ml) containing triethylorthoformate (5% by volume). The resultant solution was warmed for several minutes and cooled to room temperature. The solid product formed was separated by filtration, washed with a small volume of hot ethyl acetate and dried under reduced pressure.

All the other complexes were synthesised by using the respective metal salt solution (0.001 mol) in minimum volume of hot, absolute ethyl alcohol, containing 10% triethylorthoformate as dehydrating agent. To this solution, the ligand (0.001 mol) in hot absolute alcohol (10 ml) was added and the resulting solution was warmed for several minutes and then left aside until precipitation was complete. The product was isolated by filtration, washed with a small volume of hot absolute ethanol and then dried under reduced pressure over P_4O_{10}.

B. RESULTS AND DISCUSSION

The properties, structures and geometries of the complexes were established with the help of analytical,- physico-chemical-and spectral data.

1. Characterisation of ligands

The structures of the ligands, DFIT and MDPIT, have already been established with the help of analytical- and spectral data. The details are given in Chapter IV.

2. Formulae and general properties of the complexes

Complexes of DFIT with $CrCl_3$, $MnCl_2$, $FeCl_3$, $Co(NO_3)_2$, CdX_2, where X = OAc, Cl, Br or NO_3 , AgX, where X = OAc or NO_3 and Ag_2SO_4 were synthesised. We were not able to prepare nickel complexes of this ligand. With MDPIT, complexes were synthesised using $CrCl_3$, NiX_2,where, X = OAc, Cl or NO_3 and $Zn(OAc)_2$. No solid complexes were isolated in the case of other metal ions, such as Mn(II), Fe(III), and Co(II).

All these complexes are stable in air. The analytical data of the complexes are given in Tables 1 and 2. Elemental analyses data of the complexes of DFIT correspond to the general formulae ML_2X_2, where M = Cr(II), Mn(II), Fe(II) or Co(II); MLX, where M = Ag(I);[Ag_2L_2(SO4)(H2O$)_2$] and MLX_2, where M = Cd(II). The complexes of MDPIT have the following stoichiometries, ML'_2X_2, where M = Cr(II) or Ni(II) and $ML'X_2$, where M = Zn(II). In all these complexes X corresponds to OAc,Cl, Br, or NO_3.

TABLE 1

Analytical data of complexes of 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione (DFIT) (L)

Complex	Molecular formula	Molecular weight	Colour	Found (calculated) %				
				Metal	C	H	N	Anion
$[CrL_2Cl_2]$	$CrC_{22}H_{16}N_4S_2O_4Cl_2$	587	Blue	7.98 (8.8)	44.2 (44.9)	2.9 (2.7)	9.3 (9.5)	11.22 (12.09)
$[MnL_2Cl_2]$	$MnC_{22}H_{16}N_4S_2O_4Cl_2$	590	Pale-pink	9.1 (9.3)	44.3 (44.7)	2.82 (2.7)	10.02 (9.49)	11.98 (12.03)
$[FeL_2Cl_2]$	$FeC_{22}H_{16}N_4S_2O_4Cl_2$	591	Green	9.21 (9.45)	44.02 (44.6)	2.68 (2.70)	9.40 (9.47)	12.09 (12.01)
$[CoL_2\ Cl_2]$	$CoC_{22}H_{16}N_4S_2O_4Cl_2$	594	Pink	9.82 (9.9)	44.2 (44.4)	2.89 (2.69)	9.44 (9.42)	11.08 (11.95)
$[AgL\ (OAc)(H_2O)]$	$AgC_{13}H_{13}N_2SO_5$	416	Light-yellow	26.08 (25.86)	35.93 (37.42)	3.02 (3.11)	6.80 (6.70)	--
$[AgL(NO_3)(H_2O)]$	$AgC_{11}H_{10}N_3SO_6$	419	Light-yellow	24.30 (25.67)	32.08 (31.44)	2.50 (2.38)	10.92 (10.00)	--
$[Ag_2L_2(SO_4)(H_2O)_2]$	$Ag_2C_{22}H_{10}N_4S_3O_{10}$	813	Light-yellow	27.09 (26.49)	32.40 (32.44)	2.42 (2.5)	6.89 (6.88)	
$[CdL\ (OAc)_2]$	$CdC_{15}H_{14}N_2SO_6$	462	Brown	24.03 (24.3)	39.02 (38.92)	3.92 (3.02)	6.02 (6.05)	--
$[Cd\ L\ Cl_2]$	$CdC_{11}H_8N_2SO_2Cl_2$	415	Brown	26.92 (27.05)	30.98 (31.77)	1.20 (1.90)	6.08 (6.74)	
$[CdLBr_2]$	$CdC_{11}H_8N_2SO_2Br_2$	504	Brown	22.13 (22.28)	26.12 (26.16)	1.83 (1.58)	5.69 (5.55)	32.89 (31.72)
$[CdL(NO_3)_2]$	$CdC_{11}H_8N_4SO_8$	468	Brown	28.19 (28.18)	34.40 (35.45)	1.98 (1.70)	11.03 (11.95)	--

TABLE 2

Analytical data of complexes of 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H- imidazolin-2-thione (MDPIT) (L')

Complex	Molecular formula	Molecular weight	Colour	Found (calculated) %				
				Metal	C	H	N	Anion
[CrL'$_2$Cl$_2$]	$CrC_{34}H_{32}N_2S_2O_4Cl_2$	749	Blue	6.01 (6.94)	53.93 (54.47)	4.08 (4.27)	3.89 (3.73)	9.42 (9.47)
[NiL'$_2$(OAc)$_2$]	$NiC_{38}H_{38}N_4S_2O_8$	802	Dark-green	7.38 (7.32)	55.82 (56.85)	4.39 (4.73)	6.93 (6.98)	--
[NiL'$_2$Cl$_2$]	$NiC_{34}H_{32}N_4S_2O_4Cl_2$	755	Bluish-green	8.01 (7.77)	54.93 (54.03)	4.03 (4.23)	7.42 (7.41)	9.21 (9.4)
[NiL'$_2$(NO$_3$)$_2$]	$NiC_{34}H_{32}N_6S_2O_{10}$	808	Green	7.92 (7.26)	50.48 (50.49)	3.92 (3.96)	10.02 (10.39)	
[ZnL'(OAc)$_2$]	$ZnC_{21}H_{22}N_2SO_6$	496	White	12.92 (13.17)	50.79 (50.77)	4.43 (4.43)	5.89 (5.64)	--

The molar conductances of all the complexes were determined using their 10^{-3}M solutions in DMF. The values were compared with standard ones[118] and found that the complexes act as non-electrolytes, indicating the coordinated nature of the anions. The insolubility of these complexes in common solvents supports this observation.

3. Magnetic behaviour

The magnetic susceptibility values of all the complexes were determined using a Gouy balance at room temperature. The values are given in Tables 3 and 4.

Chromium in its complexes, usually, exists in two different oxidation states +2 and +3. They have different magnetic properties. The ground term of octahedral complex (both high-spin and low-spin) of Cr^{3+} is $^4A_{1g}$ and no orbital contribution is expected. The observed value of magnetic moment is 3.77 B.M. which is less than the spin-only value, 3.88 B.M. Tetrahedral complexes of Cr(III) are rare[50].

The ground term of high-spin octahedral Cr(II) is ^5E_g, hence no orbital contribution is expected. The expected magnetic moment value is 4.90 B.M. which corresponds to four unpaired electrons. The low-spin, octahedral Cr(II) has a ground term $^3T_{1g}$ and hence orbital contribution is expected. The experimental value (3.27 B.M.) is higher than the spin-only value (2.83 B.M.) for two unpaired electrons. Tetrahedral complexes of Cr(II) are also rare.

The chromium complexes under the present investigation register magnetic moments 4.93 and 4.99 B.M., respectively. These values indicate that chromium is in +2 oxidation state and is in a high-spin, octahedral environment.

Eventhough ,both high-spin and low-spin complexes of Mn(II) are known,[38] majority of them are high-spin[88] type. The ground term of high-spin Mn(II) (both tetrahedral and octahedral) is $^6A_{1g}$ and no orbital contribution is expected. Hence a magnetic moment value very close to the spin-only value for five unpaired electron (5.92 B.M.) is expected. The ground term for octahedral low-spin Mn(II) is $^2T_{1g}$ with orbital contribution and hence the experimental value (2.50 B.M.) of magnetic moment is greater than the spin-only value for one unpaired electron (1.73 B.M.). In the present case, the observed magnetic moment value is 5.98 B.M. for $[Mn(DFIT)_2Cl_2]$ indicating its octahedral geometry.

Fe(III) is isoelectronic with Mn(II) and the magnetic moment values are same as for the Mn(II) ion. The complexes of Fe(II) show different magnetic properties depending upon the geometry. In high-spin octahedral complexes, the ground term of Fe(II) is $^5T_{2g}$ which results in orbital contribution. Hence the experimental value of magnetic moment (5.45 B.M.) is greater than the spin-only value for four unpaired electrons (4.90 B.M.). Low-spin, octahedral complexes of Fe(II) possess orbital singlet ground state $^1A_{1g}$ with no unpaired electron and hence the magnetic moment value expected is zero.

TABLE 3

Molar susceptibilities and magnetic moments of 1,3-dihydro-4,5-difuranyl –2H-imidazolin-2-thione (DFIT) (L)

Complex	$\chi_M \times 10^{-6}$ cgs units	$-\chi_D \times 10^{-6}$ cgs units	$\chi_C \times 10^{-6}$ cgs units	μ (B.M.)
[$CrLCl_2$]	9814	315	10130	4.93
[$MnLCl_2$]	14587	317	14904	5.98
[$FeLCl_2$]	11566	318	11885	5.34
[$CoLCl_2$]	9065	315	9380	4.74
[AgLX]	Diamagnetic			
[$CdLX_2$]	Diamagnetic			

χ_M = molar susceptibility

χ_D = diamagnetic correction

χ_C = corrected molar susceptibility.

X = OAc, Cl, Br, NO_3 or SO_4

TABLE 4

Molar susceptibilities and magnetic moments of complexes of 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione (MDPIT) (L')

Complex	$\chi_M \times 10^{-6}$ cgs units	$-\chi_D \times 10^{-6}$ cgs units	$\chi_C \times 10^{-6}$ cgs units	μ (B.M.)
$[CrL'_2Cl_2]$	9967	410	10378	4.99
$[NiL'_2(OAc_2)]$	4231	415	4649	3.34
$[NiL'_2Cl_2]$	4185	408	4594	3.32
$[NiL'_2(NO_3)_2]$	4121	417	4538	3.30
$[ZnL'(OAc)_2]$	Diamagnetic			

χ_M = molar susceptibility
χ_D = diamagnetic correction
χ_C = corrected molar susceptibility.

In the present investigation, $[Fe(DFIT)_2Cl_2]$ registers a magnetic moment of 5.34 B.M., indicating that iron is in the +2 oxidation state and has an octahedral geometry.

The magnetic properties of Co(II) and Ni(II) complexes are discussed in detail in Chapter III. The cobalt(II) complex of DFIT, $[Co(DFIT)Cl_2]$ shows a magnetic moment of 4.74 B.M. indicating its octahedral geometry. The Ni(II) complexes of MDPIT, $[Ni(MDPIT)_2(OAc)_2]$, $[Ni(MDPIT)_2Cl_2]$ and $[Ni(MDPIT)_2(NO_3)_2]$ show magnetic moments of 3.34, 3.32 and 3.30 B.M. respectively. Octahedral geometry can, therefore, be assigned to these complexes.

As expected, the Ag(I) and Cd(II) complexes of DFIT and Zn(II) complex of MDPIT are diamagnetic in nature.

