TRANSITION METAL COMPLEXES OF SCHIFF BASES DERIVED FROM PIPERONAL AND DIAMINES

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CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of the research work carried out by **Mr. Prasad M. Alex** under my supervision in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry of the University of Calicut and further that no part thereof has been presented before for any other degree.

Dr. K.K. Aravindakshan
(Supervising Teacher)

DECLARATION

I, Prasad M. Alex, here by declare that this thesis entitled **Transition Metal Complexes of Schiff Bases Derived from Piperonal and Diamines**, submitted to the University of Calicut in partial fulfilment of the requirements of 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, this thesis has not previously formed the basis for award of any other degree, diploma or similar title.

Prasad M. Alex

Calicut University Campus,
10th Novemberr 2005.

PRASAD M. ALEX

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PREFACE

Schiff base derivatives and their metal complexes, which are known since 19th century, have played a key role in the development of coordination chemistry and have found wide range applications. These include biochemical, analytical, catalytic and therapeutic applications and biomimetic activities. The ability of Schiff bases to form stable complexes with transition metal ions has spurred interest in such compounds. Schiff bases derived from the condensation of diamines with carbonyl compounds represent an important class of chelating agents, the metal complexes of which have been studied widely. They have found wide applications in chemistry and possess diverse physiological activities. Piperonaldehyde is a biologically important compound and its Schiff bases are reported to show striking antimicrobial activities. Therefore, it was decided to synthesise and characterise metal complexes of Schiff bases derived from piperonaldehyde and various diamines.

In this study, three Schiff base ligands and their complexes with several transition metal ions were synthesised. Piperonaldehyde on condensation with ethylenediamine, 1,3-propanediamine and *o*-phenylenediamine yielded the ligands. Their coordination behaviors with metal ions of the first transition series had been studied and 90 new solid complexes were synthesised. They were characterised using different physico-chemical techniques and geometries had been assigned to them. Thermal analyses of some of these complexes were carried out and kinetic parameters for different stages of decomposition were calculated. The antifungal activities of some of these compounds against *Phytophthora capsici*, the pathogen which causes quick wilt disease in Black pepper had also been investigated in this study.

The thesis is divided into three parts. The Part I entitled 'Synthesis and Characterisation' has been further subdivided into five chapters. The first chapter starts with a general introduction and gives a very brief review of the research work carried out on coordination compounds of Schiff bases, especially, those derived from diamines and the scope of present investigation. Chapter II describes the reagents used, the methods of preparation, and the physico-chemical methods employed for the characterisation of the ligands and complexes. The synthesis and characterisation of complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with the ligands, bis(piperonaldehyde)ethylenediimine, bis(piperonaldehyde)-1,3-propanediimine and bis(piperonaldehyde)-o-phenylenediimine are discussed in the Chapters III, IV and V, respectively. Acetates, chlorides, bromides, nitrates and perchlorates of the above metals were used for the synthesis of complexes.

In the Part II of the thesis, 'Thermal Studies' the thermal decomposition behaviours of 9 metal complexes synthesised during the present investigation are presented. This part is divided into two chapters and the first chapter gives a general introduction into the methods adopted for thermal decomposition studies and a brief review of thermal studies on transition metal complexes. The second chapter deals with results of thermal analyses, including the kinetic parameters for the different stages of decomposition.

The Part III of the thesis, 'Antifungal Studies' comprises of studies on biological activities of the ligands and some of the metal complexes synthesised here. There are two chapters, of which the first is an introductory one, which explains the significance of the investigation and the methods used for it. A brief review of researches carried out in this field is also given. The results of the antifungal studies undertaken are explained in the second chapter.

The references cited in the text are arranged in serial order at the end of each part of the thesis.

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PART I

SYNTHESIS AND CHARACTERISATION

CHAPTER I

INTRODUCTION

Coordination chemistry offers rich opportunities for theoretical speculation, model building, preparation of compounds in the unusual valence states and chance to break down the distinction between inorganic and organic chemistry through 'inter-marriage' of organic groups with metal atoms in coordination compounds. Impact of the development of this branch on the realm of inorganic chemistry is so profound that the number, variety and complexity of coordination compounds continue to grow even in this century.

There is scarcely any branch of inquiry in chemical science which seems more likely than coordination chemistry, to lead to important developments during a few more decades. Perhaps the most significant synthetic break-through in coordination chemistry in the 18th century was the observation by Tassart, a French chemist that ammonia combined with a cobalt ore to yield a reddish brown product, which is most likely the first known coordination compound. For more than one century the theoretical knowledge and explanatory prowess of chemists found much wanting in correlating and explaining the unique behaviour of these maverick compounds. Secure foundation for the theory of coordination chemistry was laid by Werner at the end of 19th century.

The principal historian of coordination chemistry, G.B. Kauffman made the undeniable point that the name, Alfred Werner is synonymous with coordination chemistry, the field in which he played a central and monopolistic role. In fact Werner's theory is a classical example for Thomas Kuhn's idea of 'paradigm shift in science'.[1] Important land marks in the history of coordination chemistry are summarized in the Table-1. The theoretical progress in coordination chemistry culminated in molecular orbital theory and ligand field theory which give comprehensive and quantitative explanations of the structure, geometry, electronic spectra and magnetic properties of these compounds.

Vast diversity in the synthesis of coordination compounds has led to equally vast and diversified applications in areas as different as pharmaceuticals and polymer products, paints and fungicides, analytical chemistry and photo-conductors, novel catalysts and diagnostic imaging agents. The life process in nature flourishes because of coordination compounds too. Chlorophyll, haemoglobin, vitamin B-complex and many enzymes are all coordination compounds and the phenomenon of coordination plays a vital role in their functions

Almost always, a coordination compound is a compound of a transition metal. Ions of these metals with their partly filled d orbitals, having strong perturbing nature, are very adept in complex formation. From metal to metal, and from oxidation state to oxidation state, the complex forming tendency, structure and geometry of the complexes and their physical and chemical properties vary widely.

Table-1 Historical land marks of coordination chemistry

Year	Name	Contribution
1798	Tassaert	First cobaltammonates observed.
1822	Gmelin	Cobalt ammonateoxalates prepared:
1851	Genth, Claudet	$CoCl_36H_2O$,$CoCl_35H_2O$ and other cobaltammonates prepared
1869	Blomstrand	Chain theory of ammonates
1884	Jørgensen	Amendments to chain theory
1892	Werner	Werner's dream about coordination compounds
1902	Werner	Three postulates of coordination theory proposed
1911	Werner	Optical isomers of *cis*-$[CoCl(NH_3)(en)_2]X_2$ resolved
1914	Werner	Non-carbon-containing optical isomers resolved
1927	Sidgwick	Lewis' ideas of bonding applied to coordination compounds
1933	Bethe and Van Vleck	Crystal field theory

The uses and applications of transition metals and their ions were known from the pre-scientific era itself. By complexation, their properties are modified in many interesting ways. Therefore, systematic studies on new complexes of transition metals have much relevance.

A. Schiff bases as complexing agents

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Schiff[2] in 1864. The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R′, where R and R′ are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. These compounds are also knows as anils, imines or azomethines.

Several studies[3-9] showed that the presence of a lone pair of electrons in an sp^2 hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents,[7-13] especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a 5 or 6 membered ring with the metal ion. Versatility of Schiff base ligands and biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable.

B. Applications of Schiff bases and their complexes- a brief review

A thorough and exhaustive account of the vivid applications of Schiff bases and their complexes in a broad spectrum of fields is beyond the scope of this review. But an attempt is made to bring to light some of the more recent and important examples of such applications

1. As catalysts

Recent studies showed that transition metal complexes of Schiff bases have emerged as highly efficient catalysts in various fields of synthesis and other useful reactions. Synthetic chemists sometimes seek to imitate the efficiency and elegance of the biosynthetic machinery by designing biomimetic reactions that approximate natural reaction pathways. Probably the most astonishing biomimetic reactions are processes, which combine several transformations in sequence and produce complicated structures from comparably simple starting materials, in a simple laboratory operation. In such a simple but elegant method, Matsumoto *et.al.*[14] used Co(II), Mn(II) and Fe(II) with the Schiff base ligand, bis(salicylaldehyde)ethylenediimine (salen) as catalyst for the synthesis of carpanone in good yield by the oxidation of *trans*-2-(1-propenyl)-4,5-methylnedioxyphenol with molecular oxygen.

Genet *et.al.*[15] reported the use of chiral complexes of palladium with Schiff bases in the sterioselective synthesis of α-amino acids. Palladium complex of benzophenoneimine of glycine methyl ester acted as prochiral nucleophile in allylic alkylations.

The role of Schiff base catalysts in the synthesis of quality polymers is also equally important. A series Schiff base ruthenium complexes which, acted as catalysts in the field of atom-transfer radical polymerisation were reported to be synthesised.[4] When activated with trimethylsilyldiazomethane, these complexes showed good catalytic activity in ring opening metathesis polymerisation of norborene and cyclooctene. The activities for both types of reactions were reported to be depending upon the steric, bulk and electron donating ability the Schiff base ligand and optimal equilibrium in atom transfer radical polymerization could be established by adjusting the steric and electronic properties of the Schiff base ligand. Control over polymerization was verified for two substrates, namely methylmethacrylate and styrene.

Cameron *et.al.*[16] synthesised and characterised potentially tridentate Schiff base ligands having the general formula, $[3,5\text{-Bu}^t{}_2\text{-2-(HO)C}_6\text{H}_2\text{CH= NL}]$, where L = $\text{-CH}_2\text{CH}_2\text{NMe}_2$, $(2\text{-PhO})\text{C}_6\text{H}_4\text{-}$, $2\text{-CH}_2\text{C}_5\text{H}_4\text{N}$ and $8\text{-C}_9\text{H}_6\text{N}$ (quinoline) On reaction with Me_3Al at room temperature they formed complexes of formulae, $[(3,5\text{-Bu}_2{}^t\text{-2-(O)C}_6\text{H}_2\text{CH=NL)AlMe}_2]$. Among these, the complexes with L = $\text{-CH}_2\text{CH}_2\text{NMe}_2$ and $2\text{-CH}_2\text{C}_5\text{H}_4\text{N}$ had been characterised crystallographically. Further reaction of the dimethyl compounds with $\text{B(C}_6\text{F}_5)_3$ afforded the cationic systems, $[(3,5\text{-Bu}_2{}^t\text{- 2-(O)C}_6\text{H}_2\text{CH =N L)-AlMe}]^+$ of which those with L = $\text{-CH}_2\text{CH}_2\text{NMe}_2$ and $(2\text{-PhO})\text{C}_6\text{H}_4\text{-}$ were found to be ethylene polymerisation catalysts.

A special catalytic application of Schiff base complexes was reported by Kim *et.al.*[17] Electrochemical reduction of thionyl chloride had been carried out at glassy carbon and molybdenum electrodes with surface modified by binuclear tetradentate Schiff base, (3,3,'4,4'-teterasalycildineimino-1,1-biphenyl) complexes of Co(II), Fe(II), Ni(II) or Cu(II). The catalyst molecules were adsorbed on the electrode surface and reduced thionyl chloride resulting in the formation of oxidised catalyst molecule. The reduction current of thionyl chloride were increased and the reduction potentials were shifted to the negative region.

Llobet *et.al.*[18] reported the development of a selective catalyst for the oxidation of 3,5-di-t-butylcatechol to 3,5-di-t-butyl-1,2-benzoquinone. They synthesized a new macrocyclic hexaaza binucleating Schiff base ligand L, where L = 3,7,11,19,23,27 hexaazatricyclo[27.3.1.1(13,17)]tetratriaconta-1(32),2,11,13(14),15, 17(34),18,27,29(33),30-decaene by the direct condensation of *m*-phthalaldehyde and 3,3'-iminobis(propylamine). The macrocyclic ligand formed a dinuclear Cu(I) complex that reacted with molecular oxygen to form $[Cu_2L(O_2)]^{2+}$. It had been shown that this complex was an efficient and selective catalyst for the oxidation of 3,5-di-*t*-butylcatechol to 3,5-di-*t*-butyl-1,2-benzoquinone in the presence of 1 atm of O_2. Furthermore, the measured initial rate constants revealed that it reacted much faster than any of the related macrocyclic systems reported earlier, it was claimed.

Unique asymmetric catalysis of *cis*-$^{\beta}$ metal complexes of salen, bis-(salicylaldehyde)ethylenediimine and the related Schiff-base ligands was brought to light by Tsutomu Katsuki.[19] The article summarised the generation of *cis*-$^{\beta}$ metallosalen and its related complexes, their structural features, and their application to asymmetric syntheses. Chiral complexes of salen and its related tetradentate Schiff base ligands adopted three different configurations, *trans, cis*-$^{\alpha}$ and *cis*- $^{\beta}$. According to the report, eventhough the *trans*-complexes had been widely used as catalysts for various asymmetric reactions, recent studies have disclosed that *cis*- $^{\beta}$ metallosalen and its related complexes showed unique asymmetric catalyses that cannot be achieved by *trans*-metallosalen complexes.

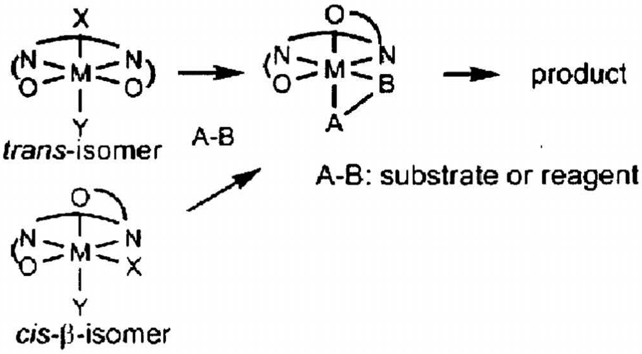


Fig. 1-Asymmetric catalysis of *cis*-$^{\beta}$ metal complexes of salen type Schiff base ligands

2. Biomedical applications

Schiff base complexes play an essential role in the development of diverse group of molecules having biomedical applications, such as synthesis of new antimicrobial agents, developing new generation drugs and anticancer agents, inventing biomimetic pathways, etc. Next part of this review intends to demonstrate the significant progress made in these areas. Recently, notable advances are made in the area of oncoligical studies with a view to developing anti-cancer agents by using Schiff base complexes.

Changzheng *et.al.*[20] reported the synthesis, characterisation and anti-tumour activities of nicotinamido-4-bis(2-chloroethyl)aminobenzaldimine (NBAB) and its Cu(II) complex. The spectrochemical and analytical studies suggested that the complex, $[Cu(NBAB)_2(NO_3)_2]$ had an elongated octahedral structure and NBAB behaved as a bidentate ligand in the keto form. Antitumour activities of the ligand and the complex against L_{1210}, murine leukaemia and K_{562} were investigated. The activity of the ligand was found to be superior to nitrogen mustard (2,2'-chlorodi-ethylamine hydrochloride) against L_{1210} and inferior to nitrogen mustard against K_{562}, but the activity of the complex against both cell lines was reported to be superior to that of nitrogen mustard.

Metesanz *et.al.*[21] synthesised, characterised and studied the cytotoxic activities and DNA binding of Pd(II) complex of benzylbis(thiosemicarbazone). According to the report, the spectroscopic and X-ray diffraction studies suggested a triclinic crystal system for [PdL]DMF, where L = bideprotanated benzylbis(thio-semicarbazone), in which the palladium atom was tetracoordinated by SNNS atoms from L. The cytotoxic activities of the complex against several human, monkey and murine cell lines (HeLa, Vero, Pam-212 and Pam-*ras*) were investigated and compared to those of *cis*-platin. They reported that the complex showed good anti-tumour properties. It showed IC_{50} values (concentration required for 50% inhibition) in a μM range similar to that of *cis*-platin. Moreover, the compound displayed notable cytotoxic activity in Pam-*ras* cells, resistant to *cis*-platin. The analysis of interaction of the compound with DNA secondary structure by means of circular dichorism spectroscopy indicated conformational changes on the double helix, which were different from those induced by *cis*-platin.

Kuz'min *et.al.*[6] investigated the anticancer activities of a series of macrocyclic Schiff bases of 2,6-bis(2- and 4-formylaryloxymethyl)pyridines. Some equations correlating the anticancer activity and structural parameters of the molecules studied were also presented in this paper. The report claimed that the influence of structures of the investigated substances on the anticancer activity, as reflected by the parameters studied, could be established.

Tai *et.al.*[22] had synthesised, characterised and studied the antitumour activities of the transition metal complexes namely, $[Mn(L)_2]$, $[Ni(L)_2 0.5H_2O]$ $[Cu(L)_2 4H_2O]$ and $[Zn(L)_2 0.5H_2O]$, where HL = Schiff base derived from trimethylolaminomethane and salicylicaldehyde. The complexes were characterised by elemental analysis, IR, ^1H NMR and UV spectra and TG-DTA studies. Tentative structures for these complexes had been proposed. The antitumour activity against human leukaemia cells of the free ligand and its Mn(II), Ni(II) and Cu(II) complexes were studied. According to the report the inhibitory effects were, in the case of Ni(II) complex, significantly higher than the free ligand and the other complexes and therefore, its possible clinical use was being explored.

Yet another promising application in the biomedical field was reported by Urena *et.al.*[23] They synthesised and characterised the complexes of Ni(II), Cu(II), Zn(II) and Cd(II) containing hydrazones, derived from 6-amino-5-formyl-1,3-dimethyluracil and nicotinic- and isonicotinic acid hydrazides. All the complexes were reported to be monomeric and four-coordinate, with three binding sites being occupied by the dinegative tridentate ligand, which makes two-, five- and six-membered chelate rings, and the fourth position occupied by either water or ammonia. The coordination of the organic ligand took place through the deprotonated nitrogen atom from the 6-amino group, the azomethine nitrogen atom and the oxygen from the hydrazide moiety. Experimental data indicated that neither the carbonyl oxygen atom from the uracil ring nor the endocyclic nitrogen atom from pyridine was involved in the coordination to the metal. The molecular structure of both ligands had been designed in a way that the activity of hydrazones was attempted to be combined with that of the uracil derivatives. Thus, the coordinating capacity through both the azomethine nitrogen and carbonyl oxygen atoms of hydrazones had been enhanced with two new basic atoms available for metal ligation, from the five-substituted uracil derivative. The presence of uracil ring was expected to contribute structural analogy with the species found in biological systems. This aspect was expected to be useful to their potential pharmacologic applications because the azomethine bond could be hydrolyzed in the acidic pH of cancer cells, liberating the uracil derivative, which could act as an efficient alkylating or antimetabolite drug.

Recently, Schiff base complexes are becoming very likely candidates as effective drugs against viral and bacterial deceases also. For example, Toshiko Takeuchi *et.al.*[24] pointed out that Co(III) complexes with Schiff bases could inhibit the replication of occular herpes virus. These complexes have high affinity for nitrogenous donors such as histidine residues and according to the report they could bind to and inhibit an enzyme that is crucial for viral replications. $[Co(acacen)(NH_3)_2]^+$, (H_2acacen = Schiff base ligand derived from acetylacetone and ethylenediamine) was found to be an effective irreversible inhibitor of thermolysin at milli-molar concentrations and it could also inhibit human α-thrombin. Actual ligand exchange with an active site, histidine, was the proposed mechanism. The activity of thermolysin and thrombin can be protected by binding a reversible inhibitor to the active site before addition of the complexes.

Chohan *et.al.*[25] synthesised and characterised a new Schiff base ligand, N-(2-furanylmethylene)-2-aminothiadiazole and the Co(II) and Ni(II) complexes with it. The Schiff base acted as tridentate ligand during the complexation reaction with Co(II) and Ni(II) ions and the complexes had the composition $[M(L)_2]X_n$, where M = Co(II) or Ni(II), L = N-(2-furanylmethylene)-2-aminothiadiazole, X = NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$ or $CH_3.CO_2^-$ and n =1 or 2, and showed octahedral geometries. The ligand and the complexes were screened for antibacterial activities against the bacterial strains, *Escherichia coli, Staphylococcus aureus* and *Pseudomonas aeruginosa*. It was reported that the complexes were generally more active than the Schiff base.

Raman *et.al.*[26] synthesised, characterised and tested the antimicrobial activities of neutral complexes of VO(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the Schiff base derived from benzil and 2-aminobenzyl alcohol. The structural features had been arrived from their microanalytical, IR, UV-Vis, ^{1}H NMR, Mass and ESR spectral data. The Co(II), Ni(II), Cu(II) and Zn(II) complexes exhibited square-planar geometry, the Mn(II) chelate showed an octahedral environment and the VO(II) chelate existed in a square-pyramidal geometry. The monomeric and non-electrolytic natures of the complexes were evidenced by their magnetic susceptibility and low conductance data. The *in vitro* biological screening effects of the compounds were tested against six bacteria, namely *Staphylococcus aureus, Bacillus* *subtilis, Klebsiella pneumoniae, Salmonella typhi, Pseudomonas aeruginosa* and *Shigella flexneri* by serial dilution method. Most of the complexes had higher activities than that of the free Schiff base and the control as indicated by the minimum inhibitory concentration values.

Schiff base complexes are nowadays being probed for novel biological applications for their special properties such as protective action against DNA damage. El-Khawaga[27] had reported the protective action of Cu(II) complex of the Schiff base derived from ethylenediamine and ethylacetate against DNA damage induced by *m*-chloroperbenzoic acid using a novel DNA unwinding technique. The broken strands in calf thymus DNA could be detected with great sensitivity by exposing it to alkaline solutions and monitoring the rate of strand unwinding. Fluorometric analysis of DNA unwinding (FADU) is a reliable method for detecting single-strand DNA breaks, as an index of DNA damage, induced by photosensitizer. In this investigation *m*-chloroperbenzoic acid (CPBA) was used as a photosensitizer in the photodamage of calf thymus DNA. When the DNA was exposed to ionizing radiation, the radicals produced, in the irradiated sample, modified the base-pair regions of the double strands. The protective action of copper salt, Schiff base formed from ethylene diamine and ethyl acetate and its Cu(II) complex against DNA damage photoinduced by CPBA was studied by fluorescent probe. Treatment of DNA with 5, 10, 50, 100, or 200 μM CPBA produced 75%, 48%, 38%, 32% and 30% double-stranded DNA remaining, respectively, after 30 min of alkaline treatment at 15°C. Treatment of calf thymus DNA irradiated with CPBA with a dose of 1μM of the complex produced 96% double-stranded remaining protected under the same conditions compared with irradiated DNA without addition of Cu(II) complex of Schiff base.

In the area of medical investigation, Schiff base complexes find applications even as diagnostic tools as cited in the following example. Synthesis of the ligand, benzoylhydrazone of α-oxo-pentanedioic acid (H_2LPB), and its six rare earth (La, Pr, Nd, Sm, Gd and Er) complexes was reported by Zhengyin *et.al.*[28] The composition and the properties of the complexes were established by analytical and spectral methods. The ligand and the complexes had been studied to explore MRI activities (as contrast agents). The toxicity of the complex in animals also had been tested and LD_{50} value was reported.

The biomimetic activity of Schiff base complexes may be illustrated by the following example. Hotchandani *et.al.*,[29] in an effort to obtain synthetic analogues of water-oxidizing complex (WOC) of photosystem II (PS II) of plant photosynthesis, prepared manganese and cobalt complexes of a new Schiff base, bis(α-nitroso-β-naphthol)ethylenediimine (niten) which is a bis(salicylaldehyde)ethylenediimine (salen) type of ligand. The structures of the ligand and the complexes were established by spectral studies and elemental analysis. Cyclic and square-wave voltametric measurements had been performed to assess their redox characteristics. Both the complexes underwent several reduction processes in cathodic negative potential region at more or less similar potentials. As these reductions were found to be more or less independent of the nature of the metal, they were considered to be ligand-localised. Although similar in negative region, a marked difference in the behaviour of the complexes was observed in anodic region. While the cobalt complex was electrochemically inactive in the positive potentials up to +1.0 V vs. Ag /AgCl, the manganese complex displayed two oxidation waves at + 0.25 and + 0.5 V vs. Ag /AgCl. It was suggested that the presence of oxidation wave in manganese complex at + 0.5 V vs. Ag/AgCl or + 0.7 V vs. NHE showed that this complex could catalyse the oxidation of water and can, thus, simulate the WOC of PS II.

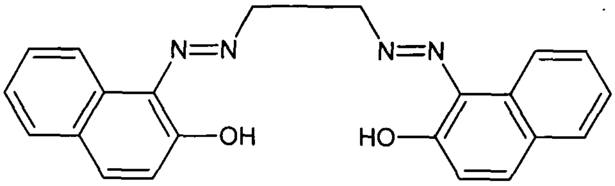


Fig 2a-Suggested structure for bis(α-nitroso-β-naphthol)ethylenediimine (niten)

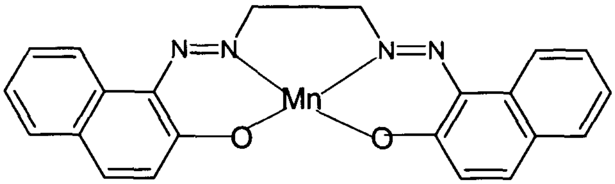


Fig 2b- Suggested structure for Mn(II) (niten) complex

3. Analytical applications

Beyond the traditional applications[9,30-33] as analytical regents and indicators in qualitative, quantitative and colorimetric analyses, Schiff bases have emerged as analytical tool for the precise determination of even traces of metals found in the physiological systems of animals and human beings. The application of the complex of Al(III) with salicylidene-*o*-aminophenol for the fluorometric determination of nucleic acids was an important development in this direction.[34] In buffer medium of hexamethylene tetraamine–HCl at pH 5.9, the complex showed a fluorescence peak at 508 nm with excitation at 410 nm. If nucleic acid was present, it reacted with the complex within 8 min at room temperature to produce a non-fluorescent product, resulting in the decrease of fluorescence intensity of the aluminium complex. On the basis of this, a new fluorometric method for nucleic acids determination had been proposed. It was claimed that in comparison to some established fluorometric methods, this procedure was sensitive, selective, reliable, reproducible and practical.

The use of Schiff bases as analytical reagents for the spectrophotometric determination of Al(III), with a view to developing an ELISA application, is another interesting advancement in this area. Aluminium is a toxic element for the central nervous system and its possible effects include amyotrophic lateral sclerosis from Alzheimer's disease. Mocanu *et.al.*[35] synthesised a new N_2O_2 type of Schiff base ligand, salicylhydrazidone-2-hydroxyacetophenone by condensing *o*-hydroxyacetophenone with salicilylyhdrazide. The ligand, due to its structure, showed good complexing capacity towards Al(III) ions and formed a stable yellow complex with the ions at a pH of 4.6. The stability constant of the complex was determined spectrophotometrically. It showed maximum absorbance at 370 nm and the absorbance was proportional to Al(III) concentration in the 0.05 to 0.45 μg/ml range of field concentration. This provided an effective method for spectrophotometric determination of Al(III) in blood samples. It was also found that Schiff bases of different structures formed from *o*-hydroxy carbonyl combinations and salicylhydrazide showed capacity to complex to some other metal ions. The toxicity of the Schiff base and the Al(III) complex was also tested and compared and the complex was reported to be acutely more toxic. This chelate was used to generate metal specific monoclonal antibodies, with a view to establishing an ELISA test kit for the determination of Al in physiological samples.

The development of a polymer membrane electrode, based on a Schiff base which is selective to silver ions and can be used as a sensor for Ag^+ ions is yet another application of Schiff base as a sophisticated analytical tool. Mahajan *et.al.*[36] prepared PVC membrane containing the Schiff base, *p*-tert-butylcalix[4]arene derivative as ionophore. The membrane electrode was highly selective to silver ion and exhibited good linear response over a wide concentration range of $1.0\text{x}10^{-1}$ to$1.0\text{x}10^{-5}$ M. The detection limit of electrode was $6.31\text{x}10^{-6}$ M. The calix[4]arene based membrane electrode exhibited enhanced selectivities for silver ion over other cations and the response was stable over a wide pH-range of 1.0-6.0. The response time of the sensor was 30 seconds and the membrane could be used for more than 6 months without observing any divergence. The sensor could be applied also as an indicator electrode for potentiometric titration of Ag^+ ions with Cl^-. It was found to be possible to determine Ag(I) in the natural water spiked with silver, with this electrode assembly.

The applications of Schiff base dyes as mere colouring agents is giving way to cutting edge applications as biolabels and tracer analytical agents. Briggs *et.al.*[37] synthesised highly fluorescent Schiff base aluminium complex which could be used as a novel biolabel. Starting from 3-(4-hydroxyphenyl)propanoic acid, formylation at the position ortho to the phenolic group, followed by condensation with *ortho*-aminophenol gave a new Schiff base ligand. This acidic Schiff base on reaction with *N*-hydroxy succinimide gave N-hydroxysuccinimidyl ester. This on non-aqueous complexation with $AlEt_2Cl$ gave a novel fluorescent biolabel displaying a Stokes shift of 100 nm. The efficacy of the new system was demonstrated by its attachment to rabbit IgG.

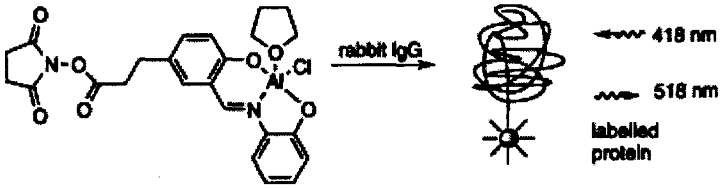


Fig-3 Fluorescent Schiff base aluminium complex as biolabel

Papic *et.al.*[38] reported the synthesis, characterization and applications of two new Schiff bases namely, 2-(2-pyridylmethyleneamino)phenol (PMAP) and 2-(2-quinolylmethyleneamino)phenol (QMAP) and their nickel complexes. It was found that, for the Ni-PMAP complex, two ligands were bonded to one metal ion, giving a neutral complex with one molecule of water, probably bonded in the inner sphere of the complex. With QMAP, nickel formed cationic complexes with a metal-to-ligand ratio of 2:2 and two molecules of acetate as anions. The solution properties of Ni-QMAP were investigated at different pH. The chromophoric properties of the complex were enhanced with increase in pH, while stability decreased with time. The application of QMAP as a spectrophotometric reagent for the determination of small amounts of nickel was investigated. Adherence to Beer's law was observed from 0.00 to 5.00 μg/ml at pH 8, which was found to be the most suitable pH in respect to sensitivity and acceptable time-stability of the complexes. Dyeing properties of both the complexes were investigated on polyamide-66. The influence of the addition of another phenyl ring to the ligand molecule on the dyeing properties of the complex was also investigated.

C. Complexes of Schiff base derived from diamines

Schiff bases derived from the condensation of diamines with carbonyl compounds represent an important class of chelating agents, the metal complexes of which have been studied widely. These compounds possess high chelating tendency due to the presence of two azomethine groups and offer structural diversity, synthetic viability and vivid applications. They can be obtained by condensing diamines with carbonyl compounds in the 1:2 molar ratio. Schiff bases of 1,2- and 1,3-diamines are expected to easily form chelate rings involving metal ion and both the nitrogen atoms. There is possibility for the formation of bridged bimetallic or even polymeric complexes in the case of Schiff bases derived from polymethylene diamines due to steric factors. A brief review of recent reports on the synthesis, characteri-sation and applications of complexes of Schiff bases derived from diamines is attempted here.

Mahapatra *et.al.*[39] synthesised binuclear complexes of Co(II), Cu(II), Cd(II) and Hg(II) with tetradentate Schiff base (H_2L) derived from benzoin and *m*-phenylenediamine. The cobalt complex was assigned the formula M_2L_2 $4H_2O$ and the copper, cadmium and mercury complexes were assigned the general formula, M_2L_2, where L = doubly deprotonated Schiff base ligand. The compounds were characterised by elemental analysis, electrical conductance and magnetic susceptibility measurements, IR and UV-Vis. spectral studies. A binuclear octahedral configuration was assigned to the cobalt complex, binuclear square-planar configuration to the copper complex and tetrahedral configuration to the cadmium and mercury complexes.

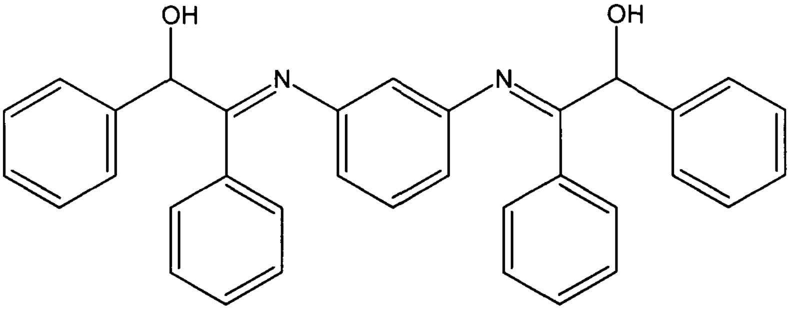
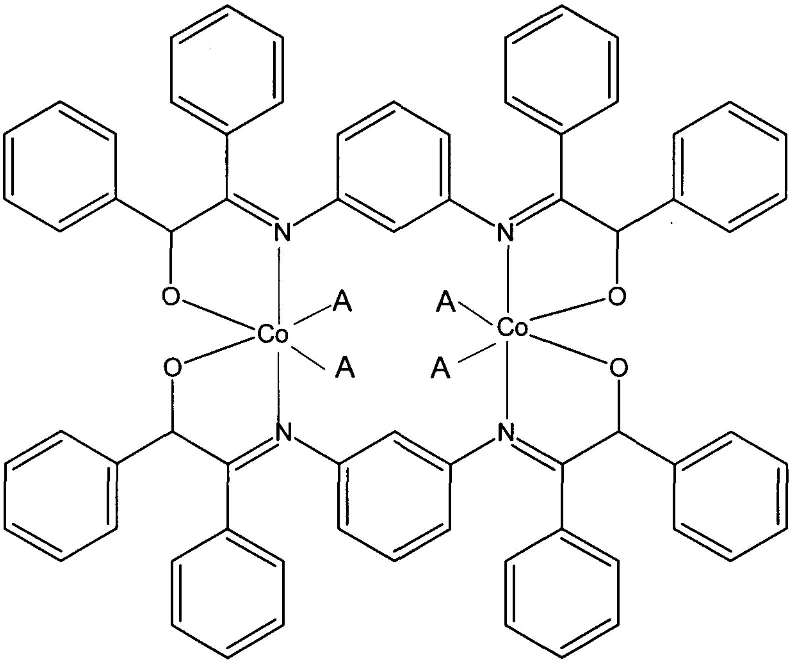


Fig-4a Schiff base derived from benzoin and m-phenylene diamine (H_2L)



where A = H_2O

Fig-4b Cobalt complex of benzoin m-phenylenediamine Schiff base ($M_2L_2\,4H_2O$)

Satyanarayan Pal and Samudranil Pal[40] reported the synthesis, structural determination and properties of *trans*-dichlororuthenium(II) complexes with N_4-donor Schiff bases. 2-Pyridine-carboxaldehyde on condensation with linear diamines namely, 1,2-diaminoethane,1,3-diaminopropane and 1,4-diaminobutane gave tetradentate Schiff bases '*paen*', '*papn*' and '*pabn*', respectively. The reactions of hydrated $RuCl_3$ with these ligands in boiling methanol gave complexes of general formula, *trans*-$[RuLCl_2]$, where L='*paen*', '*papn*' or '*pabn*'. The complexes were characterised by analytical, spectroscopic and electrochemical data. All the complexes were found to be diamagnetic and electrically non-conducting. Thus in all the complexes the metal ions were in +2 oxidation state. The molecular structures of *trans*-$[Ru(papn)Cl_2]$ and *trans*-$[Ru(pabn)Cl_2]$ in the solid state had been determined by X-ray crystallography. The neutral ligand coordinated via two pyridine-N and two imine-N atoms. The chloride ions satisfied the remaining two *trans*-sites resulting in octahedral geometries. The ^1H NMR spectra of all the complexes in $CDCl_3$ solutions also indicated *trans* arrangement of the chloride ions. Electronic spectra of the complexes in dichloromethane solutions displayed intense metal-to-ligand charge-transfer bands in the range 595–656 nm. Cyclic voltaograms of the complexes in acetonitrile solutions displayed a reversible oxidation response in the potential range 0.26–0.40 V (vs. saturated calomel reference electrode) due to Ru^{III}/Ru^{II} couple. According to the report, the central chelate ring size formed by the ligand strongly influenced the spectral and redox features of these complexes.

Jeong *et.al.*[41] synthesised and characterised tetradentate Schiff base ligands derived from 2-hydroxy-1-naphthaldehyde and aliphatic diamines namely, ethylenediamine, 1,3-diamino propane, 1,4-diamino butane, and 1,5-diaminopentane and their Cu(II) complexes. Complexes were prepared from the free ligands and copper acetate. The ligands and their Cu(II) complexes were characterised by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, UV-Vis spectra, molar conductance, and thermogravimetric analysis. The mole ratio of ligand to copper had been identified to be 1:1, with a four-coordinate configuration. The electrochemical redox process of the ligands and their Cu(II) complexes in DMF solutions was investigated by cyclic-voltammetry, chronoamperometry, differential pulse-voltammetry and controlled potential coulometry. The redox process of Cu(II) complexes was found to be a one electron transfer in quasi-reversible and diffusion-controlled reaction. The electrochemical redox potentials and the kinetic parameters of the Cu(II) complexes were found to be affected by the chelate ring size of the Schiff base ligands.

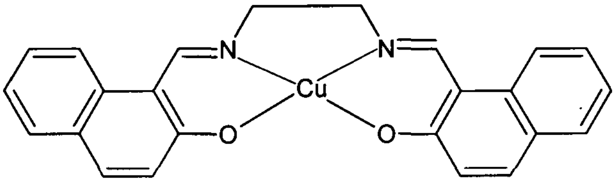
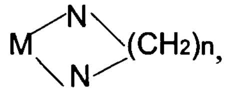


Fig-5 Suggested structure for the Cu(II) complex of the Schiff base, bis(2-hydroxy-1-naphthaldehyde)ethylenediimine

The bridging ability of quadridentate Schiff base ligands was reported to be determined by steric requirements.[9] Bridging could be more probable in the case of polymethylene derivatives, because of the inherent difficulty in forming the ring,  when n > 3 and of the decrease in steric hindrance in the formation of polynuclear complexes. Such a polymeric structure had been proposed for N,N′-polymethylene-bis(salicyladeneiminato)nickel(II) complexes.[42]

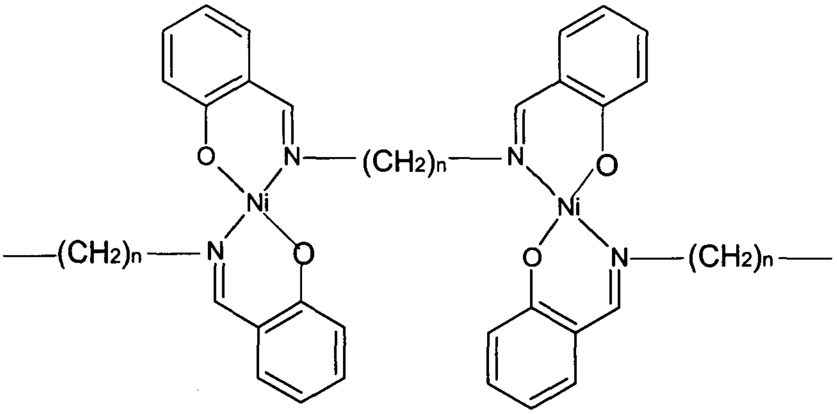


Fig-6 Polymeric structure proposed for of N,N′-polymethylene-bis(salicyladeneiminato)nickel(II) complexes

The synthesis and characterisation of Mn(II) and Mn(III) complexes of new tetradentate Schiff base ligands derived from 1-hydroxy-2-naphthaldehyde and aliphatic diamines, $H_2N(CH_2)_nNH_2$, where n = 2, 3, 4, or 10 and their reactions with molecular oxygen were reported by McAuliffe *et.al.*[43] The structure and reactivity of the Mn(II) complexes depended on 'n', the length of the carbon chain of the diamine moiety. When n = 2, 4, or 10 planar complexes, (MnL) were formed and when n = 3 the pseudo-octahedral ones, $[MnL(H_2O)_2]$ were obtained, where H_2L = N,N'-ethylene-, propane-1,3-diyl-, butane-1,4-diyl-, or decane-1,10-diyl-bis(1-hydroxy-2-naphtylmethyleneimine). These manganese species absorbed approximately 0.5 mol O_2 per mol of Mn to form dimeric di-μ-oxomanganese(IV) complexes, $[(MnLO)_2]$. This reaction in N,N-dimethylformamide was surprisingly much faster for the complex, $[MnL(H_2O)_2]$ than for the planar species. Some Mn(III) complexes of the formula $[MnL(H_2O)]ClO_4$ were also reported to be synthesized.

Jensen *et.al.*[44] reported the elucidation of the geometry of some Schiff base complexes of diamines. The structure and geometry of 1:1 complexes of Cu(II) with Schiff bases, formed by condensing 1,2-diamines with 2,4-dihydroxybenzophenone and 2,5-dihydroxyacetophenone were investigated. The circular dichroism spectral data indicated that these complexes had a non-planar structure in solution which contradicted the square-planar geometry suggested earlier.

Oxovanadium(II) complexes of new tetradentate Schiff bases, derived from 2-hydroxy-1-naphthaldehyde and some diamines, *viz, o*-phenylenediamine, ethylenediamine and propylenediamine were synthesised by Pandeya *et.al.*[45] The complexes were characterised using magnetic susceptibility data, IR, electronic- and ESR spectra.

Complexes of VO(II), Mn(II), Ni(II), Cu(II) and Zn(II) with tetradentate N_2O_2 type Schiff base, derived from the condensation of *o*-phenylenediamine and acetoacetanilide had been synthesised and characterised by Raman *et.al.*[46] The ligand was formed by the condensation of *o*-phenylenediamine with acetoacetanilide in alcohol, which when refluxed with metal chlorides in alcoholic medium yielded the complexes. The complexes were characterised on the basis of microanalytical, molar conductance and magnetic susceptibility data and IR, UV–visible, ^{1}H NMR and ESR spectra. According to the report, IR and UV–Vis spectral data suggested that all the complexes were having square-planar geometry, except the Mn(II) and VO(II) chelates, which were of octahedral and square-pyramidal geometries, respectively. The magnetic susceptibility data and low conductance values clearly indicated the monomeric and neutral nature of the complexes.

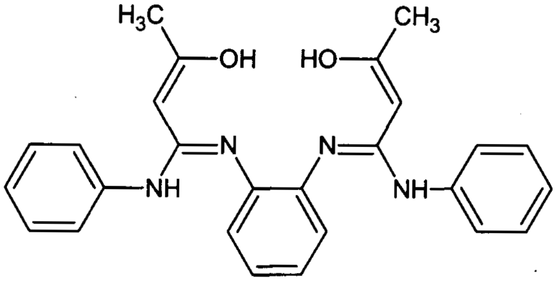


Fig-7a Schiff base ligand, acetoacetanilido-*o*-phenylenediamine

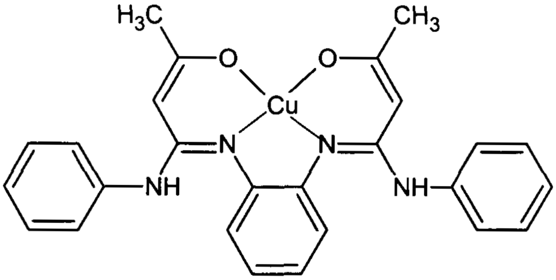


Fig-7b Cu(II) complex of the Schiff base acetoacetanilido-*o*-phenylenediamine

In another report, Tai *et.al.* [47] presented the synthesis and characterisation of a novel Schiff base ligand derived from 2,2'-bis(p-methoxyphenylamine) and salicylicaldehyde (bpmpasal) and the complexes of Cu(II), Co(II) and Mn(II) with it. Their spectral properties and electrochemical behaviours were also investigated. Using elemental analysis data, the complexes were formulated as ML, where L is the doubly deprotonated Schiff base. The authors concluded that the disappearance of the O-H band (of the free ligand), in the IR spectra of the metal complexes indicated that the OH group was deprotonated and coordinated to the metal ion as $-O^-$ and the shift of C=N stretching band to a lower frequency by about 29 cm^{-1} indicated the coordination of azomethine nitrogen atom. The new IR bands appearing at 420 ~ 430 and 541 ~ 560 cm^{-1} were assigned to (M-O) and (M-N) vibrations, respectively.

In addition, no new bands at 1610 ~ 1550 and 1420 ~ $1300cm^{-1}$ were observed, indicating that the complexes did not contain CH_3COO^- anions, which was also in accordance with the elemental analysis data for the complexes. It was suggested that the complexes were square-planar or nearly square-planar, coordinated according to the common stereochemistry of this type of compounds.

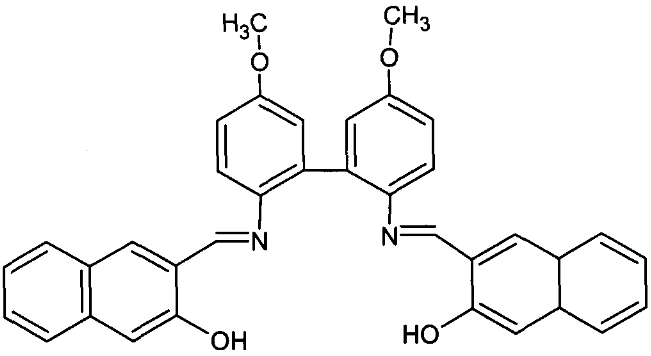


Fig-8a Schiff base ligand derived from 2,2'-bis(p-methoxyphenylamine) and salicylicaldehyde (bpmpasal)

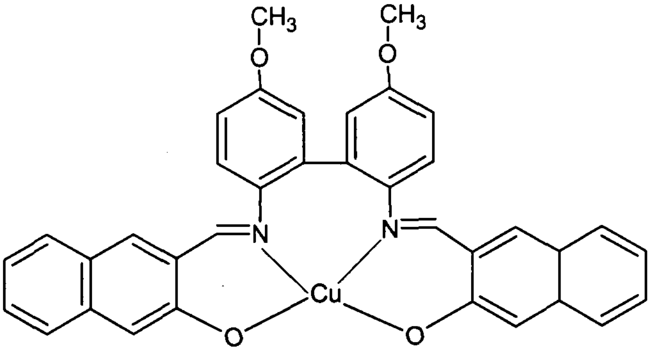


Fig-8b Suggested structure for Cu(II) complex of (bpmasal)

The synthesis and characterisation of ruthenium(III) complexes of Schiff bases, derived from heterocyclic compounds and the electrochemical studies on them were reported by Karthikeyan *et.al.*[48] A series of hexacoordinated Ru^{III}–PPh_3 complexes of general formula $[RuCl(PPh_3)L]$, where L = tetradentate Schiff bases derived by the condensation of 2-furaldehyde or thiophene-2-carboxyaldehyde with alkyl and aryl diamines, were synthesised. The complexes were characterised by elemental analyses, spectroscopic and cyclic voltammetric studies. All of the complexes were found to be paramagnetic. Coordination of the Schiff base appeared to occur through the two nitrogen and two heterocyclic oxygen or sulphur atoms. The Ru(III) centre was suggested to be in a distorted octahedral N_4Cl_2 coordination sphere.

