STUDIES ON SOME NEW METAL COMPLEXES OF THE SCHIFF BASES DERIVED FROM TRIAZOLES AND FLAVAZOLES

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CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of research work carried out by the author under my supervision in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology.

Kochi-22
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PREFACE

This thesis deals with the synthesis, characterisation and catalytic activity studies of some new Schiff base complexes derived from 2-phenyl-1,2,3-triazole-4-carboxaldehyde and 1-phenylflavazole-3-carboxaldehyde. The elucidation of the structure of these complexes is based on conductance and magnetic susceptibility measurements, TG/DTG studies, infrared, UV-Vis.-Near IR and EPR spectral studies.

The thesis is divided into nine chapters. Chapter I of the thesis presents an introduction to the coordination chemistry of Schiff bases with emphasis on aspects relevant to the theme of the present work. In Chapter II, details of the preparation and purification of the ligands are given. Various physico-chemical methods employed in the characterisation of the metal complexes are also included in the same chapter.

Chapters III, IV, and V of the thesis deal with the synthesis and characterisation of metal complexes of the Schiff bases derived from 2-phenyl-1,2,3-triazole-4- carboxaldehyde. In Chapter III, copper(II) complexes of 2-phenyl-1,2,3-triazole-4-carboxalidineaniline (PTCA) are discussed. Studies on some cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 2-phenyl-1,2,3-triazole-4-carboxaldehyde thiosemicarbazone are presented in Chapter IV. Chapter V of the thesis describes the synthesis and characterisation of cobalt(II) complexes of 2-phenyl-1,2,3-triazole-4-carboxaldehyde semicarbazone.

Chapters VI, VII and VIII of the thesis deal with the studies on some metal complexes of Schiff bases derived from 1-phenylflavazole-3-carboxaldehyde. Synthesis and characterisation of cobalt(III), nickel(II), copper(II) and zinc(II) complexes of 1-phenylflavazole-3-carboxaldehyde thiosemicarbazone are presented in Chapter VI, while those of cobalt(II) and copper(II) complexes of 1-phenylflavazole-3-carboxaldehyde semicarbazone and cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 1-phenylflavazole-3-carboxalidine-2-aminophenol are presented in Chapters VII and VIII respectively.

Transition metal complexes of many Schiff bases are found to satisfy the requirements for acting as catalysts for the oxidation of organic substrates. Among the various oxidants, dioxygen is very attractive due to its low cost and availability from liquid air; however, it usually reacts with organic substrates only in presence of a catalyst. The above mentioned complexes were screened for their catalytic activity. The results of these studies are described in Chapter IX.

Results described in this thesis have been published / are under publication as given below :

1. "New complexes of copper(II) with a Schiff base derived from 2-pheny-1,2,3-triazole-4-carboxaldehyde and aniline", K. K. M. Yusuff and C. Krishnakumar, *Synth. React. Inorg. Met-Org. Chem.,* 23 (5), 695 (1993).

2. "Thermal and catalytic activity studies of some Schiff base complexes of copper(II) derived from 2-phenyl-1,2,3-triazole-4-carboxaldehyde and aniline",
K. K. M. Yusuff and C. Krishnakumar, *React. Kinet.Catal. Lett.,* 49 (2), 437 (1993).

3. New octahedral complexes of the Schiff base derived from 2-phenyl-1,2,3-triazole-4-carboxaldehyde and thiosemicarbazide",
K. K. M. Yusuff and C. Krishnakumar, *Synth. React. Inorg. Chem.* (in press).

4. "Thermal and spectral studies of 2-phenyl-1,2,3-triazole-4-carboxaldehyde semicarbazone complexes of cobalt(II)",
K. K. M. Yusuff and C. Krishnakumar, *Thermochim. Acta* (Communicated).

5. "New transition metal complexes of the Schiff bases derived from 1-phenylflavazole-3-carboxaldehyde"
K. K. M. Yusuff and C. Krishnakumar, *Transition Met. Chem.,*(Communicated).

CONTENTS

Chapter II EXPERIMENTAL TECHNIQUES

Chapter III 2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALIDENE-ANILINE COMPLEXES OF Cu(II)

Chapter IV 2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALDEHYDE THIOSEMICARBAZONE COMPLEXES OF Co(II), Ni(II), Cu(II) AND Zn(II)

Chapter V 2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALDEHYDE SEMICARBAZONE COMPLEXES OF Co(II)

Chapter VI 1-PHENYLFLAVAZOLE-3-CARBOXALDEHYDE THIOSEMICARBAZONE COMPLEXES OF Co(III), Ni(II), Cu(II) AND Zn(II)

Chapter VII 1-PHENYLFLAVAZOLE-3-CARBOXALDEHYDE SEMICARBAZONE COMPLEXES OF Co(II), Ni(II) AND Cu(II)

Chapter VIII 1-PHENYLFLAVAZOLE-3-CARBOXALDEHYDE 2-AMINOPHENOL COMPLEXES OF Co(II), Ni(II), Cu(II) AND Zn(II)

Chapter IX THERMAL AND CATALYTIC ACTIVITY STUDIES OF SOME OF THE SCHIFF BASE COMPLEXES DERIVED FROM 2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALDEHYDE AND 1-PHENYLFLAVAZOLE-3-CARBOXALDEHYDE

CHAPTER I

INTRODUCTION

Metal complexes of Schiff bases have occupied a central place of importance in the development of coordination chemistry. The literature on these complexes range from the purely synthetic to modern physico-chemical as well as biochemically relevant studies. Many Schiff base complexes are found to have antibacterial, antifungal, antiinflammatory and antileukaemic properties[1-3]. Furthermore, these complexes find application as catalysts for a number of oxidation reactions[4].

Metal complexes derived from Schiff bases have been known since 1840. First Schiff base type complex was synthesised by Ettling[5] by the reaction of cupric acetate, salicylaldehyde and aqueous ammonia. He isolated a dark green crystalline product which was later known to be bis(salicylaldimino)copper(II). The aryl derivatives of this compound were isolated in 1869 by Schiff[6]. Since then, a large number of Schiff base complexes have been prepared and even now they comprise the major portion of the current literature on coordination chemistry. The chemistry of Schiff bases and their complexes has been repeatedly reviewed by several workers[7-15].

Schiff base can be represented by the general formula $R\text{-}CH{=}N\text{-}R'$, where R and R' are various substituents. These compounds contain the azomethine group (-RC=N-). They are formed by the condensation of primary amines with compounds containing active carbonyl group.

$$RR'CO + R'NH_2 \longrightarrow RR'C{=}NR' + H_2O$$

The experimental conditions for the formation of Schiff bases depend on the nature of amine and carbonyl compounds. Usually, it is better to remove water formed during the reaction by distillation or by using an azeotrope-forming solvent[16,17]. This is necessary in the case of diaryl or arylalkyl ketones. However, aldehydes and dialkyl ketones can usually be condensed with amines without the removal of water. Aromatic aldehydes react smoothly under mild conditions and at relatively low temperatures in a suitable solvent. In the condensation of aromatic amines with aromatic aldehydes, electron withdrawing substituents in the para position of the amines decreases the rate of reaction. When such groups are on the para position of the aldehyde, the rate of reaction was found to be increased[18].

The stability of the Schiff base complexes depends on the strength of the C=N bond, basicity of the imino group and steric factors. The presence of a second functional group with a replaceable hydrogen atom, preferably a hydroxyl group very near to the imine group allows the ligand to form a fairly stable four, five, or six membered ring on chelation to the metal atom. The role of the metal ions in these complexes seems to involve both stabilization and trapping of the Schiff base, and in addition it also ensures the planarity of the system.

The general methods of preparation of Schiff base complexes are given below:

(a) Complexation in the basic medium

In this method the metal ion and the Schiff base are allowed to react in alcoholic or aqueous alcoholic solution containing a base like acetate or hydroxide.

(b) Condensation method

The aldehyde metal complex formed by the interaction of the metal ion and aldehyde is refluxed with a slight excess of amine in solvents like ethanol, chloroform and dichloromethane.

(c) Template reaction

Planar quadridentate complexes can be prepared by this method[19,20]. The formation of macrocyclic rings is favoured by the presence of a cation of appropriate size that it can serve to hold the partially formed ligand in position as the remainder of the ring being synthesised. This process is called the template effect. Addition of salicylaldehyde to an aqueous solution of tetrakis(ethylenediammine)dichlorodinickel(II)chloride containing a few drops of pyridine results in the formation of $[Ni(Salen)_2]$ in 94% yield.

(d) Mechano-chemical method

In this method the complex is prepared by rubbing metal surfaces with ligands in solution.

A systematic study of Schiff base complexes was done by Pfeiffer and co-workers in 1931[21]. Because of the great synthetic flexibility of Schiff base formation, a large number of Schiff bases of different structural types have been synthesised. The main reason for the enormous amount of work in this field is due to the wide possibilities of synthesising a large number of Schiff base ligands with a single aldehyde, and each of these Schiff bases are able to form a considerable number of metal complexes. This is true with most of the aldehydes, especially with salicylaldehyde. In the exhaustive review on the metal complexes of Schiff bases by Holm et al[15], more than half of the discussion is confined to the Schiff base complexes derived from salicylaldehyde. Even though the amount of work done on the metal complexes of the Schiff bases derived from other aldehydes is considerably less compared to salicylaldimines, the literature on these complexes would still be enormous. It would be difficult to discuss all these types of complexes, and hence we limit our discussion to the Schiff base complexes derived from thiosemicarbazides and semicarbazides.

Metal complexes of thiosemicarbazones

In recent years, considerable interest has been evoked by the metal complexes of first transition series metal ions with sulphur donor Schiff bases having NS or ONS donor atoms. Among the various Schiff bases, thiosemicarbazones are of great importance because of their antimicrobial action[22,23]. Many of these are active against influenza, protozoa, smallpox and certain kinds of tumour. They have been suggested as possible pesticides and fungicides. A large number of thiosemocarbazones have been prepared by the condensation of aliphatic, aromatic or heterocyclic aldehydes or ketones with thiosemicarbazide.