4. Electronic spectra

The electronic spectral bands of the complexes are given in Tables 5 and 6. Six-coordinate Cr(II) has a d^4 configuration, which leads to either a quintet (^5E_g) or a triplet ($^5T_{1g}$) ground state. For the triplet ground state, several spin-allowed bands would be expected, since there are more than one triplet excited states. However , for quintet ground state the only one excited quintet state is $^5T_{2g}$ and therefore, the electronic spectrum exhibits a single band corresponding to the only spin-allowed transition, $^5E_g \rightarrow {}^5T_{2g}$ at 710 nm. Such complexes are blue in colour[122].

The Cr(II) complexes of DFIT and MDPIT investigated here register weak bands around 710 nm, which supports the observation that Cr is in +2 oxidation state in these complexes. This is further supported by the blue colour of these complexes. The magnetic moment values also supplement this. Thus, it can be inferred that during complex formation, the Cr(III) is reduced to Cr(II) by the ligands. The reducing nature of these ligands is already observed in the complex formation reactions with Cu(II) salts.

Majority of Mn(II) complexes are of high-spin type. In octahedral Mn(II) complexes, there are no spin-allowed d-d transitions. All are multiplicity-and Laporte forbidden[89]. In tetrahedral complexes, the d-d transitions are spin-forbidden. However, as there is no centre of symmetry in tetrahedral molecule, the d-d transitions are no longer Laporte forbidden, and they are more intensely coloured than octahdral ones[126].

The Mn(II) complex investigated here does not register any characteristic bands in the visible region. The complex is pale-pink in colour and hence it has an octahedral geometry.

Iron(III) is isoelectronic with Mn(II), with a ground state $^6A_{1g}$. Since there is no excited state with multiplicity 6, all electronic transitions in high-spin Fe(III) complexes are doubly forbidden i.e., Laporte- as well as spin forbidden[127]. Consequently all bands are very weak. In Fe(II), there is only one spin-allowed transition. The high-spin octahedral Fe(II) ion gives pale- green solution and there is an absorption at about 1000 nm[122]. In the Fe(II) complex of DFIT, a weak band is observed at 988 nm. The complex is pale-green in colour. Thus, the magnetic moment measurements, electronic spectrum, colour and the analytical data of the complex show that iron is in +2 oxidation state. Thus, it can be inferred that Fe(III) is reduced to Fe(II) during complex formation.

The reduction of Cu(II) to Cu(I) by thione ligands during complex formation is well documented[38,108,109]. The Fe(II) complexes of unsubstituted imidazolin-2-thione are also reported[128]. Lobana[65] reported the formation of $[Fe(HPyS)_2Cl_2]$ by the reaction of $FeCl_3$ and pyridine-2-thione (HPyS), where the ligand reduced Fe(III) to Fe(II). From the magnetic measurement and electronic spectral data, it can be deduced that DFIT and MDPIT reduce Cr(III) and Fe(III) to Cr(II) and Fe(II), respectively, during complex formation.

The Co(II) complex of DFIT, $[Co(DFIT)_2Cl_2]$, registers three bands at 1169, 614 and 497 nm which may be assigned, respectively, to $^4T_{1g} \rightarrow {}^4T_{2g}$ (F), $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions of an octahedral Co(II) complex.

The Ni(II) complexes of MDPIT, $[Ni(MDPIT)_2(OAc)]$, $[Ni(MDPIT)_2Cl_2]$ and $[Ni(MDPIT)_2(NO_3)_2]$ register intense bands near 400 nm and two weak bands around 720 and 1170 nm. These may be, respectively, due to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$,

${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transitions, characteristic of octahedral Ni(II) complexes.

TABLE 5

Electronic spectral bands of complexes of 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione(DFIT) (L) and their assignments

Complex	Bands (nm)	Assignments	Geometry
$[CrL_2Cl_2]$	711	${}^5E_g \rightarrow {}^5T_{2g}$	octahedral
$[FeL_2Cl_2]$	988	${}^5T_{2g} \rightarrow {}^5E_g$	octahedral
$[CoL_2Cl_2]$	1169 614 497	${}^4T_{1g} \rightarrow {}^4T_{2g}$ ${}^4T_{1g} \rightarrow {}^4A_{2g}$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	octahedral

TABLE 6

Electronic Spectral bands of complexes of 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione(MDPIT)(L') and their assignments

Complex	Bands (nm)	Assignments	Geometry
$[CrL'_2Cl_2]$	709	${}^5E_g \rightarrow {}^5T_{2g}$	octahedral
$[NiL'_2(OAc)_2]$	415 725 1170	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$	octahedral
$[NiL'_2(Cl_2)]$	395 710 1175	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$	octahedral
$[NiL'_2(NO_3)_2]$	400 720 1175	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$	octahedral

5. Infrared spectra

The significant IR spectral bands of the two ligands and their complexes, along with their assignments are given in Tables 7- 9.

The absence of ν_{SH} at 2500 cm^{-1} in the spectra of free ligands, together with presence of ν_{NH} as well as the four characteristic thioamide bands confirm the thione tautomer to be the dominant form of the ligands in solid state. The four characteristic thioamide bands of the two ligands are identified and the details are given in Chapter IV. The position of ν_{NH} at a lower frequency is indicative of the presence of N–H.....S bonds in solid ligands. Since the 4 and 5 positions of the imidazole ring are substituted with same groups, both NH groups are identical which is indicated by the existence of only one band corresponding to $\nu_{NH.}$

The ν_{NH} bands in the spectra of the Cr(II), Mn(II), Fe(II), Co(II) and Cd(II) complexes of DFIT split in into two bands; one at a lower frequency region while the other at a higher frequency region. . In the free ligand, the NH is hydrogen bonded to S and hence ν_{NH} has a low value. The situation is, however, complicated by the fact that the heterocyclic thiones can readily form hydrogen-bonds with anions in the complex[124,125]. Thus, the shift in ν_{NH} to low frequency most likely results from a combination of factors including electronic changes within the molecule upon coordination as well as hydrogen-bonding effects. But the splitting of ν_{NH} to two bands shows that one of the nitrogen atoms takes part in coordination[110]. The shift of one of these bands to higher frequency region may be due to the absence of hydrogen-bonding with the sulphur atom of the ligand. This is an indication of the S coordination because coordination through S atom decreases the electron availability on it and hence reduces the chance of hydrgen-bonding. Thioamide band I which has major contributions from ν_{CN} and δ_{CH}, shows negative shift of 20-75 cm^{-1} in the spectra of the complexes[110]. This also indicates the presence of N- coordination in these complexes.

The thioamide bands II, III and IV have contributions from $\nu_{C=S}$ and the coordination of the metal through S atom should, therefore, cause negative shifts in these bands. In the spectra of the complexes, all the three bands show negative shifts indicating that the ligands coordinate through the thione sulphur atoms[110,115]. Thus, the IR spectra show that DFIT acts as a bidentate, neutral ligand coordinating through one of the nitrogen atoms and the thione sulphur atom in its complexes with Cr(II), Mn(II), Fe(II), Co(II) and Cd(II).

In Ag(I) complexes of DFIT, $[Ag(DFIT)(OAc)(H_2O)]$, $[Ag(DFIT)(NO_3)(H_2O)]$ and $[Ag_2(DFIT)_2(SO_4)(H_2O)_2]$, presence of coordinated water is indicated by a broad band near 3400 cm^{-1}. The ν_{NH} shows a positive shift indicating the non- participation of N in coordination[115]. The thioamide band I which has contribution from $\nu_{C=N}$, shows a slight positive shift, confirming the non-participation of N in coordination. However, the thioamide bands II, III and IV which have contributions from $\nu_{C=S}$, show considerable negative shifts, indicating the coordination of ligand through the thione sulphur atom[115]. Thus, in Ag(I) complexes, DFIT act as a neutral monodentate ligand coordinting through thione S atom.

The changes occurred in the IR spectrum of MDPIT on coordination are almost similar in its complexes with Cr(II), Ni(II) and Zn(II) complexes. The ν_{NH} splits into two components, one shifted to a lower frequency and other to a higher value. The changes are similar to that seen in the complexes of DFIT with Cr(II), Mn(II), Fe(II), Co(II) and Cd(II). The thioamide bands show the same kind of changes. These changes indicate that in these complexes, MDPIT acts as bidentate, neutral ligand coordinating through thione sulphur - as well as one of the imide nitrogen atoms.

a) IR features of coordinated anions in the complexes

(i) Acetato complexes

The separation between $\nu_{as\ CO_2^-}$ and $\nu_{s\ CO_2^-}$ decides the mode of coordination of acetate radical. In the four acetato complexes discussed in this chapter, [Ag(DFIT)(OAc)(H_2O)], [Cd(DFIT)($OAc)_2$], [Ni($MDPIT)_2$($OAc)_2$] and [Zn(MDPIT)($OAc)_2$] the separation between these two bands is large, indicating the monodenticity of acetate radical.

TABLE 7

Significant IR spectral bands (cm $^{-1}$) of 1,3-dihydro-4,5-difuranyl-2H- imidazolin-2-thione (DFIT)(L), its complexes and their assignments

DFIT(L)	[CrL_2Cl_2]	[MnL_2Cl_2]	[FeL_2Cl_2]	[CoL_2Cl_2]	Assignments[@]
	3180	3185	3240	3210	
3126	3118	3124	3131	3138	ν_{NH}
1645	1646	1658	1626	1650 (sh)	$\nu_{C=C}+\nu_{C-N}$
1548	1546		1527	1520	
1508 (sh)	1507)	1500		1500	TA I
1480	1460	1460	1467	1381	
1394 (sh)	1391	1381	1387	1348	
1222	1208	1208	1195	1182	TA II
1020	1016	980	1016	1016	TA III
815	811	805	797	811	TA IV
690	691	680	685	671	δ_{NH}
592	585	585	598	592	$\nu_{C=S}$

[@] TA = Thioamide band

TABLE 8

Significant IR spectral bands (cm^{-1}) of 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione (DFIT)(L), its complexes and their assignments

DFIT (L)	[Ag L(OAc)H_2O]	[AgL(NO_3)(H_2O)]	[$Ag_2L_2(SO_4)(H_2O)_2$]	[CdL$(OAc)_2$]	[$CdLCl_2$]	[$CdLBr_2$]	[CdL$(NO_3)_2$]	Assignments[@]
	3390	3409	343		3280	3240	3210	ν_{OH} of coordinated water
3126	3144	31160	3180	3188	3138	3144	3131	ν_{NH}
1645	1650	1639	1653	1686	1692	1692	1633	$\nu_{C=C} + \nu_{C=N}$
1548	1553	1553	1546	1553	1540	1553	1507	
1508	1510	1507	1513					TA I
1480	1474	1480	1476	1454	1454	1454	1427	
1394	1387	1381	1381	1384	1387	1387	--	
1222	1155	1149	1155	1408	1149	1155	1155	TA II
1020	1016	1016	983	1016	1023	1016	1016	TA III
815	804	804	738	751	751	751	758	TA IV
690	658	651	670	650	670	680	--	δ_{NH}
592	570	585	585	590	585	585	590	$\nu_{C=S}$
	1600			1650				νas of COO^-
	1434			1440				νs of COO^-
		1441					1450	ν_1 of NO_3^-
		1301					1255	ν_2 of NO_3^-
		1076					1070	ν_4 of NO_3^-
			1215 1089 917 625 460					SO_4^{--}

[@] TA = Thioamide band

TABLE 9

Significant IR spectral bands (cm^{-1}) of 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione (MDPIT) (L'), its complexes and their assignments

MDPIT (L')	$[CrL'_2Cl_2]$	$[NiL'_2(OAc)_2]$	$[NiL'_2Cl_2]$	$[NiL'_2(NO_3)_2]$	$[ZnL'(OAc)_2]$	Assignments[@]
	3277	3277	3270	3271	3250	
3045	3039	3038	3038	3051	3005	ν_{NH}
1610	1633	1633	1606	1613	1620	$\nu_{C=C} + \nu_{C=N}$
1570	1566	1567	1550	1563	1527 (sh)	
1514	1507	1507	1507	1507	1500	TA I
1458	1407	1414	1401	1408	1417	
1373	1295	1296	1387	1381	1367	
1249	1241	1248	1241	1248	1248	
1211	1215	1208	1205			TA II
1174	1169	1174	1175	1169	1169	
1090	1023	1023	1023	1030	1023	TA III
792	678	744	730	784	731	TAIV
536	539	539	522	539	539	$\nu_{C=S}$
		1613			1573	ν_{as} of COO^-
		1450			1454	ν_{as} of COO^-
				1442		ν_1 of NO_3^-
				1295		ν_2 of NO^{3}-
				1109		ν_4 of NO_3^-

[@] TA = Thioamide band

(ii) Halo complexes

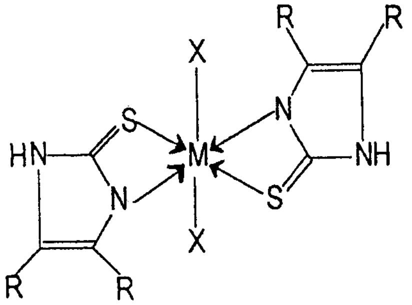
The status of the halide radicals cannot be determined from the IR spectra alone, because the M–X stretching frequency is below the range of the instrument used (X = Cl or Br). However, the elemental analytical- and conductance data indicate their coordinated nature.