Kumar *et.al.*[49] synthesised and characterised Co(II) complexes with two Schiff base ligands derived from furfuraldehyde and phenylene diamines, named as furfurlidene-*m*-phenylenediamine (fdmpda) and furfurlidene-*o*-phenylenediamine (fdopda). Six complexes of Co(II) had been characterised on the basis of elemental analysis, molar conductivity, magnetic moments, electronic and ^{1}H-NMR spectral measurements and were assigned the formulae, $[Co(fdopda)_2Cl_2]$, $[Co(fdopda)_2(NO_3)_2]$, $[Co(fdopda)_2(CH_3COO)_2]$, $[Co(fdmpda)_2(NO_3)_2]$, $[Co(fdmpda)Cl_2]$ and $[Co(fdmpda)_2(CH_3COO)_2]$. Coordination through azomethine nitrogen and oxygen of the furan ring had been proposed.

The use of bis(salicylaldehyde)ethylenediimine (salen) type Schiff bases as analytical reagents for spectrophotometric determination of manganese from pharmaceutical products was reported by Tantaru *et.al.*[50] By condensing ethyl-*o*-hydroxybenzene with ethylenediamine, a salen-type Schiff base was obtained. This

Schiff base exhibited a good capacity of complex formation with Mn(II), giving a brown complex. The complex showed maximum absorbance at 460 nm with a molar absorbtivity, $\varepsilon = 9.8 \times 10^4$. The complex was reported to have maximum stability at pH 6.0. The combination ratio was established by iso-molar series method to be 1:2 (metal : ligand). The absorbance was proportional to Mn(II) concentration in the range of 10-70 μg ml^{-1}. In this range, the Lambert-Beer law was obeyed, the linearity coefficient being 0.9989. Under these conditions, the complexation reaction of Mn(II) was interfered by other cations such as, Fe(II), Fe(III) and Ni(II). The results obtained for spectrophotometric determination of Mn(II) using this Schiff base as reagent were successfully applied to pharmaceutical products containing Mn(II) cation.

A general approach for constructing *cis*-diamines suitable for assembly into N_2O_2 type Schiff base complexes was reported by Shearer *et.al.*[51] A reliable and efficient method of synthesis of water soluble Ni(II) complex of a salen type ligand, useful in probing nucleic acid structure was described. Two equivalents of an aryl lithium reacted with 1,4-dimethylpiperazine-2,3-dione to form a symmetric α-dione. This material was then converted to its dioxime and reduced by $TiCl_4/NaBH_4$ to yield the *meso*-diamine. Condensation of this diamine and salicylaldehyde followed by coordination of nickel and final methylation generated the desired water soluble and redox active complex.

In the quest for new anticancer agents, Osinsky *et.al.*[52] studied the biological activity of Co(III) complexes of tetradentate Schiff bases derived from diamines and different biogenic nitrous bases or analogous ligands. Some cobalt(III) complexes with the basic structure, [Co(acacen)$(NH_3)_2$]Cl (H_2acacen = bis(acetylacetone)ethylenediimine) and their analogues with different ligands were tested. Transplanted rodent tumours [Guerin carcinoma, Walker-256 carcinoma, Lewis lung carcinoma (3LL), melanoma B16, adenocarcinoma Ca755] were used in this study. Complexes were given intraperitonially or intravenously. Local hyperthermia (LHT) was performed by microwave unit. The tumours were irradiated by 190 kV X-rays at 1.23 Gy/min (RT). Tumour-response to treatment was estimated by standard methods. The above cobalt complexes displayed substantial anticancer, in particular antimetastatic activity. Moreover, these complexes enhanced the antitumour effect of LHT as well as RT. Some other analogues of the above mentioned complexes with other biogenic bases were reported to be under design and investigation. According to the report, results indicated that "inorganic" cobalt complexes could be regarded as prospective selective anticancer agents with significant modifying activity.

Dey *et.al.*[53] investigated antimicrobial, insect sterilizing and ovicidal activity of twenty one mixed ligand complexes Co(II) and Co(III), including those with the Schiff base derived from salicylaldehyde and *o*-phenylene diamine. Three of these Co(III) complexes were reported to exhibit broad anti-microbial spectra, including against human bacterial pathogens, dermatophytes and plant pathogenic fungi, while one exhibited feeble activity against a human pathogenic bacterium. The corresponding Co(II) complexes were found to be inactive, while the free ligands showed reduced activity compared with the Co(III) complexes. According to the report, change in biological activity induced by a particular complex appeared to depend on the composition of the first coordination sphere. Two of these complexes showed 50% inhibition of the conidial germination of *Helminthosporium oryzae* and *Alternaria triticina*. These results indicated their potential for use against human and plant pathogenic microbes. Three of these Co(III) complexes were tested for insect sterilising and ovicidal activities on *Dysdercus koenigi F.* Positive sterilizing and ovicidal actions of the complex, $[Co(bsop)(NH_3)_2]NO_3$, (where bsop-H_2 is the Schiff base derived from salicylaldehyde and *o*-phenylene diamine) were observed. Possible mechanism(s) of all these activities were also suggested.

Takeuchi *et.al.*[54] investigated selective inhibition of human α-thrombin by cobalt(III) complexes with Schiff bases belonging to the 'acacen' class. Human α-thrombin, associated with the blood coagulation cascade, converts fibrinogen into fibrin, which ultimately forms the blood-clots. Thrombolytic activity has been linked to reocclusion of coronary arteries after thrombolytic therapy following heart attacks and, therefore, is an attractive choice for the development of new inhibitors. Co(III) complexes with Schiff base of the class, 'acacen' could bind to histidine residues in active sites and on enzyme surfaces in a random fashion. Spectroscopic and chromatographic evidences indicated that the binding of these complexes was controlled by axial ligand substitution. The binding of complexes of the acacen class to one or more histidines, including thrombin, reduced the enzymatic activity. The investigation concluded that the reaction of an active site-directed peptide linked to a cobalt chelate led to selective, irreversible inhibition of thrombin. It was also suggested that further work on such peptide chelate conjugates could yield powerful and highly selective inhibitors towards a variety of enzyme targets.

Zhao *et.al.*[55] investigated spectoscopically the photochromatic character of the diamine Schiff bases N,N'-bis(salicylidene)-1,2-diaminoethane (BSE) and N,N'-bis(salicylidene)-1,6-hexanediamine (BHE). The photochromism of these Schiff bases was studied by steady-state and time-dependent fluorescence, UV-Vis spectroscopy and theoretical chemistry calculations. The experimental results showed that BSH could perform the photochromism easier than BSE, which was suggested to be due to the molecular topology difference.

Bruno Rindone and Guido Galliani[56] reported that bis(salicylaldehyde)-ethylenediiminecobalt(II) catalysed oxidation of aromatic amines with oxygen. The report suggested that the catalysis of complexed ions in the oxidation of aromatic amines with oxygen could mimic biological detoxification reactions. The catalysis of cobalt(II) complexes with Schiff bases had been used mainly in the oxidation of phenols with oxygen. In such cases quinone and quinone dimers were the reaction products. In the reported investigation, the reaction of aromatic amines with oxygen in refluxing methanol in the presence of cobalt(II) complex of bis(salicylaldehyde)-ethylenediimine was studied. N-butyl anilines of formulae, X-C_6H_4-NH-*n*Bu, where X = -H, *m*-CH_3, *m*-OCH_3, *m*–Cl, *p*-CH_3 or *p*-OCH_3, underwent dealkylation to yield the corresponding primary amine. Neither oxygen alone nor $COCl_2$ and oxygen were able to perform this transformation under comparable conditions. Some mechanistic indications were also suggested on the basis of studies on kinetic isotopic effect.

Tsukahara *et.al.*[57] synthesised and characterised binuclear type of Cu(II) complex with Schiff base derived from diamine and linked to Viologen *via* number 3 and 4 of methylene groups. They studied the intra- and intermolecular electron-transfer reactions of Viologen-linked Cu(II) Schiff base complexes also. Probable mechanisms for electron transfer reaction were suggested on the basis of a pulse radiolytic study in acetonitrile. A trinuclear copper(II) Schiff base complex linked to Viologen *via* number 5 of methylene groups was also synthesised and characterised.

Bottcher *et.al.*[58] investigated the structural, spectroscopic and electrochemical properties of complexes of Co(III) with the Schiff base ligand, 'acacen' and a series of related ligands. Electronic structure calculations indicated that the absorption between 340 and 378 nm in the spectra of Co(III) complexes could be assigned to the lowest π-π^* intra-ligand charge-transfer transitions. This investigation suggested that equatorial ligand substitutions affected reduction potentials less than the axial ligand changes, consistent with an electronic structural model in which dz^2 was populated in forming Co(II). This investigation was taken up with a view to evaluating the role of axial binding of Co(III) to bimolecules in the biological activity of Co(III) Schiff base complexes.

D. Schiff bases derived from piperonal and their complexes

3,4-methylenedioxybenzaldehyde (piperonal) and other compounds containing 3,4-methylenedioxy groups were reported to be biologically active.[59,60] Schiff bases derived from piperonal can be expected to be good complexing agents of interesting properties, including biological activities. But literature survey revealed that works on Schiff bases of piperonal and their complexes were scanty. A very brief review on these compounds follows.

The synthesis, characterization and the studies on biological activities of a series eleven Schiff bases obtained by the condensation of piperonal with the substituted anilines [H_2N-C_6H_4-*p*-X, where X= H, Cl, Br, I, CH_3, C_2H_5, OCH_3, OC_2H_5, COOH, NO_2 or $SO_3^-Na^+$] were reported by Echevarria *et.al.*[5] Their ^{1}H- and ^{13}C NMR spectra were obtained and the Hammett correlations, including chemical shifts and the substituent constants were studied. According to the reported data, significant linear and bilinear correlations were observed for iminic carbon (C-α) and C-1 of aniline moiety showed significant resonance effect on chemical shifts correlations. The chemical shifts for C-4 of aniline moiety were highly affected by substituents, especially for halogens in the expected direction.

The biological activities of the above Schiff bases against some micro-organisms, *viz*, bacteria, yeasts and fungi were also tested. The method of two-fold serial dilution in Sabourand-dextrose liquid medium was resorted to in the assay against fungi and the results were expressed in minimal inhibitory concentrations (MIC). The filamentous dermatophytes namely, *Microsporum canis*, *Microsporum gypseum*, *Trichophyton rubrum* and *Epidermophyton floccosum* were the fungi used in the assay. Most of the Schiff bases were found to possess good antimicrobial activities, and especially against *Epidermophyton floccosum*, for which the most active compounds were those containing *p*- Br, Cl, C_2H_5, NO_2 or OCH_3 aniline moiety. Assays with bacteria and yeasts were performed by the agar well diffusion method and the compounds were found to be inactive.

Teijido *et.al.*[61] studied the reactions of $Pd(OAc)_2$ complexes with the Schiff base ligands derived from 3,4-$[O(CH_2)_nO]C_6H_3C(H)$=NR, where n =1, 2; R =

Cy-3,4-(OCH_2O)$C_6H_3CH_2$-) which produced binuclear cyclometallated products in which each palladium atom is C and N bonded to a deprotonated organic ligand, and to two acetate groups which bridged both metal centers. The regioselectivity of the cyclo-metallation processes was discussed by ^{1}H-NMR spectroscopy and X-ray diffraction studies.

Another work on regioselectivity of the cyclometallation processes involving piperonal based Schiff bases was reported by Castro-Juiz *et.al.*[62] The reaction of the Schiff base ligand 3,4-(OCH_2O)C_6H_3C(H)=NCH_2[3,4-(OCH_2O) C_6H_3] with Pd$(OAc)_2$ yielded two endocyclic cyclometallated compounds, [Pd{3,4-(OCH_2O)-C_6H_2C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]}(μ-O_2CMe)]$_2$ and [Pd{3,4-(OCH_2-O)C_6H_2-C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]}(μ-O_2CMe)]$_2$ which were separated by fractional crystallization. The corresponding cyclopalladated dimers with bridging chloride ligands were prepared by a metathesis reaction with aqueous sodium chloride. Treatment of the latter compounds with tertiary phosphines in the appropriate molar ratio gave the mono-and dinuclear compounds. The structure of the compound, [Pd{3,4-(OCH_2O)C_6H_2C(H)=NCH_2[3,4-(OCH_2O)C_6H_3]}(μ-O_2CMe)]$_2$ was determined by X-ray diffraction analysis. The molecular configuration was identified as a dimeric form of the *anti*-isomer with the cyclopalladated moieties in an `open-book' arrangement, linked by two acetate bridging ligands.

E. Scope of present investigation

Literature survey helped to conclude that Schiff bases of diamines are excellent chelating agents and their complexes exhibit wide range structural variety and broad spectrum of advanced applications such as biomimetic, antitumor, antimicrobial and antifungal activities and as sophisticated analytical agents. The survey also revealed that Schiff bases of piperonal are not widely studied, but a few, which are studied, show considerable biological activity. Moreover, complexes of Schiff bases derived from diamines and piperonal could not be found in the survey. But it is only logical to expect various diamines and piperonal to combine in 1:2 molar ratios to give very interesting Schiff base ligands. Hence the synthesis of Schiff bases derived from piperonal and ethylenediamine, propylenediamine and *o*-phenylenediamine and their complexes with transition metal ions are taken up here. These compounds can be expected to act as excellent chelating agents because of the presence of two azomethine groups. Metal ions of the first transition series can probably coordinate with these neutral bidentate ligands. When the metal ion and the ligand react in 1:1 molar ratio, there is the possibility of anion coordination as well.

Three Schiff base ligands mentioned above and their complexes with several typical transition metal ions, such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) were synthesized. The acetates, chlorides, bromides, nitrates and perchlorates of these metal ions were used for complexation. Different anions were used with view to obtaining structural variety, varied physical- and chemical proprieties and much more diverse biological applications. In order to establish the structures of the ligands and the complexes, elemental analysis, conductance and magnetic susceptibility measurements and ^{1}H NMR, IR and electronic spectral analysis were used. The thermal decomposition behaviours of a number of selected complexes were studied by TG-DTG techniques. Antifungal activities of the ligands and a number of selected complexes were also investigated.

CHAPTER II

MATERIALS AND METHODS

A brief account of the reagents and apparatus used and the methods adopted for the synthesis and characterization of the ligands and complexes are presented here. Detailed descriptions are provided in appropriate contexts.

A. Materials

Analar grade chemicals (BDH, Sarabhai, E.Merck or Glaxo) were used for the synthesis. For the preparation of the ligands piperonaldehyde, ethylenediamine, 1,3-propanediamine and *ortho*-phenylene diamine were used.

The metal salts used for the synthesis of the complexes were the acetates, chlorides, bromides, nitrates and perchlorates of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II). Bromides and perchlorates were prepared by reacting freshly prepared carbonates of these metals with hydrobromic- and perchloric acids, respectively, and then evaporating the solutions over a water bath and drying the crystals over P_4O_{10}.

The solvents made use of for the synthesis, purification and analyses of the lignds and the complexes were ethanol, methanol, acetone, diethyl ether, petroleum ether, dimethyl formamide and dimethyl sulphoxide. Solvents such as ethanol and methanol were purified by standard methods.[63]

B. Synthesis of ligands and complexes

Three Schiff base ligands, namely, bis(piperonaldehyde)ethylenediimine, bis(piperonaldehyde)-1,3-propanediimine and bis(piperonaldehyde)-*o*-phenylenediimine were synthesised. Ethanolic solutions of the diamine and the aldehyde were mixed in 1:2 molar ratios. In the case of ethylenediamine, the mixture was refluxed for about 1h and the solution was cooled to get the solid Schiff base precipitated. Propanediamine gave precipitate of Schiff base on simply stirring it with a solution of the aldehyde. But *o*-phenylenediamine was refluxed with the aldehyde solution for about 3h and the solution was cooled and concentrated to obtain the precipitate. Everytime the precipitate was filtered off, washed with water and a few ml of ethanol and recrystallised from hot ethanol.

Complexes were prepared by refluxing a mixture of the solutions of the metal salt and the ligand in appropriate molar ratios. The solvents used were methanol, ethanol, acetone *etc*. In many cases the complex was precipitated during refluxing itself, which were separated, washed with suitable solvent and dried. In other cases, after refluxing for about 2-3 h, the solution was concentrated over a water bath and the pasty mass obtained was washed repeatedly with diethyl ether and/or petroleum ether and/or acetone to get the solid complex separated. It was then dried over anhydrous $CaCl_2$.

C. Instruments and methods of analysis

The purity of the compounds was checked by standard methods of semimicro analyses. Known methods were adopted for the estimation of metal contents of the complexes.[64] A definite quantity of the complex was digested 3 or 4 times with a mixture conc. nitric acid, hydrochloric acid and perchloric acid and the residue was extracted with distilled water and the solution was used for the estimation. Copper was estimated iodometrically using standard thiosulphate solution. Manganese and cobalt were estimated complexometrically using EDTA. Cr(III) was oxidised to dichromate using excess persulphate, unreacted persulphate was then destroyed by boiling and a known amount of standard ferrous ammonium sulphate solution was added. Excess of ferrous was estimated using standard dichromate and thus the chromium content was calculated. Nickel and iron were estimated by gravimetric methods. Nickel was precipitated as $[Ni(dmg)_2]$ in an ammoniacal medium. Iron was precipitated as $Fe(OH)_3$ using excess of ammonia and the precipitate was ignited to obtain anhydrous ferric oxide.

The anions present in complexes were estimated by standard methods.[64] Chloridee and bromides were estimated by Volhards method, after sodium carbonate fusion and dissolution in nitric acid. For the estimation of perchlorates, the Kurz's method was followed. [64] Carbon, hydrogen and nitrogen were estimated by using Hitachi CHN-O rapid analyzer at CDRI, Lucknow. The melting points of ligands and complexes were noted using standard melting point apparatus. Conductance measurements were carried out at room temperature using Systronics Conductivity Bridge 305 and dip-type cell with 10^{-3} M solutions of the complexes in DMF.[65]

Magnetic susceptibilities of the complexes at room temperature were measured using Gouy type magnetic balance. Diamagnetic corrections were applied using Pascal constants for various atoms and structural units.[66] From the corrected molar susceptibilities, effective magnetic moments were calculated.

The infrared spectra of the ligands and the complexes were recorded in the range 4000-400 cm^{-1} on a Schimadzu FTIR-8101 spectrophotometer with KBr pellets at CDRI, Lucknow. The solid-state electronic spectra of complexes were recorded by the procedure recommended by Venenzi[67], using a Schimadzu UV-1601 spectro-photometer. The complex was powdered and mixed uniformly with paraffin wax. A strip of filter paper smeared with this paste was used as the sample and another smeared with pure paraffin was used as the reference. The ^1H NMR spectra of the ligands were recorded in DMSO-d_6 on a Varien 300 NMR spectrometer at RRL, Trivandrum. The thermal analyses of the complexes were done at NIT, Trichi using a Perkin Elmer TGA-7 Analyser, having the following operational characteristics: heating rate, 10 K per min; atmosphere, static air; sample size, 6-10mg; crucible, platinum. Independent pyrolytic studies of the complexes were carried out in order to check the mass-loss data obtained from TG experiments. A known mass of the complex was heated to about 820 °C in a silica crucible and the percentage of mass-loss was compared with that obtained from TG data. The chemical identification of the residue was also done. The antifungal studies were done at IISR, Calicut. Further experimental details are provided in the respective chapters. Library references were carried out at the University of Calicut, RRL Trivandrum and IISc Bangalore. Online search was also resorted to.

CHAPTER III

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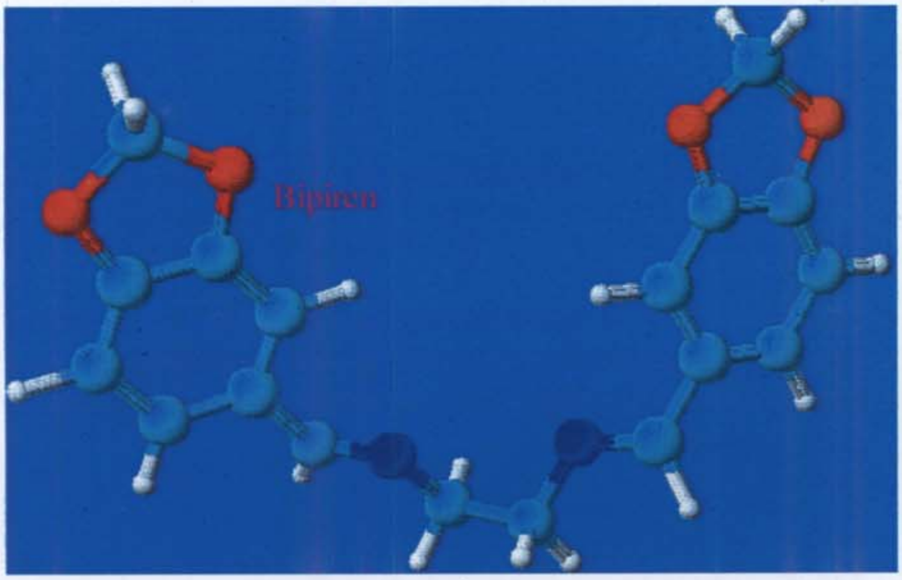
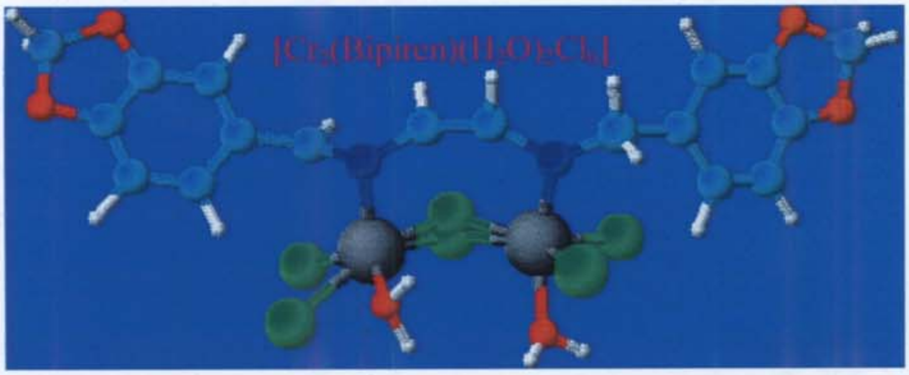

Bipiren


[Cr_2(Bipiren)(H_2O)$_2$$Cl_6$]

CHAPTER III

Cr(III), Mn(II), Fe(III), Co(II), Ni (II) AND Cu(II) COMPLEXES OF BIS(PIPERONALDEHYDE)ETHYLENEDIIMIE

(Bipiren)

Due to their good complexing properties,[7-10,58] biological activities[27,52,68] and analytical applications[32,50,69] ethylenediamine and its Schiff bases of different denticity, as well as their metal complexes, have been the subject of many studies. Apparently, the most studied among them are the complexes with tetradentate bis(salicylaldehyde)ethylenediimine.[9,56,57,70] Earlier works have clearly shown that, the coordinating possibility of ethylenediamine could be improved by condensing with a variety of carbonyl compounds.[7-10,70-72] A search through literature revealed that no work has been done on the transition metal complexes of the Schiff base derived from ethylenediamine and piperonaldehyde. The present investigation involved the synthesis of a new type of bidentate/tetradentate ligand formed by the condensation of ethylenediamine with piperonaldehyde. The choice of piperonal as the carbonyl compound in the present programme stemmed from the fact that many compounds containing 3,4-dioxymethylene groups showed pronounced biological activities.[5,59,60] This ligand system (Fig-1) has two nitrogen donor sites and two dioxymethylene groups, which also may offer coordination. Therefore, it is indeed a prudent and worthwhile endeavour to synthesise and characterise the complexes of bis(piperonaldehyde)ethylenediimine (Bipiren)*(L) and to conduct detailed investigations on the structure, thermal stabilities and biological activities of these compounds.

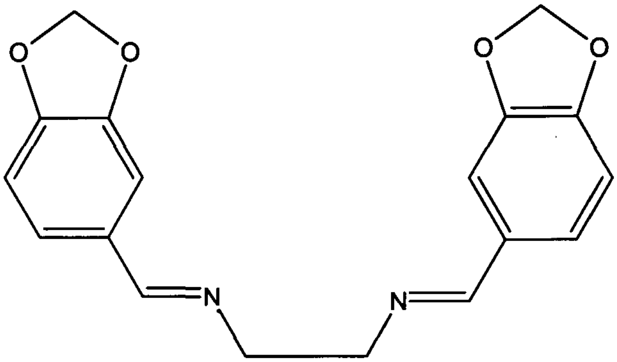


Fig-1 Suggested structure for bis(piperonaldehyde)ethylenediimine, (Bipiren) (L)

A. Experimental

1. Materials and methods

Specifications regarding the reagents used, the procedural details adopted for the synthesis and characterization of the ligand and the complexes are given in Chapter II.

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*The systematic name of the compound is: N,N'-bis[1,3-benzodioxol-5-ylmethylene]ethane-1,2-diamine. But for the sake of convenience the name 'bis(piperonaldehyde)ethylenediimine' and the short form 'Bipiren' are adopted in this thesis.

2. Synthesis of the ligand, bis(piperonaldehyde)ethylenediimine (Bipiren)

Ethylenediamine (1.20 g) in ethanol was mixed with a solution of piperonaldehyde (6.04 g) in ethanol in 1:2 molar ratio and was refluxed for about 1h and then cooled. The white precipitate formed was filtered off, washed with water and a few ml of alcohol and then purified by dissolving in hot ethanol and recrystallised from ethanol. The substance was then dried over anhydrous $CaCl_2$. (yield = 88 %)

3. Synthesis of complexes of bis(piperonaldehyde)ethylenediimine

Complexes of the ligand with several salts of Cr(III), Mn(II), Fe(III), Co(II), Ni (II) and Cu(II) were synthesised. Acetates, chlorides, bromides, nitrates and perchlorates of these metals were used for the synthesis.

a) Complexes of Cr (III), Mn (II) and Fe (III)

The complexes were prepared by refluxing the methanolic solutions of the metal salt and the ligand in 1:1 molar ratio for about 2-3 h. When the solubility of the salt in methanol was very low, as in the case of the acetates, it was dissolved in a methanol-water mixture containing minimal amount of water and was then added to methanolic solution of the ligand while refluxing. After refluxing for about 2-3 h, the reaction mixture, in each case, was concentrated over a water bath and the pasty mass obtained was washed repeatedly with diethyl ether and/or petroleum ether and/or acetone to get the solid complex separated. It was then dried over anhydrous $CaCl_2$.

b) Complexes of Co (II)

Complexes of Co(II) were also prepared by method similar to the one described above, but solutions of the ligand and metal salts in acetone were used. In the case of the acetate complex, salt was dissolved in acetone-water mixture and added to refluxing solution of the ligand in acetone. After refluxing for about 2-3 h, the solution was concentrated over a water bath and was washed repeatedly with diethyl ether and/or petroleum ether to get the solid complex separated. It was then dried over anhydrous $CaCl_2$.

c) Complexes of Ni (II)

Complexes of Ni(II) were also prepared by refluxing a mixture of the methanolic solutions of the metal salt and the ligand in 1:1 molar ratio for about 2-3 h. Here again nickel(II) acetate was dissolved in methanol-water mixture and added to refluxing solution of the ligand. Nickel chloride complex precipitated while refluxing, which was separated, washed and dried. In the case acetate, bromide, nitrate and perchlorate, after refluxing for about 2-3 h, the complexes were separated by the method of changing solvent as described above.

d) Complexes of Cu(II)

Complexes of Cu(II) were also prepared by refluxing a mixture of the methanolic solutions of the metal salt and the ligand in 1:1 molar ratio for about 2-3 h. In the case of $CuCl_2$ and $CuBr_2$, the complexes were precipitated while refluxing, and filtered off and washed with a little ethanol and dried over anhydrous $CaCl_2$. In the case of nitrate, acetate and perchlorate, after refluxing for 2-3 h, the complexes were separated by the method of changing solvent as described above.

B. Results and discussion

The data obtained from analytical and physico-chemical studies have been correlated in a logical way to explain the properties, bonding and structures of the compounds.

1. Characterisation of the ligand, Bipiren

The ligand, Bipiren was white non-hygroscopic solid with a melting point of 160 °C. TLC established its homogeneity and purity and the analytical data showed close agreement with the suggested formula of $C_{18}H_{16}O_4N_2$, for bis(piperonaldehyde)ethylenediimine. It was further characterised by ^1H NMR and IR spectral studies.

a) ^1H NMR spectrum

The ^1H NMR spectrum of the ligand, Bipiren was recorded in DMSO-d_6 (Table-1). The spectrum exhibited a number of signals that were characteristic of the compound.[73,74] The peak observed at δ value, 8.21-8.22 ppm was assigned to the azomethine protons in the molecule. The signals observed in the range 7.50-6.84 ppm were assigned to the different types of aromatic protons in the piperonal moieties. The singlet peak at 5.96 ppm was assigned to the methylinic protons of the dioxymethylene group in the piperonal moiety of the ligand. The inductive effect of the two oxygen atoms deshielded the methylenic protons and this resulted in the higher δ value for these protons. The peak in the range 3.86-3.84 ppm was assigned to the methylinic protons from the ethylene diamine moiety of the ligand. The inductive effects of the nitrogen atoms might be responsible for the high value.

b) IR spectrum

IR spectrum of the ligand, Bipiren showed a number of absorption bands which were the characteristics of different groups present in it. Assignments were done on the basis of analogous structures, known earlier[75,76] (Table-2). The bands present at 1639 and 1255 cm^{-1} were assigned to the C=N and C-N stretchings, respectively. The characteristic frequency due to the stretching of C=O in the aromatic aldehyde group of piperonal moiety, at 1690 cm^{-1} was not present in the spectrum, which indicated that the condensation was complete. The band at 3050 cm^{-1} might be assigned to the aromatic C-H stretching and that at 2905 cm^{-1} to the C-H stretching of the methylene group ($>CH_2$). The bands due to the in plane bending of the aromatic C-H are usually found in the range 1250 to 950 cm^{-1}. The bands present at 1191, 1099 cm^{-1} were assigned to these modes of vibrations. The band identified at 926 cm^{-1} was the characteristic absorption frequency of the dioxymethylene group of piperonal moiety.[76] The most characteristic frequencies of aromatic groups are found below 900 cm^{-1}, usually in the range 600-900 cm^{-1}, due to the out of plane bending vibration of the aromatic C-H. The absorptions by Bipiren at 873 and 813 cm^{-1} were assigned to these modes of vibrations.

Table-1 Significant ^{1}H NMR Peaks of Bipiren and their assignments

Chemical shift* (δ ppm)	Proton assignment
8.22-8.21s	Two -CH=N-
7.50s 7.06-7.04m 6.86-6.84m	Aromatic protons
5.96s	Two $-CH_2-$ (of dioxymethylene groups)
3.86-3.84s	Two-CH_2- (of ethylene diamine moiety)

* s = singlet, m = multiplet

Table-2 Significant IR bands of Bipiren and their assignments

Band frequency* (cm^{-1})	Assignment
3050	ν aromatic C-H
2905	ν C-H (methylene)
2839	ν C-H (=CH-)
1639s	ν >C=N-
1494 1446	ν ring C-C
1255s	ν >C-N-
1191 1099	δ in plane C-H (aromatic)
926	δ -O-CH_2-O-
873 817	δ out of plane C-H(aromatic)

* s = strong

2. Formulae and general properties of complexes

All the complexes were found to be coloured, photo-stable and non-hygroscopic solids. The solubility of these complexes in common organic solvents was very low, but they were soluble in DMF and DMSO. The analytical data (Tables 3-8) and molar conductance values in DMF (Tables 9-14) showed that the complexes had the following formulae.

Hydroxo complexes were obtained when metal acetates were used as the starting materials in the synthesis, instead of obtaining the expected acetato ones. The hydroxo and chloro complexes of all the metal ions and the bromo complexes of Cr(III) and Fe(III) showed bimetallic or polymeric nature and this could be due to the bridging nature of hydroxo, chloro, bromo and Bipiren ligands. The spectral and magnetic data also confirmed the suggested formulae.

a) $[M_2LA_6(H_2O)_2]$, where M = Cr(III) or Fe(III) and A = OH^- , Cl^- or Br^-

b) $[MLA_3(H_2O)]$, where M = Cr(III) or Fe(III) and A = NO_3^- or ClO_4^-

c) $[M_2LA_4(H_2O)_2]$, where M = Mn(II) and A = Cl^- or OH^-

or M = Ni (II) or Cu (II) and A = Cl^-

d) $[MLA_2(H_2O)_2]$, where M = Mn(II) and A = Br^- or ClO_4^-

or M = Co (II) and A = Br^-, $NO3^-$ or ClO_4^-

or M = Ni (II) and A = Br^-or $ClO4^-$

or M = Cu (II) and A = Br^-

e) $[ML(H_2O)_4] A_2$, where M= Mn(II) or Cu (II) and A = NO_3^-

f) $[M_2LA_4]$, where M = Co (II) and A = Cl^-, OH^-

or M = Ni (II) or Cu (II) and A = OH^-

g) $[ML(H_2O)_2]A_2$, where $M = Ni(II)$ and $A = NO_3^-$

or $M = Cu(II)$ and $A = ClO4^-$

3. Molar conductance

Molar conductances of 10^{-3} M solutions in DMF of the Bipiren complexes were determined at room temperature and the values are given in Tables 9-14. The range of molar conductance[65] in DMF for 1:1, 1:2, 1:3 electrolytes are 65-90, 130-170, 200-240 ohm^{-1} cm mol^{-1} respectively, and for 1:4 electrolytes it is above 450 ohm^{-1} cm mol^{-1}. Most of the complexes showed values, lower than that expected for 1:1 electrolytes, indicating their non-electrolytic nature. The nitrato complexes of Mn(II) and Ni(II) and the nitrato and perchlorato complexes of Cu(II) showed high values of conductance, corresponding to those for 1:2 electrolytes. They were assigned formulae accordingly. Analytical data and spectral studies also supported the suggested formulae.

4. Magnetic behaviour

The Gouy balance was used to determine magnetic susceptibility values of the complexes at room temperature. $Hg[Co(NCS)_4]$ was used as the calibrant.[77] Diamagnetic corrections were applied using Pascal constants for various atoms and structural units.[65] The magnetic susceptibilities, diamagnetic corrections and the effective magnetic moment values calculated from the corrected magnetic susceptibilities are given in the Tables15-20.

Table-3 Analytical data of Cr(III) Bipiren complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated) %				
					Metal	C	H	N	Anion
Biperen (L)	$C_{18}H_{16}O_4N_2$	324	Colourless	88		66.74 (66.67)	4.94 (4.93)	8.61 (8.64)	
$[Cr_2L(OH)_6(H_2O)_2]$	$Cr_2C_{18}H_{26}O_{12}N_2$	566	Brown	65	19.23 (18.37)	37.64 (38.16)	4.67 (4.59)	4.72 (4.95)	
$[Cr_2LCl_6(H_2O)_2]$	$Cr_2C_{18}H_{20}O_6N_2Cl_6$	677	Green	67	16.12 (15.36)	30.85 (31.91)	2.74 (2.95)	4.01 (4.14)	32.6 (31.46)
$[Cr_2LBr_6(H_2O)_2]$	$Cr_2C_{18}H_{20}O_6N_2Br_6$	944	Greenish yellow	62	11.83 (11.02)	21.84 (22.88)	2.04 (2.12)	2.84 (2.97)	52.14 (50.85)
$[CrL(NO_3)_3((H_2O)]$	$CrC_{18}H_{18}O_{14}N_5$	580	Green	88	9.12 (8.97)	36.34 (37.24)	2.98 (3.10)	11.7 (12.07)	
$[CrL(ClO_4)_3 (H_2O)]$	$CrC_{18}H_{18}O_{17}N_2Cl_3$	693	Green	87	7.86 (7.51)	30.5 (31.19)	2.46 (2.60)	3.96 (4.04)	43.91 (43.11)

*F. wt. = Formula weight

Table-4 Analytical data of Mn(II) Bipiren complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated) %				
					Metal	C	H	N	Anion
Bipiren(L)	$C_{18}H_{16}O_4N_2$	324	Colourless	88	-	66.74 (66.67)	4.94 (4.93)	8.61 (8.64)	
$[Mn_2L(OH)_4(H_2O)_2]$	$Mn_2C_{18}H_{24}O_{10}N_2$	538	Yellowish brown	71	21.12 (20.45)	39.43 (40.15)	4.32 (4.46)	5.1 (5.20)	
$[Mn_2LCl_4(H_2O)_2]$	$Mn_2C_{18}H_{20}O_6N_2Cl_4$	612	Yellowish brown	68	18.21 (17.97)	34.93 (35.29)	3.14 (3.27)	4.35 (4.58)	23.62 (23.20)
$[MnLBr_2(H_2O)_2]$	$MnC_{18}H_{20}O_6N_2Br_2$	575	Yellowish brown	82	9.12 (9.57)	38.13 (37.57)	3.52 (3.48)	4.93 (4.87)	27.15 (27.83)
$[MnL(H_2O)_4](NO_3)_2$	$MnC_{18}H_{24}O_{14}N_4$	575	Yellowish brown	79	9.08 (9.57)	38.2 (37.57)	4.42 (4.17)	9.54 (9.74)	
$[MnL(ClO_4)_2(H_2O)_2]$	$MnC_{18}H_{20}O_{14}N_2Cl_2$	614	Yellowish brown	76	8.74 (8.96)	36.11 (35.18)	3.31 (3.26)	4.72 (4.56)	31.93 (32.41)

*F. wt. = Formula weight

Table-5 Analytical data of Fe(III) Bipiren complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated) %				
					Metal	C	H	N	Anion
Bipiren(L)	$C_{18}H_{16}O_4N_2$	324	Colourless	88		66.74 (66.67)	4.94 (4.93)	8.61 (8.64)	
$[Fe_2L(OH)_6(H_2O)_2]$	$Fe_2C_{18}H_{26}O_{12}N_2$	574	Orange	67	20.34 (19.51)	36.81 (37.63)	4.38 (4.53)	4.59 (4.88)	
$[Fe_2LCl_6(H_2O)_2]$	$Fe_2C_{18}H_{20}O_6N_2Cl_6$	685	Orange	63	17.12 (16.35)	30.86 (31.53)	2.81 (2.92)	3.92 (4.10)	43.67 (42.86)
$[Fe_2LBr_6(H_2O)_2]$	$Fe_2C_{18}H_{20}O_6N_2Br_6$	952	Orange	64	12.2 (11.76)	21.9 (22.69)	2.0 (2.10)	2.81 (2.94)	51.9 (50.42)
$[FeL(NO_3)_3((H_2O)]$	$FeC_{18}H_{18}O_{14}N_5$	584	Orange	82	10.1 (9.59)	36.1 (36.99)	2.96 (3.08)	11.2 (11.99)	
$[FeL(ClO_4)_3(H_2O)]$	$FeC_{18}H_{18}O_{17}N_2Cl_3$	697	Orange	79	8.46 (8.04)	30.1 (31.01)	2.43 (2.58)	3.87 (4.02)	43.6 (42.86)

*F. wt. = Formula weight

Table-6 Analytical data of Co(II) Bipiren complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated) %				
					Metal	C	H	N	Anion
Bipiren(L)	$C_{18}H_{16}O_4N_2$	324	Colour-less	88		66.74 (66.67)	4.94 (4.93)	8.61 (8.64)	
$[Co_2L(OH)_4]$	$Co_2C_{18}H_{20}O_8N_2$	510	Greenish blue	61	23.83 (23.14)	41.77 (42.35)	3.78 (3.92)	5.22 (5.49)	
$[Co_2LCl_4]$	$Co_2C_{18}H_{16}O_4N_2Cl_4$	584	Bright green	64	21.82 (20.20)	35.48 (36.97)	2.61 (2.74)	4.63 (4.80)	25.1 (24.32)
$[CoLBr_2(H_2O)_2]$	$CoC_{18}H_{20}O_6N_2Br_2$	579	Orange	67	11.01 (10.19)	36.67 (37.31)	3.32 (3.45)	4.72 (4.84)	28.3 (27.63)
$[CoL(NO_3)_2(H_2O)_2]$	$CoC_{18}H_{20}O_{12}N_4$	543	Orange brown	82	11.64 (10.87)	38.39 (39.78)	3.43 (3.68)	9.97 (10.31)	
$[CoL(ClO_4)_2(H_2O)_2]$	$CoC_{18}H_{20}O_{14}N_2Cl_2$	618	Orange	79	8.93 (9.55)	35.22 (34.95)	3.36 (3.24)	4.62 (4.53)	31.48 (32.20)

* F. wt. = Formula weight

Table-7 Analytical data of Ni(II) Bipiren complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated) %				
					Metal	C	H	N	Anion
Bipiren (L)	$C_{18}H_{16}O_4N_2$	324	Colour-less	88		66.74 (66.67)	4.94 (4.93)	8.61 (8.64)	
$[Ni_2L(OH)_4]$	$Ni_2C_{18}H_{20}O_8N_2$	509	Gray	59	23.75 (23.05)	41.87 (42.40)	3.73 (3.93)	5.13 (5.50)	
$[Ni_2LCl_4(H_2O)_2]$	$Ni_2C_{18}H_{20}O_6N_2Cl_4$	619	Greenish yellow	63	19.32 (18.95)	33.96 (34.87)	3.13 (3.23)	4.43 (4.52)	23.71 (22.93)
$[NiLBr_2(H_2O)_2]$	$NiC_{18}H_{20}O_6N_2Br_2$	579	Green	73	10.91 (10.14)	38.42 (37.33)	3.24 (3.46)	4.71 (4.84)	29.01 (27.65)
$[NiL(H_2O)_2]$ $(NO_3)_2$	$NiC_{18}H_{20}O_{12}N_4$	543	Brown	75	11.72 (10.82)	38.66 (39.81)	3.53 (3.69)	11.1 (10.32)	
$[NiL(ClO4)_2(H_2O)_2]$	$NiC_{18}H_{20}O_{14}N_2Cl_2$	582	Green	72	9.92 (9.50)	33.89 (34.97)	3.13 (3.24)	4.36 (4.53)	33.43 (32.22)

* F. wt. = Formula weight

Table-8 Analytical data of Cu(II) Bipiren complexes

Compound	Empirical formula	*F.wt.	Colour	Yield %	Found (calculated) %				
					Metal	C	H	N	Anion
Bipiren(L)	$C_{18}H_{16}O_4N_2$	324	Colour -less	88	-	66.74 (66.67)	4.94 (4.93)	8.61 (8.64)	
$[Cu_2L(OH)_4]$	$Cu_2C_{18}H_{20}O_8N_2$	519	Brown	63	25.19 (24.47)	40.89 (41.62)	3.71 (3.85)	5.17 (5.40)	
$[Cu_2LCl_4(H_2O)_2]$	$Cu_2C_{18}H_{20}O_6N_2Cl_4$	629	Blue	61	21.13 (20.19)	33.53 (34.34)	2.95 (3.18)	4.38 (4.45)	23.37 (22.58)
$[CuLBr_2(H_2O)_2]$	$CuC_{18}H_{20}O_6N_2Br_2$	584	Green	58	11.21 (10.88)	35.99 (37.02)	3.24 (3.43)	4.69 (4.80)	29.1 (27.42)
$[CuL(H_2O)_4](NO_3)_2$	$CuC_{18}H_{24}O_{14}N_4$	584	Bluish green	69	11.32 (10.88)	36.2 (37.01)	3.92 (4.11)	9.12 (9.60)	
$[CuL(H_2O)_2](ClO_4)_2$	$CuC_{18}H_{20}O_{14}N_2Cl_2$	623	Brown	71	10.80 (10.20)	33.84 (34.70)	3.11 (3.21)	4.28 (4.50)	32.61 (31.97)

* F. wt. = Formula weight

Table-9 Molar conductance in DMF of Cr(III) Bipiren complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[Cr_2L(OH)_6(H_2O)_2]$	28.46
$[Cr_2LCl_6(H_2O)_2]$	-
$[Cr_2LBr_6(H_2O)_2]$	28.43
$[CrL(NO_3)_3((H_2O)]$	56.25
$[CrL(ClO_4)_3(H_2O)_]$	14.82

Table-10 Molar conductance in DMF of Mn(II) Bipiren complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[Mn_2L(OH)_4(H_2O)_2]$	21.4
$[Mn_2LCl_4(H_2O)_2]$	12.24
$[MnLBr_2(H_2O)_2]$	42.8
$[MnL\ (H_2O)_4](NO_3)_2$	148.42
$[MnL(ClO4)_2(H_2O)_2]$	41.6

Table-11 Molar conductance in DMF of Fe(III) Bipiren complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[Fe_2L(OH)_6(H_2O)_2]$	23.92
$[Fe_2LCl_6(H_2O)_2]$	16.32
$[Fe_2LBr_6(H_2O)_2]$	24.63
$[FeL(NO_3)_3((H_2O)]$	49.45
$[FeL(ClO_4)_3\ (H_2O)]$	51.82

Table-12 Molar conductance in DMF of Co(II) Bipiren complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[Co_2L(OH)_4]$	-
$[Co_2LCl_4]$	11.51
$[CoLBr_2(H2O)_2]$	42.47
$[CoL(NO_3)_2(H2O)_2]$	31.83
$[CoL(ClO_4)_2(H2O)_2]$	36.59

Table-13 Molar conductance in DMF of Ni(II) Bipiren complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[Ni_2L(OH)_4]$	28.21
$[Ni_2LCl_4(H_2O)_2]$	14.69
$[NiLBr_2(H_2O)_2]$	31.21
$[NiL(H_2O)_2]\ (NO_3)_2$	137.44
$[NiL(ClO4)_2(H_2O)_2]$	26.68

Table-14 Molar conductance in DMF of Cu(II) Bipiren complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[Cu_2L(OH)_4]$	-
$[Cu_2LCl_4(H_2O)_2]$	13.1
$[CuLBr_2(H_2O)_2]$	38.06
$[CuL(H_2O)_4](NO_3)_2$	162.23
$[CuL(H_2O)_2](ClO4)_2$	138.45

Table-15 Magnetic data of Cr(III) complexes of Bipiren
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d 10^{-6}$	$\chi_{eff}\ 10^{-6}$	μ_{eff} B.M.
$[Cr_2LCl_6(H_2O)_2]$	4837	156	4993	3.49
$[Cr_2L(OH)_6(H_2O)_2]$	4185	119	4304	3.24
$[Cr_2LBr_6(H_2O)_2]$	4892	188	5080	3.52
$[CrL(NO_3)_3((H_2O)]$	5743	240	5982	3.82
$[CrL(ClO_4)_3 (H_2O)]$	5970	297	6268	3.91

Table-16 Magnetic data of Mn(II) complexes of Bipiren
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d 10^{-6}$	$\chi_{eff}\ 10^{-6}$	μ_{eff} B.M.
$[Mn_2L(OH)_4(H_2O)_2]$	9813	111	9924	4.92
$[Mn_2LCl_4(H_2O)_2]$	8997	136	9133	4.72
$[MnLBr_2(H_2O)_2]$	14066	253	14319	5.91
$[MnL(H_2O)_4]\ (NO_3)_2$	15024	231	15255	6.10
$[MnL(ClO4)_2(H_2O)2]$	15490	269	15759	6.20

Table-17 Magnetic data of Fe(III) complexes of Bipiren
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d 10^{-6}$	$\chi_{eff}\ 10^{-6}$	μ_{eff} B.M.
$[Fe_2L(OH)_6(H_2O)_2]$	8406	119	8525	4.56
$[Fe_2LCl_6(H_2O)_2]$	10175	156	10331	5.02
$[Fe_2LBr_6(H_2O)_2]$	9736	188	9924	4.92
$[FeL(NO_3)_3((H_2O)]$	15115	240	15355	6.12
$[FeL(ClO_4)_3 (H_2O)]$	14168	297	14465	5.94

B.M.= Bohr Magneton

χ_m = Molar susceptibility χ_{eff} = Effective susceptibility

χ_d = Diamagnetic correction μ_{eff} = Effective magnetic moment

Table-18 Magnetic data of Co(II) complexes with Bipiren
T = 303 K

Complex	$\chi_m.10^{-6}$	$\chi_d.10^{-6}$	$\chi_{eff}.10^{-6}$	μ_{eff} B.M.
$[Co_2L(OH)_4]$	4391	101	4492	3.31
$[Co_2LCl_4]$	4669	126	4795	3.42
$[CoLBr_2(H_2O)_2\}$	9350	253	9604	4.84
$[CoL(NO_3)_2(H_2O)_2]$	10112	220	10331	5.02
$[CoL(ClO_4)_2(H_2O)_2]$	10823	220	11043	5.19

Table-19 Magnetic data of Ni(II) complexes with Bipiren
T = 303 K

Complex	$\chi_m.10^{-6}$	$\chi_d.10^{-6}$	$\chi_{eff}.10^{-6}$	μ_{eff} B.M.
$[Ni_2L(OH)_4]$	-	-	-	D
$[Ni_2LCl_4(H_2O)_2]$	2325	136	2461	2.45
$[NiLBr_2(H_2O)_2]$	4348	253	4601	3.35
$[NiL(H_2O)_2]\ (NO_3)_2$	-	-	-	D
$[NiL(ClO4)_2(H_2O)_2]$	4587	208	4795	3.42

Table-20 Magnetic data of Cu(II) complexes with Bipiren
T = 303 K

Complex	$\chi_m.10^{-6}$	$\chi_d.10^{-6}$	$\chi_{eff}.\ 10^{-6}$	μ_{eff} B.M.
$[Cu_2L(OH_4]$	680	101	781	1.37
$[Cu_2LCl_4(H_2O)_2]$	726	136	862	1.45
$[CuLBr_2(H_2O)_2]$	1572	253	1825	2.10
[CuL	1355	252	1607	1.98
$[CuL(H_2O)_2]\ (ClO4)_2$	1265	231	1496	1.90

D = Diamagnetic, B.M. = Bohr Magneton

χ_m = Molar susceptibility, χ_{eff} = Effective susceptibility

χ_d = Diamagnetic correction, μ_{eff} = Effective magnetic moment

The complexes of Cr(III), having a d^3 configuration, are mostly of the octahedral type with a ground term $^3A_{2g}$.[78] The spin-orbit coupling constant for Cr(III) is very low and its complexes are expected to show magnetic moments very close to the spin-only value for three unpaired electrons and usually show moments in the range 3.70 to 3.90 B.M.[78] In the case of polynuclear complexes there is the possibility of magnetic exchange between neighbouring chromium ions through the bridging ligands leading to antiferromagnetic coupling. Due to this reason, slightly lower values were reported for polynuclear complexes.[78] In the present investigation the hydroxo, chloro and bromo complexes of Cr(III) showed magnetic moments of 3.24, 3.49 and 3.52 B.M., respectively, in all probability indicating their bimetallic or polymeric nature and subsequent anti-ferromagnetic coupling.[79-81] The nitrato and perchlorato complexes showed magnetic moments of 3.82 and 3.91B.M., respectively, indicating sufficient magnetic dilution.[80,82] These observations along with other physico-chemical data pointed towards octahedral geometry for all the Cr(III) complexes, investigated here.