Biological activity of the ligand can be increased by modifying the thiosemicarbazide ligand. Modification can be done by (1) exchanging the S atom of the thiocarbonyl group by oxygen or selenium, (2) exchanging the point of attachment of the thiosemicarbazide, (3) making substitution on the terminal N atom and (4) varying the aldehyde or ketone.

Synthetic methods for thiosemicarbazones have been well discussed by Klayman et al[24]. In a more recent report by Scovill[25], a trans-amination reaction has been made use for the preparation of thiosemicarbazone from N-methyl-N-phenyl-thiosemicarbazide.

Preparations of complexes have been accomplished in a variety of solvents at different pH values and at different temperatures. These different preparative conditions and changes in the nature of substituents attached to nitrogen atom of the thiosemicarbazones yielded cationic, neutral or anionic complexes.

In solution, thiosemicarbazones exist as an equilibrium mixture of thione(I) and thiol(II) tautomers. (Fig. 1.1).

$R=N-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-NH_2$ $\qquad$ $R=N-N=\overset{SH}{\overset{|}{C}}-NH_2$

(I) (II)

Fig. 1.1 Tautomeric structure of thiosemicarbazone.

The thione(I) acts as a neutral bidentate ligand while the deprotonated thiol can act as a singly charged bidentate ligand. In most of the metal complexes of thiosemicarbazones, the ligand is found to be in the neutral form. Padhye[26] and co-workers have prepared a cobalt complex containing both the tautomeric forms of the ligand, 2-hydroxy-1,4-naphthaquinone thiosemicarbazone. The formation of such a mixed ligand tautomeric complex is generally accompanied by oxidation of the central metal ion.

In most of the complexes, the thiosemicarbazone remains in the cis configuration (Fig.1.2.)

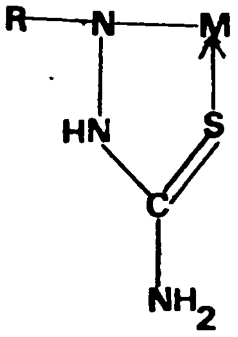


Fig. 1.2 Cis configuration of thiosemicarbazone complexes.

The attachment to the metal atom is usually through the thione/thiol S atom and the hydrazine N atom in a bidentate manner. Thiosemicarbazone complexes reported so far are predominantly those of the latter half of the transition metal ions. This might be due to the preference for soft S-atom of the ligand (soft base) to interact strongly with soft acids. Thus the low spin d^8 ions, Pd(II), Pt(II), and Au(II) and d^{10} ions Cu(I), Ag(I), Au(I) and Hg.II) exhibit higher stability constants with thiosemicarbazones[27]. However thiosemicarbazone complexes without S coordination are also known and those have been prepared through a template reaction[28].

The stereochemistries adopted by thiosemicarbazone ligand while interacting with transition metal ions depend essentially upon the presence of an additional coordination centre in the ligand moiety and charge of the ligand, which in turn is influenced by the thione $\rightleftharpoons$ thiol equilibrium. For example, benzaldehyde thiosemicarbazone is generally found to act as a neutral bidentate ligand depending upon the pH of the medium yielding complexes of the type $[ML_2X_2]$ where (M = Co(II), Ni(II), Cu(II) or Fe(II) and L = the ligand in the thione form and X= the monoanionic ligand) where as the salicylaldehyde thiosemicarbazone is found to act as a tridentate uninegative ligand yielding compounds of the type ML_2 which may be spin free or spin paired[29].

Thiosemicarbazones are not so strong as other soft base ligands like cyanide, diarsine and certain charged S-ligands. Thione forms cannot cause any spin pairing in metal complexes[30]. But thiol forms can lead to low spin complexes of Co(II) and Ni(II)[31], however they are not capable of causing spin pairing in their Fe(III) complexes.

A few reviews on metal complexes of thiosemicarbazones have appeared in the literature. A review on the important developments in the structural chemistry of transition metal complexes of thiosemicarbazones was appeared in 1985[26]. Campbell[32] has made a comprehensive review on the coordination chemistry of thiosemicarbazide and thiosemicarbazone, which provides details of the thermodynamic, structural, magnetic and electronic properties of their metal complexes. Recently West and Liberta have reviewed papers dealing with the spectral, structural and biological properties of some thiosemicarbazone complexes of copper(II)[33].

Metal complexes derived from the following thiosemicarbazone ligands were synthesised and characterised. A list of such complexes are set out in Table I.1

Table I.1 Metal complexes of thiosemicarbazones.

Metal	Ligand	Ref
Iron(II)	acetone thiosemicarbazone	34
:	1-formylisoquinoline thiosemicarbazone	34
:	4-methyl-5-amino-1-formylisoquinoline thiosemicarbazone	34
:	4-(m-amionophenyl)-2-(formylpyridine) thiosemicarbazone	34

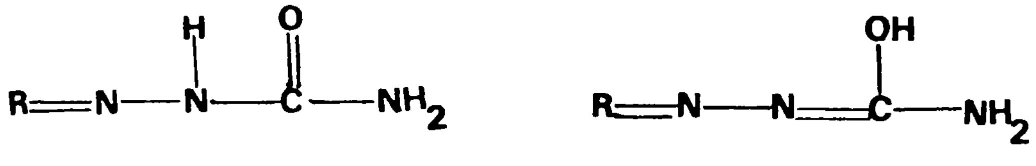
Metal	Ligand	Ref
Iron(II)	2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one thiosemicarbazone	35
Iron(III)	1-formylisoquinoline thiosemicarbazone	34
:	4-methyl-5-amino-1-formylisoquinoline thiosemicarbazone	34
:	4-(m-amionophenyl)-2-(formylpyridine) thiosemicarbazone	34
Iron(III)	acetoacetanilide thiosemicarbazone	53
Cobalt(II)	p-anisaldehyde thiosemicarbazone	36
:	2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one thiosemicarbazone	35
:	benzylmethyl-ketone thiosemicarbazone	37
:	2-furfuraldehyde thiosemicarbazone	38
:	propiophenone thiosemicarbazone	39
:	4-(2-thiazolyl)-1-(2-acetylfuran) thiosemicarbazone	40
:	4-(m-amionophenyl)-2-(formylpyridine) thiosemicarbazone	41
:	piperonaldehyde 3,4-methylene-oxybenzaldehyde thiosemicarbazone	42
:	quinoxaline-2-carboxaldehyde thiosemicarbazone	49
	2-phenyl-1,2,3-triazole-4-carboxaldehyde thiosemicarbazone	50
:	p-acetamidobenzaldehyde thiosemicarbazone	51

Metal	Ligand	Ref
Cobalt(II)	isatin 4(2-pyridyl)-3-thiosemicarbazone	52
:	acetoacetanilide thiosemicarbazone	53
Nickel(II)	p-anisaldehyde thiosemicarbazone	36
:	4-(methoxy benzaldehyde)-4-phenyl-3-thiosemicarbazone	43
:	benzylmethylketone thiosemicarbazone	44
:	propiophenone thiosemicarbazone	39
Nickel(II)	1-(o-aminoacetato-phenone)-4-phenyl thiosemicarbazone	45
:	quinoxaline-2-carboxaldehyde thiosemicarbazone	49
:	2-phenyl-1,2,3-triazole-4-carboxaldehyde thiosemicarbazone	50
:	p-acetamidobenzaldehyde thiosemicarbazone	51
:	isatin 4(2-pyridyl)-3-thiosemicarbazone	52
:	Acetoacetanilide thiosemicarbazone	53
Copper(II)	Indane-1,2,3-trione mono thiosemicarbazone	46
:	propiophenone thiosemicarbazone	39
:	4-(m-amionophenyl)-2-(formylpyridine) thiosemicarbazone	41

Metal	Ligand	Ref
Copper(II)	2-formylpyridine thiosemicarbazone	47
:	2-acetylpyridine thiosemicarbazone	47
:	4,5-dimethyl pyrazole-3-carboxaldehyde thiosemicarbazone	48
:	4-(2-thiazolyl)-1-(2-acetylfuran) thiosemicarbazone	40
:	benzylmethylketone thiosemicarbazone	37
:	quinoxaline-2-carboxaldehyde thiosemicarbazone	49
:	2-phenyl-1,2,3-triazole-4-carboxaldehyde thiosemicarbazone	50
:	acetoacetanilide thiosemicarbazone	53
:	isatin 4(2-pyridyl)-3-thiosemicarbazone	52
Zinc(II)	isatin 4(2-pyridyl)-3-thiosemicarbzone	52
:	p-acetamidobenzaldehyde thiosemicarbazone	51

Metal complexes of Semicarbazones

Schiff base complexes having oxygen coordination is important both structurally and biologically. These types of compounds include Schiff base complexes derived from semicarbazide, aminoacids, aminophenols etc.[54-56] The oxygen atoms are coordinated in most cases to a transition metal ion to secure the stability of the complex. In solution semicarbazone exists as an equilibrium mixture of keto(I) and enol(II) forms.



$R{=}N{-}NH{-}C({=}O){-}NH_2$ $\qquad$ $R{=}N{-}N{=}C(OH){-}NH_2$

(I) (II)

Fig. 1.2 Tautomeric structure of semicarbazone.

Semicarbazone acts as a bidentate or tridentate ligand depending on the aldehyde residue attached to semicarbazide moiety. In most of the complexes semicarbazone remain in the trans configuration.

Salicylaldehyde semicarbazone a potentially tridentate ligand, is found to act as a bidentate monoanion because of the nonparticipation of the carbonyl oxygen[57] of the semicarbazone moiety. This seems to be a typical ligation behavior of aryl derivatives and has been termed the flip-tail bidenticity of semicarbazone ligand. The interaction of potentially tridentate dibasic semicarbazone ligand with cobalt(II) salts yields complexes which are diamagnetic[58]. A number of metal complexes of semicarbazones have been synthesised and characterised. A list of such complexes are given in Table.I.2.

Table-I.2 Metal complexes of semicarbazones.