(iii) Nitrato complexes

The magnitude of splitting of ν_1 and ν_2 of nitrate radical decides its denticity in complexes[117,119]. The magnitude of splitting is high in the three nitrato complexes discussed in this chapter, indicating the monodenticity of nitrate radical.

C. CONCLUSIONS

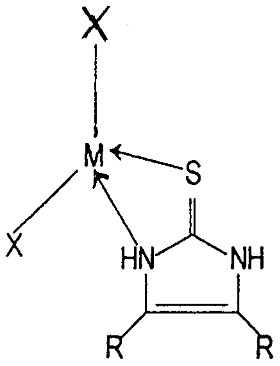
Sixteen new complexes of imidazolin-2-thiones via. 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione (DFIT) and 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione (MDPIT), were prepared and characterised by physico-chemical- and spectral studies. The complexes had general formulae $[ML_2X_2]$, where M = Cr(II), Mn(II), Fe(II), Co(II) or Ni(II), $[MLX_2]$, where M = Cd(II) or Zn(II) and $[MLX(H_2O)]$, where M = Ag(I). The sulphato complex of Ag(I) with DFIT, however, had a dimeric structure $[Ag_2L_2(SO_4)(H_2O)_2]$. In all these cases L = DFIT or MDPIT and X = OAc, Cl, Br or NO_3. Based on magnetic measurements and electronic spectral studies geometries had been assigned to them. The Cr(II), Mn(II), Fe(II), Co(II) and Ni(II) complexes had an octahedral geometry, the Cd(II) and Zn(II) complexes had a tetrahedral geometry and the Ag(I) complexes were triangular. In the Ag(I) complexes, DFIT act as neutral monodentate ligand coordinating through the thione sulphur atom alone, while in all other complexes, the ligands act as bidentate neutral ones coordinating through thione sulphur- and one of the ring N atoms. The structures of the complexes are represented as follows. **I-IV.**



Where M = Cr(II), Mn(II), Fe(II) Co(II) or Ni(II)

X = OAc, Cl, Br, NO_3 and R = C_4H_3O, C_7H_7O or C_6H_5O

I

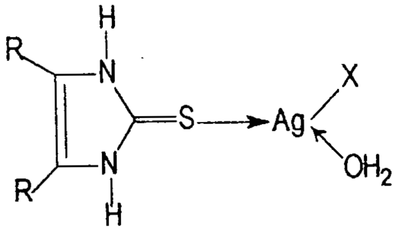


where M = Cd(II) or Zn(II)

X = Cl, Br, NO_3 or OAc

and R = C_4H_3O, C_7H_7O or C_6H_5O

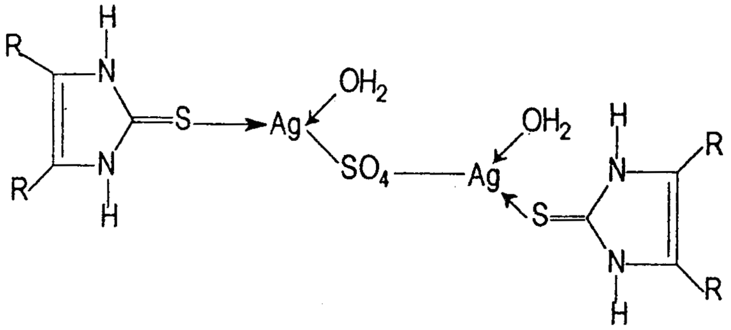
II



X = oAc or NO

and R = C_4H_3O, C_7H_7O or C_6H_5O

III



IV where R = C_4H_3O, C_7H_7O or C_6H_5O

PART II
INTRODUCTION

Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

Part II

Thermal Decomposition Studies

CHAPTER I

INTRODUCTION

Thermal decomposition studies are extensively used in all fields of research. In thermal analysis, some physical parameter of a system is measured as a function of temperature. Thermogravimetry (TG), differential thermal analysis (DTA) ,etc. are examples of such methods.

In TG, a sample is continuously weighed as it is heated at a constant, preferably, linear rate[129]. The resultant weight change Vs. temperature curve thus obtained gives informations concerning the thermal stability and composition of the original sample, intermediate compound and the final residue. The curve is quantitative in that the stoichiometry of the compound can be calculated at any temperature. The shape of the curve is determined by the kinetic parameters of decomposition such as reaction order, frequency factor and energy of activation. The utility of the method is its simplicity.

In differential thermal analysis (DTA), the temperature of a sample and a thermally inert reference material are compared, as the sample is heated at a uniform rate. The temperature difference between the sample and reference material is recorded as a function of temperature. The reference material should not undergo any decomposition during heating.

A. REACTION KINETICS BY THERMOGRAVIMETRY

The use of thermogravimetry as a tool for the elucidation of the reaction kinetics for solid- or liquid state thermal decomposition is quite attractive. The solid-solid transformations have been summarized by Lukaszewski and Redfern[130], as follows:

1. $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$
2. $A_{(s)} + B_{(s)} \rightarrow AB_{(s)} + C_{(g)}$
3. $A_{(s)} + B_{(s)} \rightarrow C_{(s)} + D_{(s)}$
4. $A_{(s)} \rightarrow B_{(s)} + C_{(l)}$
5. $A_{(s)} + B_{(g)} \rightarrow C_{(s)}$

Of these different types, much attention has been devoted to kinetic studies of reactions of the type 1.

Two different methods are used in kinetics study by thermogravimetry:

1. Isothermal method in which a plot of weight change Vs. time is obtained at constant temperature.

2. Non-isothermal method in which a plot of weight changes Vs. temperature is obtained under dynamic temperature conditions, at a linear rate of heating. From the plots, the kinetic parameters like energy of activation (E), Arrhenius pre-exponential factor (A) and change in entropy (ΔS) can be calculated. Different equations are derived using differential-, integral- or approximation methods.

The basis of all these derivations is the general kinetic equation

$$\frac{dx}{dt} = k\ x^n \qquad \text{......................} (1)$$

where x is the amount of sample undergoing reaction, n is the order of reaction and k is the specific reaction rate. The temperature dependence of the specific reaction rate is expressed by Arrhenius equation

$$k = A\ e^{-E/RT} \qquad \text{.........................} (2)$$

where R is the gas constant. Combining equations (1) and (2),

$$\frac{dx}{dt} = A\ e^{-E/RT}\ x^{n} \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

All the equations used for the determination of kinetic parameters are derived from this equation. There are several equations, from which we have selected three, namely, Coats-Redfern, Horowitz-Metzger and MacCallum-Tanner, which are given below.

Coats and Redfern[131,132]

$$\ln\left[\frac{1-(1-\alpha)^{(1-n)}}{(1-n)\,T^{2}}\right] = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad \ldots\ldots(4)$$

Horowitz-Metzger[134]

$$\ln\left[\frac{1-(1-\alpha)^{(1-n)}}{(1-n)}\right] = \ln\frac{AR\,T_s^{2}}{\phi E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^{2}} \qquad \ldots\ldots\ldots(5)$$

MacCallum – Tanner[133]

$$\ln\left[\frac{1-(1-\alpha)^{(1-n)}}{(1-n)}\right] = \log\frac{AE}{\phi R} - 0.483\,E^{0.435} - \frac{(0.449+0.217E)\times 10^{3}}{T} \qquad \ldots\ldots\ldots(6)$$

where ϕ is the linear heating rate, T_s is the temperature of maximum decomposition and $\theta = (T - T_s)$.

The order of the reaction is calculated by using a method suggested by Horowitz-Metzer in a previous work[135]. Certain objections against this type of calculations were raised by some researchers[136].

B. THERMAL DECOMPOSITION STUDIES OF METAL COMPLEXES OF PYRAZOLIN-5-ONES AND IMIDAZOLIN-2-THIONES – A REVIEW

Thermal decomposition studies of metal complexes can give supplementary informations regarding their structures. The weight change Vs. temperature curve obtained gives information concerning the thermal stability-and composition of the complex. Therefore, thermal analysis can be used as a valuable technique for structural elucidation of metal complexes. Literature survey revealed that in recent years TG and DTA are used for structural determination along with other spectral studies. The kinetic parameters like activation energy, Arrehnius factor, entropy change, etc. can be calculated for the different stages of decomposition[137-139]. Different equations can be used for the calculation.

Kuncheria reported the thermal decomposition data of Cu(II) complexes of N_1-isonicotinoyl-3-methyl-2-pyrazolin-5-one.[14] These studies were carried out as a part of structural elucidation of the complexes. All the complexes decomposed in a single stage and the end products, in all the cases were CuO. The end products were identified by chemical analyses and through independent pyrolytic studies. Absence of coordinated water in these complexes was confirmed with the help of TG studies.

Thermal decomposition studies of metal complexes of unsubstituted imidazolin-2-thiones, their methyl derivatives and their saturated analogues were reported[140-142]. The thermal decomposition of Co(II) complexes of 1-methylimidazolin-2-thione (mimt) with a general formula $Co(mimt)_2X_2$, where X = Cl, Br or I had been studied in air and argon by means of TG and DTG techniques. The DTA of these complexes were carried out in nitrogen, and the reaction enthalpies from the melting- and decomposition endotherms were derived. The end products of decomposition in air had been identified by their X-ray powder patterns. Thermal analyses showed that all complexes decomposed in two stages. In the case of the chloro-and bromo complexes, two-third of (mimt) molecules were lost in the first stage and the remainder, along with the halogen atoms were lost in the final stage of the decomposition. But the decomposition pattern was slightly different for the iodo complex. However, in all cases, the final stage represented the formation of Co_3O_4.

Jordan and Raper[141] reported the thermal decomposition behaviours of Co(II) and Ni(II) complexes of 1,3-dimethylimidazolin-2-thione. These complexes had a general formula $M(Dmimt)_2X_2$, where M = Co(II) or Ni(II) and X = Cl, Br or I. All these complexes degraded to the respective oxides. The decomposition had been carried out in air and argon. The reaction enthalpies were calculated from

DTA in nitrogen. In all the cases the end products were identified by X-ray powder diffraction studies.

Thermal analyses of Co(II) and Ni(II) complexes of imidazolin-2-thiones (imdt) are also reported[142,143]. The thermal decomposition of the Ni(II) complexes of (imdt), $[Ni(imdt)_4X_2]$ where X = Cl or Br had been studied in air and in argon by means of TG and DTG as well as in nitrogen by DTA[135]. These complexes decomposed in three stages and the end products in both the cases were NiO which was confirmed by X-ray diffraction studies. Quantitative DTA had been used to derive reaction enthalpies from the melting-and decomposition endotherms of (imdt) and its complexes in nitrogen. The factors which govern the reaction enthalpies of these complexes had also been discussed here.