Mn(II) ions usually form high-spin octahedral complexes, but a few low-spin octahedral complexes and some tetrahedral ones are also known.[78] In the case of high-spin octahedral and tetrahedral complexes of Mn(II), the spin-only magnetic moment value of d^5 configuration, in the range of 5.92 B.M., is expected. However, in many high-spin octahedral complexes the observed values are in the range 5.65 to 6.10 B.M.[78] Low-spin octahedral Mn(II) complexes are expected to have a spin-only value of 1.73 B.M., but many such complexes show magnetic moments in the range of ~2.5 B.M. A large number of Mn(II) complexes with Schiff bases have been found to show magnetic moments appreciably below the spin-only value, in the range of 4.74 to 5.50 B.M.[83,84] Obviously, they are magnetically non-dilute. Among the Mn(II) complexes presently investigated, the hydroxo and chloro complexes showed magnetic moments of 4.72 and 4.92 B.M., respectively. The probable bimetallic or polymeric nature and the consequent anti-ferromagnetic coupling in these complexes could be considered as the reason for low values.[85-87] The bromo, nitrato and perchlorato complexes showed magnetic moments in the range 5.91 to 6.20 B.M. This, along with other data supported octahedral geometry for all the Mn(II) complexes, investigated here.[26,78,85]

Iron(III) is usually high-spin in nearly all of its complexes, except those with the strongest ligands.[78] The high-spin d^5 octahedral configuration of Fe(III) is expected to give a magnetic moment, close to the spin-only value of 5.90 B.M., as the ground state has no orbital angular momentum.[78] Lower values are reported for polynuclear complexes and also in some other complexes due to the spin-crossover phenomenon.[78,80] In the present investigation, the hydroxo, chloro and bromo Fe(III) complexes showed magnetic moments of 5.02, 4.56 and 4.92 B.M., respectively. The low values could be considered as an indication of the polymeric- or bimetallic nature of these complexes.[78,80,88] The nitrato and perchlorato complexes showed magnetic moments of 6.12 and 5.94 B.M., respectively. Obviously, these complexes are high-spin with probable octahedral symmetry.[78,89]

The magnetic properties of Co(II) complexes depend on their geometries. In the high-spin octahedral complexes of Co(II), the ground term is $^4T_{1g}$, which results in considerable orbital contribution. Hence the observed magnetic moment values are in the range 4.70 - 5.20 B.M., which are higher than the spin-only value for three unpaired electrons.[78] The low-spin octahedral Co(II) complex has ground state ^2E_g and hence no orbital contribution is expected. Therefore, the observed values are very close to the spin-only value for one unpaired electron, *i.e.*, 1.73 B.M.[78,90] In the tetrahedral, high-spin complexes of Co(II) the ground term is $^4A_2$ and there is no orbital contribution. The expected magnetic moment is close to the spin-only value for the three unpaired electrons, *i.e.*, 3.87 B.M. However, the observed values are usually in the range 4.40 ~ 4.80 B.M. The high values are due to spin-orbit coupling perturbations.[78,91] In the case of four coordinate low-spin complexes, which are square-planer in geometry, it is difficult to predict accurately the magnetic properties. A magnetic moment above 1.73 B.M., the spin-only value for one unpaired electron, is expected and values in the range 2.20-2.70 B.M. are observed.[77,78] In the present investigation, the hydroxo and chloro complexes of Co(II) showed magnetic moments of 3.31, 3.42 B.M., respectively, indicating tetrahedral geometries.[90,92] The electronic spectra and the bright-green colour of the compounds also pointed towards the tetrahedral geometry. The slightly lower values indicated magnetic non-dilution and this might be due to polymeric- or bimetallic nature of the complexes and the resulting anti-ferromagnetic coupling.[78,93] Other cobalt(II) complexes, which were investigated here, showed magnetic moments in the range 4.84-5.19 B.M., which corresponded to those of high-spin octahedral geometry with sufficient magnetic diluion.[8,89,94,]

As far as magnetic properties are considered, the complexes of Ni(II) can be classified into three categories,[78] which are the six coordinate octahedral, paramagnetic complexes with ^3A_2g ground term, the four coordinate square-planar diamagnetic complexes with a spin-singlet ground term and the four coordinate approximately tetrahedral paramagnetic complexes with a triplet ground term. The octahedral complexes show magnetic moments in the range 2.90-3.30 B.M. because no orbital contribution is expected, as the ground term is ^3A_2g. A slightly higher value than the spin-only moment is observed for these complexes because of the spin-orbit coupling or higher state mixing with ground state. For tetrahedral ones, there is an appreciable orbital contribution of the $^3T_1$ ground state and the magnetic moment values are in the range 3.60-4.00 B.M. Large distortions and inequalities in the field of coordinated ligands may result in magnetic moments with small orbital contributions and the observed values can be as low as 3.20 B.M.[78,91] Ni(II) square-planar complexes have a spin-singlet ground state and hence they are diamagnetic.[78] Among the complexes of Ni(II) investigated here, the hydroxo and nitrato complexes were found to be diamagnetic in nature, indicating square-planar geometries.[46,95] The chloro complex showed a low magnetic moment of 2.45 B.M., which could be due to its bimetallic- or polymeric nature and the subsequent antiferromagnetic coupling.[78,96] But the greenish-yellow colour of the complex and its electronic spectrum indicated an octahedral geometry. The bromo and the perchlorato complexes showed the magnetic moments of 3.35 and 3.42 B.M., respectively, indicating octahedral geometry, which was further supported by their green colour and electronic spectra.[94,97]

The Cu(II) complexes usually have distorted octahedral geometry, but many complexes of square-planar or approximately tetrahedral geometry are also known.[78] However, stereochemistry has little effect on the magnetic moments of Cu(II) complexes and values slightly above the spin-only value for one unpaired electron, are expected.[78] A regular octahedral Cu(II) complex has the ground term

^2Eg and hence there is probability of no orbital contribution. The spin-only value corresponding to one unpaired electron is 1.73 B.M., but the observed values are usually in the range 1.80-2.10 BM. The slightly higher value is due to the spin-orbit coupling.[78] In regular tetrahedral Cu(II) complexes the ground term being a triplet state ($^3T_2$), orbital contribution is expected and theoretically predicted value of magnetic moment is 2.20 B.M.[98] But the observed values usually fall in the range 1.95-2.00 B.M.[99] In the present investigation, the hydroxo and chloro complexes of Cu(II) showed magnetic moments of 1.37 and 1.45 B.M., respectively. The lower values indicated some sort of molecular association that could be achieved through either a direct copper–copper interaction and/or magnetic exchange interaction through a bridging ligand.[78,94,100] The bromo, nitrato and perchlorato complexes were found to have magnetic moments in the range 1.90 to 2.10B.M., indicating sufficient magnetic dilution.[78,94] Other physico-chemical data supported these inferences and indicated square-planar geometries for the hydroxo and perchlorato complexes and octahedral geometries for the chloro, bromo and nitrato complexes.

5. Electronic Spectra

The electronic spectra of complexes depend on the energies of metal d orbitals, their degeneracy and the number of electrons distributed in them. These features are in turn controlled by the oxidation state of the metal, number and type of the ligands and the geometry of the complex. [101] Therefore, valuable informations regarding the structure, geometry and the splitting of d orbitals of coordination compounds can be obtained from their electronic spectra. The solid-state electronic spectra of complexes, presently investigated, were recorded by the procedure

Table-21 Electronic spectral bands of Cr(III) Bipiren complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[Cr_2L(OH)_6(H_2O)_2]$	542 442	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
$[Cr_2LCl_6(H_2O)_2]$	582 384	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
$[Cr_2LBr_6(H_2O)_2]$	552 401	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrL(NO_3)_3((H_2O)]$	563 412	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrL(ClO_4)_3(H_2O)]$	558 418	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral

Table-22 Electronic spectral bands of Mn(II) Bipiren complexes and their assignments

Complex	Bands* (nm)	Assignment	Geometry
$[Mn_2L(OH)_4(H_2O)_2]$	393 w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
$[Mn_2LCl_4(H_2O)_2]$	398w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
$[MnLBr_2(H_2O)_2]$	402 w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
$[MnL(H_2O)_4](NO_3)_2$	369w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
$[MnL(ClO_4)_2(H_2O)_2]$	384w	$^6A_1g(F) \rightarrow {}^4T_{2g}(G)$	Octahedral

*w = weak

Table-23 Electronic spectral bands of Fe(III) Bipiren complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[Fe_2L(OH)_6(H_2O)_2]$	492 398	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
$[Fe_2LCl_6(H_2O)_2]$	512 402	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
$[Fe_2LBr_6(H_2O)_2]$	502 399	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
$[FeL(NO_3)_3((H_2O)]$	488 401	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
$[FeL(ClO_4)_3(H_2O)]$	505 399	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral

Table-24 Electronic spectral bands of Co(II) Bipiren complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[Co_2L(OH)_4]$	1641 652 514	$^4A_2(F) \rightarrow {}^4T_2(F)$ $^4A_2(F) \rightarrow {}^4T_1(F)$ $^4A_2(F) \rightarrow {}^4T_1(P)$	Tetrahedral
$[Co_2LCl_4]$	1627 673 501	$^4A_2(F) \rightarrow {}^4T_2(F)$ $^4A_2(F) \rightarrow {}^4T_1(F)$ $^4A_2(F) \rightarrow {}^4T_1(P)$	Tetrahedral
$[CoLBr_2(H2O)_2]$	1015 622 478	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
$[CoL(NO_3)_2(H2O)_2]$	1115 678 409	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
$[CoL(ClO_4)_2(H2O)_2]$	1098 589 423	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral

Table-25 Electronic spectral bands of Ni(II) Bipiren complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
[$Ni_2L(OH_4$]	610 413	$^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1E_g$	Square-planar
[$Ni_2LCl_4(H_2O)_2$]	1140 700 410	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
[$NiLBr_2(H_2O)_2$]	1148 710 389	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
[$NiL(H_2O)_2$] $(NO_3)_2$	548 394	$^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1E_g$	Square-planar
[$NiL(ClO4)_2(H_2O)_2$]	1152 726 398	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral

Table-26 Electronic spectral bands of Cu(II) Bipiren complexes and their assignments

Complex	Bands* (nm)	Assignment	Geometry
[$Cu_2L(OH)_4$]	790 468	$^2B_{1g} \rightarrow {}^2A_{1g}$ CT	Square-planar
[$Cu_2LCl_4(H_2O)_2$]	694b	$^2E \rightarrow {}^2T_2$	Distorted octahedral
[$CuLBr_2(H_2O)_2$]	730b	$^2E \rightarrow {}^2T_{2g}$	Distorted octahedral
[$CuL(H_2O)_4](NO_3)_2$	655b	$^2E \rightarrow {}^2T_2$	Distorted octahedral
[$CuL(H_2O)_2$] $(ClO4)_2$	810 442	$^2B_{1g} \rightarrow {}^2A_{1g}$ CT	Square-planar

*b = broad

recommended by Venenzi.[67] The important spectral bands of the complexes and their probable assignment are given in the Tables 21-26

Most of the Cr(III) complexes are octahedral and their electronic spectra are well studied.[101,102] For the d^3 configuration in an octahedral field the following three spin allowed transitions are expected.

$^4A_2g \rightarrow {}^4T_{1g}(P) \sim 600\text{-}400$ nm

$^4A_2g \rightarrow {}^4T_{2g} \quad \sim 420\text{-}310$ nm

$^4A_2g \rightarrow {}^4T_{1g}(F) \quad \sim 275$ nm

In the spectra of all the Cr(III) complexes, in the present investigation, two bands were identified in the ranges 582-542 and 442-384 nm and were assigned to the $^4A_2g \rightarrow {}^4T_{1g}(P)$ and the $^4A_2g \rightarrow {}^4T_{2g}$ transitions in an octahedral geometry.[103-105] Other data also supported octahedral geometry for these complexes.

The majority of Mn(II) complexes are of high-spin d^5 configuration, having octahedral geometry. A high-spin octahedral field gives spin-forbidden as well as parity-forbidden transitions.[101,102] Hence, the absorptions of the octahedral Mn(II) complexes are very weak and they are commonly pale in colour. Usually the tales of CT bands overlap with weak the transitions, thus obscuring them. However, the following two weak transitions can be identified in their spectra.[85,106]

$^6A_{1g} \rightarrow {}^4T_{1g} \qquad \sim 550$ nm

$^6A_{1g} \rightarrow {}^4E_g$ or $^4A_{1g} \quad \sim 400$ nm

In the Mn(II) tetrahedral complexes, the transitions are still spin-forbidden but not parity-forbidden, and the transitions are, therefore, about 100 times stronger and the complexes have a noticeable pale-yellow or green colour. They can show yellow-green fluorescence as well.[107] In the present investigation, electronic spectra of the Mn(II) complexes showed a number of weak bands around 400 nm which were assigned to d-d transitions in an octahedral field.[85,106,108] The pale yellow or brown colour of the complexes also supported octahedral geometry for them.

Just like the Mn(II) complexes, the majority of Fe(III) complexes are also of high-spin configuration, generally having the octahedral geometry. The d^5 configuration in a high-spin octahedral field gives rise to spin-forbidden as well as parity-forbidden transitions.[101,109] Hence, the octahedral Fe(III) complexes are pale in colour and the absorption is very weak. The tales of CT bands overlap commonly with weak transitions and thus obscure them. In the present investigation, all the complexes of Fe(III) were found to be pale and gave only weak bands in the range 400-500 nm. These were assigned to d-d transitions of Fe(III) ion in an octahedral field.[94,110]

Octahedral and tetrahedral geometries are common among the Co(II) complexes. The octahedral complexes are generally pale red or purple in colour.[107] They have a spin-quartet ground state and there are three significant electronic transitions to the excited quartet states in the following ranges.[101,102,111]

$^4T_{1g}$ (F) → $^4T_{2g}$ (F) ~1250-1000 nm

$^4T_{1g}$ (F) → $^4A_{2g}$ (F) ~ 700-500 nm

$^4T_{1g}$ (F) → $^4T_{1g}$ (P) ~ 500-400 nm.

The second transition, *i.e.* $^4T_{1g}$ (F) → $^4A_{2g}$ (F) is a two electron process because the ground state, $^4T_{1g}$ (F) is derived mainly from $t_{2g}^5e_g^2$ configuration and the excited state, $^4A_{2g}$ (F) is derived form $t_{2g}^3e_g^4$ configuration.[154] Therefore, this transition is usually about 10^{-2} times weaker than the other transitions. The spectrum is generally dominated by the highest energy transition and may be complicated by spin-orbit coupling perturbations resulting in poor resolution of several of these bands. The tetrahedral Co(II) complexes are generally deep-blue in colour and give more intense transitions.[107] They also have a spin-quartet ground state and the three spin-allowed transitions are,[101,102]

$$^4A_2\,(F) \rightarrow {}^4T_2(F) \quad \sim 1600\text{ nm}$$

$$^4A_2\,(F) \rightarrow {}^4T_1\,(F) \quad \sim 650\text{ nm}$$

$$^4A_2\,(F) \rightarrow {}^4T_1\,(P) \quad \sim 500\text{ nm}$$

Both environments give rise to bands in the same region around 500 nm, although tetrahedral complexes more frequently exhibit maxima near 650-700 nm. Therefore, the best spectral indicator of stereochemistry in these cases is the intensity of absorption, especially when the spectrum is complicated by the overlap with a strong charge-transfer tail.[101,102] Square-planar complexes of Co(II) are generally dark-brown in colour and give weak and broad bands in the region 1200 – 1000 nm.[112]

In the present investigation, the spectra of the bright greenish-blue hydroxo and chloro complexes of Co(II) showed intense transitions. Bands were present at 1641-1627, 652-673 and 514-501 nm and were assigned, respectively to the $^4A_2(F) \rightarrow {}^4T$ (F), $^4A_2(F) \rightarrow {}^4T$ (F) and $^4A_2(F) \rightarrow {}^4T_1(P)$ transitions in a tetrahedral geometry.[101,113-115] The spectra of the bromo, nitrato and perchlorato complexes of Co(II), investigated here, showed transitions corresponding to octahedral geometries. Bands were present in the ranges 1115-1018, 678-589 and 478-404 nm in their spectra. They were assigned, respectively, to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions.[8,89,94] The orange colour of the complexes and other physico-chemical data also supported octahedral geometry.

The spectra of large number of octahedral complexes of Ni(II) are studied by Jorgensen.[116,117] Three spin-allowed transitions are expected for the d^8 configuration in an octahedral field.[101] These transitions give rise to bands usually in the following ranges.

$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ~1100 -900 nm

$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ~ 715-530 nm

$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ~ 400-340 nm

The ratio of the wave numbers of the first and second transitions lies in the range 1.6-1.8, which is one of the distinguishing characteristic of the octahedral complexes of Ni(II).[101] In weak fields, the second band may be split due to spin-orbit coupling that mixes $^3T_1g(F)$ and ^1E_g states. Most of the tetrahedral complexes of Ni(II) have intense blue or green colour unless the ligands also have absorption bands in the visible region. The two readily accessible bands in the spectrum of tetrahedral Ni(II) complexes are the following.[101,102]

$^3T_1\ (F) \rightarrow {}^3A_2\ (F)$ ~ 1500 -1250 nm

$^3T_1\ (F) \rightarrow {}^3T_1\ (P)$ ~ 700 - 590 nm

The square-planar complexes of NI(II) are generally red, yellow or brown. This may be due to the presence of absorption bands of medium intensities in the range 600-450 nm.[107] However, other colours do occur when additional bands, such as charge- transfer bands are present. The different probable transitions and the band-ranges are given below.[102,118] Charge-transfer transitions usually overlap the second and third bands.

$^1A_{1g} \rightarrow {}^1A_{2g}$ ~ 600-570 nm

$^1A_{1g} \rightarrow {}^1B_{1g}$ ~ 480 nm

$^1A_{1g} \rightarrow {}^1E_g$ ~ 400 nm

Among the complexes of Ni(II), investigated here, the chloro, bromo and perchlorato ones showed transitions corresponding to octahedral geometry. Bands were identified in the ranges 1152-1140, 726-700 and 410-394 nm and were assigned, respectively, to the $^3A_2g(F) \rightarrow {}^3T_{2g}(F)$, $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$ transitions.[94,119,120] The ratio of wave numbers of the transitions assigned as $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ was found to be in the range 1.6 to 1.8 and this confirmed octahedral geometries for them. The spectra of the hydroxo and nitrato complexes of Ni(II) showed transitions corresponding to the square-planar geometry. The bands at 610 and 548 nm were assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ and those at 413 and 394 nm to the $^1A_{1g} \rightarrow {}^1E_g$ transitions.[46,95,118] The analytical data also supported these assumptions.

In the case of Cu(II) complexes, a greenish-blue colour is associated with penta- or hexa-coordinated Cu(II) and brown and violet colours usually indicate tetra-coordinated Cu(II).[121,122] However, tailing of CT bands into blue region can impart red or brown colour irrespective of the geometry. For octahedral Cu(II) complexes, a band due to the transition, $^2E_g \rightarrow {}^2T_{2g}$ is expected. But the observed band is usually very broad and clearly contain several components which is a result of tetragonal distortion due to Jahn-Teller effect.[101] In tetrahedral Cu(II) complexes, d-d transitions occur in the range 1400-1000 nm.[121,122] The square-planar or distorted octahedral complexes of Cu(II) absorb in the region 1000-500 nm.[121,122] If this region is blank, it can be inferred that the complexes have tetrahedral geometry.

In the spectra of chloro, bromo and nitrato complexes of copper(II), presently investigated, bands appeared at 694, 730 and 655 nm, respectively, and were assigned to the $^2E \rightarrow {}^2T_2$ transitions in a distorted octahedral geometry.[119,123] The greenish-blue colour of the complexes also supported this assignment. In the case of the spectra of hydroxo and percholrato complexes, bands appeared at 790 and 810 nm respectively, which were assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions in square-planar geometry.[26,46,94,95] The brown colour and analytical data of the complexes also supported this assumption.

6. Infrared spectra

a) Complexes

As a very powerful and versatile tool for structural and analytical studies, the IR spectroscopy is extremely useful for the identification and characterisation of compounds and in assigning structures and geometries to them. The significant vibrational bands of the complexes, investigated here, and the assignments are given in the Tables 27-32. Assignments are made on the basis of comparison with similar known systems.[75,76,124,125]

All the complexes of Bipiren showed considerable down shift in the characteristic absorption frequency of the azomethine group. This could be taken as

Table-27 Significant bands in the IR spectra of Cr(III) Bipiren complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})								
	ν O-H (coordinated H_2O or OH^-)	ν C=N	νNO_3^- (coordinated)	νClO_3^- (coordinated)	(coordinated water)		δ $O\text{-}CH_2\text{-}O$	ν M-N	ν M-O
					ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren (L)		1639s					926m		
$[Cr_2L(OH)_6(H_2O)_2]$	3420s 3345b	1583m					926m	522m	432m
$[Cr_2LCl_6(H_2O)_2]$	3424b	1598s			961m	637w	929m	537w	443w
$[Cr_2LBr_6(H_2O)_2]$	3423b	1600m			958m	631w	928m	551m	436w
$[CrL(NO_3)_3((H_2O)]$	3236b	1593m	1447m 1361w 1034sh		964m	633w	927m	519w	446m
$[CrL(ClO_4)_3 (H_2O)]$	3433b	1597m		1117m 1038m 934w	956m	638w	928m	544w	417m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-28 Significant bands in the IR spectra of Mn(II) Bipiren complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})								
	ν O-H (coordinated H_2O or OH^-)	ν C=N	νNO(asy.) (free NO_3^-)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
					ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren (L)		1639s					926m		
[$Mn_2L(OH)_4(H_2O)_2$]	3381s 3256b	1597m					-	621w	519m
[$Mn_2LCl_4(H_2O)_2$]	3410b	1619m			958m	635w	-	605w	506w
[$MnLBr_2(H_2O)_2$]	3398b	1594s					927m	625m	514w
[$MnL(H_2O)_4$]$(NO_3)_2$	3402b	1600m	1384s		962m	633w	-	616m	504m
[$MnL(ClO_4)_2(H_2O)_2$]	3433b	1 595s		1118m 1040w 941w	960m	636w	926m	631m	525m

*s-strong, m-medium, w-weak, b-broad, asy-asymmetric

Table-29 Significant bands in the IR spectra of Fe(III) Bipiren complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})								
	ν O-H (coordinated H_2O or OH^-)	ν C=N	νNO_3^- (coordinated)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
					ρK_{rock} (H_2O)	ρ$_{wagg}$ (H_2O)			
Bipiren (L)		1639s					926m		
$[Fe_2L(OH)_6(H_2O)_2]$	3430s 3284b	1595m					926m	605w	490m
$[Fe_2LCl_6(H_2O)_2]$	3370b	1600m			957m	636w	926m	678w	420w
$[Fe_2LBr_6(H_2O)_2]$	3430b	1598m					927m	627m	482m
$[FeL(NO_3)_3((H_2O)]$	3434b	1596m	1445m 1348m 1036sh		959m	636w	928m	620m	452m
$[FeL(ClO_4)_3(H_2O)]$	3440b	1598m		1116m 1040m 934w	962m	633w	928m	630w	438m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-30 Significant bands in the IR spectra of Co(II) Bipiren complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})								
	ν O-H (coordinated H_2O or OH^-)	ν C=N	νNO_3^- (coordinated)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
					ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren (L)		1639s					926m		
$[Co_2L(OH)_4]$	3257s	1590s					927m	519m	412m
$[Co_2LCl_4]$	-	1626m			957m	636w	927m	479m	-
$[CoLBr_2(H2O)_2]$	3412b	1587m					928m	570w	485w
$[CoL(NO_3)_2(H2O)_2]$	3413b	1597m	1449m 1326m 1041w		961m	634w	927m	506m	454w
$[CoL(ClO_4)_2(H2O)_2]$	3428b	1595s		1119m 1049w 938w	959m	637w	928m	498m	414w

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-31 Significant bands in the IR spectra of Ni(II) Bipiren complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})								
	ν O-H (coordinated H_2O or OH^-)	ν C=N	νNO(asy) (free NO_3^-)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
					ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren (L)		1639s					926m		
[$Ni_2L(OH)_4$]	3417s	1626s					927m	469m	418m
[$Ni_2LCl_4(H_2O)_2$]	3415b	1624m			959m	635w	-	482m	418w
[$NiLBr_2(H_2O)_2$]	-	1626s					926m	467m	413w
[$NiL(H_2O)_2$] $(NO_3)_2$	3390b	1631m	1385s		962m	633w	927m	477w	414w
[$NiL(ClO4)_2(H_2O)_2$]	3382b	1633s		1120m 1049w 936w	960m	636w	927m	440m	412w

*s-strong, m-medium, w-weak, b-broad, asy-asymmetric

Table-32 Significant bands in the IR spectra of Cu(II) Bipiren complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})								
	ν O-H (coordinated H_2O or OH^-)	ν C=N	νNO(asy.) (free NO_3^-)	νClO(asy) νClO(sy) (free ClO_4^-)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
					ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren (L)		1639s					926m		
$[Cu_2L(OH_4]$	3390s	1595s					927m	489s	414m
$[Cu_2LCl_4(H_2O)_2]$	3348b	1569s			958m	636w	-	528m	480w
$[CuLBr_2(H_2O)_2]$	-	1564s					927m	524m	472m
$[CuL(H_2O)_4](NO_3)_2$	3417b	1624s	1385s		961m	634w	926m	509m	428m
$[CuL(H_2O)_2](ClO_4)_2$	3302b	1585m		1112s 981w	960m	633w	927m	524w	472w

*s-strong, m-medium, w-weak, b-broad, asy-asymmetric

an indication for the coordination of the nitrogen atoms of both the azomethine groups. The band at 1639 cm^{-1} was absent in all the complexes. Instead bands appeared in the ranges of 1600-1583, 1619-1595, 1600-1595, 1626-1595, 1633-1624 and1624-1564 cm^{-1} in the Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) complexes, respectively, and were assigned to the coordinated azomethine groups present in them.[47,89,94, 95]

The characteristic absorption frequency of the dioxymethylyne group was found to be present in the spectra of majority of the Bipiren complexes at the same frequency as it was observed in the ligand spectrum. This indicated the non-involvement of dioxymethylene groups in coordination in these complexes. But in a few cases, either this band was absent or significantly shifted to lower frequency region. The hydroxo and chloro complexes of Mn(II), the chloro complexes of Ni(II) and Cu(II) showed significant shift or absence of this band. Hence, it could be reasonably assumed that one of the oxygen atoms of the dioxymethylene groups had been coordinated in them.[76]

In addition to these, new bands were present in the lower frequency region of the spectra of all these complexes. These bands appeared in the ranges, 544-519 and 446-417 cm^{-1} in the spectra of Cr(III) complexes, 631-605 and 525-506 cm^{-1} in those of Mn(II) complexes, 678-605 and 490-420 cm^{-1} in the Fe(III) complexes, 570-479 and 485-412 cm^{-1} in the Co(II) complexes, 482-440 and 418-412 cm^{-1} in the Ni(II) complexes and 528-489 and 480-414 cm^{-1} in the Cu(II) complexes. The first one was assigned to the stretching vibrations of M–N bonds and the second one to that of the M–O bonds, formed during complexation.[47,95,124,126]

The M-O band may be either due to coordinated nitrate-, perchlorate- or hydroxyl anion or water molecule, or due to the coordination of the oxygen atoms of the dioxymethylene groups. In the chloro complex of Co(II), such a band was not present, indicating the absence of Co-O bond.

The broad bands present in the region ~ 3440-3236cm^{-1} in the spectra all the complexes of Cr(III), Mn(II) and Fe(III), in the bromo, nitrato and perchlorato complexes of Co(II), in the chloro and nitrato complexes of Ni(II) and in the chloro, nitrato and perchlorato complexes of Cu(II) were assigned to the O-H stretchings of coordinated water.[94,95,124,127] The presence of coordinated water molecules in these complexes, was further supported by the presence of bands in the ranges ~965-955 and ~640-630 cm–^{1}, owing to $\rho K_{rock}(H_2O)$ and $\rho_{wagg}(H_2O)$, respectively.[94,128] Elemental analyses data also corresponded to the presence of coordinated water molecules in these complexes.

b) IR features of coordinated anions in the complexes

IR spectroscopy can be used to determine the status of anions in complexes

i) Hydroxo complexes

The hydroxo complexes were synthesised using the corresponding metal acetates. The IR spectrum of acetate ion is well studied. Asymmetric and symmetric stretchings of the (CO_2^-) of free acetate radical absorb around ~1560cm^{-1} and

~1415cm^{-1}, respectively[124,129,130] When the carboxylic group acts as a unidentate ligand, one of the C-O bonds experiences enhanced double bond character and this gives rise to a higher frequency shift to one of the (CO_2^-) stretching bands. Hence, the separation between the two bands is much larger than that in the free ion. When it acts as a bidentate ligand, the trend turns to the opposite direction and the separation becomes smaller than that in the free acetate ion. Moreover, in complexes where it acts as bridging ligand, the two starching frequencies are close to the values for the free ion.[129-131] Eventhough, metal acetates were used in the synthesis of these complexes, in their spectra, the characteristic bands of either free or coordinated acetate ions could not be identified.[94,131] The strong absorption bands present at 3420, 3381, 3430, 3257, 3417 and 3390 cm^{-1} in the spectra of the hydroxo complexes of Cr(III), Mn(II), Fe(III), Ni(II),Co(II) and Cu(II), respectively, were assigned to the O-H stretching frequency of the hydroxo groups,[94,132] which were coordinated to the metal ions. Elemental analyses data and conductance values of these complexes also supported the assumption that instead of acetate ions, hydroxyl ions were coordinated in them.

ii) *Halo complexes*

The bands due to M-Cl or M-Br vibrations are usually observed below 400 cm^{-1} which was out of range of the instrument used in this investigation.[124,130] The analytical data indicated the presence of 2 halogen atoms per metal ion in the case of Mn(II), Co(II), Ni(II) and Cu(II) complexes and 3 halogen atoms per metal ion in the case of Cr(III) and Fe(III) complexes. Non-conducting nature of the complexes showed that the halogen atoms were coordinated to the metal ions.

iii) Nitrato complexes

Free nitrate ion has D_{3h} symmetry and its spectrum is simple. The totally symmetric NO stretching mode is IR inactive, but the doubly degenerate NO stretching mode gives rise to strong band in the range ~1390 cm^{-1}.[124,130] There are two more IR active deformation modes, one of which is doubly degenerate at 830 cm^{-1}, and the other at 720 cm^{-1}. When nitrate ion is coordinated, its effective symmetry is reduced to C_{2V} and the degenerate state splits and all modes become IR active. Kunchandi and Indrasenan[132] reported the ν_1, ν_4, ν_2 modes of vibration of the coordinated nitrate ion at 1430, 1330 and 1025 cm^{-1}, respectively. The $\nu_1$and ν_4 modes are the two split components δ_3 mode of the free nitrate ion.

In the present investigation the spectra of nitrato complexes of Mn(II), Ni(II) and Cu(II) showed sharp bands at 1384, 1385 and 1384 cm^{-1}, respectively, which corresponded to the frequency of free nitrate ion.[94,124,130] The conductance values of these complexes confirmed the presence free nitrate ions. But in the case of the nitrato complexes of Cr(III) Fe(III) and Co(II) these bands were absent and new bands appeared in the ranges 1449-1445, 1361-1326 and 1041-1036 cm^{-1}, indicating the presence of unidentate nitrate ions.[94,132,133] The non-conducting nature of these complexes confirmed the presence of coordinated nitrate ions in them.

iv) Perchlorato complexes

The perchlorate ion has T_d symmetry with a characteristic, triply degenerate Cl-O stretching mode around 1110 cm^{-1}. A weak band due to IR forbidden symmetric vibration at about 980 cm^{-1} is also present.[126,130] When the perchlorate ion acts as a unidentate ligand, symmetry lowers to the C_{3V} and bands appear near 1120, 1040 and 920 cm^{-1}. In all the perchlorato complexes, except that of Cu(II), which were investigated here, bands corresponding to monodentate perchlorate ions could be identified.[94,134] These bands appeared at 1117, 1038 and 934 cm^{-1} in the Cr(III) complex, at 1118, 1040 and 941 cm^{-1} in the Mn(II) complex, at 1116, 1040 and 934 cm^{-1} in the Fe(III) complex, at 1119, 1049 and 938 cm^{-1} in the Co(II) complex and at 1120, 1049 and 936 cm^{-1} in the Ni(II) complex. The non-conducting nature and the microanalytical data of these complexes further confirmed this assumption. In the case of the spectrum of Cu(II) perchlorato complex, bands were present at 1112 and 981 cm^{-1}(w). These bands were assigned to the presence of free perchlorate ion in this complex, which was further confirmed by its conductance studies.[124,130]

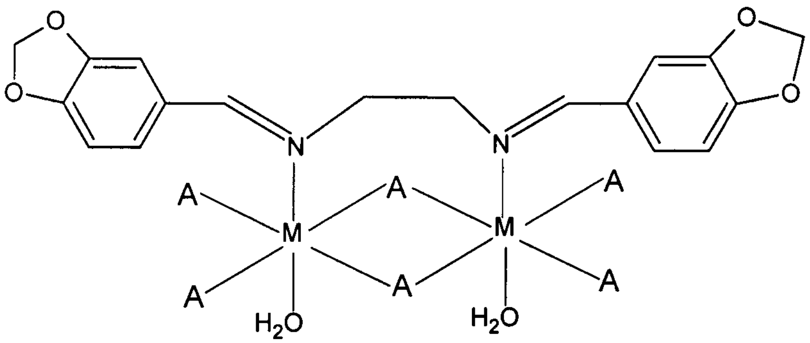
7. Thermal studies

Thermograms of the chloro complexes of Co(II), Ni II) and Cu(II) were recorded. The decomposition patterns of these complexes were in good agreement with the suggested formulae. As the end products of decomposition, metal oxides were formed and were identified chemically. Independent pyrolytic studies had also been carried out and these results agreed with the data obtained from the thermograms and the formulae suggested for these complexes. The details of the thermogravimetric studies and the explanations for the decomposition patterns are given in the Part II of this thesis.

C. Conclusions

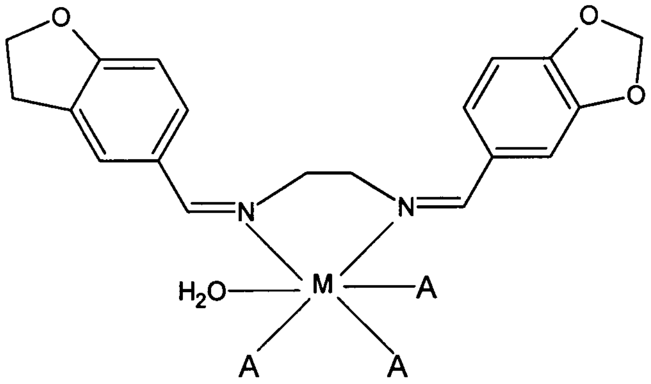
The hydroxo, chloro, bromo, nitrato and perchlorato complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with bis(piperonaldehyde)ethylenediimine (Bipiren) were synthesized. The physico-chemical properties of all the complexes were studied and they were found to have the general formulae suggested in the section B-2 of this chapter. The structures suggested for these compounds are given in Figs. 2-9.

In these complexes, Bipiren acted as a neutral bidentate- or tetradentate ligand. The dioxymethylene groups offered two additional coordination sites in the cases where Bipiren acted as a tetradentate ligand. It was also found that Bipiren acted as chelating as well as bridging ligand in certain complexes. The hydroxo and chloro complexes of all the metals were assumed to be polymeric- or bimetallic in nature, due to the bridging ability of chloro, hydroxo and the Bipiren ligands. In the case of Cr(III) and Fe(III) the bromo complexes also showed bimetallic nature. It was also found that the type of coordinations and actual geometries of the complexes depended on the nature of the metal ions and the anions getting coordinated in each case. The microanalytical, spectral, magnetic, electrical conductance and thermal data were logically correlated, and thus the formulae and structures of the complexes were established.



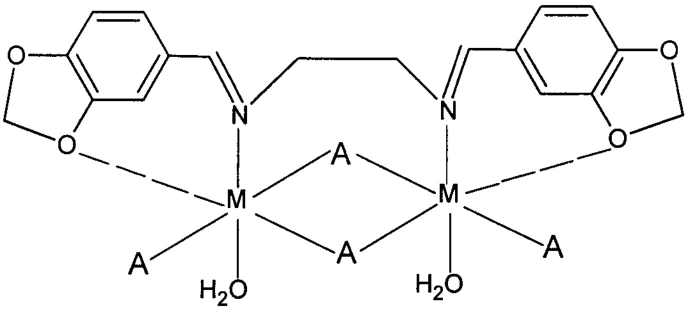
where M = Cr(III) or Fe(III) and A = OH^-, Cl^- or Br^-

Fig-2 Structure suggested for $[Cr_2L(OH)_6(H_2O)_2]$, $[Cr_2LCl_6(H_2O)_2]$, $[Cr_2LBr_6(H_2O)_2]$, $[Fe_2L(OH)_6(H_2O)_2]$, $[Fe_2LCl_6(H_2O)_2]$ and $[Fe_2LBr_6(H_2O)_2]$, where L = Bipiren.



where M = Cr(III) or Fe(III) and A = NO_3^- or ClO_4^-

Fig-3 Structure suggested for $[CrL(NO_3)_3(H_2O)]$, $[CrL(ClO_4)_3(H_2O)]$, $[FeL(NO_3)_3(H_2O)]$ and $[FeL(ClO_4)_3(H_2O)]$,where L = Bipiren.

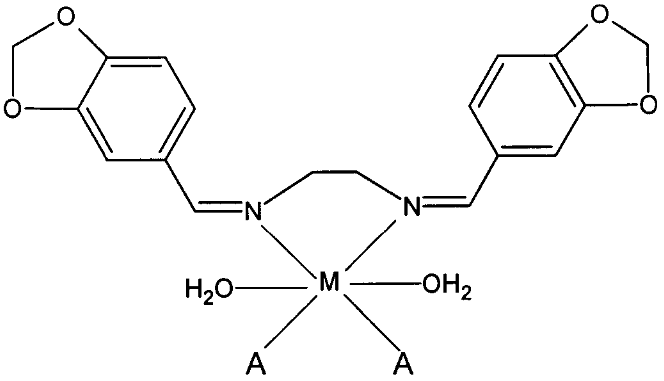


where M = Mn(II) and A = OH^- or Cl^-

or M = Ni (II) or Cu (II) and A = Cl^-

Fig-4 Structure suggested for $[Mn_2L(OH)_4(H_2O)_2]$, $[Mn_2L(Cl)_4(H_2O)_2]$

$[Ni_2L(Cl)_4(H_2O)_2]$ and $[Cu_2L(Cl)_4(H_2O)_2]$, where L = Bipiren.