Metal	Ligand	Ref.
Vanadium(IV)	2-hydroxy naphthaldehyde semicarbazone	57
	Cyclohexanone semicarbazone	58
Chromium(III)	5-chloro salicyldehyde semicarbazone	34
	diacetyl monoxime semicarbazone	34
Manganese(II)	4-methylphenylpyruvic acid semicarbazone	59
Manganese(II)	phenylpyruvic acid semicarbazone	59
Iron(III)	5-bromo salicylaldehyde semicarbazone	60
:	5-chloro salicyldehyde semicarbazone	58
Iron(II)	Acetone semicarbazone	61
Iron(II)	2-hydroxy-1,4 naphthaquinone semicarbazone	62
Cobalt(II)	isatin semicarbazone	63
Cobalt(II)	salicylaldehyde semicarbazone	58
Cobalt(III)	2-hydroxy-1,4-naphthoquinone semicarbazone	62
Nickel(II)	isatin semicarbazone	63
Copper(II)	2-hydroxy naphthaldehyde semicarbazone	57

Metal	Ligand	Ref.
Copper(II)	phenylpyruvic acid semicarbazone	59
Copper(II)	4-methylphenylpyruvic acid semicarbazone	59
Copper(II)	isatin semicarbazone	63
Zinc(II)	ethyl acetoacetate semicarbazone	64
Zinc(II)	isatin semicarbazone	63

We have made an earnest attempt to collect literature on complexes of the Schiff bases derived from triazoles and flavazoles. Unfortunately, the literature on these complexes are very scanty.[65]

Applications of Schiff base complexes

Some of the Schiff base complexes find use as catalyst in many organic reactions. Many of these complexes have antimicrobial, antimalarial and fungicidal properties.[2] They also find application in quantitative and qualitative analysis of metals.[66] Further they are also used in solvent extraction of metals[67,68]. Here we discuss only the application of Schiff base complexes as catalysts.

Catalysis by Schiff base complexes

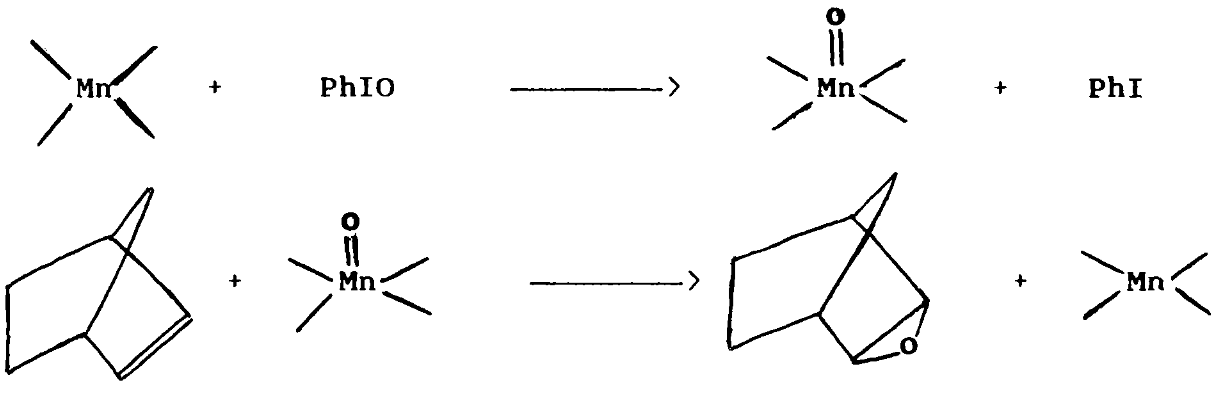
Schiff base complexes catalyse reactions like hydrolysis, carboxylation, decarboxylation, elimination, aldol condensation and redox reactions.[69-71]

Copper(II) Schiff base complexes are found to act as catalysts for the oxidative coupling of phenols[72]. They also act as catalysts for the oxidation of phenols to quinones. These complexes usually form adducts with oxygen molecules. Information about many such complexes which can be bound reversibly with dioxygen are available in the review by Basolo et.al[73].

Cobalt(II) complexes of aromatic Schiff bases form oxygenated complexes at lower temperatures (~ 0°C) possibly because these Schiff bases can readily donate electron density to the metal ion. Cobalt(II) complexes with the Schiff base ligands such as Co(Salen) [where Salen = N,N'-bis(salicylaldehyde) ethylenediimine dianion] and its analogues have been the first and most extensively investigated as reversible oxygen carriers[74-76]. Much attention has been paid on the reaction mechanism and the molecular structure of the oxygenated complexes. The molecular structure of some of the 1:2 adducts of dioxygen with Co(salen) was confirmed in solution by EPR studies and dioxygen absorption measurements. Four coordinated planar cobalt(II) Schiff base complexes readily bind dioxygen in the presence of suitable monodentate Lewis bases such as amines and solvents which increase electron density at the metal center and this cause additional stabilization of the cobalt(II)-O_2 bond. Yuriko et.al[77] have studied the high dioxygen uptake by hetero-metal binuclear Co(II)-Fe(II) Schiff base complex systems in dimethylsulphoxide under nitrogen and air by spectrophotometry and cyclic voltammetry and dioxygen uptake measurements.

The epoxidation reactions of olefins using tri and tetradentate Schiff base complexes of Fe(III) as catalysts and iodosylbenzene as the oxidant have been studied. Cyclohexene gave cyclohexene oxide, cyclohexanol and cyclohexanone as products[78]. At higher concentrations of the catalyst, high selectivity of epoxide was observed. However, only low yield was obtained. The yield of epoxide increases with increase in concentration of cyclohexene. The relative rate of epoxidation of cyclo-olefins exhibit the order: norbornene > cyclooctene > cycloheptene > cyclohexene > cyclopentene. The addition of pyridine, NaH_2PO_4 or $NaHCO_3$ was found to increase the yield of epoxide while cetyltrimethylamomonium bromide completely inhibits epoxidation[79].

Manganese(II) Schiff base complexes have also been employed as catalyst for epoxidation of olefins[80] using iodosylbenzene(PhIO) as an oxidant in acetonitrile-water solvent mixture. Binuclear Mn(II) complexes selectively catalysed the epoxidation, whereas selectivity was not observed in the case of mononuclear complexes.Among the binuclear complexes, the complex having a m-phenylenediamine bridge was found to be a superior catalyst to the one with a p-phenylenediamine bridge . The catalytic turnover number indicate that the reaction probably proceeds through a transient oxo - manganese(IV) species as shown below:



Addition of bases resulted in lower yields of epoxides with slight decrease in the rate of reaction. The retarding effect on the rates of the reaction increases with increasing basicity.

A large variety of polymer supported Schiff base complexes were synthesised and they are found to be very good oxygen carriers. The Co(II) complexes of bis(acetylacetonato ethylenediamine) or Salen can be anchored to a polymer . Such complexes act as reversible oxygen carriers even at room temperature[81]. The oxygenations in these cases can be monitored by either ESR or visible spectroscopy.

The major problem associated with the study of catalytic process is the lack of information on the nature of reactive intermediates or of the active catalyst. A method has been developed by Gassman etal[82] for the isolation and characterisation of highly reactive intermediates in homogeneous catalysis by transition metal complexes. The method involves the principle of steric exclusion type chromatography, which has been devised for the isolation of highly reactive intermediates on the surface of a porous polymer film. Analysis of these surface-isolated intermediates was carried out by X-ray photoelectron spectroscopy which provided detailed information about the complexes that resided on the surface of the film.

SCOPE OF THE PRESENT INVESTIGATION

Metal complexes of Schiff bases have received more attention due to their biological and catalytic activities. Many Schiff base complexes were found to satisfy the requirements for acting as catalysts for oxidation of organic substrates[83]. Selective oxidation or oxygenation of organic substances is important in chemical and petrochemical industries due to the wide variety of products synthesised in this route[84-86]. Among the various oxidants, dioxygen is very attractive due to its low cost and availability from liquid air; however, it usually reacts with organic substrates only in the presence of a catalyst.[86]

Because of the easy design and simple synthesis of Schiff base ligands, many interesting catalytically/biologically active complexes can be synthesised. So it was thought worthwhile to synthesize new Schiff base complexes and study their catalytic activities. Eventhough biological activity studies were not included as a part of the present investigation, we hope that the metal complexes reported herein might later find application in pharmacology, medicine etc. Complexes involving the following ligands were selected for the present study.

1. Schiff base ligand formed by the condensation of 2-phenyl-1,2,3-triazole-4-carboxaldehyde with aniline, semicarbazide or thiosemicarbazide.

2. Schiff base ligand formed by the condensation of 1-phenylflavazole-4-carboxaldehyde with semicarbazide, thiosemicarbazide and 2-aminophenol.

Several new complexes of these ligands have been synthesised and characterised using elemental analysis, conductance and magnetic measurements, IR, electronic and ESR. spectral studies, cyclic voltammetry and thermal analyses. These complexes were screened for their catalytic activity and found that some of the copper(II) complexes are very good catalysts for the oxidation of hydroquinone to quinone.

CHAPTER II

EXPERIMENTAL TECHNIQUES

Details about the general reagents used, the preparation of ligands and the various analytical and physical methods employed in the characterisation of metal complexes are presented in this chapter. Procedural details regarding the synthesis of metal complexes are given in appropriate chapters.

2.1 REAGENTS

The following metal salts were used: $Co(NO_3)_2.6H_2O$ (E. Merck, GR), $CoCl_2.6H_2O$ (E. Merck, GR), $CoBr_2$ (Aldrich, 98% pure), $Cu(CH_3COO)_2.H_2O$ (BDH, GR), $Cu(ClO_4)_2.6H_2O$, (E. Merck, GR) and $ZnCl_2$ (E. Merck, GR).

Aniline (E. Merck, GR), thiosemicarbazide (E. Merck, GR), semicarbazide hydrochloride (CDH, GR) and 2-aminophenol (CDH, GR) were also used for the present work.

Unless otherwise specified, all other reagents used were of analytical reagent grade. Solvents employed were either of 99% purity or purified by known laboratory procedures[87].