The thermal decomposition of Co(II) complexes of (imdt), $[Co(imdt)X_2]$, where X = Cl, Br or I had been studied by Jordan *et al.*[142] All the complexes, except the iodo complex, decomposed in two stages and the final products had been identified as Co_3O_4.Similar studies were reported by Raper *et al.* for Pd(II) and Pt(II) complexes of thiazole-thiones[144].

C. CONCLUSIONS

The literature survey showed that thermal decomposition studies of metal complexes of pyrazolin-5-ones and imidazolin-2-thiones were carried out for determining their structures. But no attempts had been made to calculate the kinetic parameters. Therefore, as a part of the present investigation, we have decided to record the thermograms of certain copper complexes of substituted pyrazolin-5-one and- imidazolin-2-thione and to calculate the kinetic parameters such as energy of activation, Arrhenius factor and change in entropy using Coats-Redfern, Horowitz-Metzger and MacCallum-Tanner equations.

PART II

THERMAL ANALYSES OF COPPER COMPLEXES OF SUBSTITUTED PYRAZOLIN-5-ONE AND- IMIDAZOLIN-2-THIONE

Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER II

THERMAL ANALYSES OF COPPER COMPLEXES OF SUBSTITUTED PYRAZOLIN-5-ONE AND- IMIDAZOLIN-2-THIONE

Thermograms of ten complexes of pyrazolin-5-one and imidazolin-2-thione were recorded and their stage-wise decompositions were studied in detail. The end product in each case had been identified with the help of chemical analyses and independent pyrolytic studies. Attempts were also made to calculate the kinetic parameters.

A. EXPERIMENTAL

1. Materials and methods

For the present investigation, we have selected copper complexes of two ligands. For the synthesis of these ligands and their complexes Analar Grade (BDH or E. Merck) chemicals were used. Solvents like ethanol, methanol, etc. were used after distillation.

The synthetic procedures of the two ligands and their metal complexes are described in the respective chapters of Part I of this thesis. All the complexes were dried thoroughly, powdered and the particle size was fixed in the range 150-200 BSS mesh. The thermal analyses were carried out using a Metler TA 4000 Thermal analysis system with TG 50 balance and TC 10A microprocessor. The heating rate was 20°C/min in static air.

Independent pyrolytic studies were conducted by heating a known amount of complex in a silica crucible at 800°C for 1h. The final residues were identified by chemical analyses. The weights of the final products and the percentages of mass-losses were then determined.

B. RESULTS AND DISCUSSION

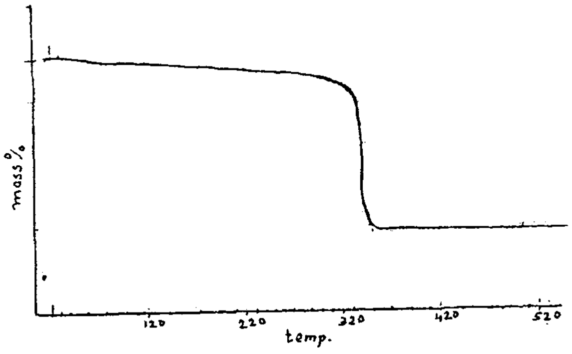
The selected compounds include five copper(II) complexes of N_1-salicylyl-3-methylpyrazolin-5-one (SMP) (L) having a general formula $[CuLX_2]$, where X = OAc, Cl, NO_3, $\frac{1}{2}SO_4$ or CNS and five copper(I) complexes of 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione (MDPIT) (L') having a general formula $[CuL'X(H_2O)]$, where X = OAc, Cl, Br or NO_3. The sulphate complex of MDPIT has the formula $[Cu_2L'_2(SO_4)(H_2O)_2]$.

The stage-wise decompositions of these complexes were examined as a part of structural characterisation. The various kinetic parameters were calculated using different equations. The mathematical equations used are discussed in Chapter I.

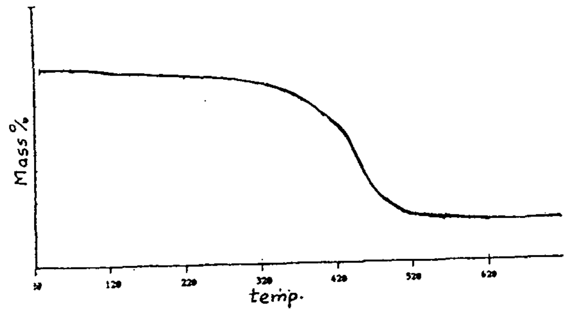
The calculations were made using a programme in Fortran 77. The decomposition data and kinetic parameters are given in Tables 1-19.

1. Decomposition data and kinetic parameters of copper(II) complexes of SMP

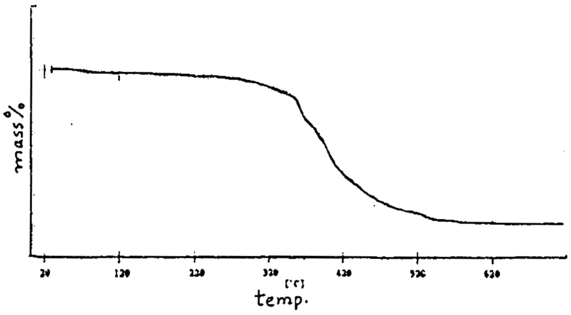
The thermograms of the Cu(II) complexes of SMP are given as I-V. the thermal decomposition data of the complexes are given in Table 1. All these complexes exhibit considerable stability towards heat. They are stable upto a temperature of 310°C.



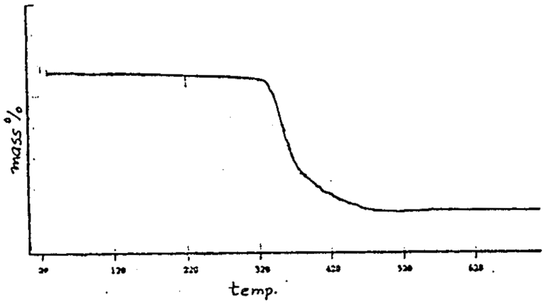
I



II


mass %
20
120
220
320
420
520
620
[°C]
temp.

III


mass %
20
120
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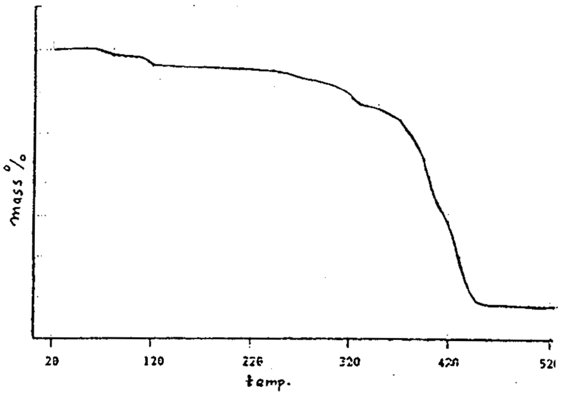
temp.

IV


mass %
20
120
220
320
420
52
temp.

V

Absence of coordinated water in these complexes is confirmed by this observation. All these complexes decompose in a single step giving stable products (CuO) between 420 and 520°C. The mass-loss data obtained from both TG- and independent pyrolysis experiments agree well with the theoretical values, which confirm the purity of the complexes.

Analyses of the data obtained using Horowitz-Metzger equation indicate that the decompositions of all these complexes follow first order kinetics. Accordingly, the kinetic parameters for the decomposition steps were evaluated using different non-mechanistic equations. The satisfactory values of correlation coefficients ($r \approx 1$) in all cases indicate good agreement with the experimental data. The values of kinetic parameters (Table 2) obtained using three different equations, i.e., Coats-Redfern, Horowitz-Metzger and MacCallum-Tanner, show that the general agreement among these methods is good, within about 10%. However, slightly higher values of kinetic data are obtained from the Horowitz-Metzger method. Similar observations were also made by other workers after a comparative study of the kinetic data obtained by using various equations[145,146]. The values of the activation entropy of decomposition of these complexes vary from –5.44 to –56.72 kcal $deg^{-1}mol^{-1}$. The negative ΔS values indicate that the activated complexes have more ordered structures than the reactants and the reactions are slower than normal. It is also observed that the values of E and A decrease in the order $[CuL(OAc)_2] > [CuL(CNS)_2] > [CuLCl_2] > [CuL(SO_4)] > [CuL(NO_3)_2]$.

TABLE 1

Thermal decomposition data of copper(II) complexes of SMP[@] (L)

Complex	Decompo-sition stage	Decomposition temp. range(°C)	Mass-loss from			Decomposition pattern
			TG	Ind. pyrolysis	Theoretical	
$[CuL(OAc)_2]$	1	320-360	78.08	79.07	80.01	$[CuL(OAc)_2] \rightarrow CuO$
$[CuLCl_2]$	1	320-450	77.90	78.06	77.44	$[CuLCl_2] \rightarrow CuO$
$[CuL(NO_3)_2]$	1	310-500	79.2	80.19	80.39	$[CuL(NO_3)_2] \rightarrow CuO$
$[CuLSO_4]$	1	320-450	79.30	78.6	79.05	$[CuLSO_4] \rightarrow CuO$
$[CuL(CNS)_2]$	1	350-520	81.02	80.59	80.00	$[CuL(CNS)_2] \rightarrow CuO$

[@] SMP – N_1-salicylyl-3-methylpyrazolin-5-one

TABLE 2

Kinetic parameters of thermal decomposition of copper(II) complexes of SMP$^{@}$ (L)

Complex	Eqn.*	E kcal mol^{-1}	A s^{-1}	ΔS kcal deg^{-1}mol^{-1}	n
$[CuL(OAc)_2]$	CR	35.82	6.29×10^{10}	-8.72	1
	HM	36.46	4.2×10^{10}	-11.34	
	MT	31.87	8.2×10^{10}	-5.43	
$[CuLCl_2]$	CR	21.10	3.3×10^{5}	-39.36	1
	HM	17.57	1.9×10^{5}	-44.94	
	MT	16.95	1.6×10^{5}	-41.17	
$[CuL(NO_3)_2]$	CR	11.80	6.15	-56.71	1
	HM	16.14	2.53	-49.33	
	MT	11.52	1.15	-42.91	
$[CuL(SO_4)]$	CR	13.20	3.3×10	-53.29	1
	HM	16.51	1.8×10	-48.54	
	MT	12.11	1.7×10	-40.91	
$[CuL(CNS)_2]$	CR	23.20	2.4×10^{5}	-35.62	1
	HM	26.17	1.3×10^{5}	-32.27	
	MT	29.77	2.6×10^{5}	-26.25	

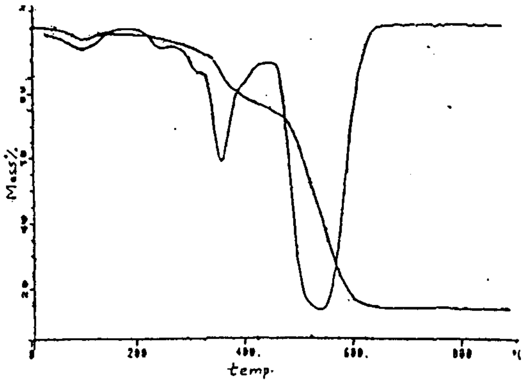
$^{@}$SMP - N_1-salicylyl-3-methylpyrazolin-5-one
*CR - Coats-Redfern
HM - Horowitz-Metzger
MT - MacCallum-Tanner
E - Energy of activation
A - Pre exponential factor
ΔS - Change in entropy
n - Order of the reaction

2. Decomposition data and kinetic parameters of copper(I) complexes of MDPIT

The thermograms of the complexes are given as **VI-X**.

a) [Cu(MDPIT)(OAc)(H_2O)]

This complex decomposes in three stages. The thermal decomposition data are given in table 3. In the first stage at 100-150°C, elimination of coordinated water takes place, producing 4.00% decrease in mass which is in close agreement with the theoretical value of 3.97%. The second stage starts at about 250°C and completes at 400°C, where elimination of coordinated acetate radical takes place. The percentage of theoretical mass-loss for the elimination of acetate radical closely agrees with the TG result. In the temperature range of 400-600°C, the complex completely decomposes to CuO with a percentage mass-loss of 83.00 against a theoretical value of 82.44%. The end product (CuO) is identified chemically. The independent pyrolytic studies are carried out and the results are in close agreement with TG-and theoretical values. Thus the thermal decomposition of this complex strongly supports the proposed structure of the complex [Cu(MDPIT)(OAc)(H_2O)].