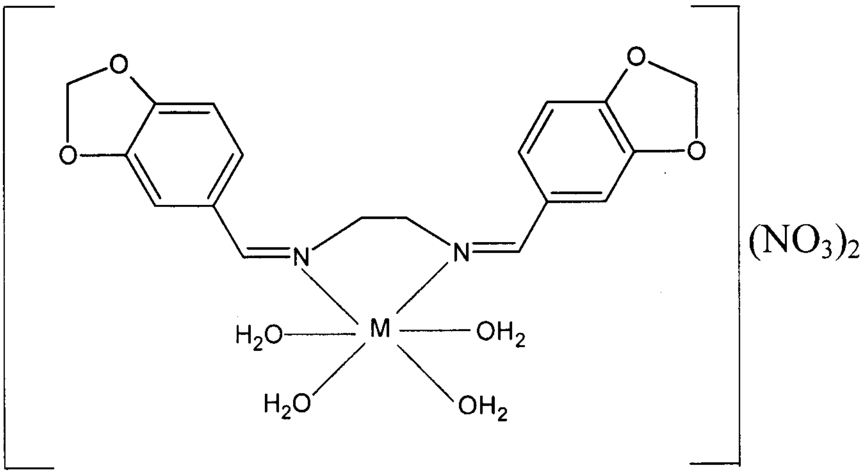
where M = Mn(II) and A = Br^- or ClO_4^-

or M= Co (II) and A = Br^-, NO_3^- or ClO_4^-

or M= Ni(II) and A = Br^- or ClO_4^-

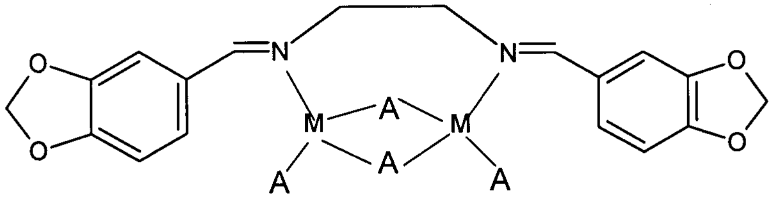
or M = Cu (II) and A = Br^-

Fig-5 Structure suggested for $[MnL(Br)_2(H_2O)_2]$, $[MnL(ClO_4)_2(H_2O)_2]$, $[CoL(Br)_2(H_2O)_2]$, $[CoL(ClO_4)_2(H_2O)_2]$, $[CoL(NO_3)_2(H_2O)_2]$, $[NiL(ClO_4)_2(H_2O)_2]$ $[NiL(Br)_2(H_2O)_2]$ and $[CuL(Br)_2(H_2O)_2]$, where L = Bipiren



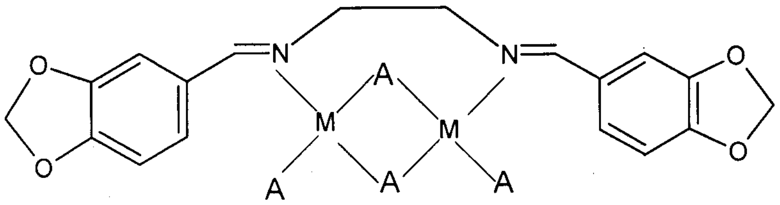
where M = Mn(II) or Cu(II)

Fig-6 Structure suggested for $[MnL(H_2O)_4](NO_3)_2$ and $[CuL(H_2O)_4](NO_3)_2$, where L = Bipiren



where M = Co (II) and A = OH^- or Cl^-

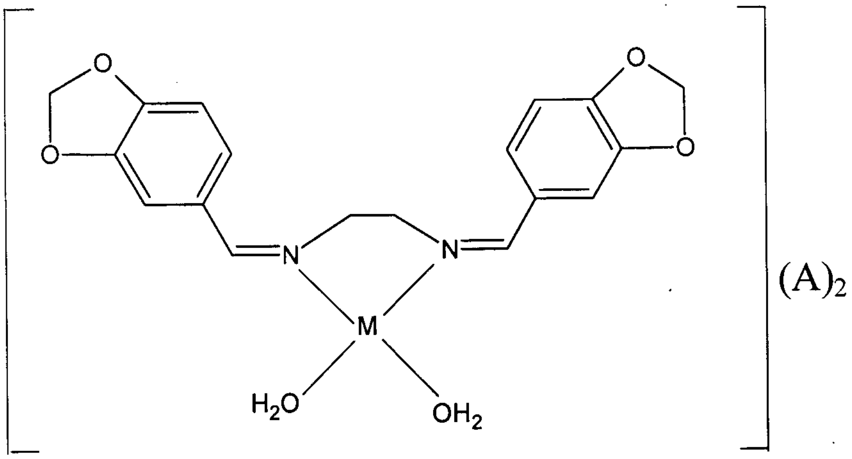
Fig-7 Structure suggested for $[Co_2L(OH)_4]$ and $[Co_2LCl_4]$, where L = Bipiren



where M= Ni (II) or Cu (II) and A = OH^-

Fig-8 Structure suggested for $[Ni_2L(OH)_4]$ and $[Cu_2L(OH)_4]$

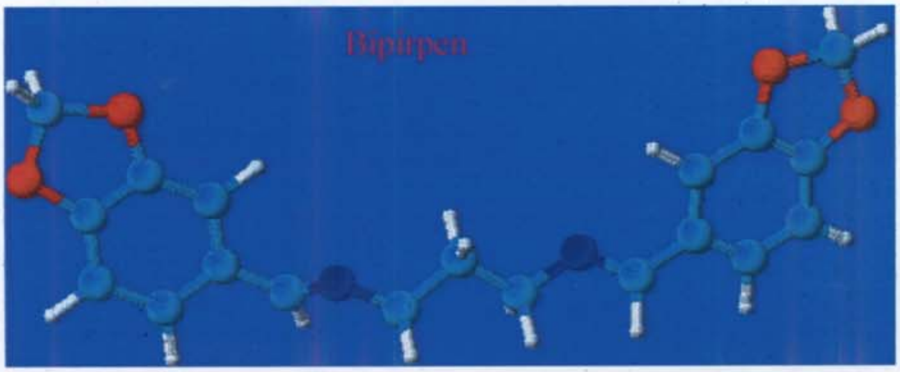
where L = Bipiren

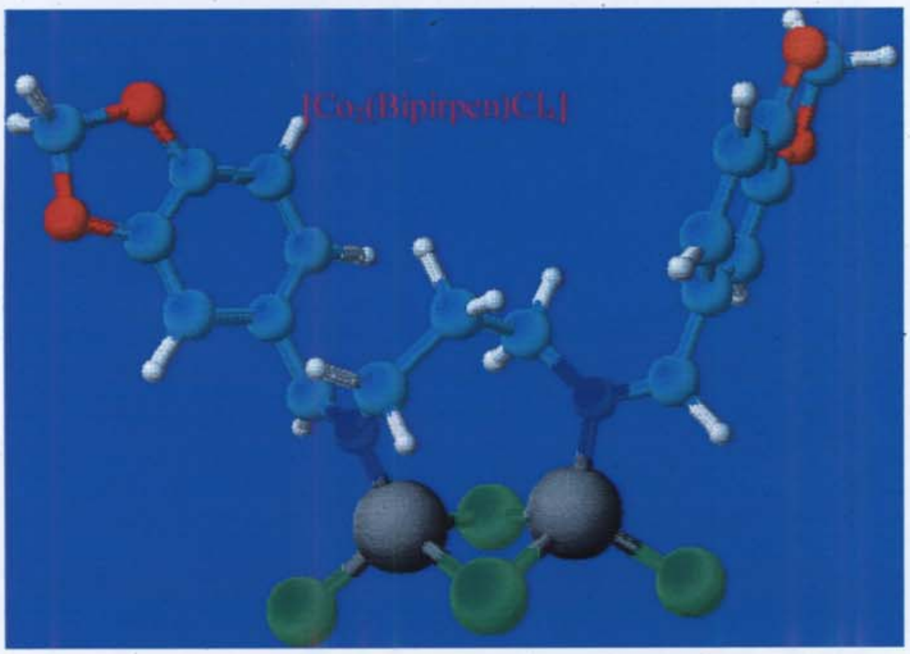


where M = Ni(II) and $A^- = NO_3^-$,
or M = Cu(II) and $A^- = ClO_4^-$

Fig-9 Structure suggested for $[NiL(H_2O)_2]\ (NO_3)_2$ and $[CuL(H_2O)_2]\ (ClO_4)_2$,
where L = Bipiren

CHAPTER IV


Bipirpen


$[Co_2(Bipirpen)CL_4]$

CHAPTER IV

Cr(III), Mn(II), Fe(III), Co(II), Ni(II) AND Cu(II) COMPLEXES OF BIS(PIPERONALDEHYDE)-1,3-PROPANEDIIMINE

(Bipirpen)

Schiff bases of 1,3-propanediamine, their derivatives and metal complexes, find a variety of synthetic,[135,136] analytical[9,33,137] and biological[52,138] applications and have been studied extensively. A perusal of earlier work revealed that the coordinating possibility of 1,3-propanediamine (propylenediamine) is enhanced by condensing with a variety of carbonyl compounds.[9,40,41,43,45] But the literature survey showed that no work has been done on the transition metal complexes of the Schiff base derived from propylenediamine and piperonaldehyde. Therefore, in the present investigation the synthesis and studies on a new bidentate/tetra dentate ligand, bis(piperonaldehyde)-1,3-propanediimine (Bipirpen)* (L), formed by the condensation of propylenediamine with piperonaldehyde and its transition metal complexes have been taken up. The use of piperonal as the carbonyl compound in these studies owed to the fact that several compounds containing the 3,4-methylenedioxy groups

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*The systematic name of the compound is: N,N'-bis[1,3-benzodioxol-5-ylmethylene]propane-1,3-diamine. But for the sake of convenience the name 'bis-(piperonaldehyde)-1,3-propanediimine' and the short form Bipirpen are adopted in this thesis.

possessed various biological activities.[5,59,60] Moreover, apart from the two nitrogen atoms of the azomethine groups, oxygen atoms of the two dioxymethylene groups are potential coordination sites in the ligand. The ligand Bipirpen (Fig-1) and its complexes with several transition metal ions, *viz*, Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) were synthesised and characterised here.

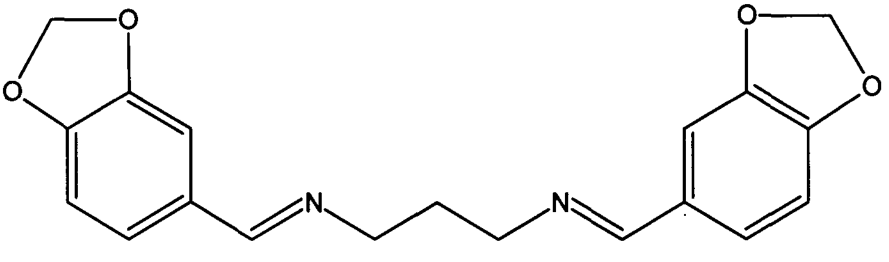


Fig-1 Structure suggested for bis(piperonaldehyde)-1,3-propanediimine (Bipirpen)

A. Experimental

1. Materials and methods

A detailed report regarding the reagents used and methods adopted for the synthesis and characterization of the ligand and the complexes are given in the Chapter II.

2. Synthesis of the ligand, bis(piperonaldehyde)-1,3-propanediimine (Bipirpen)

Ethanolic solutions of 1,3-propanediamine(1.48 g) and piperonaldehyde (6.04 g) were mixed in 1:2 molar ratio and stirred for about 15 minutes and the white precipitate formed was filtered off, washed with ethanol and then dried over anhydrous $CaCl_2$. The yield of bis(piperonaldehyde)-1,3-propanediimine was found to be 91% and the compound was recrystallised from ethanol. The melting point of the compound was found to be 139°C.

3. Synthesis of complexes of Bipirpen

Complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions with Bipirpen were synthesized in the following methods.

a) Complexes of Cr(III), Mn(II) and Fe(III)

Complexes were synthesized using acetates, chlorides, bromides, nitrates and perchlorates of these metals. Methanolic solutions of the metal salt and the ligand, mixed in 1:1 molar ratio, were refluxed for about 2-3 h. The metal acetates were dissolved in methanol-water mixture containing minimal amount of water and then added to the methanolic solution of the ligand, while refluxing. After refluxing for about 2-3 h, the solution was concentrated over a water bath to obtain a pasty mass and washed repeatedly with diethyl ether and/or petroleum ether

b) Complexes of Co(II)

Co(II) acetates, chlorides, bromides, nitrates and perchlorates were used for the synthesis of the complexes. A mixture of the solutions of the ligand and the metal salt in acetone (1:1 molar ratio) were refluxed for about 2-3 h. In the case of acetate, the salt was dissolved in acetone-water mixture and added to the reflux-ing solution of the ligand. Cobalt(II) chloride gave a precipitate, which was filtered off washed with acetone and dried over anhydrous $CaCl_2$. In other cases, after refluxing for about 2-3 h the solution was concentrated over a water bath, and the pasty mass obtained was washed repeatedly with ether and/or petroleum ether to get the solid complex separated. The complexes were then dried over anhydrous $CaCl_2$.

c) Complexes of Ni(II) and Cu(II)

Methanolic solutions of the metal salts and the ligand were mixed in 1:1 molar ratio and refluxed for about 2-3 h. Metal acetates were dissolved in methanol-water mixture containing minimal amount of water and then added to the methanolic solution of ligand, while refluxing. In the case of the metal chlorides, complexes precipitated while refluxing and were filtered off and washed with methanol. In the case of acetates, bromides, nitrates and perchlorate, after refluxing for about 2-3 h, the solutions were concentrated over a water bath and washed repeatedly with diethyl ether and/or petroleum ether and/or acetone to get the solid complexes separated. The complexes were then dried over anhydrous $CaCl_2$. In the case of copper acetate, hydroxo complex was obtained instead of the acetato complex.

B. Results and discussion

The following analytical and physico-chemical studies were done and the results had been correlated reasonably to explain the properties, structure and bonding of the compounds.

1. Characterisation of ligand

The homogeneity and purity of the ligand was established by the TLC technique. The analytical data showed close agreement with the empirical formula, $C_{19}H_{18}O_4N_2$ for bis(piperonaldehyde)-1,3-propanediimine. Further characterisation of the ligand was done by ^1H NMR and IR spectral analyses.

a) ^1H NMR spectrum

The ^1H NMR spectrum of the ligand, Bipirpen was recorded in DMSO-d_6 (Table-1) and it showed a number of characteristic signals of the compound.[73,74] The peak observed at a δ value of 8.04 ppm was assigned to the azomethine protons in the molecule. The signals due to the aromatic protons were observed in the range 7.33-6.84 ppm. The singlet peak at 5.96 ppm was assigned to the methylinic protons of the dioxymethylene groups of the piperonal moieties present in the ligand. The inductive effect of the two oxygen atoms deshielded the methylenic protons and this resulted in the higher δ value for these protons. The peaks in the ranges of 3.72-3.66 and 1.96-1.92 ppm were assigned to the methylinic protons of the propylenediamine moiety of the ligand.

Table-1 Significant ^{1}H NMR Peaks of Bipiren and their assignments

Chemical shift (δ ppm)	Proton assignment
8.04s	Two -CH=N-
7.33s 7.0-6.98m 6.87-6.84m	Aromatic protons
5.96s	Two $-CH_2-$ (of dioxymethylene groups)
3.72-3.66m	$-\underline{CH_2}-CH_2-\underline{CH_2}-$ (of propylenediamine moiety)
1.96-1.92m	$-CH_2-\underline{CH_2}-CH_2-$ (of propylenediamine moiety)

* s = singlet, m = multiplet

Table-2 Significant IR bands of Bipirpen and their assignments

Band frequency* (cm^{-1})	Assignment
3050	ν aromatic C-H
2981	ν C-H (methylene)
2905	ν C-H (=CH-)
1641s	ν >C=N-
1494 1446	ν ring C-C
1256s	ν >C-N-
1191 1099	δ in plane C-H (aromatic)
927	ν -O-CH2-O-
871 817	δ out of plane C-H(aromatic)

* s = strong

b) IR spectrum

The characteristic absorption bands of different groups present in the ligand, Bipirpen were found in its IR spectrum (Table-2). The bands present at 1641 and 1256 cm^{-1} were assigned to the C=N and C-N stretchings, respectively.[75,76] The characteristic absorption band of the dioxymethylene group of the piperonal moiety[76] was found to be present at 927 cm^{-1}. But the characteristic frequency of the aromatic aldehyde group, due to the C=O stretching,[75,76] normally observed at ~1690 cm^{-1}, could not be observed in the spectrum of the ligand, which indicated that the condensation with the amine was complete. The bands present at 2981 and 2905 cm^{-1} were assigned to the aromatic C-H and the methylene C-H stretchings, respectively. The absorptions due to the in plain bending vibrations of aromatic C-H are expected in the range 1250 to 950 cm^{-1}. The bands at 1191 and 1099 cm^{-1} could be assigned to these modes of vibrations. The bands found at 871 and 817 cm^{-1} were assigned to the out of plane bending vibrations of the aromatic C-H.[75,76]

2. Formulae and general properties of complexes

These complexes were found to be coloured, photo-stable and non-hygroscopic. They were mostly insoluble in common organic solvents, but soluble in DMF and DMSO. From the analytical data (Tables 3-8) and molar conductance values (in DMF), the following formulae were assigned to them.

When copper acetate was used for the synthesis hydroxo complex was obtained instead of the acetato complex. All other metal acetates gave the acetato complexes. The hydroxo complex of Cu(II) and the chloro complexes of all the metals showed bimetallic or polymeric nature. The tendency to form such polymeric or bimetallic structures was less in this case compared to the ligand Bipiren discussed in the previous chapter and this could be due to the larger number of -CH_2- the groups intervening the two azomethine groups in the ligand. The spectral and magnetic data also agreed to the suggested formulae.

a) $[MLA_3(H_2O)]$, where M = Fe(III) or Cr(III) and A = CH_3COO^-, Br^-, NO_3^- or ClO_4^-

b) $[M_2LA_6(H_2O)_2]$, where M = Fe(III) or Cr(III) and A = Cl^-

c) $[MLA_2(H_2O)_2]$, where M = Mn(II) or Co(II) and A = CH_3COO^-, Br^- or ClO_4^-

or M = Ni(II) and A= Br^- or $NO3^-$

or M = Cu(II) and A= Br^-

d) $[M_2LA_4(H_2O)_2]$, where M = Mn(II), Ni(II) or Cu(II) and A = Cl^-

e) $[ML(H_2O)_4]A_2$, where M = Mn(II) or Co(II) and A = NO_3^-

f) $[M_2LA_4]$, where M = Co(II) and A = Cl^-

or M = Cu(II) and A = OH^-

g) $[MLA_2]$, where M = Ni(II) and A = AcO^- or ClO_4^-

or M = Cu(II) and A = ClO_4^-

h) $[ML(H_2O)_2]A_2$, where M = Cu(II) and A = NO_3^-

3. Molar conductance

Molar conductance measurements were carried out using 10^{-3} molar solutions of the complexes in DMF, at room temperature and the values are given in Tables 9-14. Except for three complexes, all the others showed values lower than those expected for 1:1 electrolytes, indicating that they are non-electrolytes.[65] The

Table-3 Analytical data of Cr(III) Bipirpen complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
Bipirpen (L)	$C_{19}H_{18}O_4N_2$	338	Pale yellow	91		68.46 (68.01)	5.42 (5.33)	7.83 (7.94)	
$[CrL(AcO)_3(H_20)]^{**}$	$CrC_{25}H_{29}O_{11}N_2$	585	Brown	79	9.51 (8.89)	50.1 (51.28)	4.69 (4.96)	4.58 (4.79)	
$[Cr_2LCl_6(H_20)_2]$	$Cr_2C_{19}H_{22}O_6N_2Cl_6$	691	Brown .	61	14.78 (15.05)	33.74 (33.00)	3.31 (3.18)	4.14 (4.05)	29.91 (30.83)
$[CrLBr_3(H_20)]$	$CrC_{19}H_{20}O_5N_2Br_3$	648	Pale brown	72	8.32 (8.02)	34.39 (35.19)	2.88 (3.09)	3.94 (4.32)	38.12 (37.03)
$[CrL(NO_3)_3(H_20)]$	$CrC_{19}H_{20}O_{14}N_5$	594	.brown	73	9.14 (8.76)	37.68 (38.38)	3.28 (3.37)	11.52 (11.78)	
$[CrL(ClO_4)_3(H_2O)]$	$CrC_{19}H_{20}O_{17}N_2Cl_3$	707	Pale brown	69	7.72 (7.36)	31.18 (32.27)	2.73 (2.83)	3.79 (3.96)	43.22 (42.25)

*F.wt. = Formula weight, **$AcO^- = CH_3\text{-}COO^-$

Table-4 Analytical data of Mn(II) Bipirpen complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
Bipirpen (L)	$C_{19}H_{18}O_4N_2$	338	Pale yellow	91		68.46 (68.01)	5.42 (5.33)	7.83 (7.94)	
$[MnL(AcO)_2(H_2O)_2]^{**}$	$MnC_{23}H_{28}O_{10}N_2$	547	Pale brown	78	10.8 (10.05)	49.7 (50.46)	4.89 (5.12)	4.73 (5.12)	
$[Mn_2LCl_4(H_2O)_2]$	$Mn_2C_{19}H_{22}O_6N_2Cl_4$	626	Brown	69	18.5 (17.57)	35.7 (36.42)	3.42 (3.51)	4.34 (4.47)	23.8 (22.68)
$[MnLBr_2(H_2O)_2]$	$MnC_{19}H_{22}O_6N_2Br_2$	589	Pale brown	74	10.2 (9.34)	36.93 (38.71)	3.53 (3.74)	4.58 (4.75)	27.9 (27.17)
$[MnL(H_2O)_4](NO_3)_2$	$MnC_{19}H_{26}O_{14}N_4$	589	Brown	71	10.2 (9.34)	37.9 (38.71)	4.29 (4.41)	9.37 (9.51)	
$[MnL(ClO_4)_2(H_2O)_2]$	$MnC_{19}H_{22}O_{14}N_2Cl_2$	628	Pale brown	73	9.45 (8.76)	35.6 (36.31)	3.25 (3.50)	4.12 (4.46)	32.3 (31.69)

*F.wt. = Formula weight, $^{**}AcO^- = CH_3\text{-}COO^-$

Table-5 Analytical data of Fe(III) Bipirpen complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
Bipirpen (L)	$C_{19}H_{18}O_4N_2$	338	Pale yellow	91		68.46 (68.01)	5.42 (5.33)	7.83 (7.94)	
$[FeL(AcO)_3(H_20)]^{**}$	$FeC_{25}H_{29}O_{11}N_2$	589	Orange	72	10.01 (9.48)	48.98 (50.95)	4.77 (4.93)	4.68 (4.76)	
$[Fe_2LCl_6(H_20)_2]$	$Fe_2C_{19}H_{22}O_6N_2Cl_6$	699	Pale brown	67	16.42 (15.99)	32.89 (32.63)	3.03 (3.15)	3.93 (4.01)	31.87 (30.49)
$[FeLBr_3(H_20)]$	$FeC_{19}H_{20}O_5N_2Br_3$	652	Orange	73	8.97 (8.57)	34.09 (34.98)	2.97 (3.07)	4.13 (4.30)	37.98 (36.82)
$[FeL(NO_3)_3(H_20)]$	$FeC_{19}H_{20}O_{14}N_5$	598	Pale brown	71	9.82 (9.34)	37.12 (38.13)	3.18 (3.35)	11.34 (11.71)	
$[FeL(ClO_4)_3(H_20)]$	$FeC_{19}H_{20}O_{17}N_2Cl_3$	710	Orange	79	8.03 (7.86)	31.47 (32.10)	2.73 (2.82)	3.89 (3.94)	42.98 (42.02)

*F.wt. = Formula weight, $^{**}AcO^- = CH_3\text{-}COO^-$

Table-6 Analytical data of Co(II) Bipirpen complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
Bipirpen (L)	$C_{19}H_{18}O_4N_2$	338	Pale yellow	91		68.46 (68.01)	5.42 (5.33)	7.83 (7.94)	
$[CoL(AcO)_2(H_2O)_2]^{**}$	$CoC_{23}H_{28}O_{10}N_2$	551	pink	73	11.14 (10.71)	48.97 (50.09)	4.89 (5.08)	4.91 (5.08)	
$[Co_2LCl_4]$	$Co_2C_{19}H_{18}O_4N_2Cl_4$	598	Bright green	71	20.46 (19.73)	37.62 (38.13)	2.96 (3.01)	4.49 (4.68)	24.61 (23.74)
$[CoLBr_2(H_2O)_2]$	$CoC_{19}H_{22}O_6N_2Br_2$	593	pink	76	10.73 (9.95)	37.54 (38.45)	3.51 (3.71)	4.58 (4.72)	27.81 (26.98)
$[CoL(H_2O)_4](NO_3)_2$	$CoC_{19}H_{26}O_{14}N_4$	593	pink	72	10.42 (9.95)	37.56 (38.45)	4.19 (4.38)	9.28 (9.44)	
$[CoL(ClO_4)_2(H_2O)_2]$	$CoC_{19}H_{22}O_{14}N_2Cl_2$	632	pink	69	10.16 (9.34)	35.32 (36.08)	3.37 (3.48)	4.19 (4.43)	32.72 (31.49)

*F.wt. = Formula weight, $^{**}AcO^- = CH_3\text{-}COO^-$

Table-7 Analytical data of Ni(II) Bipirpen complexes

Compound	Empirical formula	F. wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
Bipirpen (L)	$C_{19}H_{18}O_4N_2$	338	Pale yellow	91		68.46 (68.01)	5.42 (5.33)	7.83 (7.94)	
$[NiL(AcO)_2]^{**}$	$NiC_{23}H_{24}O_8N_2$	515	Brown	74	12.02 (11.40)	52.58 (53.62)	4.47 (4.66)	5.23 (5.44)	
$[Ni_2LCl_4(H_2O)_2]$	$Ni_2C_{19}H_{22}O_6N_2Cl_4$	633	Yellowish green	68	19.42 (18.53)	37.10 (36.00)	3.32 (3.47)	4.31 (4.42)	23.12 (22.42)
$[NiLBr_2(H_2O)_2]$	$NiC_{19}H_{22}O_6N_2Br_2$	593	Green	75	10.22 (9.90)	37.81 (38.47)	3.54 (3.71)	4.61 (4.72)	28.01 (27.00)
$[NiL(NO_3)_2(H_2O)_2]$	$NiC_{19}H_{22}O_{12}N_4$	557	Green	78	11.03 (10.54)	40.12 (40.96)	3.74 (3.95)	9.61 (10.06)	
$[NiL(ClO_4)_2]$	$NiC_{19}H_{18}O_{12}N_2Cl_2$	596	Brown	71	9.67 (9.85)	37.42 (38.27)	2.89 (3.02)	4.57 (4.70)	34.12 (33.41)

*F.wt. = Formula weight, $^{**}AcO^{-} = CH_3\text{-}COO^{-}$

Table-8 Analytical data of Cu(II) Bipirpen complexes

Compound	Molecular formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
Bipirpen (L)	$C_{19}H_{18}O_4N_2$	338	Pale yellow	91		68.46 (68.01)	5.42 (5.33)	7.83 (7.94)	
$[Cu_2L(OH)_4]$	$Cu_2C_{19}H_{22}O_8N_2$	533	Brown	74	24.1 (23.83)	41.8 (42.78)	3.94 (4.13)	5.12 (5.25)	
$[Cu_2LCl_4(H_2O)_2]$	$Cu_2C_{19}H_{22}O_6N_2Cl_4$	643	Blue	68	20.5 (19.75)	34.73 (35.46)	3.34 (3.42)	4.23 (4.35)	23.0 (22.08)
$[CuLBr_2(H_2O)_2]$	$CuC_{19}H_{22}O_6N_2Br_2$	598	Green	78	11.3 (10.61)	37.2 (38.10)	3.52 (3.84)	4.53 (4.68)	28.1 (26.73)
$[CuL(H_2O)_2](NO_3)_2$	$CuC_{19}H_{22}O_{12}N_4$	562	Violet	74	11.7 (11.31)	39.8 (40.61)	3.79 (3.92)	9.72 (9.97)	
$[CuL(ClO_4)_2]$	$CuC_{19}H_{18}O_{12}N_2Cl_2$	601	Brown	69	11.3 (10.57)	36.8 (37.97)	2.87 (3.00)	4.43 (4.66)	34.2 (33.14)

* F.wt. = Formula weight

Table-9 Molar conductance in DMF of Cr(III) Bipirpen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[CrL(AcO)_3(H_20)]$	2.84
$[Cr_2LCl_6(H_20)_2]$	12.42
$[CrLBr_3(H_20)]$	32.29
$[CrL(NO_3)_3(H_20)]$	53.45
$[CrL(ClO_4)_3(H_20)]$	51.36

Table-10 Molar conductance in DMF of Mn(II) Bipirpen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[MnL(AcO)_2(H_2O)_2]$	13.92
$[Mn_2LCl_4(H_2O)_2]$	8.46
$[MnLBr_2(H_2O)_2]$	18.64
$[MnL(H_2O)_4]\ (NO_3)_2$	147.62
$[MnL(ClO_4)_2(H_2O)_2]$	35.87

Table-11 Molar conductance in DMF of Fe(III) Bipirpen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[FeL(AcO)_3(H20)]$	14.88
$[Fe_2LCl_6(H20)_2]$	12.71
$[FeLBr_3(H20)]$	22.46
$[FeL(NO_3)_3(H20)]$	34.59
$[FeL(ClO_4)_3(H20)]$	28.67

Table-12 Molar conductance in DMF of Co(II) Bipirpen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[CoL(AcO)_2(H_2O)_2]$	15.62
$[Co_2LCl_4(H_2O)_2]$	5.43
$[CoLBr_2(H_2O)_2]$	47.25
$[CoL(H_2O)_4]\ (NO_3)_2$	139.23
$[CoL(ClO_4)_2(H_2O)_2]$	56.84

Table-13 Molar conductance in DMF of Ni(II) Bipirpen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[NiL(AcO)_2]$	24.61
$[Ni_2LCl_4(H_2O)_2]$	4.42
$[NiLBr_2(H_2O)_2]$	48.62
$[NiL(NO_3)_2(H_2O)_2]$	51.81
$[NiL(ClO4)_2]$	19.85

Table-14 Molar conductance in DMF of Cu(II) Bipirpen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[Cu_2L(OH)_4]$	12.98
$[Cu_2LCl_4(H_2O)_2]$	2.78
$[CuLBr_2(H_2O)_2]$	38.32
$[CuL(H_2O)_2]\ (NO_3)_2$	146.24
$[CuL(ClO_4)_2]$	38.68

nitrato complexes of Mn(II), Co(II) and Cu(II) showed values, matching with those for 1:2 electrolytes.[65] They were assigned formulae accordingly. Analytical data and spectral studies also supported the assigned formulae.

4. Magnetic behaviour

The magnetic susceptibility values, diamagnetic corrections and the effective magnetic moments of the complexes calculated from the corrected magnetic susceptibilities are given in Tables 15-20.

Among the complexes of Cr(III), investigated here, the acetato, bromo, nitrato and perchlorato complexes showed magnetic moments in the range 3.80 to 3.72 B.M., indicating octahedral geometries, with sufficient magnetic dilution.[78,80,82] But the chloro complex showed a magnetic moment of 3.39 B.M. This is lower than the theoretically expected value and thus indicated magnetic non-dilution. This could be attributed to the bimetallic- or polymeric nature of the complexes and the resultant anti-ferromagnetic coupling.[78,80,81] Other data also pointed towards octahedral geometries for all the Cr(III) complexes, investigated here.

All the complexes of Mn(II), except the chloro complex, which were investigated here, showed magnetic moments in the range of 6.06-5.79 B.M., indicating that they are high-spin with probable octahedral geometry.[26,80,85] The chloro complex showed a lower value of 4.86 B.M., probably due to the bimetallic or polymeric nature with anti-ferromagnetic coupling. Other physico-chemical data also supported octahedral geometry for all the complexes of Mn(II).

Table-15 Magnetic data of Cr(III) complexes of Bipirpen
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d 10^{-6}$	$\chi_{eff}\ 10^{-6}$	μ eff B.M.
$[CrL(AcO)_3(H_20)]$	5245	307	5552	3.68
$[Cr_2LCl_6(H_20)_2]$	4549	162	4711	3.39
$[CrLBr_3(H_20)]$	5388	285	5673	3.72
$[CrL(NO_3)_3(H_20)]$	5668	252	5920	3.80
$[CrL(ClO_4)_3(H_20)]$	5518	309	5827	3.77

Table -16 Magnetic data of Mn(II) complexes of Bipirpen
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d 10^{-6}$	$\chi_{eff}\ 10^{-6}$	μ eff B.M.
$[MnL(AcO)_2(H_2O)_2]$	13464	280	13744	5.79
$[Mn_2LCl_4(H_2O)_2]$	9541	142	9683	4.86
$[MnLBr_2(H_2O)_2]$	14790	265	15055	6.06
$[MnL(H_2O)_4]\ (NO_3)_2$	14056	264	14319	5.91
$[MnL(ClO_4)_2(H_2O)_2]$	13701	281	13982	5.84

Table -17 Magnetic data of Fe(III) complexes of Bipirpen
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d 10^{-6}$	$\chi_{eff}\ 10^{-6}$	μ eff B.M.
$[FeL(AcO)_3(H20)]$	13827	299	14126	5.87
$[Fe_2LCl_6(H20)_2]$	9883	162	10045	4.95
$[FeLBr_3(H20)]$	14375	285	14660	5.98
$[FeL(NO_3)_3(H20)]$	14606	252	14857	6.02
$[FeL(ClO_4)_3(H20)]$	14010	309	14319	5.91

BM = Bohr Magneton

χ_m = Molar susceptibility χ_{eff}=Effective susceptibility

χ_d = Diamagnetic correction μ_{eff} = Effective magnetic moment

Table -18 Magnetic data of Co(II) complexes of Bipirpen
T = 303 K

Complex	χ_m 10^{-6}	$\chi_d 10^{-6}$	χ_{eff} 10^{-6}	μ eff B.M.
$[CoL(AcO)_2(H_2O)_2]$	8738	280	9018	4.69
$[Co_2LCl_4]$	5091	222	5313	3.60
$[CoLBr_2(H_2O)_2]$	10066	265	10331	5.02
$[CoL(H_2O)_4]$ $(NO_3)_2$	9420	264	9683	4.86
$[CoL(ClO_4)_2(H2O)_2]$	8930	281	9211	4.74

Table -19 Magnetic data of Ni(II) complexes of Bipirpen
T = 303 K

Complex	χ_m 10^{-6}	$\chi_d 10^{-6}$	χ_{eff} 10^{-6}	μ eff B.M.
$[NiL(AcO)_2]$	-	-	-	D
$[Ni_2LCl_4(H_2O)_2]$	2651	142	2793	2.61
$[NiLBr_2(H_2O)_2]$	4092	265	4357	3.26
$[NiL(NO_3)_2(H_2O)_2]$	3799	243	4042	3.14
$[NiL(ClO_4)_2]$	-	-	-	D

Table-20 Magnetic data of Cu(II) complexes of Bipirpen
T = 303 K

Complex	χ_m 10^{-6}	$\chi_d 10^{-6}$	χ_{eff} 10^{-6}	μ eff B.M.
$[Cu_2L(OH)_4]$	732	107	838.3	1.43
$[Cu_2LCl_4(H_2O)_2]$	830	142	972.3	1.54
$[CuLBr_2(H_2O)_2]$	1408	265	1673	2.02
$[CuL(H_2O)_2]$ $(NO_3)_2$	1365	243	1607	1.98
$[CuL(ClO_4)_2]$	1565	260	1825	2.11

B.M. = Bohr Magneton D = Diamagnetic

χ_m = Molar susceptibility χ_{eff} = Effective susceptibility

χ_d = Diamagnetic correction μ_{eff} =Effective magnetic moment

In the present investigation, the acetato, bromo, nitrato and perchlorato complexes of Fe(III) showed magnetic moment values in the range 5.87 to 6.02 B.M. Hence, it was assumed that these complexes were high-spin with probable octahedral geometry.[78,89] But the chloro complex of Fe(III) showed a lower moment of 4.95 B.M. only, indicating magnetic non-dilution. The anti-ferromagnetic coupling resulting from the bimetallic or polymeric nature of the complex might be responsible for this.[78,80,88]

The acetato, bromo, nitrato and perchlorato complexes of Co(II), which were investigated here, showed magnetic moments in the range 4.69-5.02 B.M., indicating high-spin octahedral geometries with sufficient magnetic dilution.[8,78,89] The electronic spectra and the pink colour of these complexes also supported octahedral geometries. But the chloro complex of Co(II) showed a magnetic moment of 3.60 B.M. only, which was slightly lower than the value expected for tetrahedral complex. However, the electronic spectrum and the intense blue colour of the complex confirmed this geometry. The slightly lower value could be due to the bimetallic or polymeric nature of the complex, resulting in anti-ferromagnetic coupling.[78,92,93]

Among the complexes of Ni(II), the acetato and perchlorato ones were found to be diamagnetic in nature, indicating that they were square-planar in geometry.[46,95] The chloro complex showed a magnetic moment of 2.61 B.M., lower than that expected for an octahedral complex. But the electronic spectrum and the greenish-yellow colour of the complex confirmed this geometry. The lower value could be, probably due to the bimetallic- or polymeric nature and the subsequent anti-ferromagnetic coupling in them.[78,96] The bromato and nitrato complexes of Ni(II) showed magnetic moments of 3.26 and 3.14 B.M., respectively, suggesting octahedral geometries for them.[94,97] The electronic spectra and the green colour of these complexes supported this.

In the present investigation, the hydroxo and chloro complexes of Cu(II) showed magnetic moments of 1.43 and 1.54 B.M., respectively. The lower values indicated some sort of molecular association that could be achieved through either a direct copper–copper interaction and/or magnetic exchange interaction through a bridging ligand [78,94,100] The bromato, nitrato and perchlorato complexes showed magnetic moments in the range 1.98 to 2.11 B.M. indicating sufficient magnetic dilution in these complexes.[78,84]

5. Electronic spectra

The important electronic spectral bands of the complexes and their probable assignments are given in the Tables 21-26. In the present investigation, the electronic spectra of all the complexes of Cr(III) had two bands in the ranges 548-512 and 423-392 nm. These bands could be assigned to the spin-allowed $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions for the d^3 ion in an octahedral geometry.[101,103-105] Other physico-chemical data also supported this geometry for them.

In the present investigation, the spectra of Mn(II) complexes showed a number of weak bands in the range 398-412 nm which were assigned to the spin- and parity-forbidden d-d transitions of d^5 ion in an octahedral field or to the charge-

Table-21 Electronic Spectral Bands of Cr(III) Bipirpen complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[CrL(AcO)_3(H_20)]$	542 421	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
$[Cr_2LCl_6(H_20)_2]$	548 392	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrLBr_3(H_20)]$	512 425	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrL(NO_3)_3(H_20)]$	538 423	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrL(ClO_4)_3(H_20)]$	543 409	$^4A_2g \rightarrow {}^4T_{2g}$ $^4A_2g \rightarrow {}^4T_{1g}(F)$	Octahedral

Table-22 Electronic Spectral Bands of Mn(II) Bipirpen complexes and their assignments

Complex	Bands* (nm)	Assignment	Geometry
$[MnL(AcO)_4(H_2O)_2]$	402w	$^6A_{1g}(F) \rightarrow {}^4E_g$ or $^4A_{1g}(G)$	Octahedral
$[Mn_2LCl_4(H_2O)_2]$	399 w	$^6A_{1g}(F) \rightarrow {}^4E_g$ or $^4A_{1g}(G)$	Octahedral
$[MnLBr_2(H_2O)_2]$	405w	$^6A_{1g}(F) \rightarrow {}^4E_g$ or $^4A_{1g}(G)$	Octahedral
$[MnL(H_2O)_4](NO_3)_2$	412 w	$^6A_{1g}(F) \rightarrow {}^4E_g$ or $^4A_{1g}(G)$	Octahedral
$[MnL(ClO_4)_2(H_2O)_2]$	398w	$^6A_{1g}(F) \rightarrow {}^4E_g$ or $^4A_{1g}(G)$	Octahedral

*w = weak

Table-23 Electronic Spectral Bands of Fe(III) Bipirpen complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[FeL(AcO)_3(H20)]$	409 391	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
$[Fe_2LCl_6(H20)_2]$	412 382	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral
$[FeLBr_3(H20)]$	401	$^6A_{1g} \rightarrow {}^4T_{2g}$	Octahedral
$[FeL(NO_3)_3(H20)]$	406	$^6A_{1g} \rightarrow {}^4T_{2g}$	Octahedral
$[FeL(ClO_4)_3(H20)]$	416 397	$^6A_{1g} \rightarrow {}^4T_{2g}$ CT	Octahedral

Table-24 Electronic Spectral Bands of Co(II) Bipirpen complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[CoL(AcO)_2(H_2O)_2]$	1080 687 484	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P$	Octahedral
$[Co_2LCl_4]$	1612 665 510	$^4A_2(F) \rightarrow {}^4T_2(F)$ $^4A_2(F) \rightarrow {}^4T_1\ (F)$ $^4A_2(F) \rightarrow {}^4T_1(P)$	Tetrahedral
$[CoLBr_2(H_2O)_2]$	1105 623 453	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P$	Octahedral
$[CoL(H_2O)_4]\ (NO_3)_2$	1028 587 434	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P$	Octahedral
$[CoL(ClO_4)_2(H_2O)_2]$	1073 558 443	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P$	Octahedral

Table-25 Electronic Spectral Bands of Ni(II) Bipirpen complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[NiL(AcO)_2]$	539	$^1A_1g \rightarrow {}^1B_{1g}$	Square-planar
$[Ni_2LCl_4(H_2O)_2]$	1140 700 412	$^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
$[NiLBr_2(H_2O)_2]$	1132 710 389	$^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
$[NiL(NO_3)_2(H_2O)_2]$	1154 721 392	$^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ $^3A_2g(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
$[NiL(ClO4)_2]$	534	$^1A_1g \rightarrow {}^1B_{1g}$	Square-planar

Table-26 Electronic Spectral Bands of Cu(II) Bipirpen Complexes and their assignments

Complex	Band (nm)	Assignment	Geometry
$[Cu_2L(OH)_4]$	542	$^2B_{1g} \rightarrow {}^2A_{1g}$	Square-planar
$[Cu_2LCl_4(H_2O)]$	714b	$^2E_g \rightarrow {}^2T2_g$	Distorted octahedral
$[CuLBr_2(H_2O)_2]$	743b	$^2E_g \rightarrow {}^2T2_g$	Distorted octahedral
$[CuL(H_2O)_2]\ (NO_3)_2$	572	$^2B_{1g} \rightarrow {}^2A_{1g}$	Square-planar
$[CuL(ClO_4)_2]$	536	$^2B_{1g} \rightarrow {}^2A_{1g}$	Square-planar

transfer spectra extending to the visible region.[85,101,106] The pale-yellow or orange colour of the complexes also supported octahedral geometries.

All the Fe(III) complexes, investigated here gave a number of weak bands around 416-382 nm. The spin- and parity-forbidden d-d transitions ($^6A_1g \rightarrow {}^4T_{2g}$) in an octahedral field or the charge-transfer transitions tailing into visible region probably gave rise to these bands.[94,109,110] The pale yellow or brown colours of the complexes also supported octahedral geometry.

Among the Co(II) complexes which were investigated here, the spectra of the acetato, bromo, nitrato and perchlorato complexes showed bands in the ranges 1105-1028, 687-558, 484-434 nm. These bands were assigned to the ^4T_1g(F) → ^4T_2g(F), ^4T_1g(F) → ^4A2g(F) and ^4T_1g(F) → ^4T_1g(P) transitions, respectively, in an octahedral geometry.[89,94,111] The pink colour of the complexes and other data also supported this structure. The chloro complex of Co(II) was bright-green in colour and its electronic spectrum showed intense bands at 1612, 665 and 510 nm assigned, respectively, to the $^4A_2$(F) → $^4T_2$(F), $^4A_2$(F) → $^4T_1$ (F) and $^4A_2$(F) → $^4T_1$(P) transitions, characteristic of tetrahedral geometry.[113-115] The magnetic and analytical data also supported this assumption.

In the present investigation, the spectra of acetato and perchlorato complexes of Ni(II) showed bands at 539 and 534 nm, respectively, assigned to the $^1A_1g \rightarrow {}^1B_{1g}$ transitions in a square-planar geometry.[46,95,117,118] The diamagnetic nature of the complexes also supported this geometry. The spectra of the chloro, bromo and nitrato complexes of Ni(II) showed transitions in the ranges 1132-1154, 700-721 and 412-389 nm. These were assigned to the $^3A_2g(F) \rightarrow {}^3T_2g(F)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)$ and $^3A_2g(F) \rightarrow {}^3T_1g(P)$ transitions in an octahedral geometry. The ratio of wave numbers of the first two transitions was found to be in the range 1.6-1.8, which confirmed the octahedral geometries for these complexes.[94,116,119]

In the electronic spectra of hydroxo, nitrato and perchlorato complexes of Cu(II) investigated here, broad bands appeared at 542, 572 and 536 nm respectively, which were assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions in a square-planar geometry.[26,46,96,100] The brown colour of the complexes also supported this assumption.[122] The spectra of chloro and bromo complexes of Cu(II) showed bands at 714 and 743 nm, respectively, and these were assigned to the $^2E \rightarrow {}^2T_2$ transition in a distorted-octahedral geometry.[101,119,123] The blue or green colours of the complexes also supported this geometry.[121,122]

6. Infrared spectra

a) Complexes

The significant vibrational bands of the ligand, Bipirpen and its complexes and the corresponding assignments are given in the Tables 27-32. Assignments were made on the basis of comparison with analogous systems identified earlier.[75,76,124,125]

In the spectra of all the complexes investigated here, noticeable down shifts were found in the characteristic absorption frequencies of the C=N stretching vibrations. This down shift clearly indicated the coordination of the nitrogen atoms of the azomethine groups.[46,47,94] The band at 1641 cm^{-1} was found to be shifted to the range 1631-1570 cm^{-1} which were assigned to the coordinated azomethine groups.[124]

The characteristic absorption bands of the dioxymethylene groups were found to be present without any noticeable change in frequency, in the spectra of the majority of the complexes investigated here. Therefore, it was inferred that the dioxymethylene groups were not involved in coordination with metal ions. But the chloro complexes of Mn(II), Ni(II) and Cu(II) showed significant shift or absence of this band. Hence, it was concluded that one of the oxygen atoms of the dioxymethylene group of the ligand was coordinated in these complexes.[76]

In the spectra of all these complexes, new bands appeared in the lower frequency region. In the case of the spectra of Cr(III) complexes bands were present in the range of 554-520 and 452-423 cm^{-1}, in the Mn(II) complexes in the range of 629-624 and 526-519 cm^{-1} and in the Fe(III) complexes in the range of 512-492 and 447-413 cm^{-1}. The Co(II) complexes showed new bands at 558-464 and 447-417 cm^{-1}, the Ni(II) complexes at 622 -527 and 487-431 cm^{-1} and the Cu(II) complexes at 557-524 and 505-463 cm^{-1}. The first ones of these two bands of relatively higher frequency, present in all the complexes, were assigned to the νM-N. The second ones of relatively lower frequency were also present in all the complexes, except the chloro complex of Co(II), as given in the Tables. These were assigned to the stretching vibrations of M-O bonds which were formed during complexation. The appearance of these two bands could be taken as a conclusive proof for coordination.[47,95,97,126] The M-O bands could be due to coordinated acetate, nitrate, perchlorate or hydroxyl anion or water molecule, or due to the coordination of the oxygen atom of the dioxymethylene group.

Broad bands, present in the region ~3462-3391 cm^{-1} in the spectra of all the complexes of Cr(III), Mn(II) and Fe(III), the acetato, bromo, nitrato and perchlorato complexes of Co(II), the chloro, bromo and nitrato complexes of Ni(II) and Cu(II) were assigned to the O-H stretching frequency of coordinated water molecules.[89,124,127] The appearance of bands of medium or low intensities in the ranges ~ 955-965 and ~ 630-640 cm^{-1}, due to the $\rho K_{rock}(H_2O)$ and $\rho_{wagg}(H_2O)$ vibrations,[94,128] respectively, further supported the presence of coordinated water molecules in these complexes. Analytical data also agreed to the presence of water molecules in them.

b) IR features of coordinated anions in the complexes

i) <u>Acetato complexes</u>

The spectra of the acetato complexes of Cr(III), Mn(II), Fe(III), Co(II) and Ni(II), showed bands in the ranges of 1600-1582 and 1444-1421 cm^{-1}. The separation between these two bands was much larger than the separation for the bands due to asymmetric and symmetric stretchings of free acetate ion. Therefore, the bands were assigned to the C-O stretching vibrations of the unidentately coordinated acetate ions present in them.[94,129-131] Microanalytical data and the non-conducting nature of these complexes further supported this.