2-Phenyl-1,2,3-triazole-4-carboxaldehyde was prepared[88] by the following procedure: Phenylhydrazine (0.2 mol, 20 mL) was dissolved in glacial acetic acid (20 mL) and was added to a 20% aqueous solution of glucose (50 mL). The solution was stirred well and heated on a water bath for 20 min. Yellow glucosazone separated out was filtered, washed with water and dried. Osazone(0.005 mol, 2 g) was dissolved in minimum quantity of water and $CuSO_4.5H_2O$ (3 g) was added. The solution was heated under boiling for about 3 h, and was then filtered. The volume of the filtrate was reduced to almost half under vacuum and was kept over night for the complete separation of phenylozotriazole. It was then recrystallised from hot water. Phenylozotriazole (0.0075 mol, 2 g) was then dissolved in water (75 mL) and was added to a solution of sodium metaperiodate (0.03 mol, 7.3 gm) in water (75 mL). The mixture was stirred for 10 h at 20 °C and then kept at 5 °C for 10 min. 2-Phenyl-1,2,3-triazole-4-carboxaldehyde separated out was filtered and dried. (Yield: 55%; m. p: 121 °C)

1-Phenylflavazole-3-carboxaldehyde was prepared[89] according to the following procedure: Phenylhydrazine hydrochloride (0.05 mol, 7.2 g) and glacial acetic acid (2.4 mL) was added to a solution containing glucose(1.8 g) and o-phenylenediamine (0.01 mol, 1.1 g) in water(100 mL), and the mixture was refluxed for 12 h on a boiling water bath under carbon dioxide atmosphere. The solid mass in the reaction mixture, 1-phenyl-3(D-erythro-trihydroxy propyl)flavazole, was filtered, washed with very small quantity of water, and was finally recrystallised from 1-propanol after decolourising it with animal charcoal. The recrystallised 1-phenyl-3(D-erythro-trihydroxy propyl)flavazole (0.01 mol, 3.3 g) and sodium metaperiodate (0.02 mol, 4.2 g) were dissolved in water and stirred for 8 h. Impure aldehyde remains in the mixture as a solid, and was filtered and dried. It was then dissolved in chloroform and was separated from impurities by column chromatography over neutral alumina. It was finally purified by recrystallisation from hexane.

2.2 PREPARATION OF LIGANDS

2.2.1 2-Phenyl-1,2,3-triazole-4-carboxalidene aniline

2-Phenyl-1,2,3-triazole-4-carboxaldehyde (0.01 mol, 1.73 g) was dissolved in ethanol (100 mL) and was added with constant stirring to a solution of aniline (0.02 mol, 0.95 g) in ethanol (100 mL). The mixture was stirred for one hour. The Schiff base separated out was filtered, washed with alcohol and recrystallised from chloroform. (Yield : 85%; m.p: 88°C)

2.2.2 2-Phenyl-1,2,3-triazole-4-carboxaldehyde thiosemicarbazone

An ethanolic solution (100 mL) of 2-Phenyl-1,2,3-triazole-4-carboxaldehyde (0.01 mol, 1.73 g) was added to a stirring solution of thiosemicarbazide (0.01 mol, 0.91 g) in ethanol (100 mL). The mixture was refluxed on a water bath for 3 h and allowed to cool overnight. The ligand separated out was filtered and recrystallised from hexane. (Yield: 80%; m.p: 206 °C)

2.2.3 2-Phenyl-1,2,3-triazole-4-carboxaldehyde semicarbazone

Semicarbazide hydrochloride (0.01 mol, 1.15 g) was dissolved in minimum quantity of 0.01N NaOH and the mixture was heated to boiling. The solution was cooled and tested for neutrality using pH paper. More acid or alkali was added to maintain the pH at 7. An ethanolic solution (100 mL) containing 2-Phenyl-1,2,3-triazole -4-carboxaldehyde (0.01 mol, 1.73 g) was then slowly added to the neutral solution of semicarbazide with continuous stirring. The mixture was refluxed on a water bath for 2 h. Semicarbazone separated out on cooling was filtered, washed with ethanol and recrystallised from 1-propanol. (Yield: 75%; m.p:216°C)

2.2.4 1-Phenylflavazole-3-carboxaldehyde thiosemicarbazone

1-Phenylflavazole-3-carboxaldehyde (0.01 mol, 2.74 g) was dissolved in ethanol (100 mL) and was added to a stirring solution of thiosemicarbazide (0.01 mol, 0.91 g) in ethanol (100 mL). The mixture was refluxed on a water bath for 3 h and kept overnight. The ligand separated out was filtered, washed with alcohol and recrystallised from hexane. (Yield: 80%;

m.p :224°C)

2.2.5 1-Phenylflavazole-3-carboxaldehyde semicarbazone

This compound was prepared in the same way as 2-phenyl-1,2,3-triazole-4-carboxaldehyde semicarbazone using semicarbazide hydrochloride (0.01 mol, 1.15 g) and 1-phenylflavazole-3-carboxaldehyde(0.01 mol, 2.74 g). (Yield: 65%; m.p: 220 °C).

2.2.6 1-Phenylflavazole-3-carboxalidene-2-aminophenol

1-Phenylflavazole-3-carboxaldehyde (0.01 mol, 2.74 g) was dissolved in ethanol (100 mL) and was added to a stirring solution of 2-aminophenol (0.01 mol, 1.09 g) in ethanol (100 mL). The mixture was stirred for 1 h. The ligand separated out was filtered, washed with alcohol and recrystallised from chloroform. (Yield, 80%; m.p :215 °C)

2.3 ANALYTICAL METHODS

2.3.1 Estimation of metals

In all the cases the organic part of the metal complexes was completely eliminated before the estimation of metals. The following procedure was used for the elimination of organic part of the sulphur containing complexes. A known weight of the metal complex (0.2-0.3g) was treated with conc. nitric acid (25 mL) and bromine in carbontetrachloride (20 mL). This mixture was kept for about 3 h. It was then evaporated to dryness on a water bath and converted to its sulphate by fuming with a few drops of conc. sulphuric acid several times. The resulting metal sulphate was dissolved in water and was used for the estimation of metals.

For all other cases, the elimination of organic part was done as follows. A known weight of the metal complex (0.2-0.3 g) was treated with conc. sulphuric acid (5 mL) followed by conc. nitric acid (20 ml). After completion of the vigorous reaction perchloric acid (5 mL, 60%) was added. This mixture was maintained at the boiling temperature for 3 h on a sand bath. The clear solution thus obtained was dissolved in water and this solution was used for the estimation of metals.

Gravimetric procedures[90] were used for the estimation of cobalt and nickel. Cobalt was estimated by precipitating it as $[Co(C_5H_5N)_4](SCN)_2$ using ammonium thiocyanate and pyridine. Nickel was estimated as nickel dimethylglyoximate complex by adding an alcoholic solution of dimethylglyoxime followed by ammonia solution. Iodometric method[90] was employed for the estimation of copper in the complex. Zinc was volumetrically estimated using standardised EDTA solution.

2.3.2. **CHN Analysis**

Microanalyses for carbon, hydrogen and nitrogen were done on a Heraeus CHN elemental analyser.

2.3.3. Estimation of halogen and sulphur[90]

Halogen content was determined by peroxide fusion of the sample followed by volumetric estimation using Volhard's method. For sulphur estimation, the complexes were fused with Na_2CO_3 and Na_2O_2 and the resulting sulphate was determined gravimetrically as barium sulphate.

2.4 PHYSICO-CHEMICAL METHODS

2.4.1 Conductance measurements

Molar conductances of the complexes in nitrobenzene or methanol were determined at 28 ± 2 °C using a conductivity bridge (Centuary CC 601) with a dip type cell and a platinised platinum electrode.

2.4.2 Magnetic susceptibility measurements

The magnetic susceptibility measurements were done at room temperature (28 ± 2 °C) using EG & G PARC model 155 vibrating sample magnetometer or on a simple Gouy-type magnetic balance. The Gouy tube was standardised using $Co[Hg(SCN)_4)]$ as standard recommended by Figgis and Nyholm[91]. The effective magnetic moment was calculated using the equation,

$$\mu_{eff} = 2.84\ (\chi_m{'}T)^{1/2}\ \mathrm{BM}$$

where T is the absolute temperature and $\chi_m{'}$ is the molar susceptibility corrected for diamagnetism of all the atoms present in the complex using Pascal's constants[92-95].

2.4.3 Electronic spectra

Electronic spectra were taken in solution (in the case of soluble complexes) or in the solid state by mull technique following a procedure recommended by Venanzi[96]. The procedure is as given below:

Small filter paper strips were impregnated with a paste of sample in nujol. These were placed over the entrance to the photocell housing. A nujol treated filter paper strip of similar size and shape was used as the blank.

The spectra of the complexes were recorded on a Shimadzu UV-Vis. 160 A spectrophotometer or on a Hitachi U-3410 spectrophotometer.

2.2.4 Infrared spectra

Infrared spectra of the ligands and the complexes in the region 400-4600 cm^{-1} were taken both as nujol paste and as KBr discs on a Shimadzu 8101 FTIR spectrophotometer.

2.2.5 EPR spectra

The X-band EPR spectra of a few copper complexes were taken in chloroform-toluene mixture at room temperature as well as at liquid nitrogen temperature using Varian E-112 X/Q band spectrophotometer.

2.4.6 Cyclic voltammogram

Cyclic voltammogram were recorded using an EG & G PARC Model 362 scanning potentiostat. An undivided cell was used for the study. A platinum sheet (20 mm × 20 mm) was employed as the auxiliary electrode. A platinum button electrode of area 4 mm^2 was used as the working electrode and a calomel electrode as the reference electrode. The complexes were dissolved in suitable solvent. The supporting electrolyte used was 0.1 M $LiClO_4$ solution.

2.4.7. Thermal studies

The thermal studies were done on a Shimadzu TGA 50 thermal analyser with 5-10 mg samples at a heating rate of 10°C/min. in air atmosphere using platinum crucible.