VI

TABLE 3

Thermal decomposition data of copper(I) acetate complex of MDPIT[@] (L')

Complex	Decomposition stage	Decomposition temp. range (°C)	Mass-loss from			Decomposition pattern
			TG	Independent pyrolysis	Theoretical	
[CuL'(OAc)(H_2O)]	1	100 – 150	4.00	--	3.97	[CuL'(OAc)(H_2O)] → CuL'OAc
	2	250 – 400	17.56	--	16.97	[CuL'(OAc)(H_2O)] → CuL'
	3	450 – 600	83.00	83.20	82.44	[CuL'(OAc)(H_2O)] → CuO

[@] MDPIT = 1,3-dihydro 4,5-di(4-methoxyphenyl)-2H-imidazolin-2thione.

We were not able to calculate the kinetic parameters for some stages since the computer programme that we have used was not so sophisticated to respond to all minute data involved in each step. The kinetic parameters for the decomposition stages 2 and 3 were evaluated using three equations and the values are given in Tables 4 and 5. The values show slight variations which may be due to the various assumptions made in the derivations of the equations. Both these stages have comparable energy of activation. This is to be expected because these decomposition stages involve rupture of metal-ligand bonds of similar strengths. The negative values for ΔS show a more ordered activated complex and a less than normally fast reaction.

TABLE 4

Kinetic parameters of 2nd stage decomposition of copper(I) acetate complex of MDPIT@

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal $deg^{-1}mol^{-1}$	n
Coats-Redfern	17.01	2.01×10^3	-44.96	1
Horowitz-Metzger	15.29	2.98×10^3	-48.76	1
MacCallum-Tanner	17.54	2.89×10^3	-39.67	1

@MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

TABLE 5

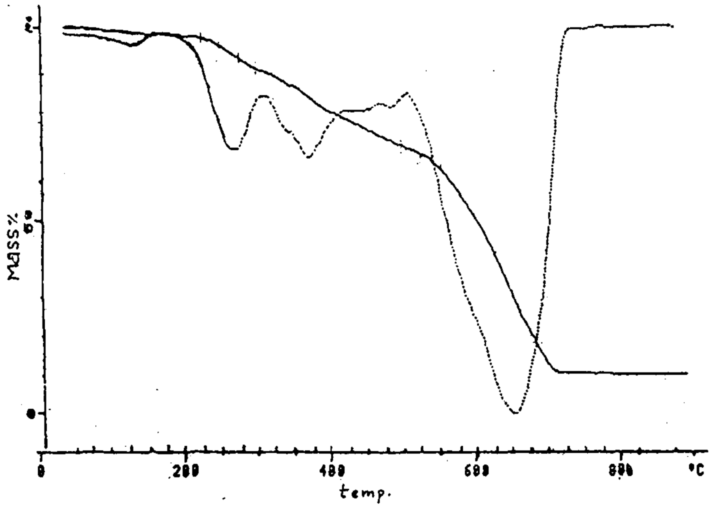
Kinetic parameters of 3rd stage decomposition of copper(I) acetate complex of MDPIT@

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal $deg^{-1}mol^{-1}$	n
Coats-Redfern	16.79	68.38	-52.16	1
Horowitz-Metzger	20.75	92.95	-41.40	1
MacCallum-Tanner	18.07	93.91	-37.80	1

@MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

b) [Cu(MDPIT)Cl(H_2O)]

The decomposition of this complex takes place in four stages. The first stage is at 100-180°C, where elimination of coordinated water takes place. In the second stage, the coordinated chloride radical gets decomposed with a mass-loss of 12.00% against a theoretical value of 12.45%. In the third stage, two methoxy groups present on the ring decompose and finally in the fourth stage, the complex completely decomposes to CuO. The percentage of mass-loss was evaluated by independent pyrolytic studies which is in close agreement with the theoretical- and TG data. The results support the proposed structure of the complex. The thermal decomposition data are given in Table 6.



VII

For the first stage, we were not able to calculate the kinetic parameters. The kinetic parameters of the 2nd, 3rd and 4th stages were calculated using the three equations. The values are given in Tables 7, 8 and 9. The activation energies of 2nd and 4th steps are comparable as these decomposition steps involve rupture of metal-ligand bands of comparable strengths. The third stage involves the elimination of two OCH_3 groups from the imidazole ring and, therefore, the activation energy is low. The more ordered natures of the activated complexes are shown by the negative values of ΔS. The reactions are slower than normal ones.

TABLE 9

Kinetic parameters of 4th stage decomposition of copper(I) chloride complex of MDPIT@

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal $deg^{-1}mol^{-1}$	n
Coats-Redfern	12.48	1.4	-60.02	1
Horowitz-Metzger	14.13	1.6	-54.92	1
MacCallum-Tanner	11.67	1.2	-58.32	1

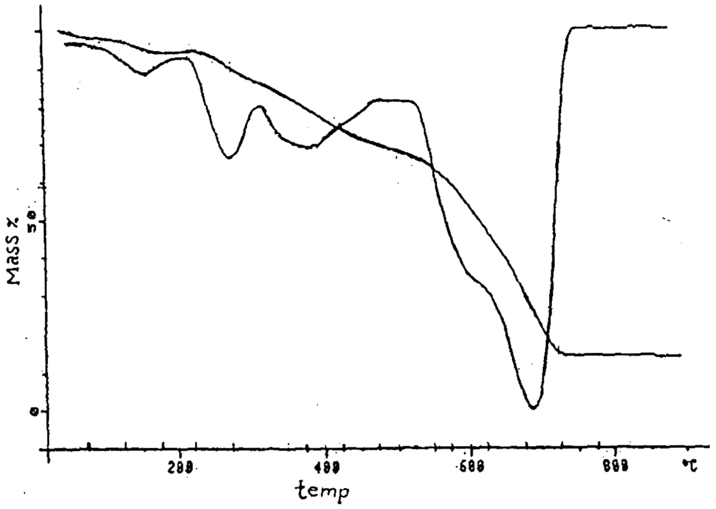
@MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre exponential factor
ΔS - Change in entropy
n - Order of the reaction

c) [Cu(MDPIT)Br(H_2O)]

The decomposition pattern of this complex is almost similar to that of [Cu(MDPIT)Cl(H_2O)]. In the first stage, the coordinated water gets decomposed in the temperature range of 100 to 150°C. In the second stage, the easily decomposable OCH_3 groups present on the ring get decomposed and then coordinated bromide radical gets eliminated in the third stage. These two stages take place continuously. The complex completely decomposes at a temperature of 600°C to CuO. This was confirmed by an independent pyrolytic study. The decomposition data of the complex are given in Table 10.

The kinetic parameters for the 2nd and 4th stages were calculated using three different equations and the values are given in Tables 11 and 12, respectively. The

3rd stage is a continuation of the 2nd and hence we were not able to calculate the parameters for the 3rd stage.



VIII

However, the energy of activation for the 2nd stage is comparatively low. Therefore, it can be inferred that the decomposition of OCH_3 groups take place before the elimination of bromide radical. As expected, the activation energy for the final decomposition step is high, as it involves the metal-ligand bond breaking. The reactions are slower than normal ones since they have more ordered activated complexes as indicated by the negative ΔS values.

TABLE 10

Thermal decomposition data of copper(I) bromide complex of MDPIT[@] L'

Complex	Decomposition stage	Decomposition temp. range (°C)	Mass-loss from			Decomposition pattern
			TG	Independent pyrolysis	Theoretical	
[CuL'Br(H_2O)]	1	100 – 150	4.30	--	3.74	[CuL'Br(H_2O)] → CuL'Br
	2	220 – 300	16.50	--	16.85	[CuL'Br(H_2O)] → [Cu(L'-2OCH_3)Br]
	3	300 – 450	35.00	--	33.72	[CuL'BrH_2O] → [Cu(L'-2OCH_3)]
	4	500 – 750	85.00	84.81	83.24	[CuL'Br(H_2O)] → CuO

[@] MDPIT = 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione

TABLE 11

Kinetic parameters of 2nd stage decomposition of copper(I) bromide complex of MDPIT$^{@}$

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal deg^{-1}mol^{-1}	n
Coats-Redfern	6.75	0.75	-60.31	1
Horowitz-Metzger	6.50	0.38	-61.66	1
MacCallum-Tanner	6.87	0.76	-46.54	1

$^{@}$MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

TABLE 12

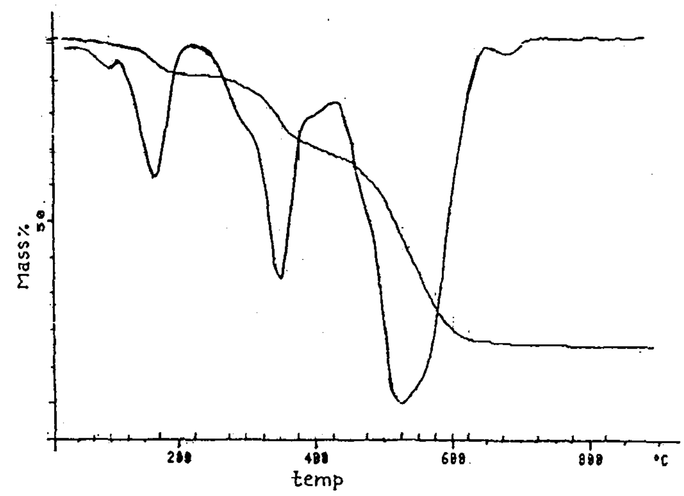
Kinetic parameters of 4th stage decomposition of copper(I) bromide complex of MDPIT$^{@}$

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal deg^{-1}mol^{-1}	n
Coats-Redfern	15.67	9.66	-56.33	1
Horowitz-Metzger	19.98	12.09	-51.31	1
Mac Callum-Tanner	17.45	18.60	-41.30	1

$^{@}$MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

d) $[Cu(MDPIT)(NO_3)(H_2O)]$

The thermal decomposition of $[Cu(MDPIT)(NO_3)(H_2O)]$ takes place in four well defined stages in the temperature range of 100-600 °C. The eliminations of coordinated water, two $-OCH_3$ groups and a nitrate radical, take place in the first three stages. Finally, in the fourth stage, the complex completely decomposes to CuO. This was confirmed by an independent pyrolytic study. The decomposition data are given in Table 13.



IX

The kinetic parameters for the different stages, except the first one, were calculated using three different equations and the data are given in Tables 14-16. The activation energies for the second and third stages are low. However, the activation energy of the 4th step, where M-L bond breaking takes place is fairly high. The negative values for ΔS indicate that the reactions are slower than normal.