Table-27 Significant bands in the IR spectra of Cr(III) Bipirpen complexes and their assignments

Compounds	Assignments and band frequencies*(cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO_3 (coordinated)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipirpen (L)		1641s						927m		
$[CrL(AcO)_3(H_20)]$	3462b	1597m	1582m 1421w			966m	637w	929m	520m	447w
$[Cr_2LCl_6(H_20)_2]$	3415b	1610m				961m	636w	928m	525w	432w
$[CrLBr_3(H_20)]$	3409b	1601s				956m	632w	927w	553w	452m
$[CrL(NO_3)_3(H_20)]$	3415b	1597m		1435m 1351w 1036sh		954m	638w	928m	554w	437w
$[CrL(ClO_4)_3(H_20)]$	3423b	1602m			1120m 1038w 946w	963m	634w	927w	534m	423w

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-28 Significant bands in the IR spectra of Mn(II) Bipirpen complexes and their assignments

Compounds	Assignments and band frequencies*(cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO(asy) (free NO_3^-)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren(L)		1641s						927m		
$[MnL(AcO)_2(H_2O)_2]$	3393b	1598m	1582w 1444m			958m	632w	928m	629m	525w
$[Mn_2LCl_4(H_2O)_2]$	3429b	1598m				964m	634w	-	627w	526m
$[MnLBr_2(H_2O)_2]$	3403b	1600s				957m	639w	928m	629w	524w
$[MnL(H_2O)_4](NO_3)_2$	3389b	1588w		1385s		961m	637w	929w	624w	521m
$[MnL(ClO_4)_2(H_2O)_2]$	3429b	1594m			1112m 1088w 944w	959m	632w	927w	625w	519m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-29 Significant bands in the IR spectra of Fe(III) Bipirpen complexes and their assignments

Compounds	Assignments and band frequencies*(cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO_3^- (coordinated)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ$_{wagg}$ (H_2O)			
Bipiren(L)		1641s						927m		
[FeL(AcO)$_3$(H20)]	3408b	1631m	1600m 1442w			964m	631w	928m	512w	434m
[Fe$_2$LCl$_6$(H20)$_2$]	3391b	1593m				959m	637w	927w	496m	421w
[FeLBr$_3$(H20)]	3410b	1631s				963m	631w	928m	492w	413w
[FeL(NO$_3$)$_3$(H20)]	3396b	1608m		1443w 1037w		960m	641w	927m	510w	447m
[FeL(ClO$_4$)$_3$(H20)]	3428b	1629m			1113m 1037w 937w	954m	638w	929w	498w	418m

s-strong, m-medium, w-weak, b-broad

Table-30 Significant bands in the IR spectra of Co(II) Bipirpen complexes and their assignments

Compounds	Assignments and band frequencies*(cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO(asy) (free NO_3^-)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren(L)		1641s						927m		
$[CoL(AcO)_2(H_2O)_2]$	3408b	1598m	1586w 1443m			959m	634w	927m	464w	417m
$[Co_2LCl_4]$	-	1629m				-	-	927m	469m	-
$[CoLBr_2(H_2O)_2]$	3410b	1598s				956m	637w	929w	558w	436w
$[CoL(H_2O)_4](NO_3)_2$	3396b	1596m		1384s		961m	632w	928w	546w	447m
$[CoL(ClO_4)_2(H_2O)_2]$	3428b	1597m			1118m 1036sh 941w	963m	635w	929w	510w	440m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-31 Significant bands in the IR spectra of Ni(II) Bipirpen complexes and their assignments

Compounds	Assignments and band frequencies*(cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO_3^- (coordinated)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren(L)		1641s						927m		
[$NiL(AcO)_2$]	-	1591m	1587m 1430w			-	-	928m	564w	487m
[$Ni_2LCl_4(H_2O)_2$]	3412b	1599m				964m	639w	-	619m	462w
[$NiLBr_2(H_2O)_2$]	3424b	1596s				958m	641w	929w	527w	453w
[$NiL(NO_3)_2(H_2O)_2$]	3429b	1592m		1423w 1354w 1026w		961m	634w	929w	542w	431m
[$NiL(ClO4)_2$]	-	1599m			1120m 1048w 932w	-	-	928m	622w	456m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-32 Significant bands in the IR spectra of Cu(II) Bipirpen complexes and their assignments

Compounds	Assignments and band frequencies*(cm^{-1})								
	ν O-H (coordinated H_2O or OH^-)	ν C=N	νNO(asy) (free NO_3^-)	νClO_3^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
					ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
Bipiren(L)		1641s					927m		
$[Cu_2L(OH)_4]$	3439s	1598m			-	-	928m	524w	482m
$[Cu_2LCl_4(H_2O)_2]$	3412b	1570m			958m	639w	-	557m	498w
$[CuLBr_2(H_2O)_2]$	3422b	1594m			959m	640w	927w	532w	467w
$[CuL(H_2O)_2](NO_3)_2]$	3386b	1587m	1384s		962m	637w	928w	557w	505m
$[CuL(ClO_4)_2]$	-	1593s		1142m 1114w 931w	-	-	927w	549w	463m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

ii) Hydroxo complex

The sharp band present at 3439 cm^{-1} in the case of the hydroxo complex of Cu(II) was assigned to the O-H stretching frequency of the coordinated hydroxo group.[94,132] The complex was synthesised using copper acetate, but in its spectrum, the characteristic bands of either free or coordinated acetate ion could not be identified.[84,130,131] Elemental analysis data also indicated the presence of hydroxyl ions in the complex and corresponded to the formula proposed for it. Hence, it was assumed that hydroxyl ions were coordinated to the metal, instead of the acetate ions.

iii) Halo complexes

The spectra of these complexes were expected to show absorption bands due to the M-Cl or M-Br vibrations below 400cm^{-1}, which was out of range of the instrument used in the present investigation.[124,130] But the microanalytical data indicated the presence of three halogen atoms per metal ion in the complexes of Cr(III) and Fe(III) and two halogen atoms per metal ion in the case of the complexes of Mn(II), Co(II), Ni(II) and Cu(II). Non-conducting nature of these complexes indicated that the halogen atoms were coordinated to the metal ions.

iii) Nitrato complexes

Among the nitrato complexes investigated here, the characteristic absorption frequencies of free nitrate ions were absent in the spectra of the complexes of

Cr(III), Fe(III) and Ni(II). Instead, bands appeared at 1435,1351 and1036 cm^{-1} in the Cr(III) complex, at 1443 and 1037cm^{-1} in the Fe(III) complex and at 1423,1354 and 1026 cm^{-1} in the Ni(II) complex. These bands were assigned to the presence of monodentate nitrate ions in them.[94,132,133] The non-conducting nature and the stochiometry of these complexes confirmed the presence of coordinated nitrate ions in them. However, the IR spectra of nitrato complexes of Mn(II), Co(II) and Cu(II) showed sharp bands at 1385, 1384 and 1384 cm^{-1}, respectively, which corresponded to the characteristic absorption frequencies of free nitrate ions. Elemental analysis data and the conductance values also confirmed the presence of free nitrate ions in these complexes.[124,130,133]

iv) Perchlorato complexes

The spectra of all the perchlorato complexes, investigated here, showed bands corresponding to unidentate perchlorate ions. These bands were found to be present in the ranges 1142-1112, 1114-1036 and 946-931 cm^{-1} and were assigned to the Cl-O stretchings of the monodentate perchlorate ion[94,124,134] The non-conducting nature and the microanalytical data of these complexes further confirmed this.

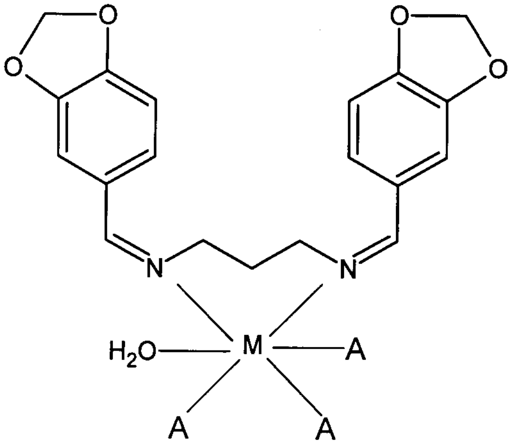
6. Thermal analyses

Thermograms of 3 complexes, namely $[Co_2LCl_4]$, $[Ni_2LCl_4(H_2O)_2]$ $[Cu_2LCl_4(H_2O)_2]$ were recorded. The decomposition patterns agreed well with the suggested formulae. The end products obtained were chemically identified as the corresponding metal oxides. Independent pyrolytic studies were also carried out and the results agreed well with the thermograms. The details of the thermogravimetric studies are given in the Part II of this thesis.

C. Conclusions

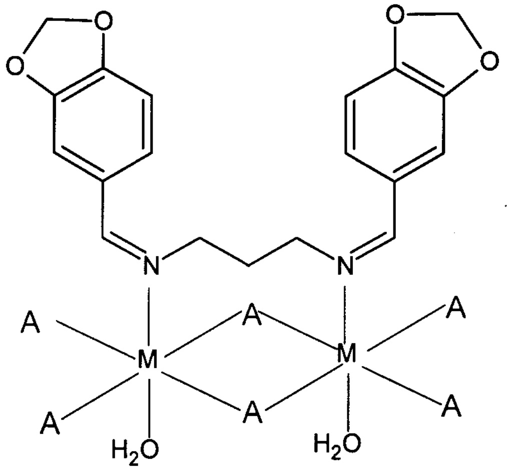
The transition metal complexes of bis(piperonaldehyde)-1,3-propanediimine were synthesised. The physico-chemical investigations of the complexes revealed the general formulae given in the subsection B-2 of this chapter.

In all the complexes, Bipirpen acted as a neutral, bidentate or tetradentate ligand. The dioxymethylene groups offered two additional sites for coordination, in the cases where Bipirpen acted as tetradentate ligand, eventhough the coordination might be weak. It was also found that Bipirpen acted as chelating as well as bridging ligand in different complexes. However, the bridging tendency of Bipirpen was less than that of the ligand, Bipiren, investigated in the previous chapter. Only the chloro complexes showed distinct tendency to form polymeric- or bimetallic complexes. The hydroxo complex of Cu(II), formed when the metal acetate was used for the preparation of the complex, also showed this tendency. The steric factors due to a larger number of -CH_2- groups, intervening the two azomethine nitrogen atoms, might be responsible for the lesser tendency of the ligand for stabilising polymeric complexes. Geometries of the complexes depended on the nature of the metal ion and the coordinating anions. The microanalytical, spectral, magnetic, electrical conductance and thermal data were logically correlated, and the formulae and structures (Fig-2-10) of the complexes were established.



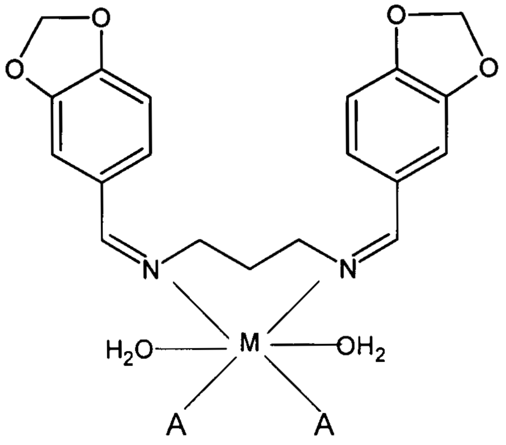
where M = Cr(III) or Fe(III) and A = CH_3-COO^-, Br, NO_3^- or ClO_4^-

Fig-2 Structure suggested for $[CrL(OOC\text{-}CH_3)_3(H_2O)]$, $[CrLBr_3(H_2O)]$, $[CrL(NO_3)_3(H_2O)]$, $[CrL(ClO_4)_3(H_2O)]$, $[FeL(OOC\text{-}CH_3)_3(H_2O)]$, $[FeLBr_3(H_2O)]$, $[FeL(NO_3)_3(H_2O)]$ and $[FeL(ClO_4)_3(H_2O)]$, where L = Bipirpen.



where M = Cr(III) or Fe(III) and A = Cl^-

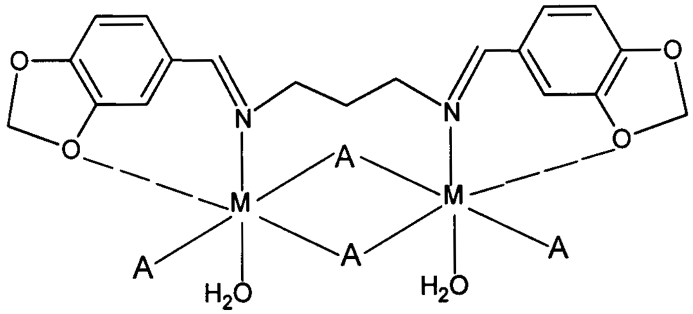
Fig-3 Structure suggested for $[Cr_2LCl_6(H_2O_2)]$ and $[Fe_2LCl_6(H_2O_2)]$, where L = Bipirpen.



Where M = Mn(II) or Co(II) and A = CH_3COO^-, Br^-or ClO_4^-

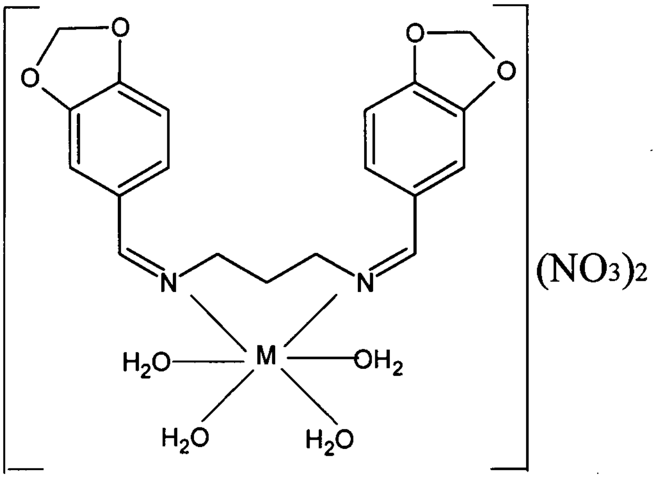
or M = Ni(II) and A= Br^- or NO_3^- or M = Cu(II) and A = Br^-

Fig-4 Structure suggested for $[MnL(OOC\text{-}CH_3)_2(H_2O)_2]$, $[MnLBr_2(H_2O)_2]$, $[MnL(ClO_4)_2(H_2O)_2]$, $[CoL(OOC\text{-}CH_3)_2(H_2O)_2]$, $[CoLBr_2(H_2O)_2]$ $[CoL(ClO_4)_2(H_2O)_2]$, $[NiLBr_2(H_2O)_2]$, $[NiL(NO_3)_2(H_2O)_2]$ and $[CuLBr_2(H_2O)_2]$, where L = Bipirpen.



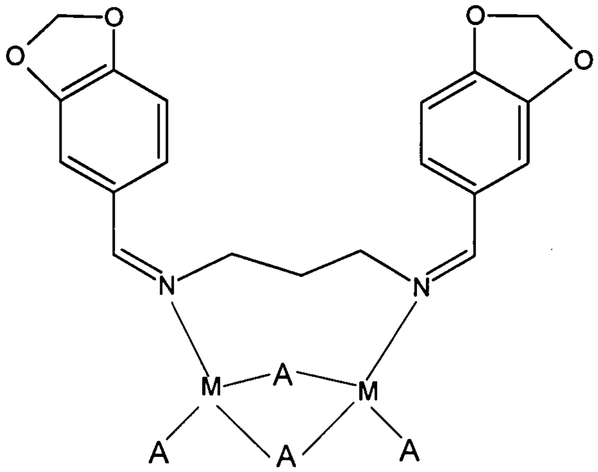
where M = Mn(II), Ni(II) or Cu(II) and A = Cl^-

Fig-5 Structure suggested for $[Mn_2LCl_4(H_2O)_2]$, $[Ni_2LCl_4(H_2O)_2]$ and $[Cu_2LCl_4(H_2O)_2]$, where L = Bipirpen.



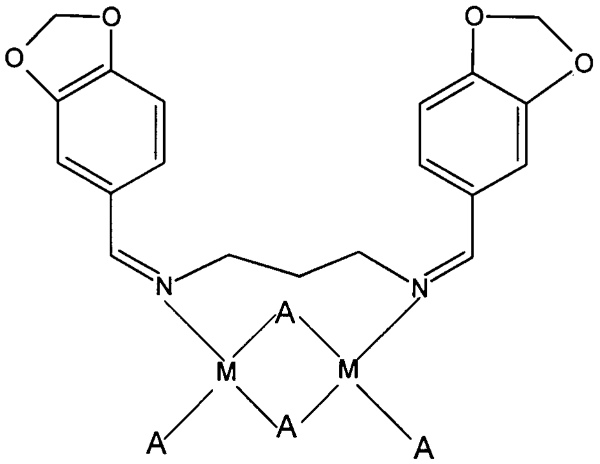
where M = Mn(II) or Co(II)

Fig-6 Structure suggested for [MnL $(H_2O)_4](NO_3)_2$ and $[CoL(H_2O)_4](NO_3)_2$, where L = Bipirpen.



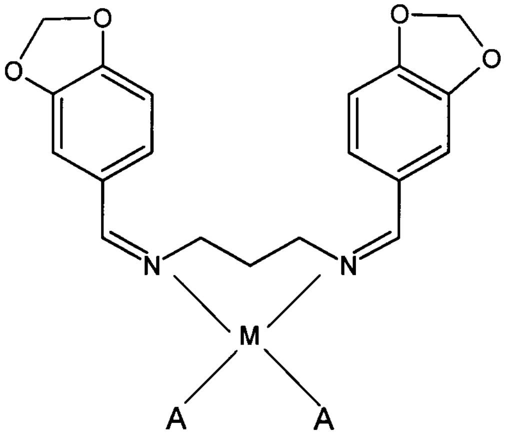
M = Co(II) and A = Cl^-

Fig-7 Structure suggested for $[Co_2LCl_4]$, where L = Bipirpen.



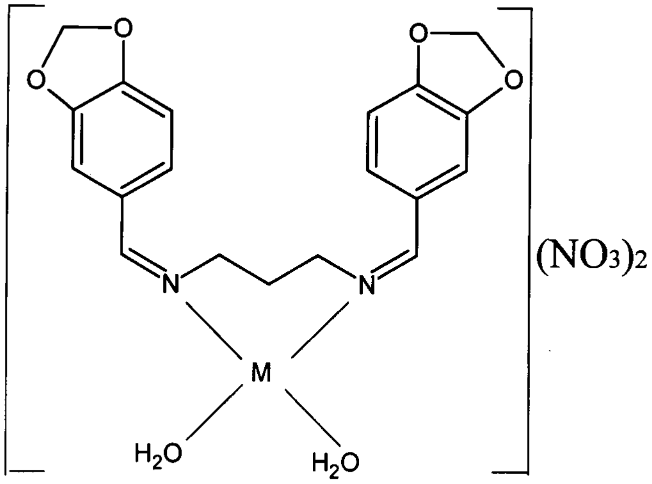
Where M = Cu(II) and A = OH^-

Fig-8 Structure suggested for $[Cu_2L(OH)_4]$, where L = Bipirpen.



Where M = Ni(II) and A = CH_3COO^- or ClO_4^- or M = Cu(II) and A = ClO_4^-

Fig-9 Structure suggested for $[NiL(OOC\text{- }CH_3)_2]$, $[NiL(ClO_4)_2]$ and $[CuL(ClO_4)_2]$, where L = Bipirpen.



where M = Cu(II)

Fig-10 Structure suggested for $[CuL(H_2O)_2]\ (NO_3)_2$, where L = Bipirpen.

CHAPTER V

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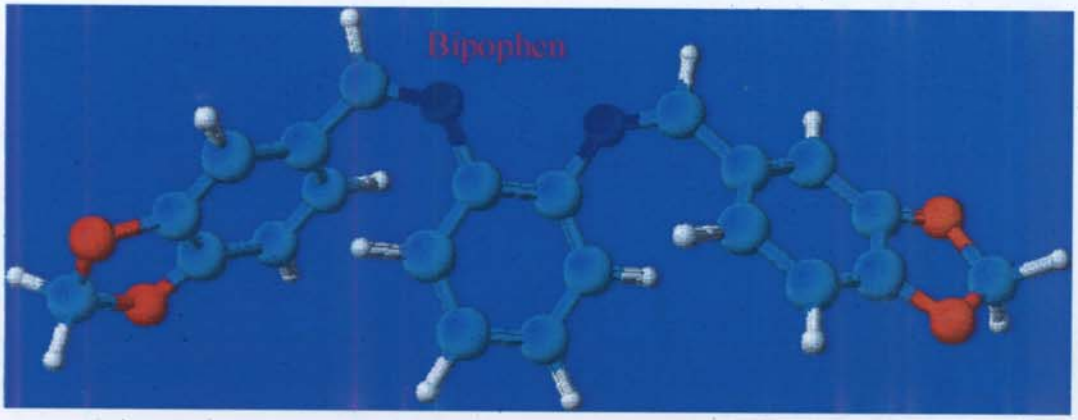
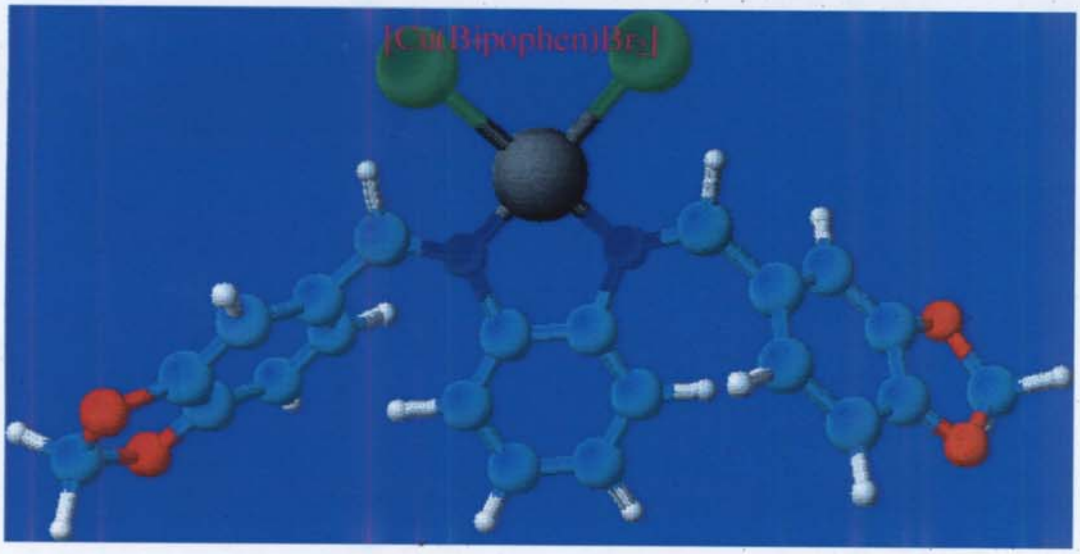


Bipophen



[Cu(Bipophen)Br$_2$]

CHAPTER V

Cr(III), Mn(II), Fe(III), Co(II), Ni(II) AND Cu(II) COMPLEXES OF BIS(PIPERONALDEHYDE)-*O*-PHENYLENEDIIMINE

(Bipophen)

There is a growing interest in the synthesis of Schiff bases of *ortho*-phenylenediamine and their metal complexes because of their wide applications in analytical,[139] biochemical,[53,140] and clinical[141] fields. Earlier works indicated that some drugs showed increased activity when administered as metal chelates rather than as organic compounds.[53,140,141] The ability of Schiff bases to form stable complexes with transition metal ions[45,46,49,53,140] has inspired interest in such compounds. A review of the literature revealed that no systematic work had been done on the transition metal complexes of the Schiff bases derived from *o*-phenylenediamine and piperonaldehyde. Therefore, the investigations on the novel Schiff base ligand bis(piperonaldehyde)-*o*-phenylenediimine (Bipophen)* (L) and its transition metal complexes were undertaken here.

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*The systematic name of the compound is: *N,N'*-bis[1,3-benzodioxol-5-ylmethylene]benzene-1,2-diamine. But for the sake of convenience the name 'bis(piperonaldehyde)-*o*-phenylenediimine' and the short form 'Bipophen' are adopted in this thesis.

The biological activities of piperonal and other compounds containing the 3,4-methylenedioxy groups are well known[5,59,60] and hence it was used as the carbonyl compound in this synthesis. The nitrogen atoms of the two azomethine groups and oxygen atoms of the two dioxymethylene groups are the potential coordination sites in this ligand. The ligand (Fig-1) and its complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) were synthesised and characterised.

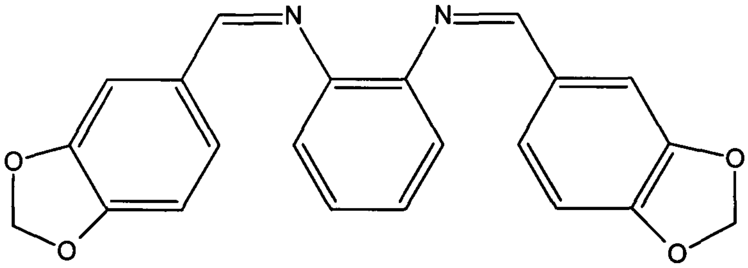


Fig-1 Structure suggested for bis(piperonaldehyde)-*o*-phenylenediimine

(Bipophen)

A. Experimental

1. Materials and methods

The specifications of the reagents used and the methods adopted for the synthesis and characterisation of the ligand and the complexes are described in the Chapter II.

2. Synthesis of the ligand, bis(piperonaldehyde)-*o*-phenylenediimine (Bipophen)

A solution of *o*-phenylenediamine (1.94 g) in ethanol was mixed with piperonaldehyde (6.04 g) in ethanol and refluxed for about 3 h. The volume of the solution was reduced to one third and was then cooled. The pale-yellow precipitate of bis(piperonaldehyde)-*o*-phenylenediimine was formed. The solid was filtered off and then recrystallised from ethanol. The compound was dried over anhydrous $CaCl_2$ (yield = 84 %).

3. Synthesis of the complexes of Bipophen

Five complexes each of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions with Bipophen were synthesised by the following methods. Acetates, chlorides, bromides, nitrates and perchlorates of these metals were used for the synthesis.

a) Complexes of Cr (III), Mn (II) and Fe (III)

Methanolic solutions of the metal salt and the ligand were mixed in 1:1 molar ratio and refluxed over water bath for about 2-3 h. Metal acetates, which are less soluble in methanol, were dissolved in a methanol-water mixture using minimal amount of water and then added to refluxing solution of the ligand in methanol. After refluxing, the solution was concentrated over a water bath and the pasty mass obtained was washed repeatedly with diethyl ether and/or petroleum ether and/or acetone to get the solid complex separated. The complexes were then dried over anhydrous $CaCl_2$.

b) Complexes of Co(II)

Complexes of Co(II) were prepared by refluxing mixtures of solutions of the ligand and metal salt in acetone mixed in 1:1 molar ratio for about 2-3 h over a water bath. Cobalt chloride gave a precipitate during refluxing, which was separated, washed with acetone and dried. The cobalt acetate was dissolved in acetone-water mixture and added to refluxing solution of the ligand. In the synthesis of acetate, bromide, nitrate and perchlorate complexes, after refluxing, the reaction mixture was concentrated over a water bath and was washed repeatedly with diethyl ether and/or petroleum ether to get the solid complexes separated. The complexes were then dried over anhydrous $CaCl_2$.

c) Complexes of Ni (II) and Cu(II)

The solutions of the ligand and the metal salts in methanol were mixed in 1:1 molar ratio and refluxed over a water bath for about 2-3 h. The metal acetates which were less soluble in methanol were dissolved in a methanol-water mixture using minimal amount of water and then added to the solution of the ligand while it was being refluxed. Nickel chloride, copper acetate, -chloride and -bromide gave solid products while refluxing. They were filtered off washed with methanol and dried over anhydrous calcium chloride. In other cases, the reaction mixtures, after being refluxed for about 2-3 h, were concentrated over a water bath to obtain a pasty mass and were washed repeatedly with diethyl ether and/or petroleum ether to get the solid complexes separated. The complexes were then dried over anhydrous calcium chloride.

B. Results and discussion

Analytical and physico-chemical studies were done systematically on these compounds and the results were correlated in a logical manner. On this basis the properties, structures and geometries of the complexes have been explained reasonably.

1. Characterization of the ligand

TLC established the homogeneity and purity of the ligand. The analytical data were found to be in good agreement with the suggested formula, $C_{22}H_{16}O_4N_2$ for bis(piperonaldehyde)-*o*-phenylenediimine. It was further characterised by IR and ^{1}H NMR spectral studies. The melting point of the compound was found to be 179°C.

a) ^{1}H NMR spectrum

The ^{1}H NMR spectrum of the ligand, Bipophen was recorded in DMSO-d_6 (Table-1). The spectrum showed a number of signals that could be assigned as the characteristic of the compound.[73,74] The peak observed at a δ value of 8.39 ppm was assigned to the two azomethine protons in the molecule. A number of multiplet signals were found in the range 7.56-6.84 ppm. They were assigned to the different types of aromatic protons of the *o*-phenylenediamine- and the piperonal moieties present in the molecule. The singlet peak observed at 5.96 ppm was assigned to the methylinic protons of the dioxymethylene groups present in ligand molecule. The

Table-1 Significant ^{1}H NMR Peaks of Bipophen and their assignments

Chemical shift* (δ ppm)	Proton assignment
8.39s	Two -CH=N-
7.56 7.42-7.34m 6.86-6.84m	Aromatic protons
5.96s	Two $-CH_2-$ (of dioxymethylene groups)

* s = singlet, m = multiplet

Table-2 Significant IR bands of Bipophen and their assignments

Band frequency* (cm^{-1})	Assignment
3078	ν aromatic C-H
2965	ν C-H (methylene)
2886	ν C-H (=CH-)
1613s	ν >C=N-
1493 1447	ν ring C-C
1248s	ν >C-N-
1135 1036	δ in plane C-H (aromatic)
930	δ -O-CH_2-O-
875 811	δ out of plane C-H(aromatic)

* s = strong

higher δ value for these protons might be due to the inductive effect of the two oxygen atoms, which deshielded them.

a) IR spectrum

The IR spectrum (Table-2) of the ligand showed a number of bands which were the characteristic of different groups present in it. The spectrum of the ligand showed absorption bands at 1613 cm^{-1} and 1248 cm^{-1} which were assigned to the C=N and C-N stretchings, respectively. The characteristic absorption band of the dioxymethylene group present at 930 cm^{-1}, could be considered as an evidence for the presence of piperonal moieties in the compound.[108] But the characteristic frequency of aromatic aldehyde group of piperonal moiety at ~1690 cm^{-1} was absent in the spectrum, which indicated that the condensation with the diamine was complete.[107,108] The band at 3078 cm^{-1} was assigned to the aromatic C-H stretching and that at 2965 cm^{-1} to the C-H stretching of the methylene groups (>CH_2). The in-plane bending vibrations of aromatic C-H are expected to cause absorptions in the range 1250 to 950 cm^{-1}. The bands present at 1135 and 1036 cm^{-1} were assigned to these modes of vibration. Similarly those at 875 and 811cm^{-1} were assigned to the out of plane bending vibrations of the aromatic C-H.

2. Formulae and general properties of complexes

The complexes were coloured, photostable and non-hygroscopic. They were found to be usually insoluble in common organic solvents, but soluble in DMF and DMSO. From the analytical data and molar conductance values in DMF, the following formulae were suggested. The spectral and magnetic evidences also confirmed the suggested formulae.

In contrast to the ligands Bipiren and Bipirpen, discussed in the previous chapters, Bipophen did not show the tendency to form polymeric or bimetallic complexes and this could be due to the benzene ring, intervening the coordinating nitrogen atoms. Similarly Bipophen gave acetato complexes, and not hydroxo complexes as in the cases of Bipiren and Bipophen, with all the metal acetates used in the synthesis. The analytical data of the complexes are given in Tables 3-8.

a) $[MLA_3(H_2O)]$, where M = Cr(III) or Fe(III)
and A = CH_3COO^-, Cl^-, Br^-, NO_3^- or ClO_4^-

b) $[MLA_2(H_2O)_2]$, where M = Mn(II) and A = CH_3COO^-, Cl^-, Br-, NO_3^-
or ClO_4^- : or M = Co(II) and A = CH_3COO^-
or M = Ni (II) and A = Cl^-

c) $[MLA_2]$, where M = Co(II) and A = Cl^-, Br^- or ClO_4^-
or M = Ni (II) and A = Br^-, CH_3COO^- or NO_3^-
or M = Cu (II) and A = CH_3COO^-, Cl^-, Br^-, NO_3^- or ClO_4^-

d) $[ML(H_2O)_2]\,(A)_2$, where M = Co(II) and A = NO_3^-
or M = Ni (II) and A = ClO_4^-

3. Molar conductance

Molar conductances of 10^{-3} molar solutions of the complexes in DMF were determined at room temperature (Tables 9-14) and they were found to be generally non-conducting or having insignificant values of electrical conductance, Table-3 Analytical data of Cr(III) Bipophen complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
(Bipophen)	$C_{22}H_{16}O_4N_2$	372	Pale yellow	84		71.12 (70.97)	4.34 (4.30)	7.49 (7.53)	
$[CrL(AcO)_3(H_2O)]$**	$CrC_{28}H_{27}O_{11}N_2$	619	Bluish gray	68	8.74 (8.41)	53.31 (54.28)	4.27 (4.36)	4.47 (4.52)	
$[CrLCl_3(H_2O)]$	$CrC_{22}H_{18}O_5N_2Cl_3$	549	Dull green	64	10.01 (9.48)	46.98 (48.13)	3.19 (3.28)	4.98 (5.10)	20.03 (19.42)
$[CrLBr_3(H_2O)]$	$CrC_{22}H_{18}O_5N_2Br_3$	682	Bluish gray	72	8.01 (7.62)	37.86 (38.71)	2.59 (2.64)	4.03 (4.11)	36.08 (35.19)
$[CrL(NO_3)_3(H_2O)]$	$CrC_{22}H_{18}O_{14}N_5$	628	Bluish gray	70	8.61 (8.28)	41.08 (42.04)	2.79 (2.87)	10.54 (11.15)	
$[CrL(ClO_4)_3(H_2O)]$	$CrC_{22}H_{18}O_{17}N_2Cl_3$	741	Bluish gray	68	7.46 (7.02)	34.71 (35.65)	2.39 (2.43)	3.71 (3.78)	41.58 (40.31)

*F. wt. = Formula weight, **$AcO^- = CH_3\text{-}COO^-$

Table-4 Analytical data of Mn(II) Bipophen complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
(Bipophen) L)	$C_{22}H_{16}O_4N_2$	372	Pale yellow	84		71.12 (70.97)	4.34 (4.30)	7.49 (7.53)	
$[MnL(AcO)_2(H_2O)_2]$**	$MnC_{26}H_{26}O_{10}N_2$	581	Orange	69	9.02 (9.47)	54.18 (53.70)	4.52 (4.48)	4.87 (4.82)	
$[MnLCl_2(H_2O)_2]$	$MnC_{22}H_{20}O_6N_2Cl_2$	534	Pale yellow	61	9.98 (10.30)	50.24 (49.44)	3.82 (3.75)	5.31 (5.24)	13.46 (13.30)
$[MnLBr_2(H_2O)_2]$	$MnC_{22}H_{20}O_6N_2Br_2$	623	Pale yellow	68	8.46 (8.83)	42.96 (42.38)	3.25 (3.21)	4.52 (4.49)	24.98 (25.68)
$[MnL(NO_3)_2(H_2O)_2]$	$MnC_{22}H_{20}O_{12}N_4$	587	Pale yellow	72	8.98 (9.37)	45.74 (44.97)	3.46 (3.41)	9.68 (9.54)	
$[MnL(ClO_4)_2(H_2O)_2]$	$MnC_{22}H_{20}O_{14}N_2Cl_2$	662	Orange	63	8.12 (8.31)	40.12 (39.88)	3.06 (3.02)	4.28 (4.23)	29.68 (30.06)

*F. wt. = Formula weight, **AcO^- = CH_3-COO^-

Table-5 Analytical Data of Fe(III) Bipophen complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
Bipophen (L)	$C_{22}H_{16}O_4N_2$	372	Pale yellow	84		71.12 (70.97)	4.34 (4.30)	7.49 (7.53)	
$[FeL(AcO)_3(H_2O)]$**	$FeC_{28}H_{27}O_{11}N_2$	623	Orange	64	9.42 (8.97)	52.89 (53.95)	4.23 (4.33)	4.45 (4.50)	
$[FeLCl_3(H_2O)]$	$FeC_{22}H_{18}O_5N_2Cl_3$	552	Pale brown	56	10.48 (10.11)	46.98 (47.80)	3.17 (3.26)	5.01 (5.07)	19.89 (19.28)
$[FeLBr_3(H_2O)]$	$FeC_{22}H_{18}O_5N_2Br_3$	686	Pale brown	58	8.72 (8.14)	37.31 (38.49)	2.59 (2.62)	4.03 (4.08)	36.78 (34.99)
$[FeL(NO_3)_3(H_2O)]$	$FeC_{22}H_{18}O_{14}N_5$	632	Pale brown	56	9.21 (8.84)	40.97 (41.78)	2.78 (2.85)	11.48 (11.08)	
$[FeL(ClO_4)_3(H_2O)]$	$FeC_{22}H_{18}O_{17}N_2Cl_3$	744	Orange	61	7.87 (7.50)	34.24 (35.47)	2.37 (2.42)	3.69 (3.76)	41.11 (40.10)

*F. wt. = Formula weight, **$AcO^- = CH_3\text{-}COO^-$

Table-6 Analytical Data of Co(II) Bipophen Complexes

Compound	Empirical formula	F.wt.*	Color	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
(Bipophen) (L)	$C_{22}H_{16}O_4N_2$	372	Pale yellow	84		71.12 (70.97)	4.34 (4.30)	7.49 (7.53)	
$[CoL(AcO)_2(H_2O)_2]$**	$CoC_{26}H_{26}O_{10}N_2$	585	Dull green	67	9.86 (10.06)	53.82 (53.33)	4.56 (4.44)	4.86 (4.79)	
$[CoLCl_2]$	$CoC_{22}H_{16}O_4N_2Cl_2$	502	Bright blue	72	11.46 (11.75)	52.81 (52.59)	3.22 (3.19)	5.64 (5.58)	14.01 (14.14)
$[CoLBr_2]$	$CoC_{22}H_{16}O_4N_2Br_2$	591	Blue	57	9.82 (9.98)	44.96 (44.67)	2.76 (2.71)	4.79 (4.74)	26.89 (27.07)
$[CoL(H_2O)_2]$ $(NO_3)_2$	$CoC_{22}H_{20}O_{12}N_4$	591	Blue	62	9.79 (9.98)	45.12 (44.67)	3.41 (3.38)	9.54 (9.48)	
$[CoL(ClO4)_2]$	$CoC_{22}H_{16}O_{12}N_2Cl_2$	630	Dark blue	66	9.28 (9.37)	42.42 (41.91)	2.59 (2.54)	4.61 (4.44)	30.92 (31.59)

*F. wt. = Formula weight, **AcO^- = CH_3-COO^-

Table-7 Analytical Data of Ni(II) Bipophen Complexes

Compound	Empirical formula	F.wt.*	Color	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
(Bipophen)(L)	$C_{22}H_{16}O_4N_2$	372	Pale yellow	84		71.12 (70.97)	4.34 (4.30)	7.49 (7.53)	
[NiL(AcO)$_2$]**	$NiC_{26}H_{22}O_8N_2$	549	Brown	62	11.22 (10.70)	55.98 (56.86)	3.93 (4.01)	4.97 (5.10)	
[NiLCl$_2$(H$_2$O)$_2$]	$NiC_{22}H_{20}O_6N_2Cl_2$	538	Pale green	70	11.34 (10.92)	48.56 (49.10)	3.63 (3.72)	5.03 (5.21)	13.91 (13.20)
[NiLBr$_2$]	$NiC_{22}H_{16}O_4N_2Br_2$	591	Pale yellow	59	10.34 (9.94)	43.92 (44.69)	2.59 (2.71)	4.62 (4.74)	27.64 (27.09)
[NiL(NO$_3$)$_2$]	$NiC_{22}H_{16}O_{10}N_4$	555	Gray	64	10.92 (10.58)	46.86 (47.59)	2.79 (2.88)	9.94 (10.10)	
[NiL(H$_2$O)$_2$](ClO$_4$)$_2$	$NiC_{22}H_{20}O_{14}N_2Cl_2$	666	Brown	68	8.68 (8.82)	36.21 (36.66)	2.82 (3.00)	4.02 (4.21)	31.01 (29.89)

*F. wt. = Formula weight, **AcO$^-$ = CH_3-COO$^-$

Table-8 Analytical Data of Cu(II) Bipophen Complexes

Compound	Empirical formula	F.wt.*	Colour	Yield %	Found (calculated)%				
					Metal	C	H	N	Anion
(Bipophen) (L)	$C_{22}H_{16}O_4N_2$	372	Pale yellow	84		71.12 (70.97)	4.34 (4.30)	7.49 (7.53)	
$[CuL(AcO)_2]$**	$CuC_{26}H_{22}O_8N_2$	554	Brown	68	12.12 (11.47)	55.74 (56.37)	3.91 (3.97)	4.94 (5.06)	
$[CuLCl_2]$	$CuC_{22}H_{16}O_4N_2Cl_2$	507	Green	72	12.61 (12.53)	51.38 (52.12)	3.06 (3.16)	5.14) (5.28)	14.36 (14.02)
$[CuLBr_2]$	$CuC_{22}H_{16}O_4N_2Br_2$	596	Brown	54	11.21 (10.66)	43.89 (44.33)	2.48 (2.69)	4.56 (4.71)	27.14 (26.87)
$[CuL(NO_3)_2]$	$CuC_{22}H_{16}O_{10}N_4$	560	Brown	62	11.92 (11.35)	46.68 (47.18)	2.71 (2.86)	9.69 (10.01)	
$[CuL(ClO_4)_2]$	$CuC_{22}H_{16}O_{12}N_2Cl_2$	635	Green	56	10.51 (10.01)	41.13 (41.61)	2.47 (2.52)	4.32 (4.41)	32.14 (31.36)

*F. wt. = Formula weight, **AcO^- = CH_3-COO^-

Table-9 Molar conductance in DMF of Cr(III) Bipophen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[CrL(AcO)_3(H_2O)]$	-
$[CrLCl_3(H_2O)]$	4.73
$[CrLBr_3(H_2O)]$	4.26
$[CrL(NO_3)_2(H_2O)]]$	38.58
$[CrL(ClO4)_3(H_2O)]$	49.52

Table-10 Molar conductance in DMF of Mn(II) Bipophen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[MnL(AcO)_2(H_2O)_2]$	3.25
$[MnLCl_2(H_2O)_2]$	24.62
$[MnLBr_2(H_2O)_2]$	15.68
$[MnL(NO_3)_2(H_2O)_2]$	44.72
$[MnL(ClO_4)_2(H_2O)_2]$	48.15

Table-11 Molar conductance in DMF of Fe(III) Bipophen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[FeL(AcO)_3(H_2O)]$	-
$[FeLCl_3(H_2O)]$	1.46
$[FeLBr_3(H_2O)]$	6.09
$[FeL(NO_3)_3(H_2O)]$	12.92
$[FeL(ClO_4)_3(H_2O)]$	32.56

Table-12 Molar conductance in DMF of Co(II) Bipophen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[CoL(AcO)_2(H_2O)_2]$	1.35
$[CoLCl_2]$	29.14
$[CoLBr_2]$	2.84
$[CoL(H_2O)_2](NO_3)_2$	139.32
$[CoL(ClO_4)_2]$	31.82

Table-13 Molar conductance in DMF of Ni(II) Bipophen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[NiL(AcO)_2]$	2.71
$[NiLCl_2(H_2O)_2]$	22.32
$[NiLBr_2]$	48.24
$[NiL(NO_3)_2]$	35.87
$[NiL(H_2O)_2] (ClO_4)_2$	132.94

Table-14 Molar conductance in DMF of Cu(II) Bipophen complexes

Complexes	Λ_m ohm^{-1}cm^{2}mol^{-1}
$[CuL(AcO)_2]$	19.06
$[CuLCl_2]$	8.24
$[CuLBr_2]$	7.45
$[CuL(NO_3)_2]$	33.24
$[CuL(ClO4)_2]$	30.18

thus indicating that they were non-electrolytes. But the nitrato complex of Co(II) and the perchlorato complex of Ni(II) showed values, corresponding to 1:2 electrolytes.[65] On the basis of the conductance values and analytical data formulae were assigned to them.

4. Magnetic behaviour

The magnetic susceptibility values, diamagnetic corrections and the effective magnetic moment values of the complexes are given Tables 15-20. All the complexes of Cr(III) investigated here, showed magnetic moments in the range 3.72 to 3.86 B.M., clearly indicating octahedral geometries with sufficient magnetic dilution.[78,80,82]

The Mn(II) complexes, investigated here, were found to have magnetic moments in the range 5.78-6.10 B.M. Accordingly, high-spin octahedral geometries with sufficient magnetic dilution were assigned to them.[26,78,85] The electronic spectra and pale-yellow or orange colours of the complexes also supported octahedral geometries for them.

In the present investigation, all the Fe(III) complexes showed magnetic moments in the range 5.78 to 6.21 B.M. Obviously these complexes are of high-spin octahedral geometry.[78,89]

Among the complexes of Co(II) which were investigated in this study, the acetato complex showed a magnetic moment of 4.92 B.M., indicating high-spin

Table-15 Magnetic data of Cr(III) complexes of Bipophen

T = 303 K

Complex	χ_m. 10^{-6}	χ_d. 10^{-6}	χ_{eff}. 10^{-6}	μ_{eff} B.M.
$[CrL(AcO)_3(H_2O)]$	5472	293	5765	3.75
$[CrLCl_3(H_2O)]$	5684	267	5951	3.81
$[CrLBr_3(H_2O)]$	5809	299	6108	3.86
$[CrL(NO_3)_3(H_2O)]$	5257	265	5522	3.67
$[CrL(ClO_4)_3(H_2O)]$	5351	323	5673	3.72

Table-16 Magnetic data of Mn(II) complexes of Bipophen

T = 303 K

Complex	χ_m. 10^{-6}	χ_d. 10^{-6}	χ_{eff}. 10^{-6}	μ_{eff} B.M.
$[MnL(AcO)_2(H_2O)_2]$	14731	275	15006	6.05
$[MnLCl_2(H_2O)_2]$	13965	258	14222	5.89
$[MnLBr_2(H_2O)_2]$	13417	279	13696	5.78
$[MnL(NO_3)_2(H_2O)_2]$	14257	256	14514	5.95
$[MnL(ClO_4)_2(H_2O)_2]$	14960	295	15255	6.10

Table-17 Magnetic data of Fe(III) complexes of Bipophen

T = 303 K

Complex	χ_m. 10^{-6}	χ_d. 10^{-6}	χ_{eff}. 10^{-6}	μ_{eff} B.M.
$[FeL(AcO)_3(H_2O)]$	14961	293	15255	6.11
$[FeLCl_3(H_2O)]$	13907	267	14174	5.88
$[FeLBr_3(H_2O)]$	13445	299	13744	5.79
$[FeL(NO_3)_3(H_2O)]$	15545	265	15810	6.21
$[FeL(ClO_4)_3(H_2O)]$	13374	323	13696	5.78

B.M. = Bohr magneton

χ_m = Molar susceptibility χ_{eff} = Effective susceptibility

χ_d = Diamagnetic correction μ_{eff} = Effective magnetic moment

Table-18 Magnetic data of Co(II) complexes of Bipophen
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d.10^{-6}$	$\chi_{eff}.10^{-6}$	μ_{eff} B.M.
$[CoL(AcO)_2(H_2O)_2]$	9649	275	9924	4.92
$[CoL_2Cl_2]$	7343	237	7580	4.30
$[CoLBr_2]$	6695	196	6891	4.10
$[CoL(H_2O)_2]\ (NO_3)_2$	7717	256	7973	4.41
$[CoL(ClO4)_2]$	8102	274	8376	4.52

Table-19 Magnetic data of Ni(II) complexes of Bipophen
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d.10^{-6}$	$\chi_{eff}.10^{-6}$	μ_{eff} B.M.
$[NiL\ (AcO)_2]$	-	-	-	D
$[NiLCl_2(H_2O)_2]$	3708	258	3965	3.11
$[NiL\ Br_2]$	-	-	-	D
$[NiL\ (NO_3)_2]$	-	-	-	D
$[NiL(H_2O)_2]\ (ClO_4)_2$	-	-	-	D

Table-20 Magnetic data of Cu(II) complexes of Bipophen
T = 303 K

Complex	$\chi_m\ 10^{-6}$	$\chi_d 10^{-6}$	$\chi_{eff}\ 10^{-6}$	μ_{eff} B.M.
$[CuL(AcO)_2]$	1520	254	1774	2.08
$[CuLCl_2]$	1395	196	1591	1.97
$[CuL\ Br_2]$	1602	258	1860	2.13
$[CuL(NO_3)_2]$	1229	235	1464	1.89
$[CuL\ (ClO4)_2]$	1729	274	2002	2.21

B.M. = Bohr magneton D = Diamagnetic

χ_m = Molar susceptibility χ_{eff} = Effective susceptibility

χ_d = Diamagnetic correction μ_{eff} = Effective magnetic moment

octahedral geometry.[8,89,94] All other complexes of Co(II) showed magnetic moments in the range 4.10 - 4.52 B.M., indicating their tetrahedral geometries.[78,92,93]

The acetato, bromo, nitrato and perchlorato complexes of Ni(II), under present investigation were found to be diamagnetic, indicating square-planar geometry.[46,78,95] But the chloro complex of Ni(II) showed a magnetic moment of 3.11 B.M., indicating octahedral geometry.[78,94,97]

In the present investigation, all complexes of Cu(II) were found to have magnetic moments in the range 1.89-2.13 B.M. indicating sufficient magnetic dilution[78,94] and hence probable monomeric nature.