CHAPTER-III

2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALIDENEANILINE COMPLEXES OF COPPER(II)

3.1 INTRODUCTION

Triazoles are important to the pharmaceuticals and agrochemical industries, since they show fungicidal, herbicidal and plant growth regulating properties[97]. They also find applications as optical brightners in textile industry and as polymer additives[98]. 2-Phenyl-1,2,3-triazole-4-carboxalideneaniline(PTCA) is interesting from the structural point of view because of the presence of three nitrogen atoms in the ring and one nitrogen atom outside the ring. We have synthesised copper(II) complexes of this ligand, and the results of our studies on these complexes are presented in this chapter.

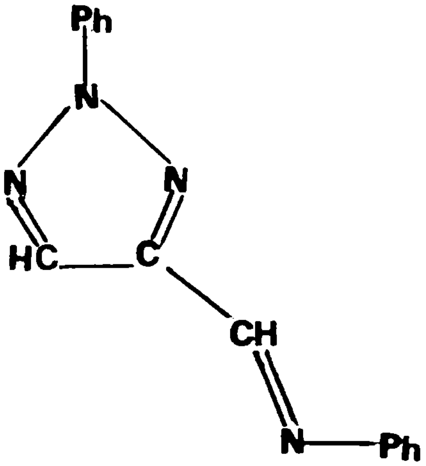


Fig 3.1 Structure of PTCA

3.2 EXPERIMENTAL

3.2.1 Materials

Details regarding the preparation and purification of the ligand, PTCA, are given in Chapter II.

3.2.2 Synthesis of the complexes

All the complexes were prepared by the following general procedure: A solution containing copper(II) salt (0.01 mol-1.7 g of $CuCl_2.2H_2O$, 2.23 g of $CuBr_2$, 1.99 g. of $Cu(OAc)_2.H_2O$ or 3.70 g of $Cu(ClO_4)_2.6H_2O$) in ethanol (100 mL) was added to a solution containing PTCA (0.02 mol, 4.96 g) in ethanol (100 mL). The mixture was refluxed on a water bath for 2-3 h. The complexes which separated out on cooling were filtered, washed with ethanol and dried *in vacuo* over anhydrous $CaCl_2$.

3.2.3 Analytical methods

Details about the analytical methods and other characterisation techniques are given in Chapter II.

3.3 RESULTS AND DISCUSSION

Attempts to form complexes of this ligand with metal salts of iron(III), cobalt(II), nickel(II) and copper(II) resulted in the isolation of solid complexes only for copper(II). The complexes isolated are non-hygroscopic, crystalline substances and are stable in air. They are soluble in DMSO, DMF, acetonitrile, nitrobenzene and chloroform. The analytical data (Table III.1)show that these complexes have the general formula $[Cu(PTCA)_2X_2]$ (X=Cl, Br or OAc, where OAc represents the acetate group). The molar conductance values (Table-III.2) reveal that all the complexes, except the perchlorato complex, are non-electrolytes in nitrobenzene. The perchlorato complex has a molar conductance value of 19.0 ohm^{-1} cm^{2} mol^{-1} which suggests that it is a 1:1 electrolyte in nitrobenzene[99]. The main reason for this slightly low value could be due to solvent interactions and the low ionic mobilities of the ions involved[99]. From the analytical and molar conductance data, the empirical formula of the perchlorato complex has been given as $[Cu(PTCA)_2(ClO_4)]ClO_4$.

3.3.1 Magnetic susceptibility measurements

Magnetic moment values are presented in Table III.2. All the complexes exhibit magnetic moment values around 1.9 BM at 28 ± 2°C . The data indicate the absence of any metal-metal interations and also exclude the possibility of these complexes having a tetrahedral structure.

Table III .2

Molar conductance and magnetic moment data.

Compound	Molar conductance (ohm^{-1} cm^{2} $mole^{-1}$)	Magnetic moment(BM)
1. $[Cu(PTCA)_2Cl_2]$	6.2	1.7
2. $[Cu(PTCA)_2Br_2]$	7	1.8
3. $[Cu(PTCA)_2(OAc)_2]$	9	1.9
4. $[Cu(PTCA)_2(ClO_4)]$ ClO_4	19	1.8

3.3.2 Infrared spectra

The infrared spectral data show that PTCA acts as a bidentate ligand coordinating through the ring N-3 atom as well as through the azomethine nitrogen atom. The ligand exhibits a band around 1590 cm^{-1} and 1635 cm^{-1} which might be due to ν(C=N) of the triazole ring[100] and ν(C=N) of the azomethine linkage respectively[101]. An additional band at 1560 cm^{-1} is found in the case of these complexes. The presence of this band and the retention of the 1590 cm^{-1} band suggest that only one of the ring nitrogen atoms is coordinated to the metal atom. In the spectra of complexes, the ν(C=N) (azomethine) band appears at 1625 cm^{-1}. This red shift clearly suggests the involvement of azomethine nitrogen atom in bonding to the metal ion[102-104]. In the case of the acetato complex, the acetate group acts as a monodentate ligand as indicated by the presence of two bands at 1615 cm^{-1} and 1340 cm^{-1} which can be assigned to ν_a(COO) and ν_s(COO) respectively[105]. Further it exhibits δ(COO) at 760 cm^{-1} which is unique for the unidentate acetate[103]. For the perchlorato complex, there are two additional bands, one at 1260 cm^{-1} and the other at 1130 cm^{-1}, which suggests that the perchlorate ion acts as a bidentate ligand[106]. In addition, two bands are observed at 980 cm^{-1} and 1080 cm^{-1} which are characteristic of the non-coordinated perchlorate group[103].

Table III .3

Infrared absorption frequencies (cm^{-1}).

L	I	II	III	IV	Assignment
2365 m	2360 m	2360 m	2365 m	2360 m	
2350 m	2350 m	2350 m	2350 m	2350 m	
1895 w	1890 w	1895 w	1890 w	1890 w	
1815 w	1815 w	1815 w	1815 w	1815 w	
1755 w	1755 w	1755 w	1780 w	1755 w	
1710 w	1710 w	1710 w	1710 w	1710 w	
1670 w	1675 w	1675 w	1675 w	1670 w	
1635 s	1620 s	1620 s	1620 s	1620 s	ν(C=N)(azomethine)
------	------	------	1615 m	------	ν_a(COO)
1590 s	1590 s	1590 s	1590 s	1590 s	ν(C=N) ring
------	1560 s	1560 s	1560 s	1560 s	ν(C=N) ring
1520 s	1520 s	1520 s	1520 s	1520 s	
1500 s	1500 s	1505 s	1500 s	1505 s	
1470 m	1480 m	1470 m	1475 m	1480 m	
1455 m	1455 m	1465 m	1455 m	1455 m	
1435 m	1430 m	1430 m	1430 m	1430 m	
1390 m	1395 m	1390 m	1390 m	1390 m	
1370 s	1360 s	1370 s	1360 s	1360 s	
-----	------	------	1340 m	-----	ν_s(COO)
1310 s	1305 s	1305 s	1305 s	1305 s	
-----	-----	-----	-----	1260 m	$\nu(ClO_4)$
1250 m	1250 m	1250 m	1250 m	1250 m	
1205 m	1205 m	1210 m	1205 m	1205 m	
1180 w	1180 w	1185 w	1180 w	1185 w	
1150 w	1150 w	1150 w	1150 w	1150 w	
------	------	-----	------	1130 m	$\nu(ClO_4)$
1105 w	1100 w	1105 w	1100 w	1105 w	
------	------	------	------	1080 m	$\nu(ClO_4)$

Table III.3 (Continued)

L	I	II	III	IV	Assignment
1040 s	1040 s	1040 s	1040 s	1040 s	
1030 m	1025 m	1030 m	1025 m	1025 m	
-----	-----	-----	-----	980 s	δ(ClO_4)
965 w	965 w	965 w	965 w	965 w	
915 m	915 m	915 m	915 m	915 m	
860 s	860 s	860 s	860 s	860 s	
790 m	785 m	785 m	790 m	785 m	
770 s	770 s	770 s	770 s	770 s	
-----	-----	-----	760 s	-----	δ(COO)
700 s	700 s	700 s	705 s	700 s	
690 s	690 s	690 s	690 s	690 s	
665 s	665 s	665 s	665 s	665 s	
620 w	620 w	620 w	625 w	620 w	
480 w	485 w	480 w	480 w	480 w	

Abbreviations : s = strong, m = medium, w = weak

L. PTCA I. $[Cu(PTCA)_2Cl_2]$, II. $[Cu(PTCA)_2Br_2]$,

III. $[Cu(PTCA)_2(OAc)_2]$IV. $[Cu(PTCA)_2(ClO_4)]ClO_4$

3.3.3 Electronic spectra

Two bands are seen in the spectra of the ligand: The band at 29140 cm^{-1} is assigned to the $\pi \longrightarrow \pi^*$ transition of the azomethine chromophore[107], and the band at higher energies (48070 cm^{-1}) is associated with the $\pi \longrightarrow \pi^*$ transition of the benzene ring[108]. In the spectra of the complexes, the band due to the azomethine chromophore is shifted to 31250 cm^{-1} indicating that amino nitrogen is involved in coordination[109]; while the band ascribed to the benzene $\pi \longrightarrow \pi^*$ transition is nearly at the same position as that of the ligand (48070 cm^{-1}). A band is also seen at 36760 cm^{-1} which may be due to a charge transfer transition. The d-d transitions are not observed, probably because they are masked by the charge transfer bands[110].