TABLE 13

Thermal decomposition data of copper(I) nitrate complex of MDPIT[@] (L')

Complex	Decompo-sition stage	Decomposition temp. range (°C)	Mass-loss from			Decomposition pattern
			TG	Independent pyrolysis	Theoretical	
$[CuL'(NO_3)(H_2O)]$	1	100 – 150	4.00	--	3.97	$[CuL'(NO_3)(H_2O)] \rightarrow CuL'NO_3$
	2	150 – 200	10.50	--	10.73	$[CuL'(NO_3)(H_2O)] \rightarrow Cu(L'\text{-}2OCH_3)(NO_3)$
	3	200 – 450	30.50	--	31.10	$[CuL'(NO_3)(H_2O)] \rightarrow [Cu(L'\text{-}2OCH_3)]$
	4	450 – 600	84.00	83.46	82.60	$[CuL'(NO_3)(H_2O)] \rightarrow CuO$

[@] MDPIT = 1,3-dihydro-4,5-di(4-methoxyphenyl)2H-imidazolin-2-thione

TABLE 14

Kinetic parameters of 2nd stage decomposition of copper(I) nitrate complex of MDPIT@

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal deg^{-1}mol^{-1}	n
Coats-Redfern	7.60	7.62	-55.31	1
Horowitz-Metzger	9.85	11.90	-49.83	1
MacCallum-Tanner	7.31	15.81	-42.58	1

@MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

TABLE 15

Kinetic parameters of 3rd stage decomposition of copper(I) nitrate complex of MDPIT@

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal deg^{-1}mol^{-1}	n
Coats-Redfern	9.01	2.80	-57.96	1
Horowitz-Metzger	7.69	5.08	-61.35	1
MacCallum-Tanner	8.39	4.081	-60.49	1

@MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

TABLE 16

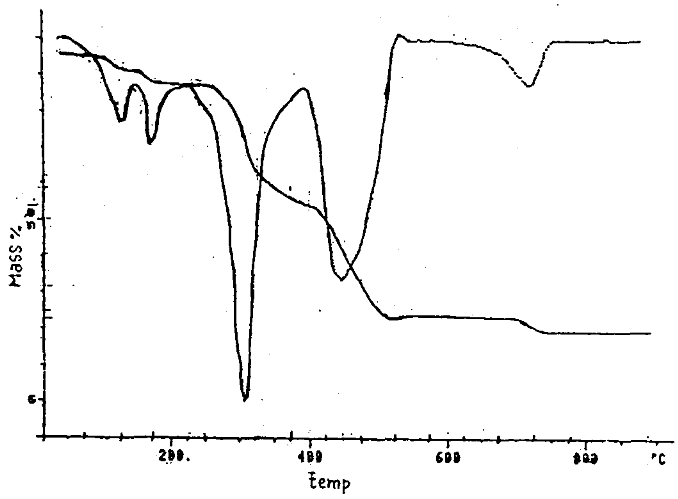
Kinetic parameters of 4th stage decomposition of copper(I) nitrate complex of MDPIT@

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal $deg^{-1}mol^{-1}$	n
Coats-Redfern	12.53	4.28	-57.66	1
Horowitz-Metzger	16.27	5.420	-52.62	1
MacCallum-Tanner	13.80	6.72	-51.66	1

@MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

e) [$Cu_2(MDPIT)_2(SO_4)(H_2O)_2$]

The thermal decomposition pattern of this complex is slightly different from those of the other complexes. The decomposition takes place in five steps. In the first step, two molecules of coordinated water are lost at a temperature range of 100-150°C. In the next step,two OCH_3 groups from the ligand get decomposed. This change takes place at a temperature range of 150-200°C. One of the ligand molecules (L') gets decomposed in the third stage and the other one (L'-2OCH_3) in the fourth stage yielding Cu_2SO_4. Finally, the complex decomposes to CuO in the fifth step. The formation of CuO was confirmed by chemical analysis of the residue and by independent pyrolytic studies. The experimental mass-loss data agree with the theoretical value and thus indicating the purity of the complex. The decomposition data are given in Table 17.



X

The kinetic parameters for the 3rd and 4th stages were calculated using the three different equations. For the other stages, we were not able to get the values by the computer programme used here. The values are given in Tables 18 and 19. The activation energies for these two steps are appreciably high which is anticipated as they involve M-L bond breaking. The ΔS values are negative and these steps have more ordered activated complexes and, therefore, the reactions are slow.

TABLE 17

Thermal decomposition data of copper(I) sulphate complex of MDPIT[@] (L')

Complex	Decomposition stage	Decomposition temp. range (°C)	Mass-loss from			Decomposition pattern
			TG	Independent pyrolysis	Theoretical	
$[Cu_2L'_2(SO_4)(H_2O)_2]$	1	100 – 150	4.4	--	4.05	$[CuL'_2SO_4(H_2O)_2] \rightarrow Cu_2L'_2SO_4$
	2	150 – 200	11.04	--	11.11	$[Cu_2L'_2SO_4(H_2O)_2] \rightarrow [Cu_2(L'_2\text{-}2OCH_3)SO_4]$
	3	200 – 400	46.16	--	46.33	$[Cu_2L'_2SO_4(H_2O)_2] \rightarrow [Cu_2(L'\text{-}2OCH_3)SO_4]$
	4	400 – 500	76.6	--	74.63	$[Cu_2L'_2SO_4(H_2O)_2] \rightarrow Cu_2SO_4$
	5	650 – 750	81.11	82.0	82.07	$[Cu_2L'_2SO_4(H_2O)_2] \rightarrow 2CuO$

TABLE 18

Kinetic parameters of 3rd stage decomposition of copper(I) sulphate complex of MDPIT@

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal deg^{-1}mol^{-1}	n
Coats-Redfern	14.84	3.89×10^3	-40.01	1
Horowitz-Metzger	16.38	4.95×10^3	-43.01	1
MacCallum-Tanner	13.76	2.5×10^3	-35.18	1

@MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

TABLE 19

Kinetic parameters of 4th stage decomposition of copper(I) sulphate complex of MDPIT@

Equation	E kcal mol^{-1}	A s^{-1}	ΔS kcal deg^{-1}mol^{-1}	n
Coats-Redfern	11.08	5.4×10^3	-56.99	1
Horowitz-Metzger	14.51	7.1×10^3	-51.89	1
MacCallum-Tanner	12.03	7.4×10^3	-53.95	1

@MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
E - Energy of activation
A - Pre-exponential factor
ΔS - Change in entropy
n - Order of the reaction

C. CONCLUSIONS

Thermograms of $[Cu(SMP)X_2]$, where X = OAc, Cl, NO_3, ½SO_4 or CNS; $[Cu(MDPIT)X(H_2O)]$, where X = OAc, Cl, Br or NO_3 and $[Cu_2(MDPIT)_2(SO_4)(H_2O)_2]$ were investigated and it was observed that the decomposition patterns supported the structures suggested for these complexes. All complexes of SMP decomposed to CuO in a single step. The decomposition patterns of the Cu(I) complexes of MDPIT were not uniform. The acetato complex decomposed in three stages while the halo-and nitrato complexes in four stages. The sulphato complex, being a dimer decomposed in a different way. But in all these complexes the coordinated water molecules were removed at a temperature range of 100-150°C and the anions got decomposed in the next stage. The methoxy groups present on the ring decomposed in a separate stage, except in the case of the acetato complex.

The kinetic parameters were calculated using three different equations, and the values obtained were comparable. The decomposition stages, especially the final ones leading to oxide formation, showed higher values of E. This was to be expected because these decomposition stages involved rupture of stronger metal-ligand bond than in the case of dehydration and elimination substituents on the ligand molecules. It is difficult to draw definitive conclusions from ΔS and A data which must await further theoretical developments in this field. One may note, however, that, processes like the dehydrations, elimination of simple groups, etc. generally tend to have lower values of ΔS and A. A negative value for ΔS further shows a more ordered activated complex and less than normally fast reaction. On the other hand, positive values of ΔS indicate less ordered activated complex and faster than normal reactions.

PART III
INTRODUCTION

Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

Part III

Antimicrobial Studies

CHAPTER I

INTRODUCTION

Heterocyclic compounds exhibit a wide spectrum of physiological- and biological activities. Research works are progressing for correlating their activities with structures.[147] The halogen, alkyl- and substituted phenyl groups present on the heterocyclic rings are expected to have special role in their biological activities[148]. Among a wide variety of nitrogen heterocyclics which have been exploited to synthesise pharmaceutically important compounds, pyrazoles, imidazoles and their derivatives have played important roles.

The importance of metal ions like Na, K, Mg, Ca, Fe, Mn, etc. in biological processes are well known. The metal complexes of heterocyclic compounds, therefore, may have interesting biological activities. The antifungal activities of metal complexes of semicarbazones, thiosemicarbazones and hydrazones were subjected to study in our laboratory[162]. Thoppil *et al* of Department of Botany, University of Calicut are involved in the investigations on microbicidal activities of essential oils[163-166]. As a continuation of these types of work done in our laboratory, we have decided to carry out some preliminary investigations on antifungal- and antibacterial activities of selected substituted pyrazolones,-thioimidazolones and their metal complexes.

A. ANTIMICROBIAL AGENTS

Antimicrobial chemotherapy has played a vital role in the treatment of human infectious diseases. Literally, hundreds of antimicrobial agents are available today. This section provides an overview of the mechanism of action of some of the antimicrobial agents.

1. Antifungal agents

The incidences of fungal infection have increased enormously in the past ten years and as a result, newer and more effective antifungal agents are being used nowadays[149-151]. Although more extensive researches in the development of antifungal agents have been done, only six of them are currently licensed for use against systemic fungal infections. They include, polyenes, azoles and pyramidine synthesis inhibitors.

a) Polyenes

Amphotericin B is a polyene microlide antibiotic, used primarily in the treatment of systemic- and life-threatening fungal infections. They act by binding to ergosterol in the fungal cell membrane, causing osmotic instability and loss of membrane integrity. The direct membrane toxicity is due, in part, to oxidative damage and is frequently fungicidal[152,153]. This effect is extended to mammalian cells in which the drug binds to cholesterol, creating high toxicity. Amphotericin B is produced by *Streptomyces nodosus* and has been used for many years in the treatment of mycotic diseases[154].

b) Azoles

The azole class of antifungal compounds was introduced in the late 1960s as a group of therapeutic agents. Four azoles have been approved for the treatment of systemic fungal diseases.They are, miconazole, ketoconazole, fluconazole and itraconazole. They inhibit fungal cytochrome P-450 dependent enzymes, resulting impairment of ergosterol synthesis and depletion of ergosterol in the fungal cell membrane.

Miconazole and ketoconazole are broad spectrum imidazole agents, active against a variety of fungal pathogens, including yeasts, dimorphic organisms and opportunistic pathogens. Itraconazole and fluconazole have been approved as orally active systemic agents with less potential toxicity than the imidazoles[156,157].

c) Pyrimidine synthesis inhibitors.

The pyramidine synthesis inhibitor, flucytosine is a water soluble- and stable compound used orally in the treatment of systemic infections caused by susceptible pathogenic- or opportunistic yeasts and other fungi. It acts as a competitive antimetabolite for uracil in the synthesis of yeast RNA and it also interferes with thymidylate synthetase[158,159].

2. Antibacterial agents

After the discovery of penicillin in the 1920s, literally, hundreds of antibacterial agents have been synthesised and dozens are currently available for clinical uses. Due to this large number, a detailed description of the mechanism of action of such compounds is beyond the scope of this thesis. Penicillins, cephalosporins, quinotones, tetracyclines, metronidazole[160], etc. are effective antibacterial agents. The mechanisms of action of each group of compounds are different. For example, the antibacterial activity of penicillins is due to their ability to inhibit a number of bacterial enzymes,namely, p enicillin-binding proteins[167], while tetracyclines inhibit protein synthesis[168].

B. ANTIMICROBIAL SUSCEPTIBILITY TESTS

Antifungal -and antibacterial susceptibility tests are similar in design. They include dilution-or diffusion methods. Dilution susceptibility methods are used to determine the minimum inhibitory concentration (MIC) of antimicrobial agents, i.e., the minimum concentration of antimicrobial agents required to kill a microorganism. The procedures for determining antimicrobial activity are carried out either by agar- or broth based methods[160]. The antimicrobial agents are usually tested at two fold serial dilutions and the lowest concentration that inhibits visible growth of an organism is recorded as the MIC.

In disk diffusion method, filter paper strips impregnated with a specified amount of the antimicrobial agents, are applied to the surface of an agar medium that has been inoculated with the test organism. Alternatively, wells of definite diameter can be cut in the medium and specified quantity of the antimicrobial agent can be added to it. The drug in the disk or well diffuses through the agar[161]. In the areas where the concentration of the drug is inhibitory, no growth occur, forming a zone of inhibition around each disc or well. The diameter of this zone can be measured ,which will give an idea of the antimicrobial activity of the drug used.