5) Electronic Spectra

The significant electronic spectral bands of the complexes and their assignments are given in Tables 21-26. In the spectra of all the Cr(III) complexes, investigated here, two bands were identified in the ranges 584-553 and 431-401 nm and they were assigned, respectively, to the spin-allowed $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions of the d^3 ions in octahedral geometries.[103-105] Other data also supported octahedral geometries for these complexes.

All the Mn(II) complexes, investigated here, showed weak bands in the range 366-402 nm which could be assigned to the spin- and parity-forbidden d-d transitions, $^6A_1g(F) \rightarrow {}^4T_2g(G)$ of the d^5 configuration in an octahedral field.[85,101,106]

Table-21 Electronic spectral bands of Cr(III) Bipophen complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[CrL(AcO)_3(H_2O)$	553 401	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrLCl_3(H_2O)]$	568 426	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrLBr_3(H_2O)]$	571 417	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrL(NO_3)_2(H_2O)]]$	578 434	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}(F)$	Octahedral
$[CrL(ClO4)_3(H_2O)]$	584 431	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}(F)$	Octahedral

Table-22 Electronic Spectral Bands of Mn(II) Bipophen complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[MnL(AcO)_2(H_2O)]$	399w	$^6A_{1g}(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
$[MnLCl_2(H_2O)_2]$	385w	$^6A_{1g}(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
$[MnLBr_2(H_2O)_2]$	402w	$^6A_{1g}(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
$[MnL_2(NO_3)_2(H_2O)_2]$	366w	$^6A_{1g}(F) \rightarrow {}^4T_{2g}(G)$	Octahedral
$[MnL_2(ClO_4)_2(H_2O)_2]$	395w	$^6A_{1g}(F) \rightarrow {}^4T_{2g}(G)$	Octahedral

Table-23 Electronic Spectral Bands of Fe(III) Bipophen Complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[FeL(AcO)_3(H_2O)]$	432 378	$^6A_{1g}\rightarrow{}^4T_{2g}$ CT	Octahedral
$[FeLCl_3(H_2O)]$	419 376	$^6A_{1g}\rightarrow{}^4T_{2g}$ CT	Octahedral
$[Fe_2LBr_6(H_2O)]$	407	$^6A_{1g}\rightarrow{}^4T_{2g}$	Octahedral
$[FeLNO_3)_3(H_2O)]$	413	$^6A_{1g}\rightarrow{}^4T_{2g}$	Octahedral
$[FeL(ClO_4)_3(H_2O)]$	423 385	$^6A_{1g}\rightarrow{}^4T_{2g}$ CT	Octahedral

Table-24 Electronic Spectral Bands of Co(II) Bipophen Complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
$[CoL(AcO)_2(H_2O)_2]$	1092 676 496	$^4T_1g(F)\rightarrow{}^4T_2g(F)$ $^4T_1g(F)\rightarrow{}^4A_{2g}(F)$ $^4T_1g(F)\rightarrow{}^4T_1g(P)$	Octahedral
$[CoLCl_2]$	1598 678 498	$^4A_2(F)\rightarrow{}^4T_2(F)$ $^4A_2(F)\rightarrow{}^4T_1(F)$ $^4A_2(F)\rightarrow{}^4T_1(P)$	Tetrahedral
$[CoLBr_2]$	1614 684 512	$^4A_2(F)\rightarrow{}^4T_2(F)$ $^4A_2(F)\rightarrow{}^4T_1(F)$ $^4A_2(F)\rightarrow{}^4T_1(P)$	Tetrahedral
$[CoL(H_2O)_2](NO_3)_2$	1634 692 482	$^4A_2(F)\rightarrow{}^4T_2(F)$ $^4A_2(F)\rightarrow{}^4T_1(F)$ $^4A_2(F)\rightarrow{}^4T_1(P)$	Tetrahedral
$[CoL(ClO_4)_2]$	1652 672 491	$^4A_2(F)\rightarrow{}^4T_2(F)$ $^4A_2(F)\rightarrow{}^4T_1(F)$ $^4A_2(F)\rightarrow{}^4T_1(P)$	Tetrahedral

Table-25 Electronic Spectral Bands of Ni(II) Bipophen Complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
[NiL $(AcO)_2$]	572	$^1A_{1g} \rightarrow {}^1B_{1g}$	Square planar
[$NiLCl_2(H_2O)_2$]	1136 714 421	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral
[NiL Br_2]	546	$^1A_{1g} \rightarrow {}^1B_{1g}$	Square planar
[NiL $(NO_3)_2$]	541	$^1A_{1g} \rightarrow {}^1B_{1g}$	Square planar
[$NiL(H_2O)_2$] $(ClO_4)_2$	587	$^1A_{1g} \rightarrow {}^1B_{1g}$	Square planar

Table-26 Electronic Spectral Bands of Cu(II) Bipophen Complexes and their assignments

Complex	Bands (nm)	Assignment	Geometry
[$CuL_2(AcO)_2$]	529	$^2B_{1g} \rightarrow {}^2A_{1g}$	Square planar
[$CuLCl_2$]	730 509	$^2E_g \rightarrow {}^2T_{2g}$ CT	Octahedral
[CuL_2 Br_2]	533	$^2B_{1g} \rightarrow {}^2A_{1g}$	Square planar
[CuL_2 $(NO_3)_2$]	521	$^2B_{1g} \rightarrow {}^2A_{1g}$	Square planar
[$CuL_2(ClO4)_2$]	734 521	$^2E_g \rightarrow {}^2T_{2g}$ CT	Octahedral

In the present investigation, complexes of Fe(III) were pale in colour and gave only weak bands around 400-500 nm. The spin- and parity-forbidden d-d transitions of the d^5 ion in an octahedral field would give rise to such weak bands.[94,101,109]

Among the Co(II) complexes, under investigation, the spectra of the acetato complex showed bands at 1092, 676 and 496 nm which corresponded, respectively, to the $^4T_1g(F) \rightarrow {}^4T_2g(F)$, $^4T_1g(F) \rightarrow {}^4A_2g(F)$ and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ transitions in an octahedral geometry[8,84,95,123,136] The pink colour of the complex also supported this geometry. The spectra of the chloro, bromo, nitrato and perchlorato complexes of Co(II) showed transitions in the ranges 1652-1598, 692-672 and 512-491 nm. These were assigned, respectively, to the $^4A_2(F) \rightarrow {}^4T_2(F)$, $^4A_2(F) \rightarrow {}^4T_1$ (F) and $^4A_2(F) \rightarrow {}^4T_1(P)$ transitions in a tetrahedral geometry.[101,113-115] The bright greenish-blue colours of the complexes and the intensity of transitions supported these assignments.

The spectra of the acetato, bromo, nitrato and perchlorato complexes of Ni(II), which were investigated here, showed absorption bands at 572, 546, 541 and 587 nm, respectively, which corresponded to the $^1A_1g \rightarrow {}^1B_{1g}$ transitions in square-planar geometries.[46,95,102,118] The analytical data also supported this geometry. The spectrum of the chloro complex showed absorption bands at 1136, 714 and 421 nm, which were assigned, respectively, to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3A_2g(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ transitions in an octahedral geometry. The ratio of wave numbers of transitions, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ was found to be in the 1.73, confirming octahedral geometry for the complex.[94,116,119]

In the electronic spectra of acetato, bromo and nitrato complexes of Cu(II), which were presently investigated, bands appeared at 529, 533 and 521 nm respectively, and they were assigned to the $^2B_{1g} \rightarrow ^2A_{1g}$ transitions in square-planar geometries.[26,46,86,100] The brown colour of the complexes also supported this geometry.[121,122] The electronic spectra of chloro and perchlorato complexes of copper showed bands at 730 and 734 nm, respectively, which were assigned to the $^2E \rightarrow ^2T_2$ transitions in distorted octahedral geometries.[101,119,123] The green colour of the complexes also supported octahedral geometries.

6. Infrared Spectra

a) Complexes

The significant vibrational absorption bands present in the IR spectra of the ligand and the complexes and their probable assignments[75,76,124,125] are given in the Tables 27-32. In the spectra of all the Bipophen complexes, the ν(C=N) was shifted to lower frequency, due to its involvement in coordination.[46,47,94,95] This band appeared in the range of 1603-1571 cm^{-1} in the spectra of these complexes. In the spectra of the majority of complexes, investigated here, the characteristic absorption band of the dioxymethylene groups appeared almost at the same frequency as in the ligand spectrum. Therefore, the non-involvement of dioxymethylene groups in coordination was inferred. However the spectra of chloro and perchlorato complexes of Cu(II) showed significant down-shifts or absence of this band. Hence, it was assumed that one oxygen atom each of dioxymethylene group was coordinated in them.[76]

Table-27 Significant bands in the IR spectra of Cr(III) Bipophen complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO_3 (coordinated)	νClO_4^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
(Bipophen) (L)		1613s						930m		
$[Cr_2LCl_6(H_20)_2]$	3415b	1592m	1578m 1412w			958m	632w	929m	592m	459w
$[CrL(AcO)_3(H_20)]$	3462b	1582m				963m	638w	928m	518m	488w
$[CrLBr_3(H_20)]$	3409b	1579s				959m	637w	930w	541w	459w
$[CrL(NO_3)_3(H_20)]$	3415b	1593m		1443m 1328w 1033sh		958m	636w	929m	506m	493m
$[CrL(ClO_4)_3(H_20)]$	3423b	1601m			1119m 1034w 942w	961m	633w	928w	542w	486m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-28 Significant bands in the IR spectra of Mn(II) Bipophen complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO_3 (coordinated)	νClO_4^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
(Bipophen) (L)		1613s						930m		
[$MnL(AcO)_2(H_2O)_2$]	3436b	1583m	1578w 1446m			963m	634w	929w	499m	433w
[$MnLCl_2(H_2O)_2$]	3403b	1593m				957w	636w	-	454w	430m
[$MnLBr_2(H_2O)_2$]	3429b	1582s				959w	637w	928m	458m	427w
[$MnL(NO_3)_2(H_2O)_2$]	3429b	1576w		1446w 1330m 1036w		964m	635w	929m	452w	429m
[$MnL(ClO_4)_2(H_2O)_2$]	3429b	1583m			1116m 1037w 936w	957w	635m	927w	451w	427m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-29 Significant bands in the IR spectra of Fe(III) Bipophen complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO_3^- (coordinated)	νClO_4^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
(Bipophen) (L)		1613s						930m		
[FeL$(AcO)_3$(H20)]	3404b	1582m	1572m 1448w			964m	631w	929m	521w	488m
[FeLCl_3(H20)]	3398b	1571m				959m	637w	928m	504m	486w
[FeLBr_3(H20)]	3409b	1601s				963m	631w	929m	509w	492w
[FeL$(NO_3)_3$(H20)]	3421b	1591m		1448m 1326w 1039w		960m	633w	930m	510w	485m
[FeL$(ClO_4)_3$(H20)]	3385b	1596m			1117m 1039w 945w	958m	638w	929m	498m	476m

*s-strong, m-medium, w-weak, b-broad

Table-30 Significant bands in the IR spectra of Co(II) Bipophen complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO(asy) (free NO_3^-)	νClO_4^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
(Bipophen) (L)		1613s						930m		
$[CoL(AcO)_2(H_2O)_2]$		1598m	1556w 1390m			964m	633w	930m	464	421
$[CoLCl_2]$	-	1579m				-	-	930m	483	-
$[CoLBr_2]$	3405b	1593s				962m	638w	929w	558	-
$[CoL(H_2O)_2]$ $(NO_3)_2$	-	1596m		1384s		963m	637w	929w	546	432
$[CoL(ClO4)_2]$	3425b	1587m			1116m 1036w 926sh	957m	634w	929w	510	440

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-31 Significant bands in the IR spectra of Ni(II) Bipophen complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO_3^- (coordinated)	νClO_4^- (coordinated)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
(Bipophen)(L)		1613s						930m		
[$NiL(AcO)_2$]		1599m	1596m 1454w			-	-	928m	486w	462m
[$NiLCl_2(H_2O)_2$]	3402b	1599m				962m	639w	929m	476m	431w
[$NiLBr_2$]	-	1596s				-	-	929w	426m	--
[$NiL(NO_3)_2$]	-	1592m		1454m 1328m 1043w		964m	637w	930m	426w	403m
[$NiL(H_2O)_2$](ClO_4)$_2$	3409b	1599m			1115s	-	-	930m	452m	426m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

Table-32 Significant bands in the IR spectra of Cu(II) Bipophen complexes and their assignments

Compounds	Assignments and band frequencies* (cm^{-1})									
	ν O-H (coordinated H_2O or OH^-)	ν C=N	ν CO (coordinated CH_3-COO^-)	νNO_3^- (coordinated)	νClO_4^- (free)	(coordinated water)		δ O-CH_2-O	ν M-N	ν M-O
						ρK_{rock} (H_2O)	ρ_{wagg} (H_2O)			
(Bipophen)(L)		1613s				-	-	930m		
$[CuL(AcO)_2]$		1598m	1550w 1448m			-	-	929m	498m	432m
$[CuLCl_2]$	-	1579m				-	-	921w	459m	-
$[CuLBr_2]$	-	1593s				-	-	930m	466m	-
$[CuL(NO_3)_2]$	-	1596m		1467m 1334w 1036w		-	-	928m	466w	433m
$[CuL(ClO4)_2]$	-	1587m			1118m 1037w 938w		-	921w	506w	426m

*s-strong, m-medium, w-weak, b-broad, sh-shoulder

The IR spectra of these complexes revealed new bands in the ranges 592–451 and 493–403 cm^{-1} and were assigned to the ν(M–N), ν(M–O) vibrations, respectively.[47,95,126] It was assumed that the M-O bonds were formed by the coordination of acetate, nitrate, perchlorate or hydroxyl ions or water molecules or oxygen atoms of the dioxymethylene groups of the ligand to the metal ions. However, in the spectra of the chloro and bromo complexes of Co(II) and Cu(II) and the bromo complex of Ni(II), the second band of relatively lower frequency was not present, indicating the absence of M-O bonds in them.

The spectra of all the complexes of Cr(III), Mn(II) and Fe(III), the acetato and nitrato complexes of Co(II), the chloro and perchlorato complexes of Ni(II) showed broad bands in the region ~3436-3385 cm^{-1} and they were assigned to the O-H stretchings of coordinated water molecules.[95,97,127] In addition, the bands present in the ranges ~ 964-955 and ~ 630-640 cm^{-1}, assigned to the $\rho K_{rock}(H2O)$ and $\rho_{wagg}(H2O)$ vibrations, respectively, were considered as conclusive proof for the coordination of water molecules in these metal complexes.[84,128] Elemental analysis data also agreed to the presence of water molecules in them.

b) IR features of coordinated anions in complexes

i) Acetato complexes

The spectra of the acetato complexes all the metal ions in this study, showed bands in the ranges, 1596-1550 and 1454-1390 cm^{-1}. These bands were assigned to the C-O stretching vibrations of the unidentate acetate ions.[94,129-131] The non-conducting nature and analytical data further supported the assumption. Unlike the ligands, Bipiren and Bipirpen, discussed in the previous chapters, Bipophen gave acetato complexes and not hydroxo complexes when the metal acetates used in the synthesis.

ii) Halo complexes

The bands due to M-Cl and M-Br vibrations are usually observed below 400 cm^{-1} which was out of range of the instrument used in this study.[124,130] However, the microanalytical data showed that two halogen atoms per metal ion were present in the Mn(II), Co(II), Ni(II) and Cu(II) complexes and three halogen atoms per metal ion were present in the Cr(III) and Fe(III) complexes. The non-conducting nature of these complexes indicated that the halogen atoms were coordinated to metal ions.

iii) Nitrato complexes

In the spectra of the nitrato complexes Cr(III), Mn(II), Fe(III), Ni(II) and Cu(II) bands appeared in the ranges of 1467-1443, 1334-1326 and 1043-1033 cm^{-1} and were assigned to the N-O vibrations of unidentate nitrate ions.[94,132,133] The stochiometry and non-conducting nature of these complexes further confirmed the presence of coordinated nitrate ions. But the spectrum of nitrato complex of Co(II) showed a sharp band at 1384 cm^{-1} that corresponded to the frequency of free nitrate ion.[124,130,133] The molar conductance value and the stochiometry also confirmed the presence free nitrate ions in this complex.

iv) Perchlorato complexes

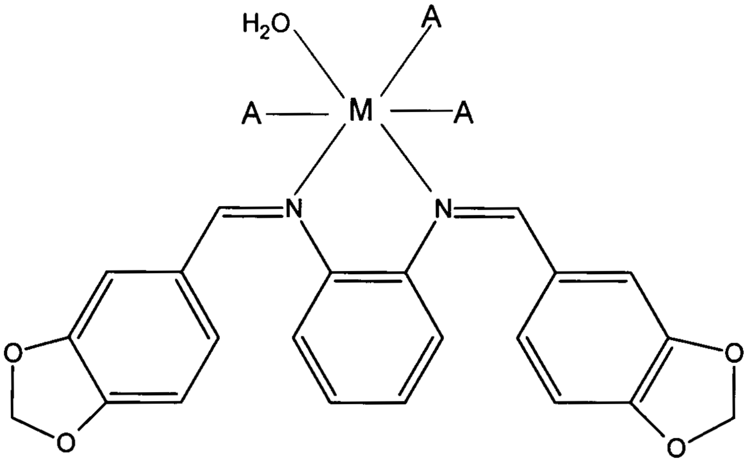
The IR spectra of the perchlorato complexes of Cr(III), Mn(II), Fe(III) Co(II) and Cu(II) showed bands in the ranges 1119-1116, 1039-1034 and 938-946 cm^{-1} which were assigned to the unidentate perchlorate ions present in them.[124,134] The analytical data and non-conducting nature of these complexes confirmed this. The spectrum of perchlorato complex of Ni(II) showed a sharp band at 1115 cm^{-1} which was assigned to free perchlorate ion.[124,130] This was further confirmed by molar conductance value and stochiometry of the complex.

7. Thermal analysis

Thermograms of three complexes of Bipophen were recorded. The decomposition patterns agreed well with the suggested formulae. Metal oxides were formed as end products and were identified chemically. Independent pyrolytic studies were also carried out and they agreed to the thermograms. The details of the thermal studies are given in the Part II of this thesis.

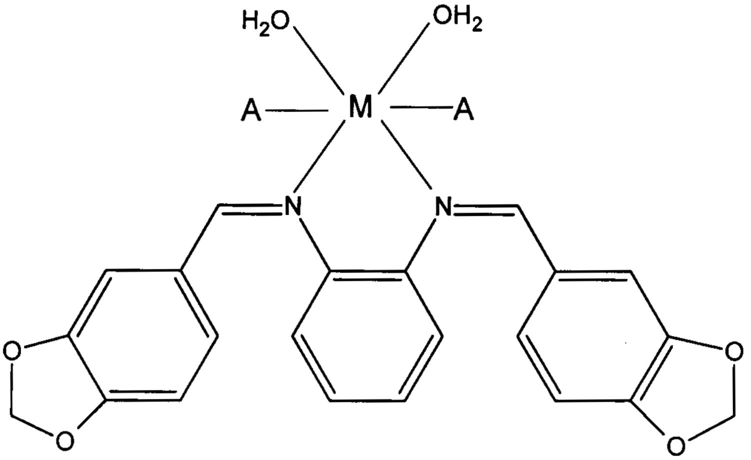
C. Conclusions

The complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with bis(piperonaldehyde)-*o*-phenylenediimine were synthesized. The physico-chemical properties of all the complexes were studied and they were found to have the general formulae given in the section B-2 of this chapter. In all the complexes, Bipophen acted as a neutral bidentate- or tetradentate ligand. The dioxymethylene groups offered two additional coordination sites in the cases where Bipophen acted as a tetradentate ligand. Unlike the ligands, Bipiren and Bipirpen, discussed in the previous chapters, Bipophen did not show bridging nature in its complexes. The benzene ring, intervening the coordinating nitrogen atoms might be responsible for this. Similarly, Bipophen reacted with all the metal acetates used in the synthesis to give acetato complexes and not hydroxo complexes as in the cases of Bipiren and Bipophen. It was found that the types of coordination and geometries of the complexes depended on the nature of the metal ions and coordinating anions. The microanalytical-, spectral-, magnetic-, conductance- and thermal data were logically correlated, and the formulae and the structures (Fig 2-8) of the complexes were established.



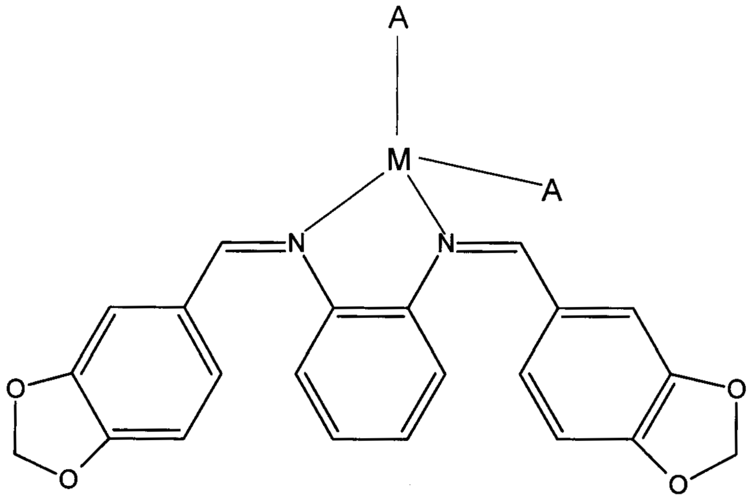
where M = Cr^{3+} or Fe^{3+} and A = CH_3COO^-, Cl^-, Br^-, NO_3^- or ClO_4^-

Fig-2 Structure suggested for Cr(III) and Fe(III) complexes of Bipophen



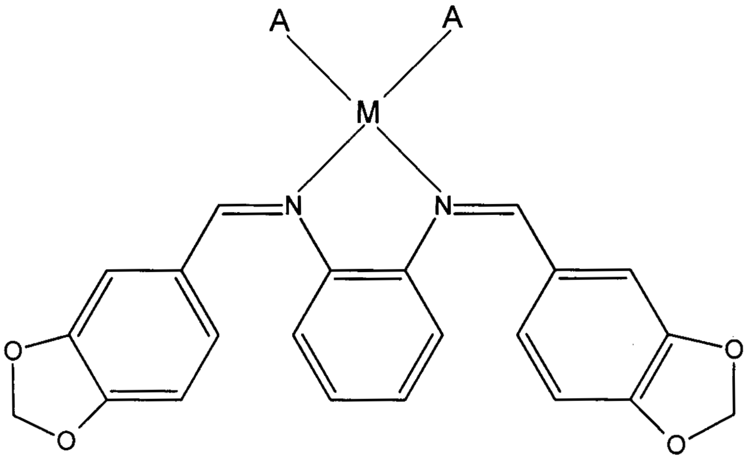
where M = Mn^{2+} and A = CH_3COO^-, Cl^-, Br^-, NO_3^- or ClO_4^-
or M = Co^{2+} and A = CH_3COO^- or M = Ni^{2+} and A = Cl^-

Fig-3 Structure suggested for Mn(II) Bipophen complexes, $[CoL(CH_3COO)_2(H_2O)_2]$ and $[NiLCl_2(H_2O)_2]$, where L = Bipophen



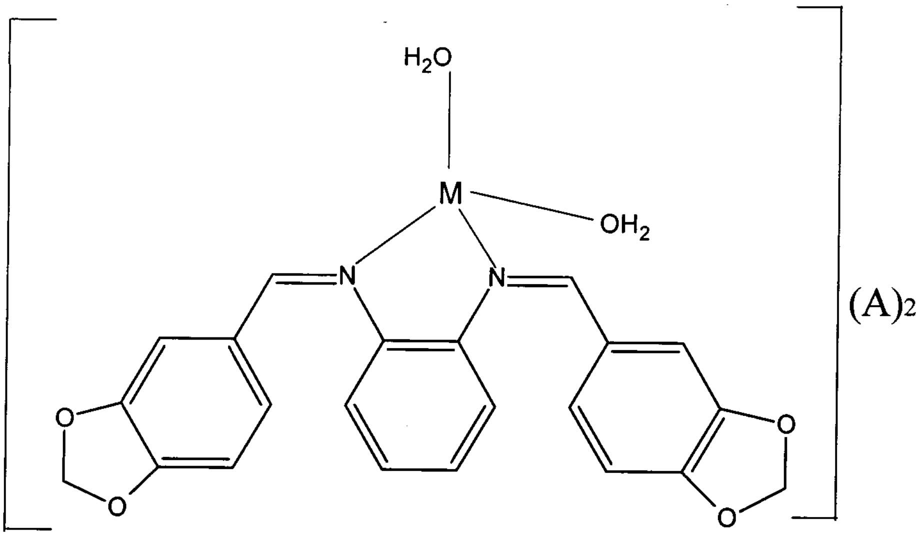
where M = Co^{2+} and A = Cl^-, Br^- or ClO_4^-

Fig-4 Structure suggested for $[CoLCl_2]$, $[CoLBr_2]$ and $[CoL(ClO_4)_2]$,
where L = Bipophen



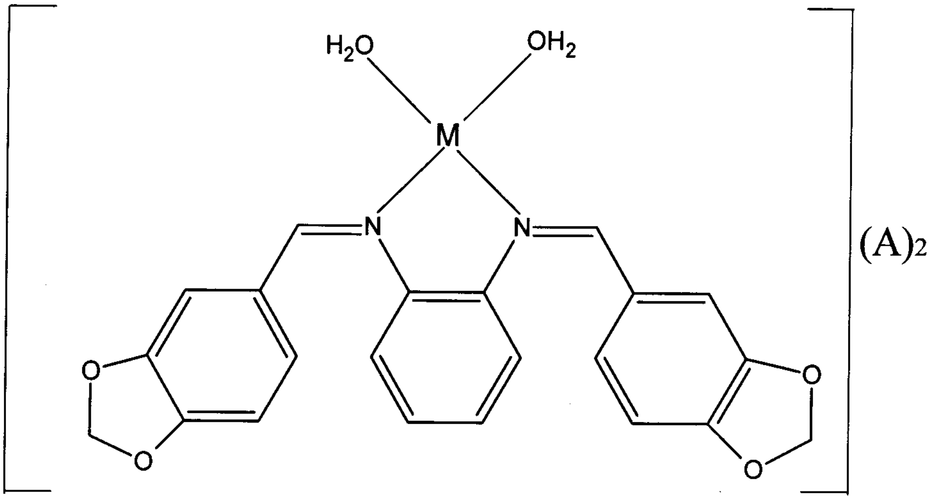
where M = Ni^{2+} or Cu^{2+} and A = CH_3COO^-, Br^- or NO_3^-

Fig-5 Structure suggested for $[NiL(CH_3COO)_2]$, $[NiLBr_2]$, $[NiL(NO_3)_2]$
$[CuL(CH_3COO)_2]$, $[CuL(Br_2]$ and $[CuL(NO_3)_2]$,
where L = Bipophen



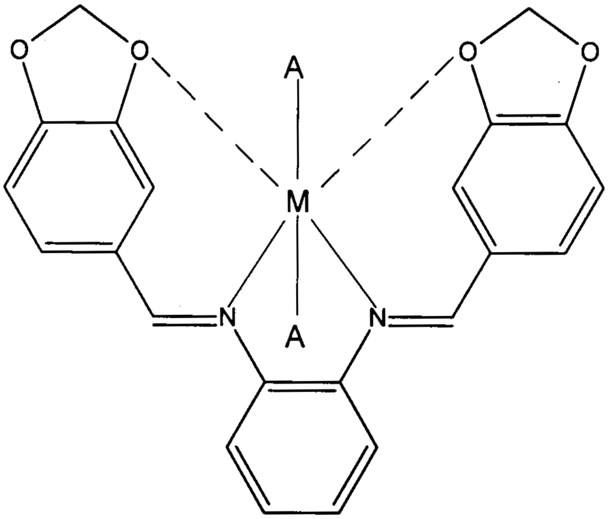
where M = Co^{2+} and $A^- = NO_3^-$

Fig-6 Structure suggested for $[CoL(H_2O)_2]\ (NO_3)_2$,
where L = Bipophen



where M = Ni^{2+} and $A^- = ClO_4^-$

Fig-7 Structure suggested for $[NiL(H_2O)_2]\ (ClO_4)_2$,
where L = Bipophen



where M = Cu^{2+} and A =Cl^-, ClO_4^-

Fig-8 Structure suggested for [$CuLCl_2$] and [$CuL(ClO_4)_2$], where L = Bipophen

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PART II

THERMAL STUDIES

CHAPTER I

INTRODUCTION

Thermal analysis is a broad term which encompasses a spectrum of related techniques. Whatever may be the specific technique, the dependence of a physical parameter of a substance is determined as a dynamic function of temperature. It may be defined as a group of techniques in which a property of the sample is monitored against time or temperature, while the temperature of the sample in a specified atmosphere is programmed.[1] The most commonly used techniques include thermogravimetric analysis (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). TG is a technique in which the mass of the sample is monitored, while DTA monitors the difference in temperature between the sample and a reference material as a function of furnace temperature or time and DSC monitors the difference in energy inputs between the sample and a reference material as a function of temperature.[2-5]

A. Thermogravimetric analysis (TG)

In this technique, the mass of a substance in an environment, heated at a controlled rate, is recorded as a function of temperature, *i.e.*, $w = f(T)$ at a constant heating rate, dT/dt or mass as a function of time, *i.e.*, $w = f(t)$ at a constant temperature. The resulting mass change versus temperature curves can give information about thermal stability and decomposition pattern of the sample, thermal stability and composition of any intermediate compound that may be formed, composition of the residue, if any and also the temperature of inception, maximum rate and completion of decomposition. The analytical instrument used is thermobalance with a furnace programmed for linear rise in temperature with time. TG curve is affected by factors like heating rate, furnace atmosphere, amount of sample, nature of sample, particle size, heat of reaction, *etc.*[2-8]

Manual differentiation of the normal thermogravimetric curve or suitable instrumentation can yield the derivative thermogram (DTG). The relationship between the rate of weight change and temperature or time is expressed by derivative thermogravimetric curve, *i.e.*, dw/dt = f (T or t). DTG curves have a number of peaks instead of steps. In these curves the area under peaks is proportional to the total weight change. DTG curves have certain similarities to DTA curves which allow to a certain extent comparisons to be made.[8-10]

B. Differential thermal analysis (DTA)

The temperatures of a sample and a thermally inert reference material are compared as sample is heated or cooled at a uniform rate. In this differential method, the temperature difference ΔT, between the sample and reference material is recorded as a function of temperature. It may be noted that the reference substance should not undergo decomposition or phase transition in the temperature range of interest.[6] DTA curves give information about enthalpy changes occurring during heating and they yield valuable informations complementary to those derived from TG curves.[4-6]

C. Kinetics

The methods of thermal analysis are widely used in chemical sciences and natural sciences, such as geology, mineralogy and metallurgy. Thermogravimetry, differential thermal analysis and other thermo-analytical methods can be used to study the solid state thermal decomposition and heterogeneous reaction kinetics[1-4] and it is possible to evaluate kinetic and thermodynamic parameters, such as rate constants, activation energy, order of reaction, frequency factor, entropy of activation, enthalpy of activation, free energy of activation, enthalpy of transition, *etc.*[1-12] The solid state transformations which an be studied by thermal analysis are summarized by Lukaszewski and Redfern [13] as follows.

1) $A(s) \rightarrow B(s) + C(g)$

2) $A(s) + B(s) \rightarrow AB(s) + C(g)$

3) $A(s) + B(s) \rightarrow C(s) + D(g)$

4) $A(s) \rightarrow B(s) + C(l)$

5) $A(s) + B(g) \rightarrow C(s)$

The above reactions may occur consecutively or simultaneously.[1] Thermogravimetry is generally concerned with only a single substance and, therefore, applicable only in the reactions (1) and (5). Other techniques, such as DTA could be used for reactions (2), (3) and (4). Of these different types, much attention has been devoted to kinetic studies of the reactions of type (1).

When the kinetic study is based on the observation of weight change, two approaches are possible in principle, *viz*, the static or isothermal method and the non-isothermal or dynamic heating method. In the isothermal method weight change is measured as a function of time at a constant temperature. The non-isothermal method involves the determination of the degree of transformation as a function of time during a linear increase of temperature.[2] The major advantage of the non-isothermal method over the isothermal method is that it requires a lesser number of experimental data and the kinetic parameters may be determined from a single thermogravimetric curve for the whole range of temperature.[2-5] Similarly, when the sample undergoes considerable reaction on being raised to required temperature , the results obtained by non-isothermal methods are more reliable. The main disadvantage of non-isothermal method is that the reaction mechanism cannot be usually determined and it gives only an overall kinetic expression. Also results in this method are more susceptible to procedural factors. However, non-isothermal method is used more commonly because it requires only a single TG experiment to compile results. Therefore, the non-isothermal method is adopted in the present study.

1. <u>The non-isothermal kinetics</u>

Two different approaches can be adopted for the evaluation of kinetic parameters of thermal decomposition reactions under non-isothermal conditions.[14] The non-mechanistic or general kinetic study is a simple extension of homogenous kinetics to solid state kinetics which is usually heterogeneous. The mechanism based study gives the physico-chemical description of the process. However, only the non-mechanistic approach was adopted in the present study.

The analytical determination of specific reaction quantities E_a and A is based on experiments performed at programmed temperature conditions. Therefore, the kinetic law and Arrhenius equation can be considered here. The foundation for calculation of kinetic data from a TG is based on the kinetic equation,

$$-dx/dt = kx^n \tag{1}$$

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

$$k = A\, e^{-Ea/RT} \tag{2}$$

where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T, the absolute temperature. The mathematical treatment of kinetic equations makes use of one of the following three methods of evaluation,

a) integral method b)differential method c) approximation method.

The relationship of x to mass-loss is given by the equation,

$$-dx = (w_o/ w_\alpha)dw \tag{3}$$

where w_o is the initial mass of the sample and w_α is the maximum mass loss. On integration of the left hand side of the equation (3) between w_α and x and the right hand side between 0 and w

$$\int_{w_\alpha}^{x} dx = -\int_{0}^{w} (w_o/ w_\alpha)\, dw \tag{4}$$

$$x = (w_o/ w_\alpha)(w_\alpha - w) \tag{5}$$

By substituting equations (5) and (2) in equation number (1) and by differentiating the logarithmic form, an expression of differential form is obtained. Integral method uses the integrated form of equation number (1), after substitution of mass-loss, w, in equations (3) and (5) *a) The integral method using the Coats-Redfern equation*[15,16]

Integral methods are generally considered to be more accurate and give quite reliable results. The disadvantages are that, the prior determination of n is required and temperature integral has to be approximated.

This method considers reactions of the type,

$$aA(s) \rightarrow bB(s) + cC$$

The rate of decomposition of A may be represented as,

$$d\alpha /dt = k(1-\alpha)^n \tag{6}$$

where $\alpha = w/w_\alpha$ the fraction of A decomposed at time, t; w is the mass-loss at time, t; w_α is the maximum mass-loss; n is the order of the reaction and k the rate constant.

At a constant rate of heating ϕ (K min^{-1})

$$\phi = dT/dt \tag{7}$$

By combining equations (6), (2) and (7) and on integrating we get,

$$\int_0^\alpha d\alpha/(1-\alpha)^n = (A/\phi)\int_0^T e^{(-Ea/RT)}\, dT \tag{8}$$

The left and side of the equation (8) as two different solutions depending upon the value of n

$$1-(1-\alpha)^{(1-n)}/(1-n) \qquad \text{for } n \neq 1 \text{ and}$$

$$-\ln(1-\alpha) \qquad \text{for } n = 1$$

In both cases the right hand side of the equation has the solution

$$(ART^2/\phi E_a)(1-2RT/E_a)\, e^{(-Ea/RT)} \tag{9}$$

After taking logarithms, the following equations are obtained.

$$\ln[1-(1-\alpha)^{(1-n)}/(1-n)\,T^2] = \ln[(AR/\phi E_a)(1-2RT/E_a)] - E_a/RT, \qquad \text{for } n \neq 1 \qquad (10)$$

and $$\ln[-\ln(1-\alpha)/T^2] = \ln[(AR/\phi E_a)(1-2RT/E_a)] - E_a/RT, \qquad \text{for } n = 1 \qquad (11)$$

The term, $\ln[(AR/\phi E_a)(1-2RT/E_a)]$ is practically constant for the thermal decomposition reactions of the above mentioned types and the plots of,

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

$\ln[-\ln(1-\alpha)/T^2]$ vs. $1/T$ for $n = 1$

result in a straight line of slope $-E_a / R$ for correctly chosen value of n. Using computer program, the best fit-value of n is determined for the decomposition of complexes and kinetic parameters are calculated based on the above non-mechanistic integral equations (10) and (11). E_a is calculated from the slope and A is found out from the intercept. The entropy of activation ΔS^* is found from the equation

$$A = (kT_s/h).e^{(\Delta S^*/R)}$$

where k is the Boltzman's constant, h is the Planck's constant and T_s is the peak temperature.

D. Thermal decomposition studies on metal complexes

Thermal decomposition studies on metal complexes give supplementary, but valuable informations regarding the structure of metal complexes. The weight change versus temperature curve affords knowledge about the thermal stability and composition of a complex. A few examples, cited here from the literature, illustrate the importance of thermal analysis as a valuable tool for the structural elucidation of metal complexes. The kinetic parameters like activation energy, Arrhenius factor, entropy of activation, *etc*, can be calculated for various stages of decomposition using different methods.[17-19]

Mandlik *et.al.*[20] reported the synthesis characterisation and thermal decomposition studies of the complexes of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO_2(VI) with a new Schiff base, 2,5-dihydroxyacetophenone isonicotinoyl hydrazone (H_2L). According to the report, the Schiff base behaved as flexidentate ligand and commonly coordinated through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of the azomethine group. Thermograms of Cr(III), Mn(III) and Fe(III) complexes indicated decompositions in two stages. The elimination of lattice- or coordinated water molecules took place in the first stage and the organic ligand degradated in the second stage. They were stable up to 60 °C, elimination of one lattice and one coordinated water molecule took place in the ranges 60–120 °C and 150–220 °C, respectively, in these complexes. The VO(IV) and UO_2(VI) complexes were stable up to 250 °C, indicating the absence of lattice or coordinated water molecules. Above 250 °C a gradual, but continuous mass-loss up to 600–680 °C occurred for all the complexes and finally horizontal curves were observed corresponding to the final stable pyrolysis products, Cr_2O_3, Mn_3O_4, Fe_2O_3, V_2O_5, ZrO_2 and U_3O_8, respectively. The activation energy was calculated by Broido and Horowitz-Metzger methods and comparable values were reported. The decomposition followed first order kinetics in all cases. On the basis of thermal activation energy, the thermal stabilities of the compounds were found to be in the order, VO(IV) > Fe(III) > Mn(III) > UO_2(VI) > Zr(IV) > Cr(III) > H_2L. The entropy of activation, free energy of activation and frequency factor had also been calculated. It was suggested that the negative value for entropy of activation indicated that the activated complexes had more ordered or more rigid structures than the reactants or intermediates and the reactions were slower than normal.

The thermal decomposition of complexes of Co(III) with Schiff base ligands was studied by Leovac *et.al.*[21] They synthesised, characterised and analysed the thermal decomposition of mixed ligand Co(III) complexes with salicylaldehyde semi-, thiosemi- and isothiosemi- carbazones and pyridine. All the compounds were reported to undergo continuous thermal decomposition and the pattern did not depend on the carrier gases up to 600 K. In argon, above this temperature the decomposition rate decreased and was not completed up to 1000 K. But in air, the decomposition of some compounds was accompanied by burning of the sample. In all cases, the decomposition of the compounds began with the departure of the pyridine ligand, followed by decomposition of the Schiff base and the end product was cobalt(III) oxide. The thermal stabilities of the investigated compounds were found to be comparable and the decomposition began around 420 K. The complex, $[Co^{III}(L^1)(py)_3][Co^{II}Cl_3(py)]$, where L^1 = salicylaldehyde semicarbazone exhibited the highest thermal stability and it decomposed above 470 K. The decomposition of $[Co(L)(py)_3]I\ 0.5I_2$, where L = salicylaldehyde semi-, thiosemi- or isothiosemi-carbazones, was followed by coupled mass spectrometry up to 600 K. As the first departing group, pyridine and its decomposition products were identified. The DSC curves were recorded in an inert atmosphere (argon) and they indicated endothermic decomposition processes.

The mode of thermal decomposition and thermal stability of transition metal complexes with dibenzo[b,f][1:5]diazocine-6:12-dione were investigated by

Saeed-ur-Rehman *et.al.*[22] on the basis of thermal decomposition curves in static air atmosphere. The dibenzo[b,f][1:5]diazocine-6:12-dione, also as called PHZD, a derivative of phenhomazine, is an eight membered cyclic diamine which was reported to behave as a bidentate ligand. Complexes of Ni(II), Cu(II), Co(II), Cd(II), Zn(II) and Hg(II) with this ligand, having the general formula $M(PHZD)_2X_2$, where X = Cl, Br or I, were synthesised and identified. The thermo-analytical investigations indicated that Ni(II), Cu(II), Co(II) and Zn(II) complexes had undergone two-step changes as temperature was raised. The decomposition of these complexes led to the formation of metal oxide at a temperature above 600 °C. In the temperature range of 110-600 °C, the main reaction was the elimination and evolution of PHZD moieties and halogen molecules. According to proposed mechanism one PHZD moiety was eliminated in the first stage and the remaining PHZD moiety and chlorine molecule in the second stage. In the case of the Cd(II) and Hg(II) complexes, the thermal decomposition took place in a single step. Non-equivalence of PHZD ligands had been inferred because of their elimination at different temperatures. On the basis of the initial temperature of decomposition, the following sequence of thermal stability had been suggested,

$$Cd > Zn > Hg > Co > Cu > Ni.$$

Arif *et.al*[23] studied thermal decomposition reactions of various copper(II) fluoride complexes of the general type $Cu(L)FxH_2O$, where L = asparagines (asp), arginine (arg), methionine (meth) or proline (pro) and x = 3 to 4, in nitrogen atmosphere using TG and DTA techniques. A possible mechanism of decomposition was suggested on the basis of the patterns of their pyrolysis. The residues obtained at the end of various decomposition processes were identified through IR spectrometry.

The kinetic parameters, such as, energy of activation (Ea) and order of reaction (n) were also determined. In general, the thermal decomposition of the complexes could be described by the following equations.

$$Cu(A)F\ xH_2O \rightarrow Cu\ (A)\ F\ nH_2O + (x - n)\ H_2O$$

$$Cu(A)F\ nH_2O \rightarrow CuF\ nH_2O + A$$

$$CuF\ nH_2O \rightarrow CuF_2 + nH_2O$$

(A = asp, meth, arg or pro; n = 1, 2 or 3 and x = 3 or 4)

With the initial decomposition temperature as the criterion of thermal stability, the thermal stability of these complexes decreases in the following order:

$$Cu\ (arg)F\ 4H_2O > Cu\ (meth)\ F\ 3H_2O > Cu\ (asp)\ F\ 3H_2O = Cu\ (pro)F\ 4H_2O$$

On the basis of activation energy as well, the highest thermal stability was displayed by the complex, Cu(arg)F $4H_2O$. The authors put forward the following conclusions from the study: (i) all the amino acid complexes showed 3-stage degradation, which also indicated the similarity of the mode of degradation, (ii) the intermediates for different stages were not stable and started decomposing immediately after their formation, (iii) the ligands appeared to be more stable than their corresponding metal complexes, (iv) in all the cases, CuF_2 was the residue, and was stable even above 800 °C, (v) the elimination of water molecules above 300 °C, suggested that these were strongly coordinated in the crystal lattice of complexes and (vi) the results of the present study revealed that thermal analysis could be useful for distinguishing the coordinated water molecules from hydrogen bonded water molecules.

Mojumdar *et.al.*[24] investigated the thermal decomposition of the following complexes (a) $Mg(ac)_2(Et_2na)_2\ 2H_2O$, (b) $Mg(Cl_3ac)_2(Et_2na)_2\ 3H_2O$ and (c) $Cu(Cl_3ac)_2(Et_2na)_2\ 3H_2O$, where ac = CH_3COO-, Cl_3ac = Cl_3CHCOO-, and Et_2na

= N,N-diethylnicotinamide), in air in the temperature range of 20-1000 °C by means of thermogravimetry (TG) and differential thermal analysis (DTA). The composition of the complexes, the solid intermediates and resultant products of thermolysis had been identified by means of elemental analyses and complexometric titrations. The possible schemes for the decomposition of the complexes were also suggested. In the first stage, water molecules were released. The loss of the volatile ligand, (Et_2na) occurred in the second stage. Both the Et_2na molecules were lost in this step. The thermal stabilities of the complexes were reported to be in the sequence: (c) < (a) < (b). The final products of the thermal decomposition were MgO in the case of (a) and (b) and CuO in the case of (c). The IR, EPR, and electronic spectral analyses indicated that Et_2na was coordinated to Mg(II) and Cu(II) through the nitrogen atom of its heterocyclic ring. The following scheme was proposed for thermal decomposition of the copper complex.

$Cu(Cl_3ac)_2(Et_2na)_2\ 2H_2O \rightarrow Cu(Cl_3ac)_2(Et_2na)_2 + 2H_2O$ (110-230°C)

$Cu(Cl_3ac)_2(Et_2na)_2 \rightarrow Cu(Cl_3ac)_2 + 2Et_2na$ (230-600°C)

$Cu(Cl_3ac)_2 \rightarrow CuO + \text{G. products}$ (600-790°C)

The DTA curve for the complex exhibited an endothermic peak at 130 °C corresponding to the loss of two molecules of water and two exothermic peaks at 340 °C and 660 °C corresponding to the decomposition reactions of two molecules each of Et_2na and Cl_3ac, respectively, with simultaneous formation of CuO. The elimination of Et_2na was an endothermic process in the complexes (a) and (b) and an exothermic process in the complex (c).

The thermal decomposition of Co(II), Cu(II), Zn(II) complexes with a new Schiff base ligand was studied by Soliman *et.al.*[12] The bivalent, tridentate ONS donor Schiff base (H_2L) was prepared by condensation of *o*-vanillin (3-methoxy salicylaldehyde) with 2-aminothiophenol. Complexes of Co(II), Cu(II) and Zn(II) with the ligand in 1:1 and 1:2 molar ratios were prepared. On the basis of spectral, elemental and thermal analyses the following formulae were suggested for the complexes, *viz*, $[ML.H_2O]H_2O$, where M = Co(II); $[ML.H_2O]$, where M = Cu(II) or Zn(II); $[M(HL)_2]H_2O$, where M = Zn(II) and $[M(HL)_2]$, where M = Co(II) or Cu(II). The dehydration of $[CoL.H_2O]H_2O$ and $[Zn(HL)_2]H_2O$ were reported to occur in the range 50-120 °C and the weight-loss corresponded to the loss of one water molecule, in each case, identified as water of hydration. The cobalt 1:1 complex was reported to lose one more water molecule above 150 °C and was suggested as the coordinated molecule. $[CuL.H_2O]$ and $[ZnL.H_2O]$ also lost one molecule of water above 150 °C which was identified as coordinated molecule. In all the complexes, decomposition of the Schiff base moiety was reported to take place in two steps, *via*, formation of unstable intermediates. The decomposition started at 195-285 °C range and ended at 490-750 °C range with simultaneous oxide formation. The kinetic- and thermodynamic parameters, such as, order of reaction, activation energy, entropy of activation, enthalpy of activation and free energy of activation were calculated on the basis of Horowitz-Metzger and Coats-Redfern equations.