3.3.4 EPR spectra

The EPR spectrum (Fig.3.2) of $[Cu(PTCA)_2Br_2]$ was recorded in chloroform-toluene mixture at liquid nitrogen temperature. Kneubuhl's procedure[111] was used to calculate the g-values. Three g-values (g_1=2.29, g_2=2.08, g_3=2.01; A_1=70, A_2=75, A_3=80) were observed which may be due to a slight variation from the octahedral structure. As the lowest g-value is less than 2.04, a compressed rhombic symmetry is indicated for the complex[112]. Hyperfine lines corresponding to g_1, g_2 and g_3 values could be located. The variation in hyperfine line intensities and

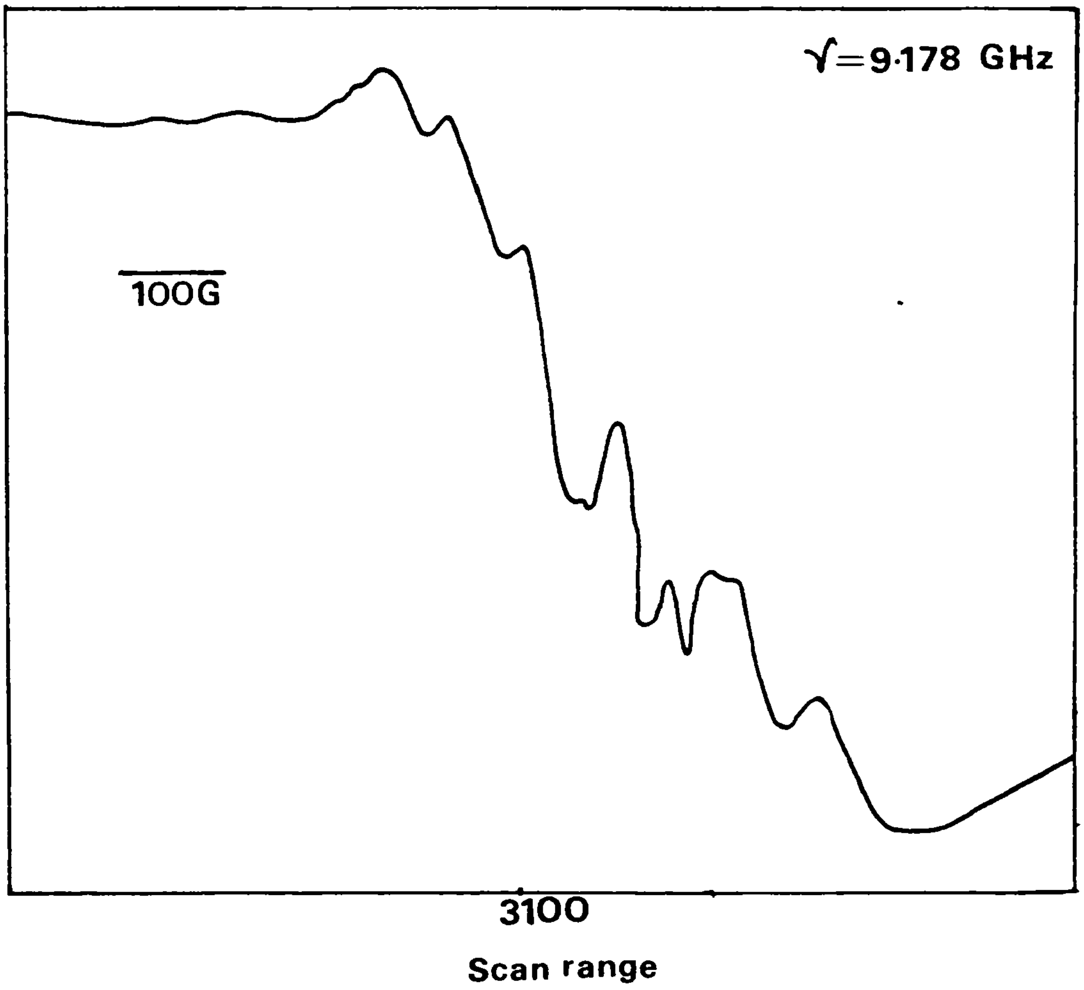


Fig 3.2 EPR spectrum of $[Cu(PTCA)_2Br_2]$ at liquid nitrogen temperature.

absence of some lines may be due to the superposition of different type of hyperfine lines.

3.3.5 Cyclic voltammetric studies

The cyclic voltammetric behavior of the complexes in dimethylsulphoxide is outlined taking $[Cu(PTCA)_2Cl_2]$ as an example. The potential was cycled between -1.6 V to +1.2 V using $LiClO_4$ as the supporting electrolyte. Fig.3.3a shows the cyclic voltammogram of the complex in oxygen free nitrogen. The complex gives three cathodic peaks and one anodic peak. The anodic peak at +0.66 V is due to the oxidation of Cu(II) to Cu(III). The graph of the peak current dependence at +0.66 V against the square root of scan rate gives a straight line showing that oxidation is reversible[113]. The cathodic peaks at +0.299 V, -0.531 V and -1.01 V are due to the reduction of Cu(III)——>Cu(II), Cu(II)——>Cu(I) and Cu(I)——>Cu(0) respectively.

On bubbling dry oxygen for 30 min. through a $[Cu(PCTA)_2Cl_2]$ solution, the following changes in cyclic voltammogram (Fig.3.3b) were observed: 1) An anodic peak appears at +0.114 V. This may be due to the presence of an oxygen adduct formed during the anodic cycle. 2) In the cathodic region a few additional peaks (not well shaped) appear at potentials greater than that required for oxygen superoxide ion reduction. The

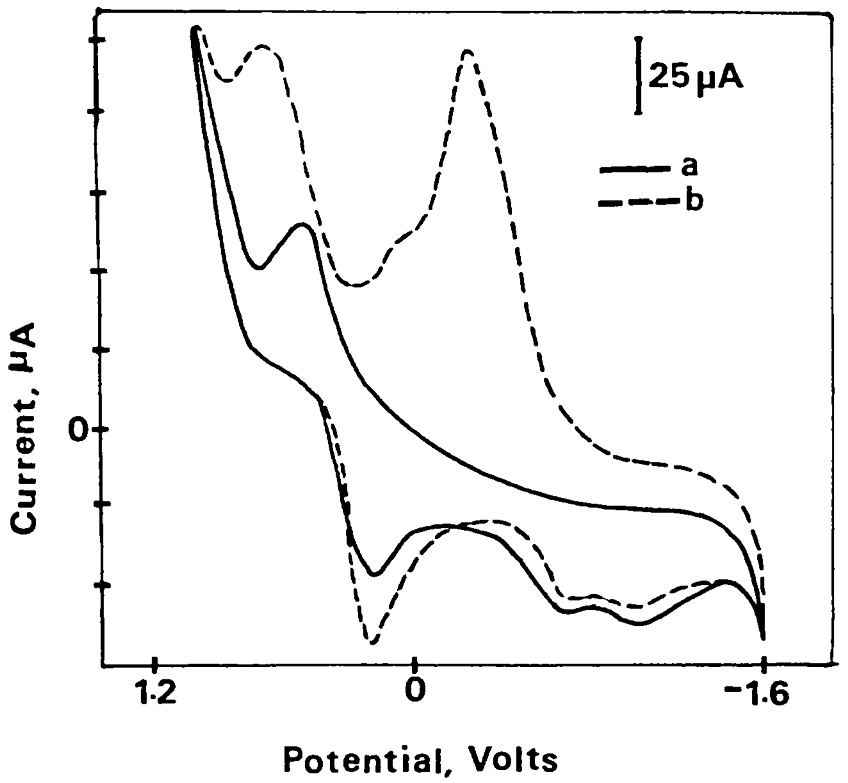


Fig 3.3 Cyclic voltammogram of $[Cu(PTCA)_2Cl_2]$.

(a) in nitrogen atmosphere, (b) in oxygen atmosphere system shows the development of another anodic peak with increase of the scan rate, which may be attributed to the formation of some metastable intermediates or conformational control of the electron transfer process[114].

3.3.6 Thermal studies

The thermoanalytical data of the chloro, bromo, and acetato complexes are given in Table III. 4. All the complexes have a wide stability range. They are stable up to 140°C, confirming the absence of any coordinated water molecules. The decomposition pattern of the complexes are similar. The mass loss at the first stage corresponds to the removal of two PTCA ligands. The decomposition is complete at the second stage and the residue left is copper(II) oxide. Based on these results the structure shown in Fig.3.5 may be assigned to the complexes.

Table-III. 4

Thermal Decomposition Data

Substance	Stage	Temperature Range in DTG	%Loss Found (Calc.)	Composition of expelled group
$[Cu(PTCA)_2Cl_2]$	I	170-420	77.1 (78.1)	2 PTCA
	II	420-840	11.0 (11.2)	2 chlorine
$[Cu(PTCA)_2Br_2]$	I	220-500	67.9 (68.8)	2 PTCA
	II	500-820	21.8 (22.3)	2 bromine
$[Cu(PTCA)_2(OAc)_2]$	I	200-500	72.8 (73.1)	2 PTCA
	II	500-800	17.0 (17.5)	2 acetate