C. FUNGAL- AND BACTERIAL STRAINS USED

Four different fungal- and three bacterial strains were used in the present investigation. Their names and characteristics[169] are given in Tables 1 and 2, respectively.

TABLE 1

Fungal strains used

Sl. No.	Fungal strain	Characteristics	Diseases caused
1.	*Aspergillus niger*	Rapidly growing, white and filamentous, becoming black	They cause infection of external ear-otomycosis
2.	*Aspergillus parasiticus*	Rapidly growing	Cause aspergillosis, which involve allergic manifestations, superficial infections, etc.
3.	*Rhizopus oryzae*	Fast growing white cottony colony at 28°C	They are the most prevalent agent of mucormycosis
4.	*Candida albicans*	They are special type of yeasts. They form white or cream colonies	Causes candidiasis

TABLE 2

Bacterial strains used

Sl. No.	Bacterial strain	Characteristics	Diseases caused
1	*Staphylococcus aureus*	They are gram positive cocci,occur in grape like clusters. They grew readily on ordinary media. The colonies are large, circular, shiny and opaque	They cause cutaneous infections like furuncles, styes, boils, abscess, carbuncles, impetigo, etc. They also cause sepsis in wounds and burns.*S. aureus* cause acute osteomyelitis. In respiratory tract it causes tonsillitis, pharyngitis, sinusitis and pneumonia.
2	*Escherichia coli*	Colonies are large thick, grayish-white and moist. Good growth ocurs on ordinary media.	Four main types of clinical syndromes are caused by *E. coli*. They are diarrhoea, urinary tract infections, pyogenic infections and septicaemia.
3	*Pseudomonas aeruginosa*	It grows well on ordinary media, producing large, opaque, irregular colonies	It is one of the agents responsible for nosocomial infections, infantile diarrhea, etc.

D. ANTIMICROBIAL ACTIVITIES OF PYRAZOLONES AND THIOIMIDAZOLONES – A REVIEW

In general, azoles are effective against most fungi that cause superficial infections of the skin and mucous membrane[170]. Although individual drug has its own useful spectrum of action, azoles as a group have clinically useful activity against *Candida albicans, Candida tropicalis, Candida glabrata, Cryptococcus neoformans, Blastomyces, Dermatitidia, Histolasma capsulatum, Coccidioidea immitis* and ring worm fungi (dermatophytes). These drugs do not appear to have any useful antibacterial- or antiparasitic activities, with the possible exception of antiprotozoal effects against *Leishmania major*[171].

The action of the azoles on mycotic biochemistry and physiology have been studied extensively[156,157]. But the mechanism by which they exert their antimicrobial effects are not yet fully elucidated. At high concentration (micromolar) the azoles are fungicidal and at low concentration (nanomolar) they are fungistatic. The fungicidal effect is associated with the damage to the cell membrane, with the loss of essential cellular constituents, such as, K ions and amino acids. The fungistatic effects of the azoles have been correlated with the inhibition of membrane bound enzymes by low concentration of azoles[170].

The azoles are known to inhibit cholesterol biosynthesis in experimental animals and to inhibit other cytochrome oxidases involved in mammalian steroid biosynthesis. The primary structural requirement for members of azole class is a weakly basic imidazole or 1,2,4 triazole ring, bonded by a nitrogen-carbon linkage to the rest of the structure. At the molecular level, the amidine nitrogen atom (N_3 in imidazole) is believed to bind the heme-iron of enzyme bound cytochrome P-450 to inhibit activation of molecular oxygen and prevent oxidation of steroidal substrates by the enzymes. The most potential antifungal azoles possess two or more aromatic rings, atleast one of which is halogen substituted[172].

Pyrazolones are found to possess promising antiviral activity[173-175]. Many pyrazolone derivatives possess antiinflammatory activity[176-179]. Irikura[180] reported that 3,5-dimethylpyrazolone has antidiabetic activity. Antibacterial activities of a series of substituted pyrazolones were studied by Hogale and Pawar[31]. They used cup-plate agar diffusion technique, using chloromycetin as standard. The compounds were found to be active against *S. aureus* and *E. coli.*

Literature survey showed that studies on the biological activities of metal complexes of substituted pyrazolones are rare. The antitumour activities of metal complexes of substituted pyrazolones were studied in our laboratory[14]. N_1-isoniotinoyl-3-methyl-5-pyrazolone (IMP) and their derivatives showed practically no cytotoxic action while their Cu(II) complexes showed remarkable activity (100% activity at 100 µg/ml concentration). The complexes of substituted

IMP showed higher activities which may be due to the presence of OH group in the compound. Some chloro-substituted compounds showed brilliant activity[14].

Thiourea and related compounds show antithyroid activity, but they are too toxic for clinical uses. The more useful drugs are 2-uracils and 2-thioimidazole derivatives. They prevent the iodination of precursors of thyroxine and tri-iodethyroxine. Methimazole and carbimazole are examples[34].

A series of imidazolidin-2-thiones and thioimidazolines were prepared by Kohn *et al* [181]. They investigated the central nervous system (CNS) depressant activity and found that the thioimidazolines exhibit more pronounced CNS depressant activity than the corresponding imidazolidine thiones.

E. CONCLUSIONS

Our literature survey clearly showed the antimicrobial activities of pyrazolones, thioimidazolnes and their derivatives. But practically no attempts were reported to study the activities of their metal complexes. Considering the importance of metal ions and heterocyclic compounds in biological systems, it would be of much interest to make a study on the antimicrobial activities of the metal complexes of substituted pyrazolones and-thioimidazolones. Hence as a part of present investigation, we have decided to conduct tests to assess the antifungal- and antibacterial activities of some metal complexes of substituted pyrazolone and- thioimidazolones that we have synthesized during the present programme of research.

PART III

ANTIFUNGAL- AND ANTIBACTERIAL ACTIVITIES OF SUBSTITUTED PYRAZOLIN-5-ONE,IMIDAZOLIN-2-THIONES AND THEIR METAL COMPLEXES

Jayasree S. “Studies on metal complexes with heterocyclic compounds ”
Thesis. Department of Chemistry , University of Calicut, 2002

CHAPTER II

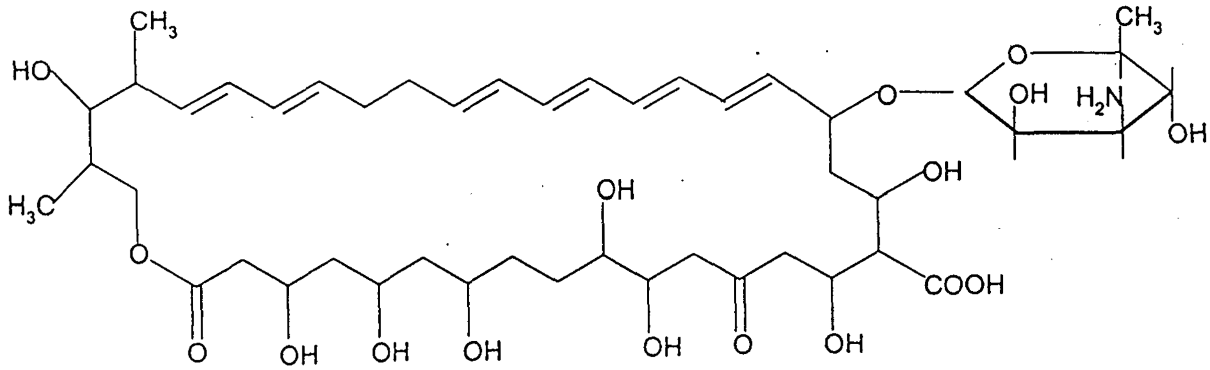
ANTIFUNGAL- AND ANTIBACTERIAL ACTIVITIES OF SUBSTITUTED PYRAZOLIN-5-ONE, -IMIDAZOLIN-2-THIONES AND THEIR METAL COMPLEXES

The antifungal activities of metal complexes of N_1-salicylyl-3-methyl-pyrazolin-5-one (SMP) having a general formula $[M(SMP)X_2]$, where M = Co(II), Ni(II) or Cu(II) and X = OAc or Cl were tested against four different fungal strains; *Aspergillus niger, Aspergillus parasiticus, Rhizopus oryzae* and *Candida albicans.* The antibacterial activities of these complexes were tested against three bacterial strains; *Staphylococcus aureus, Escherichia coli* and *Pseudomonas aeruginosa.* Antifungal- and antibacterial activities of copper(I) complexes of substituted imidazolin-2-thiones having a general formula $[CuLXH_2O]$, where L = substituted imidazolin-2-thione [DFIT, MDPIT, CPDMPIT or CPDOMPIT], and X = Cl or OAc were also tested. All the compounds showed remarkable activities against these microorganisms. The results are discussed in this chapter.

A. EXPERIMENTAL

1. Standards used

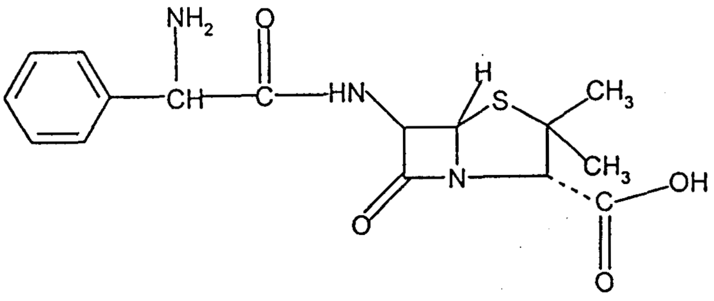
Nystatin was used as the standard for antifungal tests. Nystatin is a polyene with a molecular formula $C_{47}H_{75}NO_{17}$. The structure is given below.[182] **I**



I

Its aqueous suspension is stable for 10 min on heating to 100°C and at pH 7. For the present investigation, a 1000 ppm solution in DMSO was used as the standard.

Ampicillin was used as a standard for antibacterial studies. It is effective against a wide spectrum of bacteria. It belongs to penicillin group of antibacterial agents and its structure is as given below[182]. **II**



II

A 2000 ppm solution of Ampicillin in distilled water was prepared and two drops of the solution was used as control drug in antibacterial studies.

2. Materials and methods

Of the four pathogenic fungal strains used, three were obtained from the Department of Botany, University of Calicut (origin: MTCC Gene Bank, Institute of Microbial Technology, Chandigarh, India). *Candida albicans* and the bacterial strains were obtained from Medical College, Calicut. The cultures were maintained on nutrient agar slant. The medium used for conducting antifungal tests was Sabouraud's glucose agar for *Candida albicans* and for the other three, it was potato agar medium. Peptone and agar used were of bacteriological grade. DMSO was used as the solvent for preparing solutions of the ligands, complexes and standards used. All the other chemicals were of AnalaR grade. The antibacterial tests were conducted at Microbiology Department, Medical College, Calicut.

a) Preparation of media

The medium for demonstration of antifungal tests were prepared by the following method. 20 g potato was cut into small pieces and boiled with 100 ml distilled water. The extract was taken to which 2 g glucose and 1.5 g agar were added and boiled. Sabouraud's agar medium was prepared by adding 1 g peptone to 100 ml hot water followed by 4 g glucose and 2 g agar. The mixture was boiled to get the medium. Its pH was adjusted to 5.7 using 10% HCl. For antibacterial studies the medium used was Mueller-Hinton agar medium, which is commercially available.

b) Antifungal study

The medium was autoclaved for 15 min and when the temperature became 35-40°C, the fungal spores were scrapped and added to the medium. Mixed it well and carefully poured into clean ,autoclaved petridishes of 9 cm diameter and allowed to cool. Using an agar punch, wells (10 mm) were cut on these plates. In each well 2 drops of 2000 ppm solution of the compound were added. In each petri-plate, one well was used for DMSO and another one for the standard Nystatin. The wells were labelled properly and incubated at room temperature for 3-4 days. The plates were prepared in triplicate. The antifungal activity was measured by noting the diameter of the inhibition zone around each well. The results are presented in Tables 1-4.

c) Antibacterial study

Disc diffusion method was used for the antibacterial studies. Filter paper discs of 6 mm diameter were cut and were impregnated with two drops of the solution of complex (2000 ppm) in DMSO and they were allowed to dry. The medium was autoclaved, cooled to 40-50°C and poured into petriplates. The pH was kept at 7.2-7.4. A sterile cotton swab was dipped in the microbial suspension, excess fluid was pressed out and streaked over the entire surface of the agar plates.