E. Scope of the present investigation

The literature survey made it clear that studies on thermal decomposition of metal complexes of Schiff bases are helpful in establishing their structures. Similarly, thermogravimetry gives ideas about the stabilities and decomposition patterns of complexes. It is also evident that kinetic- and thermodynamic parameters of decomposition can be calculated from thermograms. Hence, thermogravimetric analysis of selected complexes of the ligands, bis(piperonaldehyde)ethylenediimine, bis(piperonaldehyde)-1,3-propanediimine, bis(piperonaldehyde)-*o*-phenylenediimine had been taken up here. The thermograms in air, of the chloro complexes of Co(II), Ni(II) and Cu(II) with the above mentioned Schiff base ligands were recorded. Both TG and DTG techniques were adopted.

Based on TG, the thermal stabilities and decomposition stages of the complexes were discussed .The temperature regions of stability, the temperature of inception and maximum rate of decomposition had been noted. The stages of decomposition were assigned and the final residues were identified.

The non-isothermal TG curves have been subjected to mathematical analysis using the integral method of Coats-Redfern. The kinetic parameters, *viz*, order of reaction, activation energy, frequency factor and entropy of activation were calculated. The enthalpies of activation and free energies of activation for various decomposition steps have also been calculated using the following relations.[12]

$$\Delta H^* = E_a - RT_s$$

$$\Delta G^* = \Delta H^* - T_s\Delta S^*$$

where T_s = the peak temperature of the decomposition stage investigated.

CHAPTER II

THEMAL ANALYSIS OF Co(II), Ni(II) AND Cu(II) COMPLEXES OF BIS(PIPERONALDEHYDE)ETHYLENEDIIMINE, BIS(PIPERONALDEHYDE)-1,3-PROPANEDIIMINE AND BIS(PIPERONALDEHYDE)-*O*-PHENYLENE DIIMINE

The results of thermal decomposition studies of the chloro complexes of Co(II), Ni(II) and Cu(II) with the three Schiff base ligands, bis(piperonaldehyde) ethylenediimine (Bipiren), bis(piperonaldehyde)-1,3-propanediimine (Bipirpen) and bis(piperonaldehyde)-*o*-phenylenediimine (Bipophen) are described in this chapter. Thermograms of these complexes were recorded and their stage-wise decompositions were studied in detail. The end product in each case had been identified by chemical analysis and independent pyrolytic studies. The kinetic parameters for the different stages of decomposition were also calculated.

A. Experimental

1. Materials and methods

For the present investigation, the chloro complexes of Co(II), Ni(II) and Cu(II) with the Schiff base ligands Bipiren, Bipirpen and Bipophen were selected. Analar grade reagents and solvents were used for the synthesis of the ligands and the complexes and the procedural details are given in the first part of this thesis. All the complexes were dried, thoroughly powdered and the decomposition studies were carried out using a Perkin Elmer TGA-7 Analyzer. The heating rate of 10 °C min^{-1} in static air was used. A sample mass of 6 to 8 mg was used for all the studies. The fraction of decomposition, 'α' was determined directly from the TG curves. Independent pyrolytic studies were conducted by heating a known amount of the complex in a silica crucible at 800 °C for about 1 h. Mass-loss considerations and chemical analysis confirmed that the end products were the corresponding metal oxides.

2. Treatment of data

The instrumental TG-DTG traces were replotted in Microsoft-Excel. Thermal data for the complexes are presented in Tables 1-3. The kinetic parameters calculated from the TG data using Coats-Redfern equation are given in Tables 4-6. Calculations were done using an Excel program.

B. Results and discussion

Thermograms of 9 complexes, synthesised in the present investigation, namely, [Co_2(Bipiren)Cl_4], [Ni_2(Bipiren)$Cl_4 2H_2O$], [Cu_2(Bipiren)$Cl_4 2H_2O$], [Co_2-(Bipirpen)Cl_4], [Ni_2(Bipirpen)$Cl_4 2H_2O$], [Cu_2(Bipirpen)$Cl_4 2H_2O$] [Co(Bipophen)-Cl_2], [Ni(Bipophen)$Cl_2 2H_2O$] and [Cu(Bipophen)Cl_2] were recorded. The stage-wise decompositions of these complexes were analysed as part of their structural characterisation. Various kinetic parameters were calculated using the Coats-Redfern equation.

1. Decomposition data and kinetic parameters of chloro complexes of Co(II), Ni(II) and Cu(II) with Bipiren.

The thermal decomposition curves (TG and DTG) of Bipiren complexes are reproduced in the Figs. 1-3. The temperature intervals for various steps along with the observed and calculated mass-losses are given in Table-1. The thermal decomposition of these complexes led to the formation of metal oxides at temperatures around 600 °C. A three-stage decomposition pattern was observed for the nickel(II) and copper(II) complexes of Bipiren. The first stage corresponded to the removal of two water molecules, the second to the lose of one and two piperonal moieties respectively in Ni(II) and Cu(II) complexes. The third stage represented the removal of the rest of the ligand and four chloride ions with simultaneous formation of metal oxides.[22,25,26] The dehydration reaction took place around 150 °C, indicating the presence of coordinated water molecules in the complexes.[12,20,27] The Co(II) complex did not show any mass-loss in this range and was stable up to 220 °C. This could be taken as an indication for the absence water molecules in it.[20,28] The two stages of decomposition of the Co(II) complex were similar to the second and third stages of decomposition of the Ni(II) complex. The overall mass-loss corresponded to the formation Co_3O_4, NiO and CuO, respectively, which were confirmed by chemical analysis. The mass-loss data obtained from independent pyrolytic experiments and from the thermal studies were found to be agreeable with the formulae suggested for the complexes.

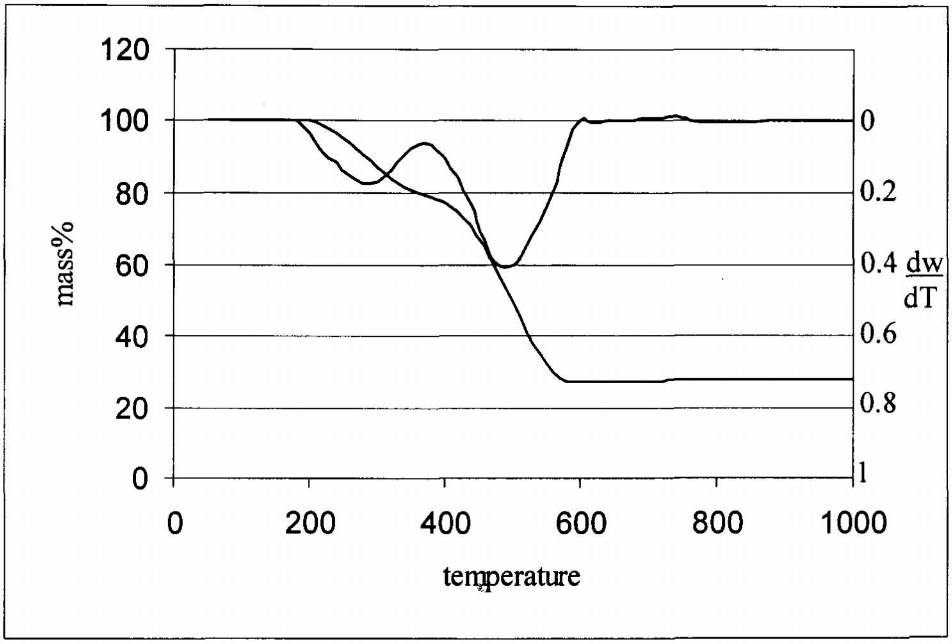

Fig-1 TG-DTG traces of [Co_2(bipiren)Cl_4]

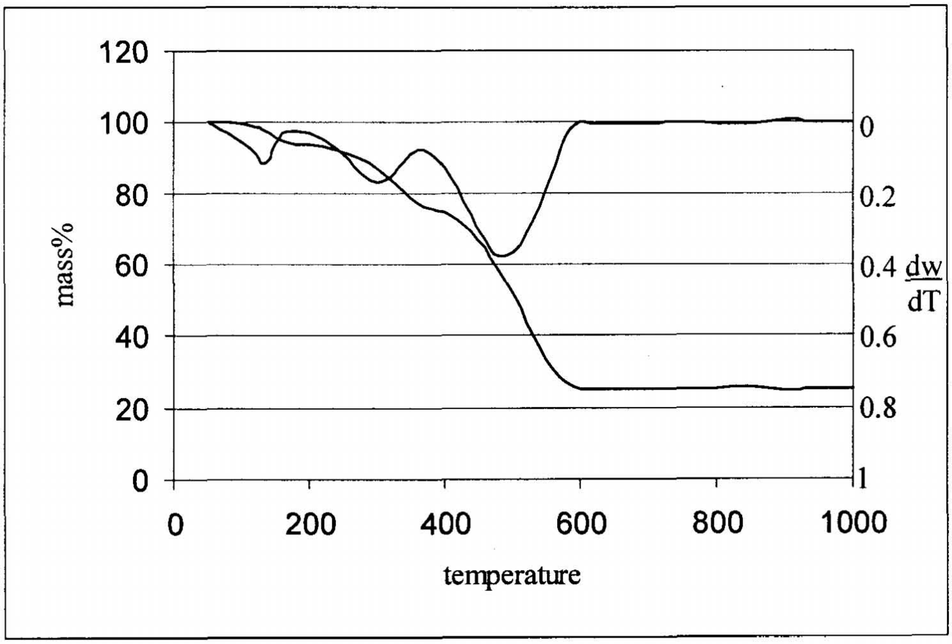

Fig-2 TG-DTG traces of [Ni_2(bipiren)$Cl_4 2H_2O$

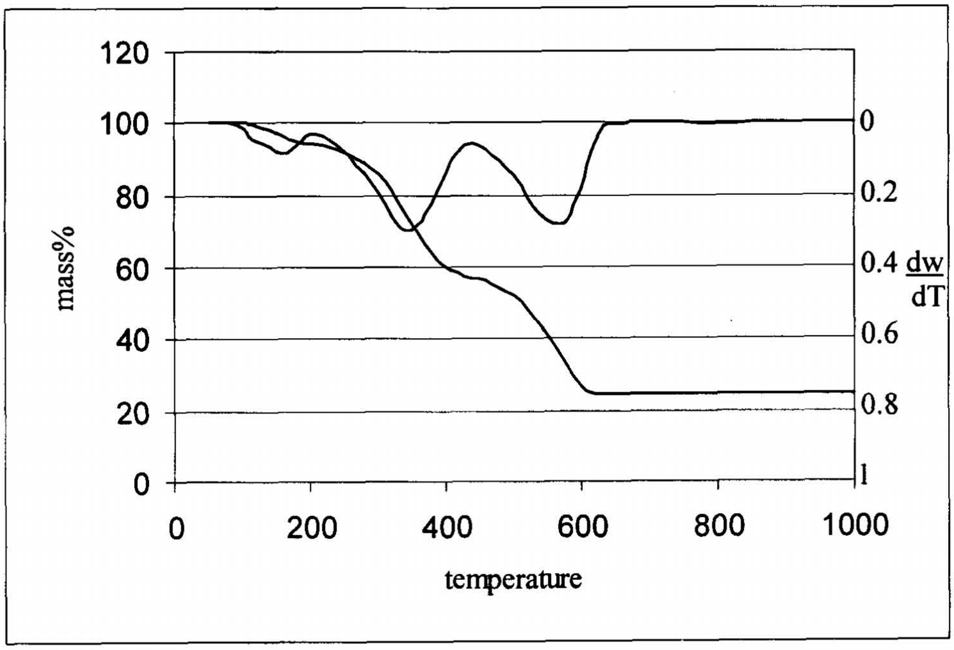

Fig-3 TG-DTG traces of [Cu_2(bipiren)$Cl_4$$2H_2O$

Table-1 Thermal decomposition data of Co(II), Ni(II) and Cu(II) Bipiren complexes

Complex	Stage	Temp range in TG	Peak temp	Loss of mass			Assignments
				From TG	Theoretical	From Pyrolysis	
Co_2LCl_4	I	220-380	290	21.3	20.7		Loss of 1 piperonal moiety
	II	380-580	490	51.4	51.8		Loss of rest of the ligand, 4 Cl^- ions & subsequent formation of metal oxide
	Total			72.7	72.5	71.9	$Co_2LCl_4 \rightarrow \frac{2}{3}Co_3O_4$
$Ni_2LCl_42H_2O$	I	110-180	135	6	5.8		Loss of $2H_2O$
	II	180-400 (220-400)*	310	19.8	19.5		Loss of 1 piperonal moiety
	III	400-600	500	48.8	50.6		Loss of remaining ligand , $4Cl^-$ ions & formation of metal oxide
	Total			75.6	74.9	75.5	$Ni_2LCl_42H_2O \rightarrow 2\ NiO$
$Cu_2LCl_42H_2O$	I	110-200	160	5.9	5.7		Loss of $2H_2O$
	II	200-460 (240-460)*	350	38.1	38.4		Loss of 2piperonal moieties
	III	460-620	560	31.2	32.2		Loss of remaining ligand, $4Cl^-$ ions & formation of metal oxide
	Total			75.2	76.3	74.7	$Cu_2LCl_42H_2O \rightarrow 2\ CuO$

*Temperature range of significant mass-loss in the stage

Table- 2 Kinetic parameters for the decomposition of Co(II), Ni(II) and Cu(II) Bipiren Complexes

Complex	Stage	E_a kJ/mol	A s^{-1}	ΔS* J/K/mol	ΔH* kJ/mol	ΔG* kJ/mol	γ	n
Co_2LCl_4	I	57.50	$5.13x10^2$	-198.31	52.81	164.47	-0.9926566	1
	II	114.59	$1.60x10^5$	-153.09	108.25	225.06	-0.9941095	1
$Ni_2LCl_42H_2O$	I	68.98	$3.01x10^6$	-123.51	65.59	115.98	-0.9997576	1
	II	59.82	$4.50x10^2$	-199.68	54.98	171.38	-0.9997821	1
	III	116.13	$1.50x10^5$	-153.76	109.70	228.56	-0.9948807	1
$Cu_2LCl_42H_2O$	I	67.51	$8.83x10^5$	-131.99	64.74	108.69	-0.9951084	1
	II	60.17	$2.58x10^2$	-204.86	54.99	182.62	-0.9972724	1
	III	149.94	$9.26x10^6$	-120.07	143.01	243.04	-0.9986331	1

The values of kinetic parameters were obtained using Coats-Redfern equation. The enthalpy of activation and free energy of activation for various decomposition steps were calculated using the following relations.[12]

$$\Delta H^{*} = E_a - RT_s$$

$$\Delta G^{*} = \Delta H^{*} - T_s\Delta S^{*}$$

The values of activation energy E_a, order parameter n, frequency factor A, entropy of activation ΔS^{*}, the enthalpy of activation ΔH^{*}, and the free energy of activation ΔG^{*} for the different stages are summarized in the Table- 2. The order parameter 'n' was chosen such that maximum value was obtained for the correlation coefficient in the Coats- Redfern equation.[15,16] The satisfactory values of correlation coefficients ($\gamma \approx 1$) in all the cases indicated good agreement with experimental data. E_a and A for different stages were found to be fairly comparable. It was also found that greater the thermal stability, the larger is the activation energy for decomposition. The negative values of entropy of activation indicated that the activated complexes had more ordered structures than that of the reactants and the reactions were slower than the normal. Comparable results were reported by other workers regarding the kinetic parameters for thermal decompositions of several metal complexes with Schiff bases.[12,20] Based on inception temperature and activation energy, for the first stage of decomposition excluding the dehydration stage, stabilities of the complexes were found to be in the order,

Cu > Ni > Co

The free energies of activation for this stage also, were in the same order.

2. Decomposition data and kinetic parameters of chloro complexes of Co(II), Ni(II) and Cu(II) with Bipirpen.

The thermograms of the Bipirpen complexes are reproduced in Figs. 4-6. The stages and temperature intervals for thermal decomposition along with the observed and calculated mass-losses are presented in Table- 3. In the case of all the three complexes, metal oxides were formed as the end products of decomposition at temperatures around 600 °C. The Ni(II) and Cu(II) complexes of Bipirpen *viz.* $[Ni_2(Bipirpen)Cl_42H_2O]$ and $[Cu_2(Bipirpen)Cl_42H_2O]$ exhibited 3-stage decomposition patterns. The removal of two water molecules occurred in the first stage. The second stage in the case of the nickel complex matched to the loss of one piperonal moiety and that in the case of copper complex indicated the lose of two piperonal moieties. In both cases, the rest of the ligand and four chloride ions were removed, with the simultaneous formation of metal oxides in the third stage.[22,25,26] The presence of coordinated water molecules in these complexes, was confirmed by the dehydration reactions, which took place around 150 °C.[12,20,27] No mass-loss was detected for the Co(II) complex up to a temperature of 200 °C indicating the absence of water molecules in it.[20,28] It decomposed in two stages which were similar to the second and third stages of decomposition of the Ni(II) complex. The total mass-losses indicated the formation Co_3O_4, NiO and CuO, respectively, which were confirmed by chemical analysis. The percentages of mass-losses from the thermal studies and from the independent pyrolytic experiments were in good agreement with theoretical values. The thermal data supported formulae, $[Co_2(Bipirpen)Cl_4]$, $[Ni_2(Bipirpen)Cl_42H_2O]$ and $[Cu_2(Bipirpen)Cl_42H_2O]$ which were suggested for the complexes.

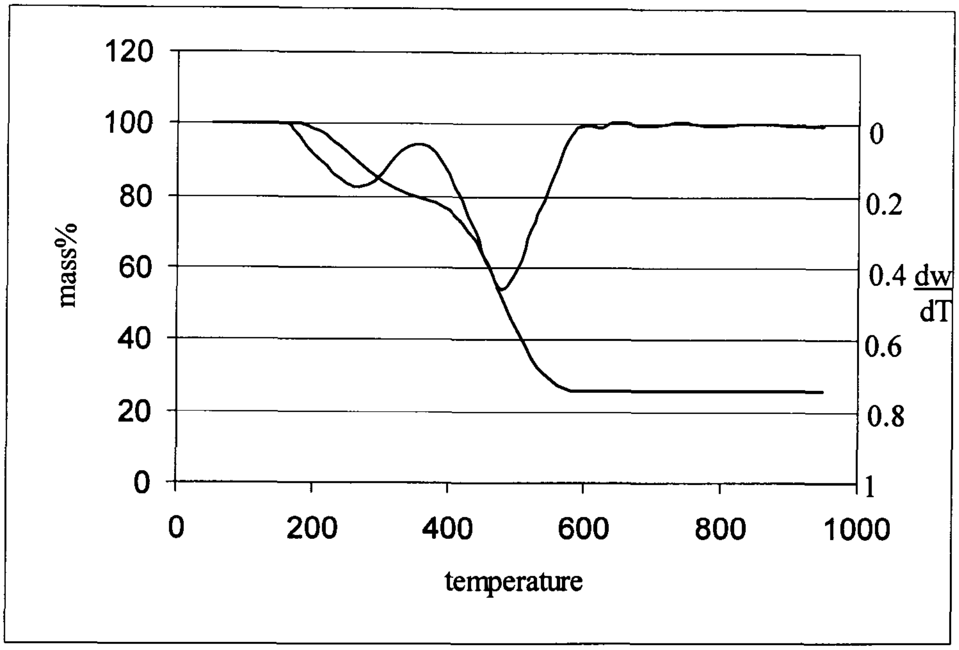

Fig-4 TG-DTG traces of [Co_2(bipirpen)Cl_4]

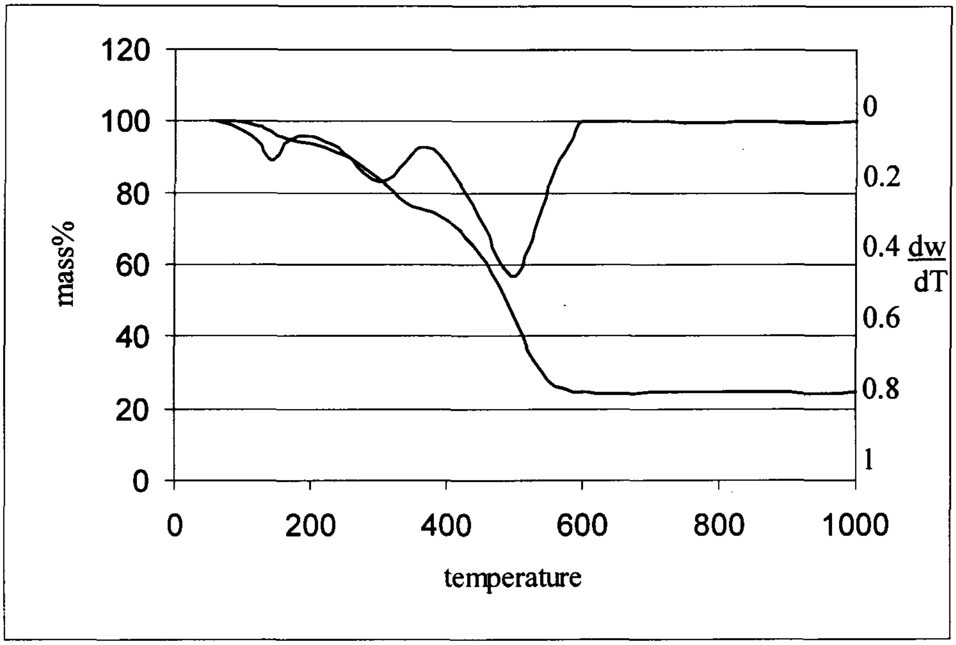

Fig-5 TG-DTG traces of [Ni_2(bipirpen)$Cl_4 2H_2O$]

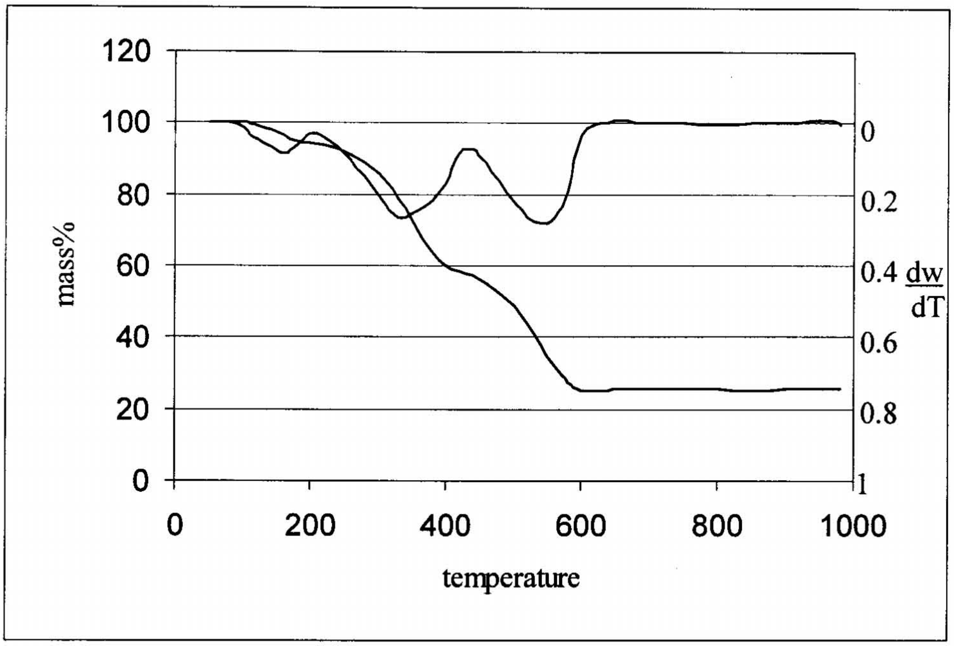

Fig-6 TG-DTG traces of [Cu_2(bipirpen)$Cl_4 2H_2O$]

Table-3 Thermal decomposition data of Co(II), Ni(II) and Cu(II) Bipirpen Complexes

Complex	Stage	Temp range in TG	Peak temp	Loss of mass			Assignments
				From TG	Theoretical	From Pyrolysis	
Co_2LCl_4	I	200-340	310	20.9	20.2		Loss of 1 piperonal moiety
	II	340-560	490	53.2	53.0		Loss of rest of the ligand, 4 Cl^- ions & subsequent formation of metal oxide
	Total			74.1	73.2	73.5	$Co_2LCl_4 \rightarrow \frac{2}{3}Co_3O_4$
$Ni_2LCl_42H_2O$	I	100-180	150	5.9	5.7		Loss of 2H2O
	II	180-380 (220-380)*	320	20.6	19.1		Loss of 1 piperonal moiety
	III	380-590	500	50.0	51.6		Loss of remaining ligand, 4Cl^- ions & formation of metal oxide
	Total			75.5	76.4	74.8	$Ni_2LCl_42H_2O \rightarrow 2\ NiO$
$Cu_2LCl_42H_2O$	I	110-200	115	5.8	5.6		Loss of 2H_2O
	II	220-440	330	37.9	37.6		Loss of 2piperonal moiety
	III	440-600	550	31.1	32.1		Loss of remaining ligand, 4Cl^- & formation MO
	Total			74.8	75.3	74.2	$Cu_2LCl_42H_2O \rightarrow 2\ CuO$

*Temperature range of significant mass-loss in the stage

Table-4 Kinetic parameters for the decomposition of Co(II), Ni(II) and Cu(II) Bipirpen Complexes

Complex	Stage	E_a kJ/mol	A s^{-1}	ΔS^* J/K/mol	ΔH^* kJ/mol	ΔG^* kJ/mol	γ	n
Co_2LCl_4	I	55.11	4.93×10^2	-198.93	50.26	166.23	-0.9939207	1
	II	113.12	1.73×10^5	-152.46	106.78	223.11	-0.9931158	1
$Ni_2LCl_42H_2O$	I	72.36	7.72×10^6	-115.97	68.84	117.90	-0.9980618	1
	II	56.73	3.71×10^2	-201.42	51.80	171.25	-0.9997985	1
	III	111.39	1.06×10^5	-156.82	104.80	229.16	-0.9967919	1
$Cu_2LCl_42H_2O$	I	66.80	7.06×10^5	-135.14	63.57	116.01	-0.9957561	1
	II	59.61	2.65×10^2	-204.38	54.60	177.84	-0.9990715	1
	III	145.59	8.83×10^6	-120.38	138.75	237.82	-0.9970325	1

The kinetic parameters were calculated by applying the Coats-Redfern equation. Table- 4 summarises the values of activation energy E_a, order parameter n, frequency factor A, entropy of activation ΔS^*, the enthalpy of activation ΔH^*, and the free energy of activation ΔG^* for the different stages. Acceptable values were obtained for the correlation coefficients ($\gamma \approx 1$) which indicated good agreement with the experimental data. The activation energies and frequency factors of these complexes for different stages were found to be fairly comparable. The values of entropy of activation were found to be negative and hence it was inferred that the activated complexes had more ordered structures than that of the reactants and the reactions were slower than the normal. Similar values were reported by other workers for the kinetic parameters of thermal decompositions of metal complexes of other Schiff bases.[12,20] Based on inception temperature and activation energy, for the first stage of decomposition, excluding the dehydration stage, stabilities of these complexes were found to be in the order

$$Cu > Ni > Co.$$

The free energies of activation for this stage also followed the same order.

3. Decomposition data and kinetic parameters of chloro complexes of Co(II), Ni(II) and Cu(II) with Bipophen

The thermograms of the Bipophen complexes, investigated here, are produced in Figs. 7-9. Table- 5 represents the temperature intervals for various steps and the observed and calculated weight-losses in these steps. The thermal decomposition of these complexes resulted in the formation of the metal oxides as end-products at temperatures around 600 °C. The Co(II) complex, *ie*, $[Co(Bipophen)Cl_2]$

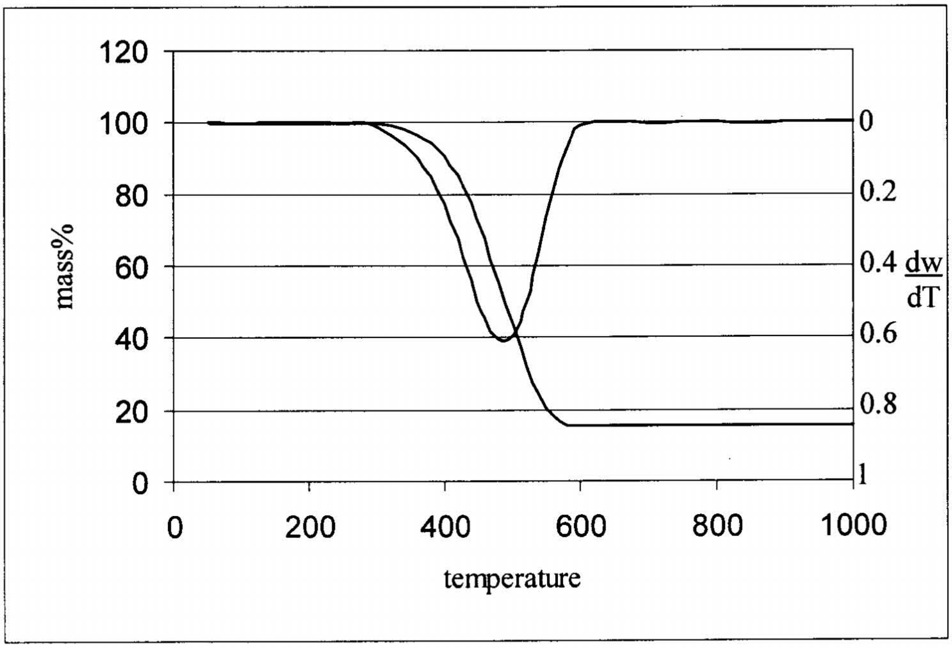

Fig-7 TG-DTG traces of [Co(bipophen)Cl_2]

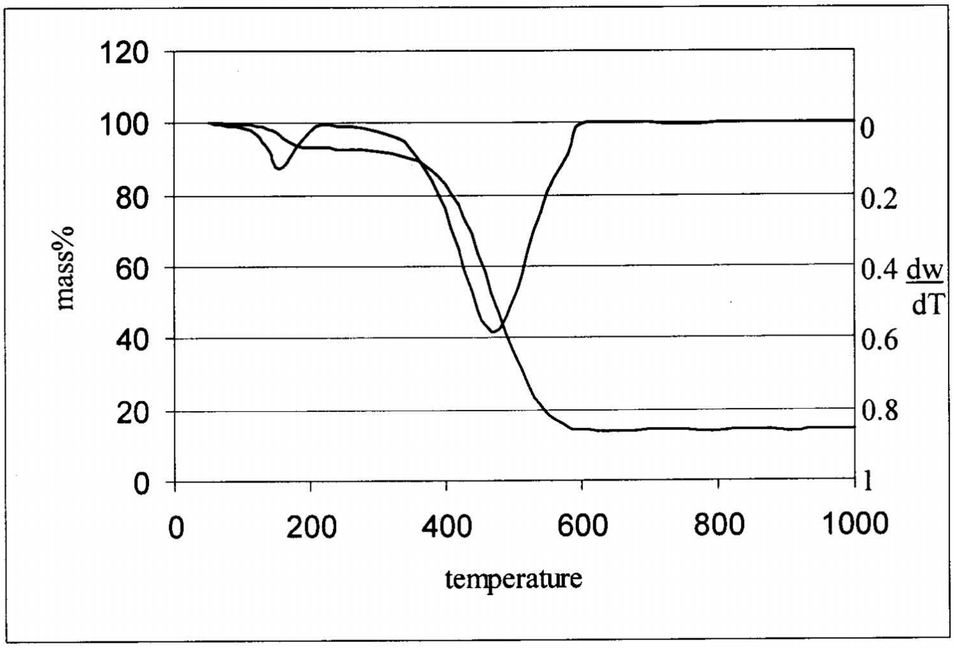

Fig-8 TG-DTG traces of [Ni(bipophen)$Cl_2 2H_2O$]

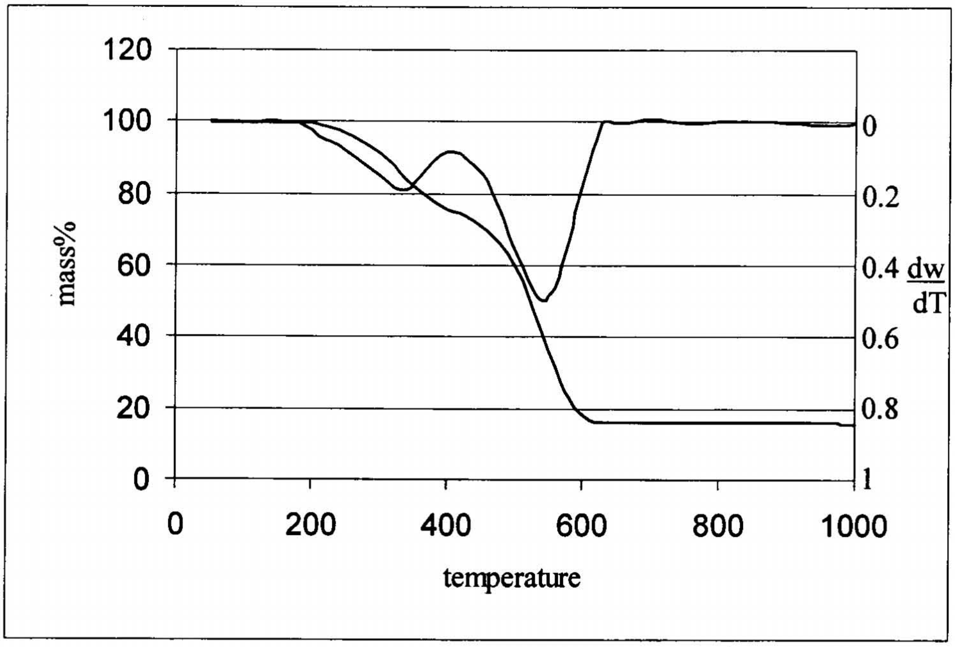

Fig-9 TG-DTG traces of [Cu(bipophen)Cl_2.2H2O]

Table-5 Thermal decomposition data of Co(II), Ni(II) and Cu(II) Bipophen Complexes

Complex	Stage	Temp range in TG	Peak temp	Loss of mass			Assignments
				From TG	Theoretical	From Pyrolysis	
$CoLCl_2$	I	310-580	490	85.7	84.2	85.2	Loss of the ligand, 4 Cl^- ions & subsequent formation of metal oxide
							$CoLCl_2 \rightarrow \frac{1}{3}Co_3O_4$
$NiLCl_2 2H_2O$	I	120-200	160	6.9	6.7		Loss of $2H_2O$
	II	300-600	470	78.8	79.4		Loss of the ligand, $4Cl^-$ ions & formation of metal oxide
	Total			85.7	86.1	85.3	$NiLCl_2 2H_2O \rightarrow NiO$
$CuLCl_2$	I	200-400	340	24.3	23.9		Loss of 1piperonal moiety
	II	400-600	560	59.6	60.4		Loss of remaining ligand, $2Cl^-$ ions & subsequent formation of metal oxide
	Total			84.1	84.3	83.8	$CuLCl_2 \rightarrow CuO$

Table-6 Kinetic parameters for the decomposition of Co(II), Ni(II) and Cu(II) Bipophen Complexes

Complex	Stage	E_a kJ/mol	A s^{-1}	ΔS^* J/K/mol	ΔH^* kJ/mol	ΔG^* kJ/mol	γ	n
$CoLCl_2$	I	84.27	$1.46 x 10^3$	-192.12	77.92	224.51	-0.9999923	1
$NiLCl_22H_2O$	I	68.51	$1.09 x 10^6$	-132.42	64.91	122.25	-0.9983816	1
	II	78.40	$6.07 x 10^2$	-199.22	72.23	220.25	-0.9985527	1
$CuLCl_2$	I	54.33	$1.32 x 10^2$	-210.16	49.23	178.14	-0.9992776	1
	II	115.98	$8.26 x 10^4$	-159.21	109.14	240.17	-0.9998626	1

underwent a single-stage decomposition in which the ligand and the two chloride ions were lost and the oxide, Co_3O_4 was formed simultaneously. The Ni(II) complex, [Ni(Bipophen)$Cl_2$2H_2O] exhibited a 2-stage decomposition, where the first stage corresponded to the removal of two water molecules in the range 120-200 °C. The dehydration reaction in this temperature range indicated that the water molecules were coordinated to the metal ion.[12,20,27] In the second stage, the ligand and two chloride ions were lost with the subsequent formation of NiO. The Cu(II) complex, [Cu(Bipophen)Cl_2] decomposed in two stages. In the first stage, one piperonal moiety was removed and in the second, the rest of the ligand and two chloride ions were lost and simultaneously cupric oxide was formed. The Co(II) and Cu(II) complexes did not show any mass loss up to 220°C. This clearly indicated that water molecules were not present in them.[20,28] The mass-loss data from independent pyrolytic experiments and the thermal studies were in good agreement and supported the formulae, suggested for the complexes.

The Coats-Redfern equation was applied to calculate kinetic parameters. The values of activation energy E_a, order parameter n, frequency factor A, entropy of activation ΔS^*, the enthalpy of activation ΔH^*, and the free energy of activation ΔG^* for the different stages are presented in the Table 6. The agreeable values of correlation coefficients ($\gamma \approx 1$) indicated good concurrence with experimental data in all the cases. E_a and A for the three complexes for different stages were found to be fairly comparable. The entropies of activation for different stages of decomposition of these complexes were found to be negative, indicating that the activated complexes had more ordered structures in comparison to the reactants and the reactions were slower than the normal. Other researchers also reported comparable values for the kinetic parameters of the thermal decomposition of metal complexes of Schiff bases.[12,20] Taking into account of the inception temperatures and activation energies for the first stage of decomposition, excluding the dehydration stage, the stabilities of the complexes were in the order,

$$Co > Ni > Cu.$$

The free energies of activation for this stage were also found to be in the same order. In comparison with the complexes of the other ligands, Bipiren and Bipirpen, the thermal stabilities of these complexes were in the reverse order. This could be attributed to the differences in decomposition reactions of the complexes of Bipophen from others and also to the differences in structures of these complexes.

C. Conclusions

The thermograms of the Co(II), Ni(II) and Cu(II) complexes of the Schiff base ligands, bis(piperonaldehyde)ethylenediimine, bis(piperonaldehyde)-1,3-propanediimine and bis(piperonaldehyde)-*o*-phenylenediimine were analysed and the stages of decomposition of each complex were logically explained. The thermograms supported and confirmed the formulae suggested for these complexes. The kinetic parameters of decomposition reactions were calculated from the thermograms by the applying the Coats-Redfern equation. The free energies of activation for different stages were also calculated and this parameter could be regarded as a reliable index for the stability of the complexes.

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PART III

ANTIFUNGAL STUDIES

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CHAPTER I

INTRODUCTION

Black pepper or *Piper nigram L,* a perennial climber, belonging to the family, *Piperacia* is one of the main exports earning spice crops of Kerala. It is believed to be originated from the high ranges of Malabar Coast of Kerala.[1] Ravages due to diseases play a major role in limiting pepper production in India.[2] Several diseases caused by fungi, bacteria, virus and mycoplasma, affect black pepper, besides nutritional disorders. The common diseases include foot-rot (quick-wilt), slow decline, stunted disease, *etc.*[2-4] Among them, foot-rot caused by *Phytophthora capsici*, is highly prevalent in almost all the pepper growing areas and is reported to inflict considerable damage to the plants. Crop lose due to foot-rot disease in Kerala is estimated to be about 10 % of the total production and in India it ranges from 20 to 30 %.[5-7]

Sudden wilting and death of plants characterise foot-rot and hence the name quick-wilt.[2] The causative agent for the disease is *Phytophthora capsici*, a devastating soil born pathogen, earlier known as *Phytophthora palmivora* MF_4.[5] This affects all parts of the plant and the infection of the underground ground portion remains undetected until a substantial portion of the root system is damaged. Hence control measures taken after noticing the symptoms become ineffective. When the fungus attacks through soil the root system is infected (root-rot) causing defoliation and complete death of the plants. Infections on the aerial portions, like leaves, spikes and stems often reach the collar causing foot-rot. The disease spreads usually in a centrifugal pattern.[8]

Phytophthora capsici, a wet weather pathogen, is active during the monsoon season (June-October) in Kerala. Contaminated soils are the main sources of inoculums of the fungus and it can survive in the infected plants for a period of 19 months.[9] The fungi spread mainly through rain splash and water.[10] The favourable conditions for the spread of this disease are heavy rainfall, high relative humidity, low temperature and shorter duration of sunshine.[10] Climatic conditions influence the life cycle of *Phytopthora*, its pathoginicity and the epidemic it causes. The distribution of inoculums decreases with distance from the infected vine and as time elapses after death of the plant. The fungus remains dormant in the form of resting spores under unfavourable conditions.[11,12]

A. Short account on *Phytophthora capsici*

Fungi, a group of spore bearing organisms lacking chlorophyll, are heterotropic in nutrition; they either infect living organisms as parasites or attack dead organic matter as saprobes or saprophytes to obtain their food. Some of the fungi form symbiotic relationship with plants as in *lichens* and *micorrhizae*. The thallus of a fungus is known as mycelium that consists of a large number of branched tubular structures each of which is individually called a hypha. The diameter of these tubular filaments may vary from 5-8 µm and they can readily be seen with the low power of compound microscope. Young mycelium is nearly transparent or hyaline and coenocytic in nature. Hyphae are usually smooth, swollen, nodose or tuberculate. Growth takes place from the tip of each hypha, but side branches of hyphae can be produced at the base. Environmental effects can cause variations in the branching pattern.

As in the case of other fungi, *Phytophthora capsici* also reproduce by vegetative, asexual and sexual means. They reproduce by asexual spores, under suitable environmental conditions, such as optimum temperature and moisture. *Phytophthora capsici* can show rapid vegetative growth depending on the nutrient status. Sporangium or more specifically a zoosporangium, which means a vessel containing zoospore, is the common characteristic of asexual spore of *Phytophthora capsici.* Sporangia are born on sporangiospores, which are similar in diameter to the hyphae. There are some species in which new sporangiospores emerge through the base of the old sporangium from which uninucleate zoospores have been released. In others new sporangiospores arise just beneath the bases of the old sporangium, that is, they are simpodial and produce more sporangia successively.[13] Sporangia may vary in size and shape. Conspicuous bud or nipple called papilla is present at the apex of the sporangia of some species. The papilla is a plug that is composed of hydrated material, which dissolves prior to the emergence of zoospore.[14-16]

In aqueous solutions or in agar media sporangium germinates by the production of germ tube that usually emerges from the tip of the sporangium (direct germination). In aqueous, medium after the temperature is reduced it germinates by the production of uninucleate biflagellate zoospores within the sporangium (indirect germination). The zoospore emerges from sporangium in a membranous vesicle that soon breaks allowing zoospores to swim away.[17-19] The vesicles of *Phytophthora* are of persistent plasma membrane in origin. The zoospores are reniform in shape with two hetrokont flagella emerging from the concave side. In *Phytopthora* a long whiplash characterize one of the flagella and shorter tinsel the other.[20] Zoospore swims for hours and eventually ceases to swim, round up and within minutes develop a cell wall; at this stage the spore is called a cyst.[21,22] Agitation, either produced artificially by shaking zoospore in a flask or naturally by their bumbing against solid surface, can induce encystement. Eventually the cysts shed their flagella and germinate by producing germtubes and mycelia. Occasionally, repeated emergence, that is, the formation of another zoospore within the cyst and its release may occur.[13,23] Zoospores are considered to be the major infectious propagules. The chlamidospore (a seed within a clock) may form terminally at the tips of hyphae or may be intercalary (between the tip and base of hyphae). It may be spherical to oval in shape and is either hyaline or deep brown. The chlamidospore may have either a thin or thick wall.

An antheridium (male component) and an oogonium (egg containing female component) constitute the sexual structure of *Phytophthora*. The oogonia are usually globose or subglobose but are, sometimes pyriform in shape. The oogonium is delimited from the hyphae by septum; the antherdium is delimited by a septum, which attaches to the oogonial incept. Oogonial incept grows through the antheridial incept. This type antheridium is known as amphigynus (surrounding the female). In some species antheridium attaches to the oogonium by contact to the lower hemispheric side of the oogonium and is called paragynus (beside the female). Meiosis or reduction division of the chromosomes from diploid to haploid nuclei occurs in the coenocytic antheridium and oogonia. The unique difference separating *Phytophthora* and other oomycetes from true fungi is the failure to form uninucleate gametes.[24-26]

The supernumerary nuclei of oogonium migrate to the periphery of the oogonium and are sequestered in the periplasm. A fertilization tube from the antheridium ruptures the oogonial wall and deposits the antheridial nucleus; a nucleus presumed to be the fusion nucleus remains along oogonial cytoplasm. The single oospore that forms within the oogonium is globose and characteristically develops a thick inner wall composed mainly of β-1,3 glucans. Prior to germination of zoospore, the haploid nuclei from the antheridium and the oogonium are fused to form the diploid nucleus. The diploid oospore germinates under suitable conditions by the production of single or multiple germ tubes at the tips, which may or not form sporangia. However, in *Phytopthora capsici* sporangia form on oospore, that germinates in distilled water.

Phytopthora and other oomycetes have a number of biological characteristics that are relatively uncommon in other fungi.[24] The major part of the life cycle is primarily diploid, where as that of the higher fungi is haploid. The cell walls of *Phytophthora* are composed of cellulose and beta glucans and not chitin, which is the cell wall component of fungi other than oomycetes.[25,26] Mycolominarin, a β-1,3 glucan is the characteristic storage carbohydrate. The species do not synthesis sterols but require an exogenous source of beta hydroxy sterols for sporulation.[30,31] Sporangia are extremely variable in shape and dimension and are predominantly tapered at the base and are caduceus with long pedestals varying in length. Black pepper isolates produce sporangia on sporangiophores that are characteristically umbellate. The species, *Phytophthora capsici* is predominantly heterothallic and antheridia are amphigynus. Oogonia are spherical or sub-spherical and hyaline to brown in colour. Dimension of oogonia from different hosts vary from 23-50 μm. *Phytopthora* is unique and its special features are to be taken into consideration while trying to control it.