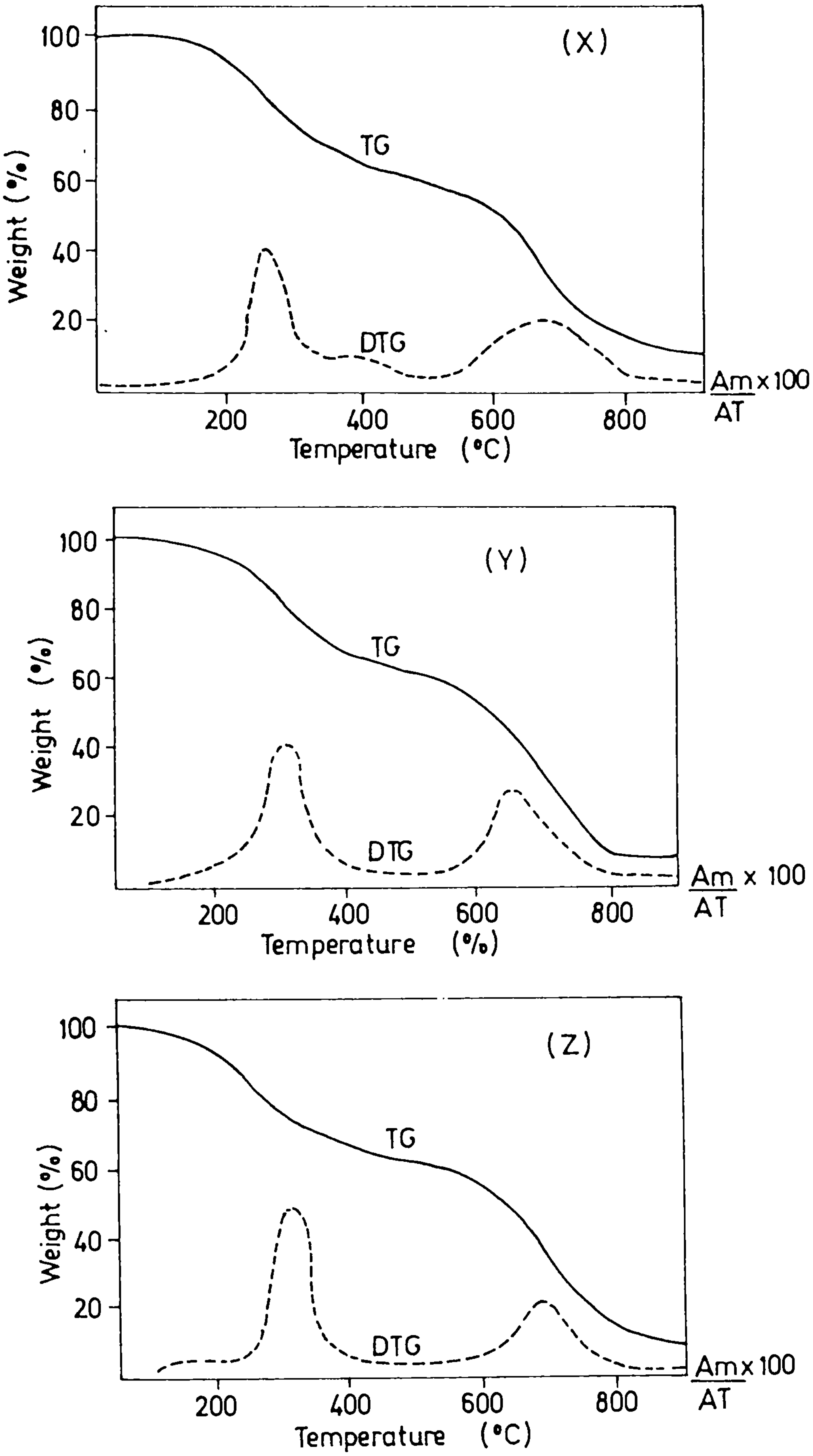


Fig. 3.4 TG/DTG traces of the complexes. X = $[Cu(PTCA)_2Cl_2]$, Y = $[Cu(PTCA)_2Br_2]$, Z = $[Cu(PTCA)_2(OAc)_2]$.

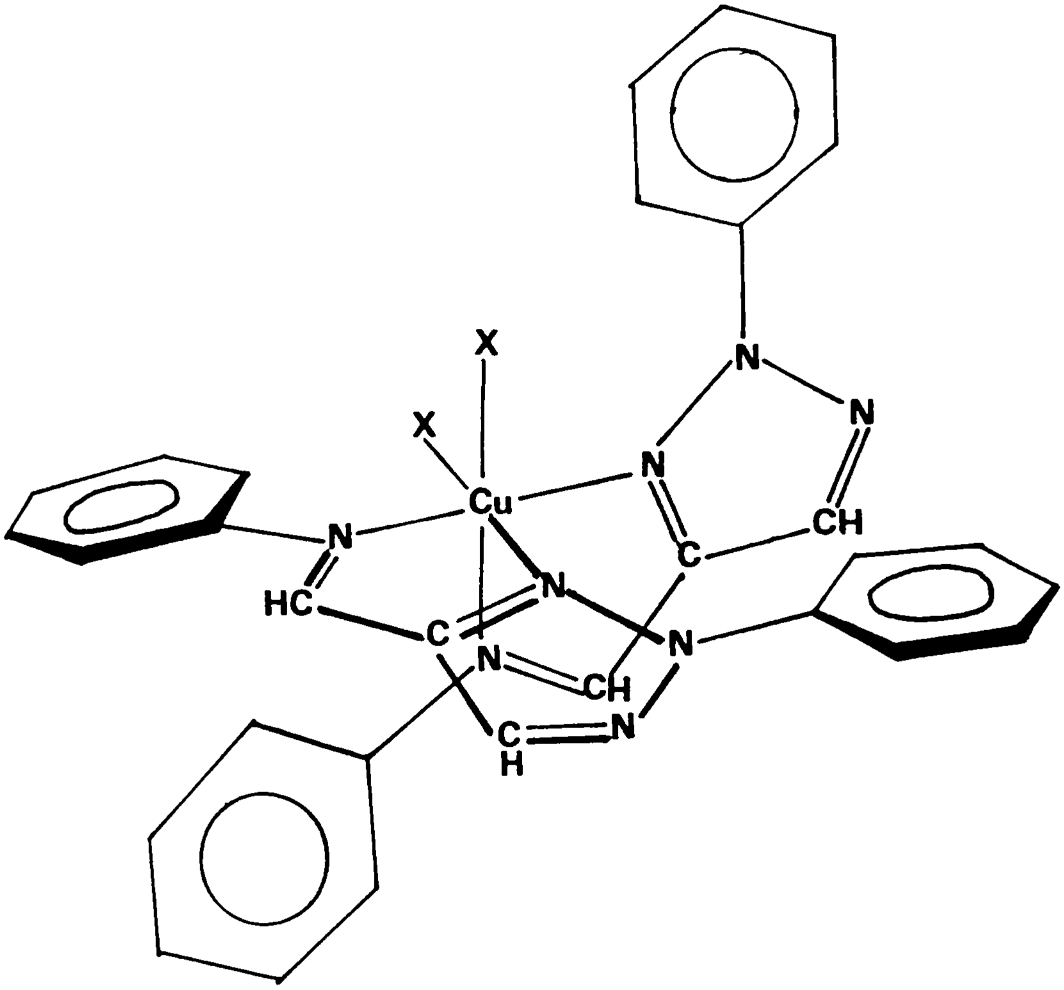


Fig. 3.5 Schematic structure of the complexes. For the perchlorato complex XX=ClO_4 with a ClO_4^- counter ion . For all the other complexes X=Cl,Br or OAc.

CHAPTER IV

2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALDEHYDE THIOSEMICARBAZONE COMPLEXES OF Co(II), Ni(II), Cu(II) AND Zn(II)

4.1. INTRODUCTION

In this chapter, our studies on the synthesis and characterisation of some transition metal complexes of 2-phenyl-1,2,3-triazole-4-carboxaldehyde thiosemicarbazone (PTSC) are presented. 2-Phenyl-1,2,3-triazole-4-carboxaldehyde thiosemicarbazone is interesting due to the many potential sites for coordination: three nitrogen atoms in the ring, one sulphur atom and three nitrogen atoms outside the ring. Furthermore, the ligand might show anticancer activity as it is capable of NNS coordination with the metal atoms. Pronounced anticancer activity has been reported for compounds having this capability[115].

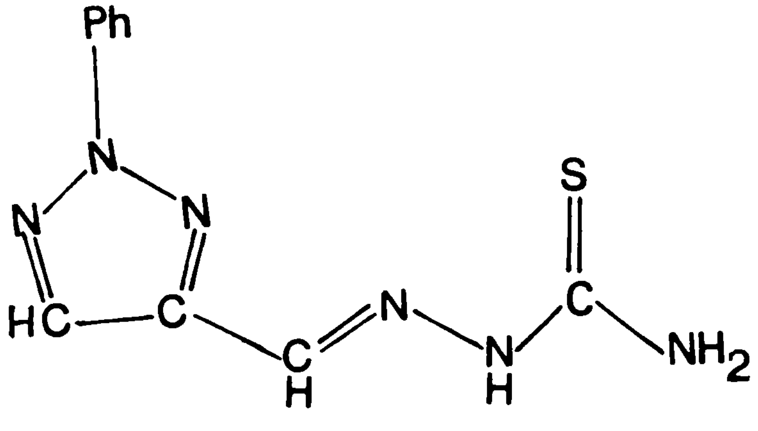


Fig 4.1 Structure of PTSC

4.2 EXPERIMENTAL

4.2.1 Materials

Details regarding the preparation and purification of the ligand are given in Chapter II.

3.2.2 Synthesis of the complexes

All the complexes were prepared by the following general procedure. The ligand PTSC (0.01 mol, 2.46 g) was dissolved in ethanol (80 mL). To this solution metal chloride (0.005 mol- 1.19 g of $CoCl_2.6H_2O$, 1.19 g of $NiCl_2.6H_2O$, 0.85 g of $CuCl_2.2H_2O$ or 0.68 g of $ZnCl_2$) in ethanol (20 mL) was added and refluxed on a water bath for 4 h. After adding sodium acetate (~ 0.25 g), the reaction mixture was refluxed for two more hours. The complexes separated out on cooling were filtered, washed with ethanol and dried over anhydrous $CaCl_2$. (Yield: 60-75%).

4.2.3 Analytical methods

Details regarding the analytical methods and other characterisation techniques are given in Chapter II.

4.3 RESULTS AND DISCUSSION

The complexes isolated are non-hygroscopic, crystalline substances and are stable in air. They are soluble in chloroform, DMSO, DMF, nitrobenzene and acetonitrile and partially soluble in ethanol and methanol. The analytical data (Table-IV.1) show that the complexes have the general formula $[M(PTSC)_2(OAc)_2]$ (where M=Co(II), Ni(II), Cu(II) or Zn(II) and OAc represents acetate group). The molar conductance values (Table IV.2) show that these complexes are non-electrolytes in nitrobenzene[99].

4.3.1 Magnetic susceptibility measurements

The magnetic moment values of the complexes are presented in Table IV.2. All the complexes exhibit magnetic moment values which are in agreement with the octahedral structure.