The discs impregnated with the complexes were placed on the surface and labelled. One disc in every plate was used for DMSO and another one for standard ampicillin. The plates were incubated for 18-24 h and the diameter of the inhibition zone was measured.

3. Interpretation of results

The diameter of zone of inhibition was measured. The diameters greater than those for the solvent and standard used were considered as measure of activity. In some cases very high activities were observed and such solutions were diluted further and tested again, so as to obtain the minimum inhibitory concentration (MIC) and the values were reported.

B. RESULTS AND DISCUSSION

The experimental results of antifungal-and antibacterial studies conducted with substituted pyrazolin-5-one,- imidazolin-2-thiones and their complexes are presented in this section. The chloro- and acetato complexes were selected for the antimicrobial studies. The diameters of zones of inhibition for the compounds, solvents and standards used are presented in different tables.

1. Antifungal activities of SMP and its Co(II), Ni(II) and Cu(II) complexes

The results of antifungal susceptibility tests conducted with SMP and its complexes are given in Table 1. The results show that almost all compounds are

TABLE 1

Antifungal activities of SMP[@] and its complexes

Conc. of solution : 2000 ppm

Compound	Diameter of inhibition zone (mm)											
	Aspergillus niger			*Aspergillus parasiticus*			*Rizopus oryzae*			*Candida albicans*		
	1	2	3	1	2	3	1	2	3	1	2	3
DMSO	8	8	8	10	10	10	10	10	10	10	10	8
Nystatin	10	10	10	10	10	10	18	18	18	11	10	10
SMP	12	11	12	32	30	30	22	17	22	25	28	24
[Co(SMP)$(OAc)_2$]	14	13	13	21	20	22	10	10	10	10	10	10
[Co(SMP)Cl_2]	14	14	14	25	28	25	12	14	12	18	18	17
[Ni(SMP)$(OAc)_2$]	10	10	10	23	22	23	20	20	20	10	10	10
[Ni(SMP)Cl_2]	12	12	11	26	28	22	40	38	40	13	14	13
[Cu(SMP)$(OAc)_2$]	10	10	11	20	20	20	18	18	18	12	12	10
[Cu(SMP)Cl_2]	10	10	10	17	22	20	32	34	30	10	10	10

[@] SMP - N_1-salicylyl-3-methylpyrazolin-5-one active against four fungal strains used. Except in the case of *Aspergillus niger*, the ligand SMP showed very high activity. But the activities of the complexes are less.

[Co(SMP)Cl$_2$] showed high activity against *Aspergillus parasiticus.* [Ni(SMP)Cl$_2$] and [Cu(SMP)Cl$_2$] showed high activities against *Rhizopus oryzae.* Hence experiments were repeated with 1000 and 500 ppm concentrations of these complexes. The results are presented in Table 2.

TABLE 2

Antifungal activities of SMP[@] and its complexes

Conc. of solution : 1000 ppm

Compound	Diameter of inhibition zone (nm)					
	Aspergillus parasiticus			*Rhizopus oryzae*		
	1	2	3	1	2	3
DMSO	8	8	8	8	8	8
Nystatin	10	10	10	10	10	10
SMP	21	21	23	10	10	10
[Co(SMP)Cl$_2$]	19	19	17	-	-	-
[Ni(SMP)Cl$_2$]	-	-	-	10	10	10
[Cu(SMP)Cl$_2$]	-	-	-	10	10	10

[@] SMP = N$_1$-salicylyl-3-methylpyrazolin-5-one

[Co(SMP)Cl$_2$] showed high activity even at 1000 ppm concentration. But [Ni(SMP)Cl$_2$] and [Co(SMP)Cl$_2$] showed very low activities at this concentration.

Therefore, it can be inferred that the MICs of these complexes are between 1000 and 2000 ppm.

The experiments were repeated with 500 ppm solution of [Co(SMP)Cl_2], but the activity was found to be less. Hence the MIC of this complex is between 500 and 1000 ppm.

2. Antifungal activities of substituted imidazolin-2-thiones and their Cu(I) complexes

The antifungal activities of four different imidazolin-2-thiones – DFIT, MDPIT, CPDMPIT and CPDOMPIT and their Cu(I) acetate- and –chloro complexes were studied using their 2000 ppm solutions. The results are given in Tables 3 and 4.

The most striking observation of this experiment was that the ligands and their complexes were not at all active against *Rhizopus oryzae*. While the complexes of DFIT and MDPIT showed only moderate activities against *Apsergillus niger*, *Aspergillus parasiticus* and *Candida albicans*, the complexes of CPDMPIT and CPDOMPIT showed remarkably high activities against these microorganisms. The high activities of the complexes of CPDMPIT and CPDOMPIT may be due to the presence of halogen substituted aromatic ring on imidazolin-2-thione.

TABLE 3

Antifungal activities of DFIT and MDPIT[@] and their Cu(I) complexes

Concentration of solution : 2000 ppm

Compound	Diameter of inhibition zone (mm)											
	Aspergillus niger			*Aspergillus parasiticus*			*Rhizopus oryzae*			*Candida albicans*		
	1	2	3	1	2	3	1	2	3	1	2	3
DMSO	8	8	8	8	8	8	8	8	8	8	8	8
Nystatin	10	10	10	12	12	11	10	10	10	10	10	10
DFIT	10	10	10	13	13	12	--	--	--	12	12	12
[Co(DFIT)(OAc)H_2O]	10	10	10	22	20	20	--	--	--	10	10	10
[Cu(DFIT)(Cl)H_2O]	10	10	10	15	15	15	--	--	--	10	10	10
MDPIT	10	10	10	10	10	10	--	--	--	10	10	10
[Cu(MDPIT)(OAc)H_2O]	10	10	10	10	10	10	--	--	--	10	10	10
[Cu(MDPIT)ClH_2O]	10	10	10	10	10	10	--	--	--	10	10	10

[@] DFIT - 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione
MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione

TABLE 4

Antifungal activities of CPDMIT and CPDOMPIT[@] and their Cu(I) complexes

Concentration of solution : 2000 ppm

Compound	Diameter of inhibition zone (mm)											
	Aspergillus niger			*Aspergillus parasiticus*			*Rizopus oryzae*			*Candida albicans*		
	1	2	3	1	2	3	1	2	3	1	2	3
DMSO	8	8	8	8	8	8	8	8	8	8	8	8
Nystatin	10	10	10	10	10	10	10	10	10	10	10	10
CPDMPIT	14	14	14	15	15	15	--	--	--	18	19	18
[Cu(CPDMPIT)(OAc)H_2O]	12	12	14	15	17	17	--	--	--	18	18	18
[Cu(CPDMPIT)ClH_2O]	13	14	13	18	18	18	--	--	--	19	19	20
CPDOMPIT	12	12	14	15	15	14	--	--	--	20	19	20
[Cu(CPDOMPIT)(OAc)H_2O]	14	14	14	14	14	14	--	--	--	19	20	19
[Cu(CPDOMPIT)ClH_2O]	15	14	15	17	17	17	--	--	--	24	23	23

[@] CPDMPIT - 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione
CPDOMPIT - 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-methylenedioxyphenyl)-2H-imidazolin-2-thione

3. Antibacterial activities of SMP and its Co(II), Ni(II) and Cu(II) complexes

Antibacterial activities of SMP and its complexes with Co(II), Ni(II) and Cu(II) chlorides were studied using ampicillins as standard. The results are given in Table 5.

SMP showed high activity against *S. aureus*, but its complexes showed comparatively low activities. [Ni(SMP)Cl_2] showed reasonably high activity against *E. coli*,while [Co(SMP)Cl_2] was active against *P. aeruginosa*. But the activities of the compounds were lower than that of the standard.

4. Antibacterial activities of substituted imidazolin-2-thiones and their Cu(I) complexes

The antibacterial activities of four substituted imidazolin-2-thiones, DFIT, MDPIT, CPDMPIT and CPDOMPIT and their Cu(I) chloride complexes were tested against three different bacterial strains. The results are given in Table 6.

Ampicillin was used as the standard. The results revealed that these ligands and their complexes were inactive against *E. coli*. The ligands showed no activity towards *S. asureus*, but the complexes showed reasonably high activities. At the same time, the ligands and complexes showed moderate activities against *P. aeruginosa*.

TABLE 5

Antibacterial activities of SMP[@] and its complexes

Concentration of solution: 2000 ppm solution

Compound	Diameter of inhibition zone (mm)								
	Staphylooccus aureus			*Escherichia coli*			*Pseudomonas aeruginosa*		
	1	2	3	1	2	3	1	2	3
DMSO	6	6	6	6	6	6	6	6	6
Amphicillin	15	15	15	15	15	15	15	15	15
SMP	15	15	15	10	10	10	10	10	10
[Co(SMP)Cl_2]	10	10	10	10	10	10	14	14	14
[Ni(SMP)Cl_2]	10	10	10	13	13	13	11	11	11
[Cu(SMP)Cl_2]	10	10	10	10	10	10	10	10	10

[@] SMP - N_1-salicylyl-3-methylpyrazolin-5-one

TABLE 6

Antibacterial activities of substituted imidazolin-2-thiones and their Cu(I) complexes

Concentration of solution : 2000 ppm

Compound[@]	Diameter of inhibition zone (mm)								
	Staphylooccus aureus			*Escherichia coli*			*Pseudomonas aeruginosa*		
	1	2	3	1	2	3	1	2	3
DMSO	6	6	6	6	6	6	6	6	6
Ampicillin	15	15	15	10	10	10	10	10	10
DFIT	--	--	--	--	--	--	10	10	10
[Cu(DFIT)Cl(H_2O)]	10	10	10	--	--	--	10	10	10
MDPIT	--	--	--	--	--	--	10	10	10
[Cu(MDPIT)Cl(H_2O)]	11	11	11	--	--	--	11	11	11
CPDMPIT	--	--	--	--	--	--	10	10	10
[Cu(CPDMPIT)Cl(H_2O)]	12	12	12	--	--	--	11	12	12
CPDOMPIT	--	--	--	--	--	--	10	10	10
[Cu(CPDOMPIT)Cl(H_2O)]	14	14	14	--	--	--	10	10	10

[@] DFIT - 1,3-dihydro-4,5-difuranyl-2H-imidazolin-2-thione
MDPIT - 1,3-dihydro-4,5-di(4-methoxyphenyl)-2H-imidazolin-2-thione
CPDMPIT - 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-dimethoxyphenyl)-2H-imidazolin-2-thione
CPDOMPIT - 1,3-dihydro-4-(2-chlorophenyl)-5-(3,4-methylenedioxyphenyl)-2H-imidazolin-2-thione

C. CONCLUSIONS

Preliminary investigations on antimicrobial activities of some of the ligands and their complexes revealed that these compounds were active against microorganisms. A detailed investigations in this regard could not be conducted due to the pathogenic nature of the microorganisms used and also due to the lack of facilities. A more clear idea of the activities of such compounds can be derived if their mechanism of action can be predicted. Hence further studies in this fields are to be promoted.

The lower activities of some complexes when compared to those of the ligands may be due to presence of bulky substituents on the heterocyclic rings, which may prevent their bonding to the heme iron. However, an accurate assessment in this regard needs further studies.

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