Within a few days or weeks after infection, the inoculums of *Phytophthora* species, which cause foliar as well as root diseases increase from low, often undetectable levels to high levels. The increase of inoculums of *Phytophthora* species is caused by the rapid production of sporangia and zoospore from infected plant tissues, when environmental conditions, most important of which is the presence of free water, are favourable thus they have short regeneration time and great reproductive capacity.[32]

B. Controlling *Phytophthora capsici*

Fungicides are compounds that either destroy a fungus or inhibit or suppress its growth. *Phytophthora capsici* shows four phases of growths, which are mycelial growth, sporangial formation, zoospore liberation and zoospore germination. A compound, which can inhibit one of these phases, could be useful as an anti-fungal agent. A number of fungicides are usually used for the control of *Phytophthora* infections and they can be classified as protective and systemic fungicides. The commonly used protective fungicides are copper compounds, especially Bordeaux mixture, copper oxy chloride and cuprous oxides, organotin compounds, dithiocarbamates (zineb, maneb, mancozeb) chlorathalonil and pthalimides (captan, captaphole, folpet).[33,34]

Organotin compounds are, particularly effective antisporulent fungicides.[35] Dithiocarbamic acid is combined with different cations to makeup fungicide that differ in certain properties. The simplest one is metham sodium (vapam), a sodium salt that is soluble in water. Ziram and ferbam are dialkyl dithiocarbamates. Nabam, zeneb, maneb and propenub are dialkyl bisdithiocarbamates. Dithioaramates are preferred to copper fungicide because they are much less phytotoxic. Some of the dithiocarbamates increase the green colour of leaves because of the added cation, such as, zinc.[33] Chlrothalonil has greater persistence in rainy weather than other protectant fungicides.

Systemic fungicides are compounds that can be taken up through roots, stems, leaves or flowers and can be translocated to other areas in the plant. This movement can be across the leaves, upward to new growth or downwards. Systemic fungicides are less prone to loss by rainfall than protective fungicides and can suppress the pathogen after the infection has occurred. The modern systemic fungicides effective against *Phytopthora* consist of different groups, which include the carabmates (prothiocarb and propamocarb), isooxazoles (hymexasol), cyanoacetamideoximes (cymoxanil), ethyl phophonates (fosetyl A1) and phenyl amides (metalaxyl). The phenyl amides, formerly called acylalanines, include metalaxyl, the acyl amino butyro lactones and the acyl amino oxazolidones.[36,37,38] Prothiocarb has a limited systemic capability and is not translocated away from the point of application. Propamocarb is an analogue of prothiocarb in which an oxygen atom replaces sulphur.

Metalaxyl gets translocated from seeds to roots; from roots to leaves and to new growths.[39,40] The systemic-curative effect of metalaxyl in plants makes it advantageous over the protective fungicides especially when infection has occurred before application. It reduces the mycelial growth of *Phytophthora capsici* by 57 percent and zoospore production by nearly 100 %. It is less susceptible to loss by rainfall. By incorporating radio active carbon, C^{14} during the synthesis of metalaxyl, its movement in the plant can be monitored by measuring the amount radioactivity in the samples of the plant tissues or by exposing tissues to X-ray films. Thus the movement of metalaxyl from root to stem and leaves above the point of application is traced by this method.[39] It is water-soluble and is marketed under several names; redomil for foliar application, apron for seed treatment and subdue for soil application. It shows a specific suppressive effect on the ribosomal RNA.[41,42] It does not usually inhibit germination of sporangia or encysted zoospores as effectively as it does mycelial growth. Even though advantageous in many respects, the development of resistance to metalaxyl within the population of target pathogen is a problem. It acts on RNA synthesis of *Phytophthora* and its mode of action is specific and probably governed by one gene.[43] If this gene mutates, the resistant propagules can dominate the population.

The phosphonate fungicides include fosetyl Al and its breakdown products, as phosphorous acid .The active ingredient is phosphonate anion, which slows the growth of the pathogen and inhibit its sporulation.[44,45] It also alters the metabolism of the pathogen in such a way that the host can mount more active and more effective defence response. Zarilimide, a new systemic benzamide fungicide is also active against *Phytophthora capsici.* The destruction of microtubule cytoskeleton and inhibition mitosis is involved in its mode of action.

In order to destroy the fungus at its source, for instance on benches in soil or in water, in an intensive glass house operation, the chemical biocides are to be used which may destroy all living organisms including plants; so they must be used with due caution. These compounds must be added to the source of *Phytophthora* inoculums in such away that plants will not be affected. Copper napthenate, sodium hypochlorite, quaternary ammonium products, sodium tetra-thiocarbonates, methyl bromide and chloropicrin, isothiocyantes, *etc*, are examples of such eradicant biocides. Sodium tetrathiocarbonate that releases CS_2 in to soil, shows promise for control of *Phytophthora.*

A number of biological control agents have also been advocated for the control of foot-rot disease.[3] Biocontrol agents like, *Gliocadium variens*, *Vesicular arbusular micorrhizae*, *Trichoderma spp*, *etc*, are also used against *Phytophthora capsici*. *Trychoderma spp* causes lysis of mycelium and zoospore and inhibits the production of sporangia.

Now a days the use of plant secondary metabolites for the control of fungi is gaining importance.[46-48] The root exudates of *Allium spp* have been reported to be inhibitory to *Phytophthora capsici.*[49] The application of nitrogenous organic substance is useful in suppressing *Phytohpthora* population in the soil. Application of a mixture of garlic and mustard in soil has been reported to be effective against the foot-rot of black pepper.[50] Water and ethanol extracts of *Piper colbrinum and Chromalaena adorata* are also found inhibitory to *Phytophthora capsici.*

C. Scope of present investigation

Even though a totally organic, pesticide-free farming is highly desirable, the diseases like foot-rot of black pepper will probably never be completely controlled without chemical fungicides. An integrated approach involving traditional, biological and chemical methods of control, combined with host resistance is the widely suggested strategy for the effective disease management.

A large number of transition metal complexes are found to possess antifungal, antitumour and antibacterial activities.[51-53] A broad spectrum of biological activities is reported to be associated with a number of ligands. It has also been established that biological activities of ligands enhance manifold as they coordinate with suitable metal ions.[54] Schiff base complexes of Mn(II), Co(II), Ni(II) and Cu(II) were reported to have antibacterial and antifungal activities.[55,56] The Complexes of Co(II), Ni(II) and Cu(II) with heterocyclic Schiff base ligands derived from 2-acetylthiophene and 2-aminothiophenol were tested for antimicrobial activities by the serial dilution method against two bacteria, *Staphylococcus Aureus* and *Escheria coli* and two fungi, *Aspergillus niger* and *Candida albicans.*[57] They were found to have considerable antifungal activities. Raman *et.al.*[58] studied the antimicrobial activities of the complexes of VO(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the Schiff base derived from benzil and 2-aminobenzyl alcohol. The *in vitro* screenings of the biological effects of these compounds were carried out against the bacteria, *Staphylococcus aureus, Bacillus subtilis, Klebsiella pneumoniae, Salmonella typhi, Pseudomonas aeruginosa* and *Shigella flexneri* by serial dilution method. Most of the complexes had higher activity compared to the Schiff base ligand and the control as indicated by the minimum inhibitory concentration values reported. Raman *et.al.*[59] reported the biological activities of the complexes of Co(II), Ni(II), Cu(II) and Zn(II) with the Schiff base derived from acetyl acetone and *p*-anisidine. They were tested for antimicrobial activity against the bacteria, *Staphylococcus Aureus, Bacillus subtilis* and *Escheria coli* and the fungi, *Aspergillus niger* by the well diffusion method using agar nutrient as the medium. In comparison to the ligand complexes were more active against all the tested organisms.

Schiff bases of diamines, especially those of *o*-phenylenediamine and their complexes were reported to show considerable biological activities.[60,61] Derivatives of piperonal and their Schiff bases were also reported to show antibacterial and antifungal activities.[62-64] The synthesis, characterization and studies on biological activity of a series eleven Schiff bases obtained by the condensation of piperonal with the substituted anilines [H_2N-C_6H_4-*p*-X, where X= H, Cl, Br, I, CH_3, C_2H_5, OCH_3, OC_2H_5, COOH, NO_2 or $SO_3^-Na^+$] were reported by Echevarria *et.al.*[64] The method of two-fold serial dilution in Sabourand-dextrose liquid medium was resorted to in the assay against fungi and the results were expressed in minimal inhibitory concentration (MIC). The filamentous dermatophytes, namely, *Microsporum canis, Microsporum gypseum, Trichophyton rubrum* and *Epidermophyton floccosum* were the fungi used in the assay. Most of the Schiff bases were found to possess good activity, and especially against *Epidermophyton floccosum*, for which the most active compounds were those containing *p*- Br, Cl, C_2H_5, NO_2 or OCH_3 aniline moiety. Assays with bacteria and yeasts were performed by the agar-well diffusion method and the compounds were found to be inactive. Earlier works had also shown that some drugs showed increased activity when administered as metal chelates rather than as organic compounds.[58-61]

In view of this, the Schiff bases derived from piperonal and various diamines namely, bis(piperonaldehyde)ethylenediimine, bis(piperonaldehyde)-1,3-propanediimine and bis(piperonaldehyde)-*o*-phenylenediimine and their complexes with Mn(II), Co(II), Ni (II) and Cu(II) were tested against the mycelial growth of *phytopthora capsici.* Based on the results of the preliminary studies a detailed investigation was undertaken to find out the inhibitory effects of the active compounds on the various stages of the growth of *phytopthora capsici*, *viz*, sporangial production, zoospore liberation and zoospore germination.

CHAPTER II

ANTIFUNGAL ACTIVITIES OF THE COMPLEXES OF BIS(PIPERONALDEHYDE)ETHYLENEDIIMINE BIS(PIPERONALDEHYDE)-1,3-PROPANEDIIMINE AND BIS(PIPERONALDEHYDE)-*O*-PHENYLENEDIIMINE

This chapter describes antifungal activities of twelve transition metal complexes of bis(piperonaldehyde)ethylenediimine (Bipiren), bis(piperonaldehyde)-1,3-propanediimine (Bipirpen), and bis-(piperonaldehyde)-*o*-phenylenediimine (Bipophen). The details of the preparation and characterisation of these complexes are presented in the Part I. As all the complexes were found to be soluble in DMSO, standard solutions were prepared in DMSO and diluted to required concentrations using sterile distilled water. The complexes in required quantity were incorporated with carrot agar medium (CA) [65] to study their effects on the growth of *Phytopthora capsici*. The complexes used in these studies were $[Co_2(Bipiren)(OH)_4]$, $[Ni_2(Bipiren)(OH)_4]$, $[Cu_2(Bipiren)(OH)_4]$, $[Co(Bipirpen)(CH_3COO)_2(H_2O)_2]$, $[Ni(Bipirpen)(CH_3COO)_2]$, $[Cu_2(Bipirpen)(OH)_4]$, $[Co(Bipophen)(CH_3COO)_2(H_2O)_2]$, $[NiL(Bipophen)(CH_3COO)_2]$ and $[CuL(Bipophen)(CH_3COO)_2]$.

A. Material and methods

The ligands and the complexes were dissolved in DMSO-water mixture (1:40) to form stock solutions of 1000 ppm. The stock solutions were then autoclaved and kept aside to be added to the carrot agar medium.[65] 200 g of fresh carrot was weighed, pealed and cut into small pieces and the pieces were minced in a blender containing 500 ml of distilled water for 40 seconds at high speed and filtered through four layers of cheese cloths, the juice was then squeezed from residue. The filtrate and 18 g of agar were then diluted to 1litre with sterile distilled water. The carrot juice was then boiled and 20 g of agar was added while stirring. This was distributed in to conical flasks and sterilized by autoclaving at 121 °C for 20 min.

Further studies were conducted by adding the test solutions to CA media just before pouring the media into plates. The effects of the ligands and complexes on mycelial growth, sporulation, sporangial production, zoospore release and zoospore germination of *Phytophthora capsici* were studied by incorporating them into CA media as specified above.

B. Experimental

1. Isolation *of Phytophthora Capsici*

Infected roots of foot-rot affected black pepper plants were collected and brought to the laboratory. They were washed several times with sterilized water and cut into small pieces of 1cm size. They were then sterilized with 0.1% solution of $HgCl_2$ for 2 min and washed with sterile distilled water three times and were blotted dry. These bits were placed in media containing PVPH (pimaricin, vancomycin, pentachloronitrobenzene and hymexasol) and incubated at 24 °C for 48-72 h.[66] The

Phytopthora growth obtained, was sub-cultured in carrot agar slab for further studies.

2. <u>Mycelial growth</u>

The ligands and complexes were dissolved in DMSO-water mixture in 1:40 ratio to form stock solutions of 1000 ppm. Different dilutions were made from the stock solutions. Poisoned food technique[67] was used for the study on mycelial growth-inhibition. Appropriate volumes of the test solutions were mixed aseptically with carrot agar medium to obtain concentrations ranging from 25 to 100 ppm so as to form a final volume of 50 ml medium in each case. 15ml each of the amended medium was poured into petri-plates. Discs of inoculums of *Phytophthora capsici* 5 mm in diameter were taken from the edges of actively growing 72 h old culture of *Phytophthora capsici* grown on CA. The culture was obtained from the national repository of *Phytophthora.* The discs were placed centrally on to the amended medium in petri-plates. Plates with DMSO concentrations, corresponding to the highest concentration of the organic solvent (0.25 %) among the test solutions served as control. Three replications were maintained for each test solution. The plates were incubated at 25 (+/-1) °C in the dark and growth of the colony was measured after 96 h of inoculation at 24 h intervals. The radial growth of mycelium was measured from three sides of the plates and the mean of these three readings was taken as the radius of the colony. The growth of the colony in the control sets were compared with that of various test solutions and the percentage inhibition was calculated using the formula,

$$\text{Inhibition (\%)} = (C - T) \times 100/C$$

where C is the radial growth in the control and T is the radial growth in the various test solutions.

3. Sporangial production

Phytopthora capsici was grown on CA in dark for 48 h at 25^0C. 5 mm discs of inoculums were taken from the edges of 48 h old culture and were used to study the effect of the ligands and metal complexes on sporulation. The ligands, Bipiren and Bipophen and six of their complexes with Co(II), Ni(II) and Cu(II), which showed significant inhibitory effects on mycelial growth, were selected for further studies. Different concentrations, such as, 25, 50, 75 and 100 ppm of test solutions, as well as the control solutions were poured into petri-plates and discs of inoculums, 5 mm in diameter from the above cultures were placed centrally on to the amended media and they were kept under florescent light for 48 to 72 h. Three replications were maintained for each test solution. Number of sporangial productions per microscopic field (20x) was counted for three different fields and the average number of sporangia per disc was calculated and the percentage of inhibition was ascertained in comparison with the control.

4. Zoospore release / indirect germination of sporangia

Fusion of cleavage vesicles and release of zoospores (zoosporogenesis or indirect sporangial germination) occur spontaneously in distilled water, in most species of *Phytophthora* and can be enhanced by chilling sporangia at about 10 °C for 30 min before immersing them in distilled water. 5 mm discs were cut from the periphery of 48 h old cultures and were allowed to sporulate by incubating in light as described above. The sporulating discs were taken in petri-plates and test solutions of different concentrations ranging from 25 to 100 ppm as well as the control solutions were poured into it and cold shock treatment was given by keeping the discs in the freezer at 4 °C for 10 min. These plates were taken out and incubated at laboratory temperature for 30 min before observation. Due to the cold shock, zoospores formed inside sporangia were released. The number of sporangia which released zoospores per microscopic field (20x) were recorded. In each slide, 5 microscopic fields were observed and inhibition percentage was calculated by comparing with the control.

5. Zoospore germination

5 mm discs, cut from the periphery of 48 h old cultures were allowed to sporulate by incubating in light as described above. Cold shock treatment was given by keeping the discs in the freezer at 4 °C for 10 min. The released zoospores were collected in test tubes and are vortexed. The zoospores settled at the bottom were collected and placed in clean cavity slides containing 5 µl of test solutions of different concentrations, ranging from 25 to100 ppm and incubated for one hour at 24 °C. Triplicates were kept for all the concentrations. 5 microscopic fields were observed in each slide, for counting the number of zoospores germinated out of the total used. Three replications with DMSO concentrations, corresponding to the highest concentration of the organic solvent (0.25 %) among the test solutions served as controls. Percentage of inhibition to zoospore germination was calculated by comparing with control.

C. Results and discussion

Antifungal activities of Mn(II), Co(II), Ni(II) and Cu(II) complexes of Bipiren, Bipirpen and Bipophen were evident from the detailed studies on the effect of these compounds on different stages of growth of *Phytopthora capsici.* The data and discussions of these studies are presented here.

1. Mycelial growth

The data for the inhibition of mycelial growth of *Phytophthora capsici* by the tested compounds are presented in Tables 1-3. The majority of them were found to be fairly active and the percentage of inhibittion increased with concentrations. Generally, the complexes were much more active than the respective ligands. Among the ligands, Bipophen was more effective than Bipiren or Bipirpen, in the inhibition of the mycelial growth. Similarly, the complexes of Bipophen were more active than those of the other ligands. Comparing the metal complexes, those of Cu(II) and Ni(II) were found to be more effective than Co(II) and Mn(II) complexes. Out of the 3 ligands and 12 metal complexes tested, 4 of them, *viz*, the Co(II), Ni(II) and Cu(II) complexes of Bipophen and the Cu(II) complex of Bipiren showed more than 60 % growth inhibition at a concentration of 50 ppm itself. The Cu(II) complex of Bipophen was the most effective among all the compounds tested. At 100 ppm, it showed 96.6 % inhibition. The LD_{50} values for the complexes of Mn(II), Co(II), Ni(II) and Cu(II) complexes of Bipophen were found to be 69, 40, 37, 26 ppm, respectively while that of the ligand, Bipophen was 64 ppm. The graphs showing the LD_{50} values for the Bipophen complexes are given in Fig-1.

Table-1 The inhibitory effects of Bipiren and its metal complexes on the mycelial growth of *phytophthora capsici*

Conc. of sample	Sample						
		Bipiren	Complex				Control
			Mn(II)	Co(II)	Ni(II)	Cu(II)	
25 ppm	Diameter mm	31.2	32.6	31.6	28.3	22.8	34
	% of inhibition	8.24	4.12	7.06	16.8	32.9	
50 ppm	Diameter mm	29	30.4	29.2	22.6	12.9	34
	% of inhibition	14.7	10.6	14.1	33.5	62.1	
75 ppm	Diameter mm	23.2	26.9	20.3	17.2	7.5	34
	% of inhibition	31.8	20.9	40.3	49.4	77.9	
100 ppm	Diameter mm	14.2	23.2	10.3	9.2	5.8	34
	% of inhibition	58.2	31.8	69.7	72.9	82.9	

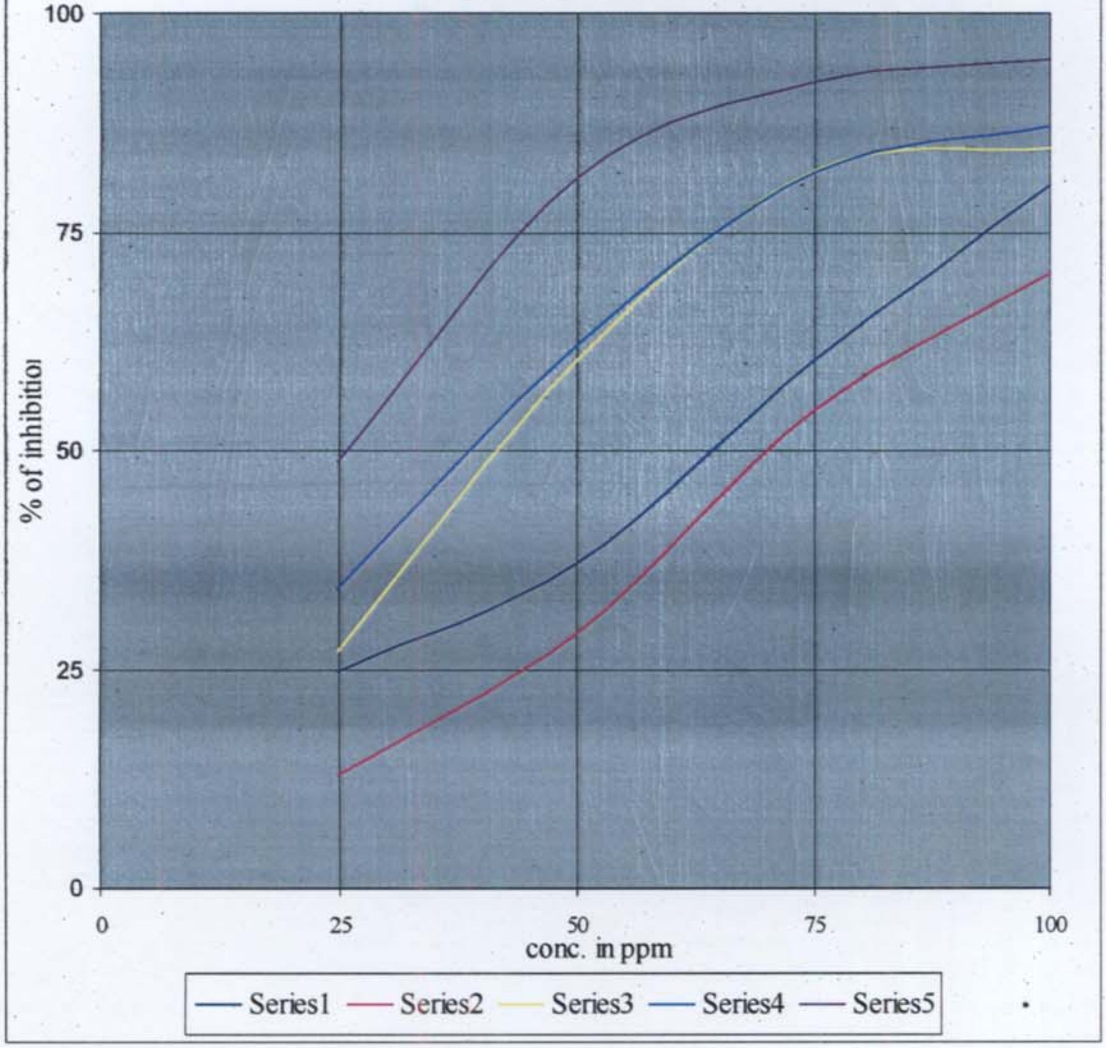
Table-2 The inhibitory effects of Bipirpen and its metal complexes on the mycelial growth of *phytophthora capsici*

Conc. of sample	Sample						
		Bipirpen	Complex				Control
			Mn(II)	Co(II)	Ni(II)	Cu(II)	
25 ppm	Diameter mm	32	33.2	32.2	30.2	28.8	34
	% of inhibition	5.88	2.35	5.29	11.2	15.3	
50 ppm	Diameter mm	30.8	32	30.9	28.4	23.6	34
	% of inhibition	9.41	5.88	9.12	16.5	30.6	
75 ppm	Diameter mm	28.2	29.2	25.8	22.9	12.8	34
	% of inhibition	17.1	14.1	24.1	32.6	62.4	
100 ppm	Diameter mm	18.6	24.8	15.8	12.6	10.1	34
	% of inhibition	45.3	27.1	53.5	62.9	70.3	

Table-3 The inhibitory effect Bipophen and its metal complexes on the mycelial growth of *phytophthora capsici*

Conc. of sample		Sample					
		Bipophen	Complex				Control
			Mn(II)	Co(II)	Ni(II)	Cu(II)	
25 ppm	Diameter mm.	25.6	29.6	24.8	22.4	17.4	34
	% of inhibition	24.7	12.9	27.1	34.1	48.8	
50 ppm	Diameter mm.	21.4	24.1	13.5	12.9	6.4	34
	% of inhibition	37.1	29.1	60.3	62.1	81.2	
75 ppm	Diameter mm.	13.5	15.4	6.1	6.2	2.7	34
	% of inhibition	60.3	54.7	82.1	81.8	92.1	
100 ppm	Diameter mm.	6.7	10.1	5.2	4.4	1.8	34
	% of inhibition	80.3	70.3	84.7	87.1	94.7	

Fig-1 The inhibitory effect of Bipophen complexes on mycelial growth; Graphical representation



Series 1 – Bipophen

Series 2, 3, 4 and 5 – Mn(II), Co(II), Ni(II) and Cu(II) complexes of Bipophen

Table-4 The inhibitory effects of Bipiren and its metal complexes on the sporangial production of *phytophthora capsici*

Conc. of sample	Sample					
		Bipiren	Complex			Control
			Co(II)	Ni(II)	Cu(II)	
25ppm	no of sporangia per field	52	49	46.6	43.2	64
	% of inhibition	18.8	23.4	27.2	32.5	
50ppm	no of sporangia per field	48.4	44.8	38.8	33.8	64
	% of inhibition	24.4	30	39.4	47.2	
75ppm	no of sporangia per field	41	32.4	26.2	15.6	64
	% of inhibition	35.9	49.4	59.1	75.6	
100ppm	no of sporangia per field	31.4	17.4	18	11	64
	% of inhibition	50.9	72.8	71.9	82.8	

Table-5 The inhibitory effects of Bipophen and its metal complexes on the sporangial production of *phytophthora capsici*

Conc. of sample	Sample					
		Bipophen	Complex			Control
			Co(II)	Ni(II)	Cu(II)	
25ppm	no of sporangia per field	47.2	45.1	43.8	42.1	64
	% of inhibition	26.3	29.5	31.6	34.2	
50ppm	no of sporangia per field	42.6	37.8	39.2	34	64
	% of inhibition	33.4	40.9	38.8	46.9	
75ppm	no of sporangia per field	31.2	20.2	19.1	3.8	64
	% of inhibition	51.3	68.4	70.2	94.1	
100ppm	no of sporangia per field	18.4	8.8	5.6	1.6	64
	% of inhibition	71.3	86.3	91.3	97.5	

Table-6 The inhibitory effect of Bipiren and its metal complexes on the sporangial release of *phytophthora capsici*

Conc. of sample	Sample					
		Bipiren	Complex			Control
			Co(II)	Ni(II)	Cu(II)	
25ppm	% of zoospore release	36.4	28	23	19	51.4
	% of inhibition	29.2	45.5	55.3	63.0	
50ppm	% of zoospore release	23.2	19	14	11	51.4
	% of inhibition	54.9	63	72.8	78.6	
75ppm	% of zoospore release	17.4	8.6	5.8	0	51.4
	% of inhibition	66.1	83.3	88.7	100	
100ppm	% of zoospore release	9.8	1.8	0	0	51.4
	% of inhibition	80.9	96.5	100	100	

Table-7 The inhibitory effect Bipophen and its metal complexes on the sporangial release of *phytophthora capcici*

Conc. of sample	Sample					
		Bipophen	Complex			Control
			Co(II)	Ni(II)	Cu(II)	
25ppm	% of zoospore release	31.8	28.2	25.4	0	51.4
	% of inhibition	38.1	45.1	50.6	100	
50ppm	% of zoospore release	25.4	18.6	0	0	51.4
	% of inhibition	50.6	63.8	100	100	
75ppm	% of zoospore release	11.8	3.4	0	0	51.4
	% of inhibition	77	93.4	100	100	
100ppm	% of zoospore release	0	0	0	0	51.4
	% of inhibition	100	100	100	100	

Table-8 The inhibitory effect Bipiren and its metal complexes on the zoospore germination of *phytophthora capsici*

Conc. of sample	Sample					
		Bipiren	Complex			Control
			Co(II)	Ni(II)	Cu(II)	
25ppm	% of zoospore germination	41.8	46.3	30.2	26.8	68.6
	% of inhibition	39.1	32.5	56	60.9	
50ppm	% of zoospore germination	36	40.2	23.4	13.2	68.6
	% of inhibition	47.5	41.4	65.9	80.8	
75ppm	% of zoospore germination	28	26.2	14.2	5.8	68.6
	% of inhibition	59.2	61.8	79.3	91.5	
100ppm	% of zoospore germination	18.6	7.8	6.8	1.8	68.6
	% of inhibition	72.9	88.6	90.2	97.4	

Table-9 The inhibitory effect Bipophen and its metal complexes on the zoospore germination of *phytophthora capsici*

Conc. of sample	Sample					
		Bipophen				Control
			Co	Ni	Cu	
25ppm	% of zoospore germination	24.8	28.3	18.6	13.2	68.6
	% of inhibition	63.8	58.7	72.9	80.8	
50ppm	% of zoospore germination	16.4	22.3	14.6	8.2	68.6
	% of inhibition	76.1	67.5	78.7	88	
75ppm	% of zoospore germination	10.2	13.2	7.4	3.8	68.6
	% of inhibition	85.1	80.8	89.2	94.5	
100ppm	% of zoospore germination	4.6	5.9	3.2	0	68.6
	% of inhibition	93.3	91.4	95.3	100	

Metal acetates were used for the synthesis of these complexes. The effects of the Mn(II), Co(II), Ni(II) and Cu(II) acetates on the mycelial growth of *phytophthora capscici* were studied earlier by other workers and the LD_{50} values of these salts were reported to be above 500 ppm.[68]

2. Sporangiogenisis

The ligands, Bipiren and Bipophen and six of their complexes with Co(II), Ni(II) and Cu(II), which showed significant inhibitory effects on mycelial growth, were selected for further studies. The data for the inhibition of sporangiogenesis effects by these compounds are presented in Tables 4-5. All the tested complexes showed considerable activity and the percentage of inhibition increased with increase in concentration. The results showed that Bipophen and its complexes were more effective than Bipiren and its complexes. At 100 ppm, Cu(II) and Ni(II) complexes of Bipophen showed inhibitory effects of 97.5 % and 91.3 %, respectively, which were higher than those of the other samples tested. At lower concentrations also these complexes showed significant inhibitory effects.

3. Zoospore release

The data for the effects of these compounds on zoospore release are given in Tables 6-7. In general, all the complexes were more active than the respective ligands in preventing zoospore release of *Phytophthora capsici*. Bipophen and its complexes were more effective than Bipiren and its complexes. Comparing the metal complexes, those of the Cu(II) were more effective than others in this stage also. The Cu(II) complex of Bipophen showed 100 % inhibition on sporangial liberation at 25 ppm itself and that of Bipiren showed only 63 % inhibition at 25 ppm. The ligand, Bipophen and its Ni(II) and Co(II) complexes of showed 100 % inhibition at 100, 50 and 100 ppm, respectively. The Cu(II) and Ni(II) and complexes of Bipiren showed 100 % inhibition at 75 and 100 ppm, respectively.

4. Zoospore germination

The data for inhibition of zoospore germination are given in Tables 8-9. Generally, the inhibitory powers of the ligands and their complexes increased with increase in concentration. Bipophen and its complexes showed considerable activity even at low concentrations. At 25 ppm, Bipophen and its Cu(II) and Ni(II) complexes showed 63.8, 72.9 and 80.8 % inhibitions, respectively. Eventhough Bipiren did not show considerable inhibitory effect at 25 ppm, its Cu(II) complex exhibited remarkably high inhibitory action, 60.9 % at 25 ppm and 97.4% at 100 ppm. In this stage also Cu(II) complex of Bipophen was found to be the most effective against *Phytopthora capsici*, among the tested samples.

D. Conclusion and scope

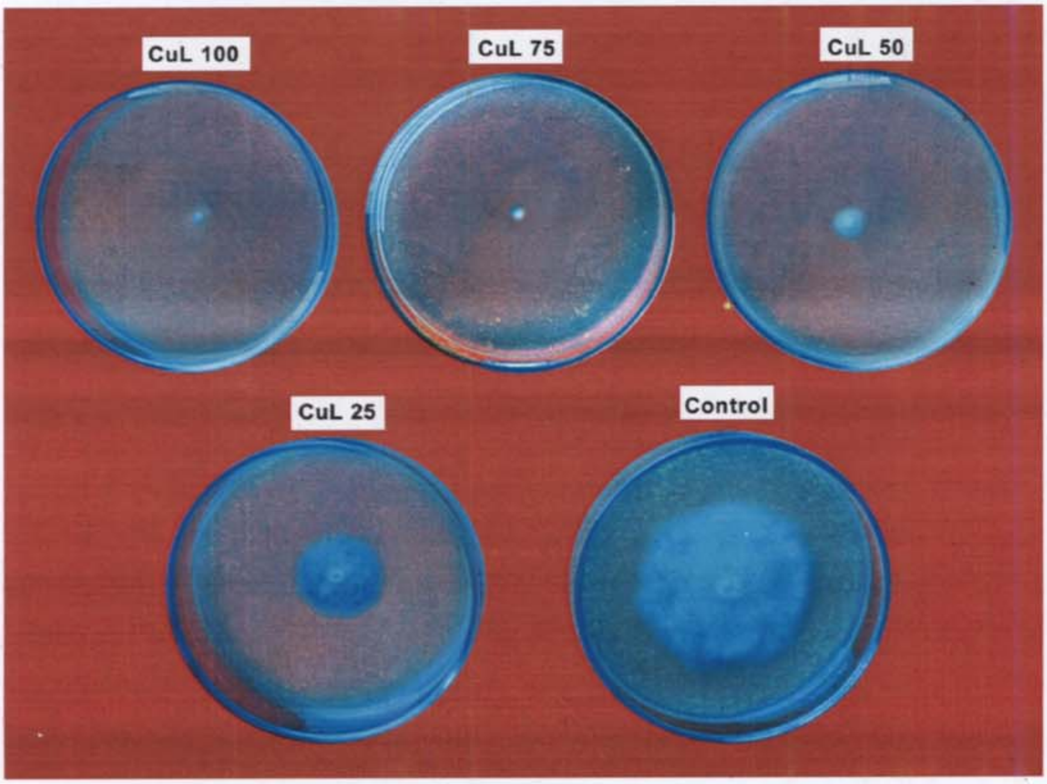
From the data it is clear that most of these complexes were inhibitory to all the four stages in the growth of *Phytophthora capsici.* The individual effects of the ligands, Bipiren, Bipirpen and Bipophen on the mycelial growth and of Bipirpen and Bipophen on the other stages of the growth of *Phytopthora capsici* showed that they were also antifungal in nature. But the metal complexes were generally found to show more antifungal activity than the parent ligands in all the four stages of investigation. The acetates of Cu(II), Co(II), Ni(II) and Mn(II) were also reported to be antifungal in nature, capable of inhibiting the mycelial growth of *Phytophthora capsici*, but the activities were generally far lower than those of the complexes.[68] Among the four stages, the inhibition was more pronounced in zoosporangial production and zoospore release. The complexes of Cu(II) were found to be the more effective than the complexes of other metal ions in retarding the growth of *Phytophthora capsici* at various stages. The Ni(II) and Co(II) complexes followed them. Among the ligands, Bipophen showed maximum inhibitory effect, followed by Bipiren. The Cu(II) complex of Bipophen was the most effective among all the tested compounds.

The higher activities of the metal complexes in comparison to the free metal ions or ligands may be explained on the basis of Overtone's concept[59,69] and chelation theory.[70,71] According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of lipid-soluble materials alone, due to which liposolubility is an important factor which controls the biological activities of drugs. On chelation, the polarity of the metal ion will be reduced to a considerable extent due to the overlap of the ligand orbitals and the partial sharing of the positive charges of the metal ions with the donor groups. Further, it increases the delocalisation of π-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocks the metal binding sites in the enzymes of the organisms.[72] These complexes may also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further involve the formation of a hydrogen bond through the azomethine group with the active centres of cell constituents, resulting in the interference with normal cell division process.[72]

Mode of antifungal activity of 1,10-phenanthroline and its Mn(II) Cu(II) and Ag(I) complexes against the pathogenic yeast, *Candida albicans* was well studied by Barry *et.al.*[73] Yeast cells exposed to these drugs showed a diminished ability to reduce 2,3,5-triphenyltetrazolium chloride (TTC), indicating a reduction in respiratory function. All the drugs promoted reductions in the levels of cytochromes *b* and *c* in the cells, while the Ag(I) complex lowered the amount of cytochrome aa_3 as well. Cells treated with 1,10-phenanthroline and its Cu(II) and Ag(I) complexes showed reduced levels of ergosterol while the Mn(II) complex induced an increase in the ergosterol concentration. The general conclusion was that the drugs damaged mitochondrial function and uncoupled the respiration. The drugs were not uniformly active and it was suggested that their bioactivity has a degree of metal ion dependency.

Therefore, the possible mechanism of action of an antimicrobial agent includes interference with cell wall synthesis, mitochondrial function, respiration, DNA function, inhibition of protein synthesis and alteration of permeability of cell membrane. In the present investigation, inhibitory effects of certain Schiff base ligands and their metal complexes on various stages of the growth of *Phytophthora capsici* were evaluated. As a continuation of this study a detailed investigation into the mechanism involved in the inhibition process is being taken up. The observation that not only the Cu (II) complexes of various Schiff bases, but the Co(II) and Ni (II) that not only the Cu (II) complexes of various Schiff bases, but the Co(II) and Ni (II) complexes also showed sufficient antifungal coactivity may open up new avenues in the quest for tackling problem of foot-rot disease in black pepper.

Photographs showing the inhibitory effects of the ligand Bipophen and complexes of it on the myceilial growth of *Phytophthora capsici* are given at the end of this chapter. L represents Bipophen and MnL, CoL, NiL and CuL represent the Mn(II), Co(II), Ni(II) and Cu(II) complexes of the ligand. The numerals 25, 50, 75 and 100 stand for the concentrations of the ligand and complexes in ppm.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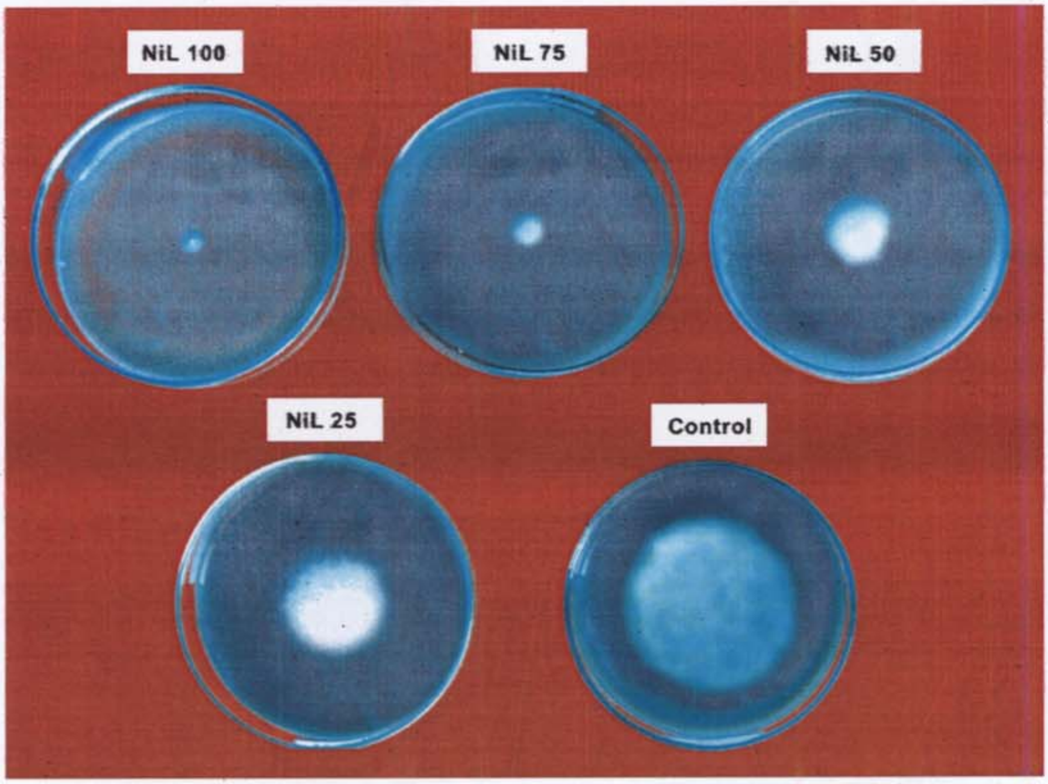
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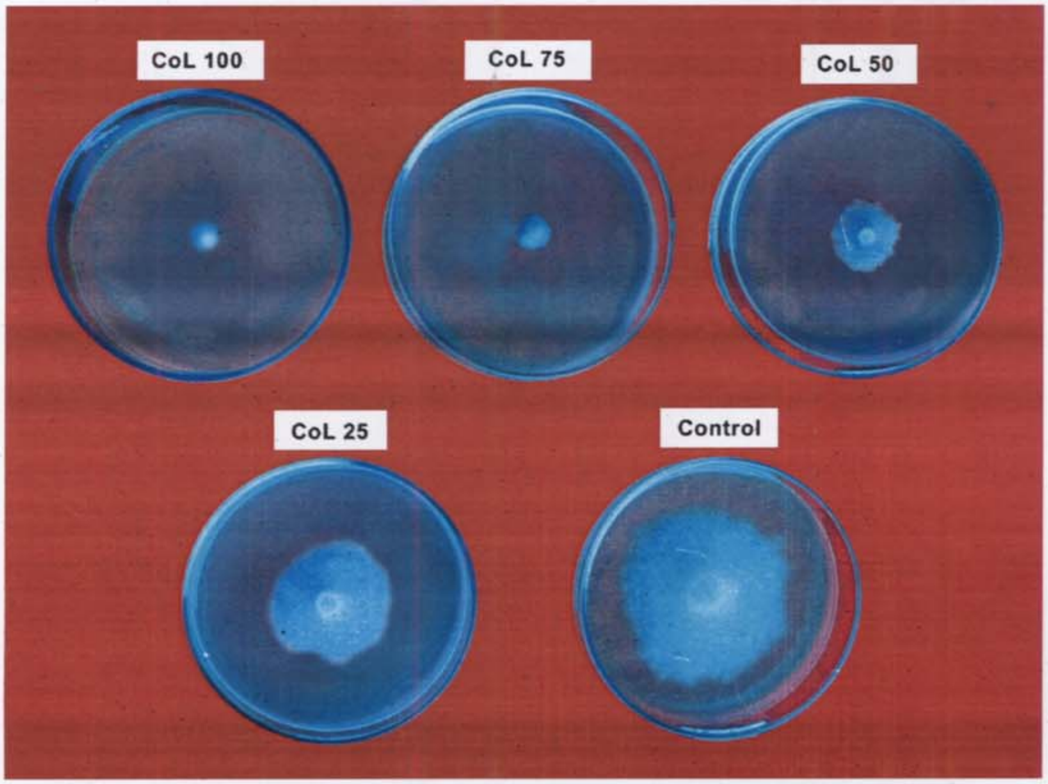
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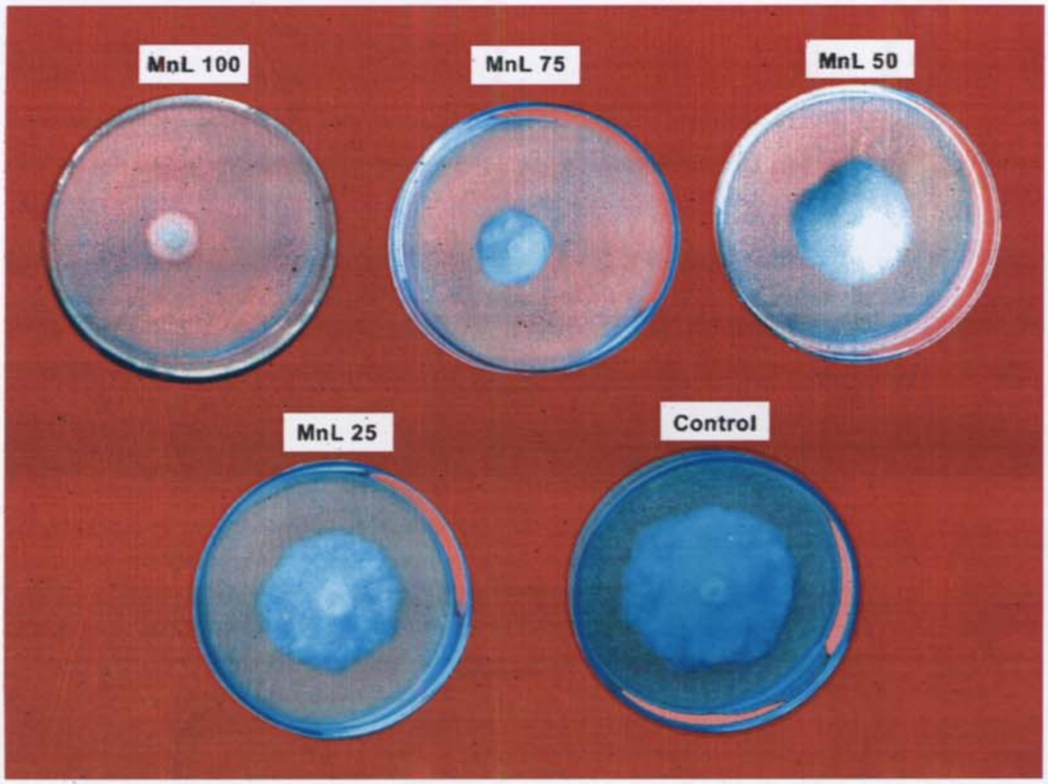
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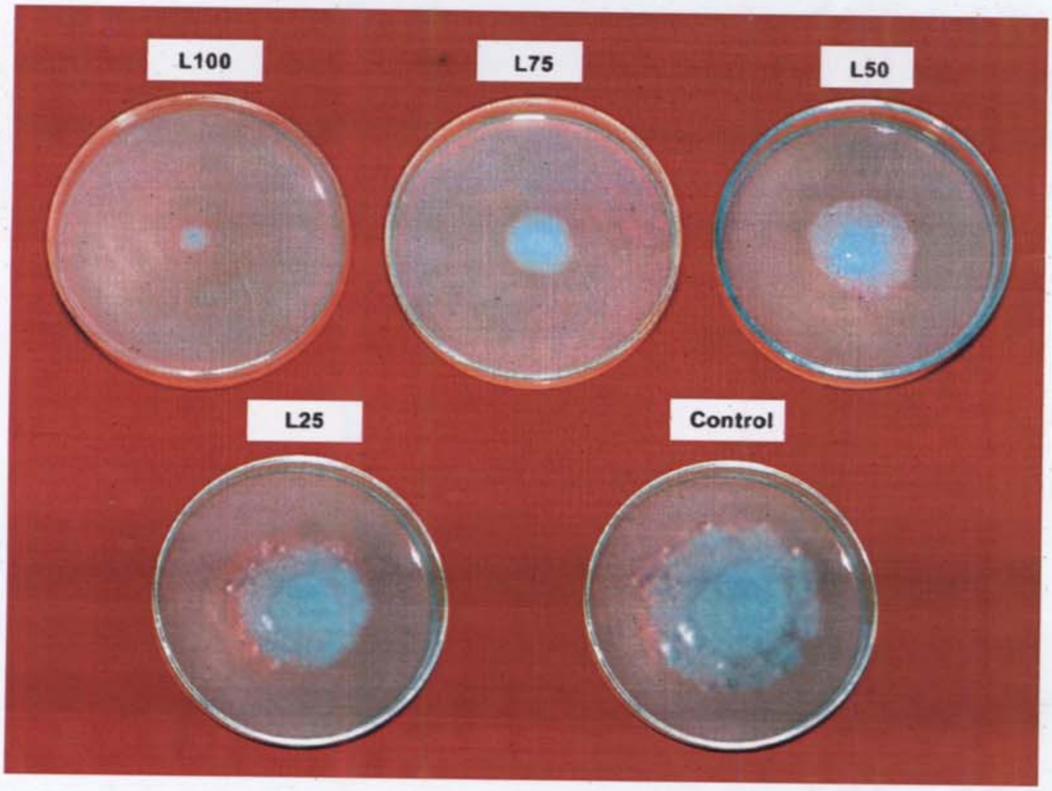
MnL 50
MnL 25
Control


L100
L75
L50
L25
Control

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