4.3.2 Infrared spectra

The infrared spectra (Table IV.3) show that PTSC acts as a bidentate ligand coordinating through azomethine nitrogen atom and thione sulphur. The ligand exhibits a band around 1590 cm^{-1} and 1635 cm^{-1} which might be due to the $\nu(C=N)$ of the triazole ring[100] and $\nu(C=N)$ of the azomethine group[101] respectively. In the spectra of the complexes the azomethine band appears at 1620 cm^{-1}, which indicates the participation of the azomethine nitrogen in bonding to the metal atom[102,103]. The retention of the band at 1590 cm^{-1} shows that ring nitrogen is not involved in

Table IV.1

Physical and Analytical data

Substance	% Yield	C (%) Found (Calc.)	H (%) Found (Calc.)	N (%) Found (Calc.)	S (%) Found (Calc.)	M (%) Found (Calc.)
$[Ni(PTSC)_2(OAc)_2]$	75	42.90	3.79	24.90	10.10	8.81
$[NiC_{24}H_{26}N_{12}S_2O_4]$		(43.08)	(3.88)	(25.13)	(9.57)	(8.78)
$[Co(PTSC)_2(OAc)_2]$	60	43.60	3.83	25.25	9.80	8.76
$[CoC_{24}H_{26}N_{12}S_2O_4]$		(43.05)	(3.88)	(25.11)	(9.57)	(8.81)
$[Cu(PTSC)_2(OAc)_2]$	70	42.50	3.78	24.67	9.35	9.50
$[CuC_{24}H_{26}N_{12}S_2O_4]$		(42.76)	(3.86)	(24.94)	(9.50)	(9.43)
$[Zn(PTSC)_2(OAc)_2]$	63	42.74	3.63	24.47	9.30	9.63
$[ZnC_{24}H_{26}N_{12}S_2O_4]$		(42.64)	(3.84)	(24.84)	(9.47)	(9.68)

Table IV.2

Molar conductance and magnetic moment data.

Compound	Molar conductance (ohm^{-1} cm^2 $mole^{-1}$)	μ_{eff} (BM)
$[Ni(PTSC)_2(OAc)_2]$	1.3	3.2
$[Co(PTSC)_2(OAc)_2]$	1.5	5.1
$[Cu(PTSC)_2(OAc)_2]$	0.3	1.8
$[Zn(PTSC)_2(OAc)_2]$	0.5	diamagnetic

Table IV.3

Infrared absorption frequencies (cm^{-1}).

L	I	II	III	IV	Assignment
3162 m	3165 m	3162 m	3162 m	3162 m	
1635 s	1620 s	1620 s	1620 s	1620 s	ν(C=N) azomethine
------	1610 m	1610 m	1610 m	1610 m	ν_a(COO)
1603 m	1603 m	1603 m	1603 m	1603 m	
1590 s	1595 s	1590 s	1595 s	1590 s	ν(C=N) ring
1570 m	1570 m	1570 m	1570 m	1570 m	
1541 w	1545 w	1541 w	1545 w	1541 w	
1503 s	1503 s	1503 s	1503 s	1503 s	
1464 w	1465 w	1464 w	1465 w	1464 w	
1427 w	1430 w	1427 w	1430 w	1427 w	
-----	1410 m	1410 m	1410 m	1410 m	
1385 s	1385 s	1385 s	1385 s	1385 s	
1360 w	1355 w	1360 w	1355 w	1360 w	
------	1325 w	1325 w	1325 w	1325 w	ν_s(COO)
1250 w	1255 w	1250 w	1255 w	1250 w	
1197 m	1197 m	1197 m	1197 m	1197 m	
1126 m	1125 m	1126 m	1126 m	1126 m	
1047 w	1047 w	1050 w	1047 w	1047 w	
904 w	904 w	904 w	904 w	904 w	
802 w	802 w	802 w	802 w	802 w	
780	765 m	760 m	760 m	765 m	ν(C=S)
------	756 m	756 m	756 m	756 m	δ(COO)
729 w	729 w	729 w	729 w	729 w	

Abbreviations : s = strong, m = medium, w = weak

L. = PTSC , I. $[Ni(PTSC)_2(OAc)_2]$ II. $[Co(PTSC)_2(OAc)_2]$,

III. $[Cu(PTSC)_2(OAc)_2]$, IV. $[Zn(PTSC)_2(OAc)_2]$, coordination to the metal atom. PTSC is capable of existing in the thione(I) and thiol(II) form. However the band due to ν(S-H) is not observed in the spectra of free ligand. Therefore, ligand exists mainly as the thione form in the solid state. In the spectra of the free ligand, ν(C=S) appears as a medium band at 780 cm^{-1}. On complexation, this band shifts to 765-760 cm^{-1} indicating the participation of sulphur atom in coordination[116]. Besides two bands which are not due to the PTSC ligand are observed at 1610 cm^{-1} and 1325 cm^{-1}, and these bands can be assigned to ν_a(COO) and ν_s(COO) respectively. Further the complexes exhibit δ(COO) at 756 cm^{-1} which suggests that the acetate acts as a unidentate ligand in these complexes[103].

4.3.3 Electronic spectra

The electronic spectral data are given in Table IV.4 All the complexes exhibit broad bands with high intensity in the region 34200 — 30000 cm^{-1} and these bands can be assigned to charge transfer transitions[117].

The Co(II) complex shows three bands indicative of high spin octahedral structure[110]. The absorption bands observed at 9830 cm^{-1} and 16940 cm^{-1} for this complex can be attributed to $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ transitions respectively. Further, a weak shoulder band observed at 25300 cm^{-1} is due to $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition. Three

Table IV.4

Electronic spectral data

Compound	Absorption Maxima (cm^{-1})	log ε
[Co(PTSC)$_2$(OAc)$_2$]	9830	1.36
	16940	1.48
	25300	1.93
	31740	5.23
[Ni(PTSC)$_2$(OAc)$_2$]	9520	1.30
	20830	1.58
	25460	1.77
	30960	5.10
[Cu(PTSC)$_2$(OAc)$_2$]	19800	1.13
	34210	5.10

spin allowed transitions are expected for octahedral Ni(II) complexes[118]. The spectrum of the Ni(II) complex exhibits bands at 9520 cm^{-1}, 20830 cm^{-1} and 25460 cm^{-1} which are attributed to $^3A_{2g} \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transitions respectively. The Cu(II) complex shows a broad band at 19800 cm^{-1} which is due to d-d transition.

4.3.4 EPR spectra

The X band EPR spectrum of $[Cu(PTSC)_2(OAc)_2]$ is shown in Fig.4.2. Kneubuhl procedure[111] was used to calculate the g-values. The complex yields two g values ($g_{\parallel} = 2.26$, $g_{\perp} = 2.081$). The greater $g_{\parallel}$ value compared to the $g_{\perp}$ value indicate that the complex has an elongated octahedral structure and also that the unpaired electron is in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state.[113] However, the $g_{\parallel}$ value is found to be less than 2.3 suggesting covalent character of the metal-ligand bond[114]. Based on these results the structure shown in Fig.4.3 may be assigned for the complexes.

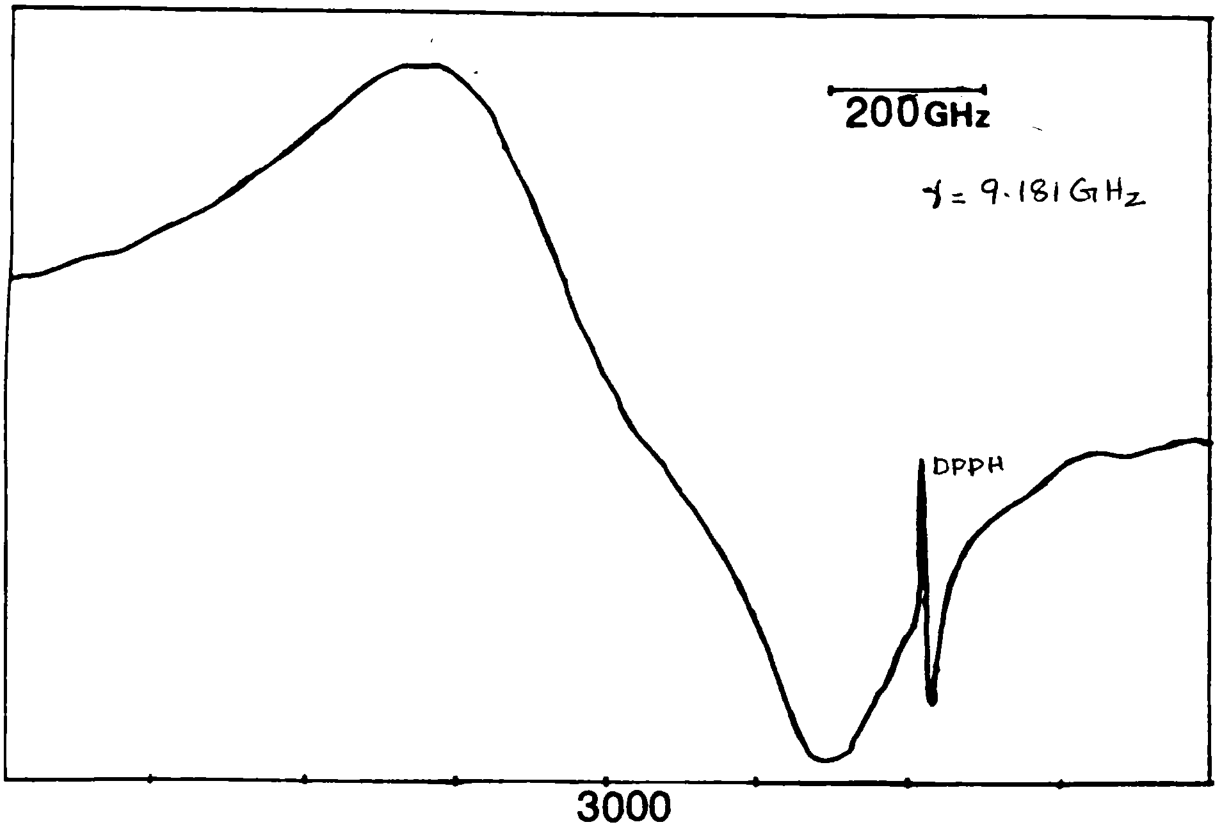


Fig. 4.2 EPR spectrm of [Cu(PTSC)$_2$(OAc)$_2$] at liquid nitrogen temperature.

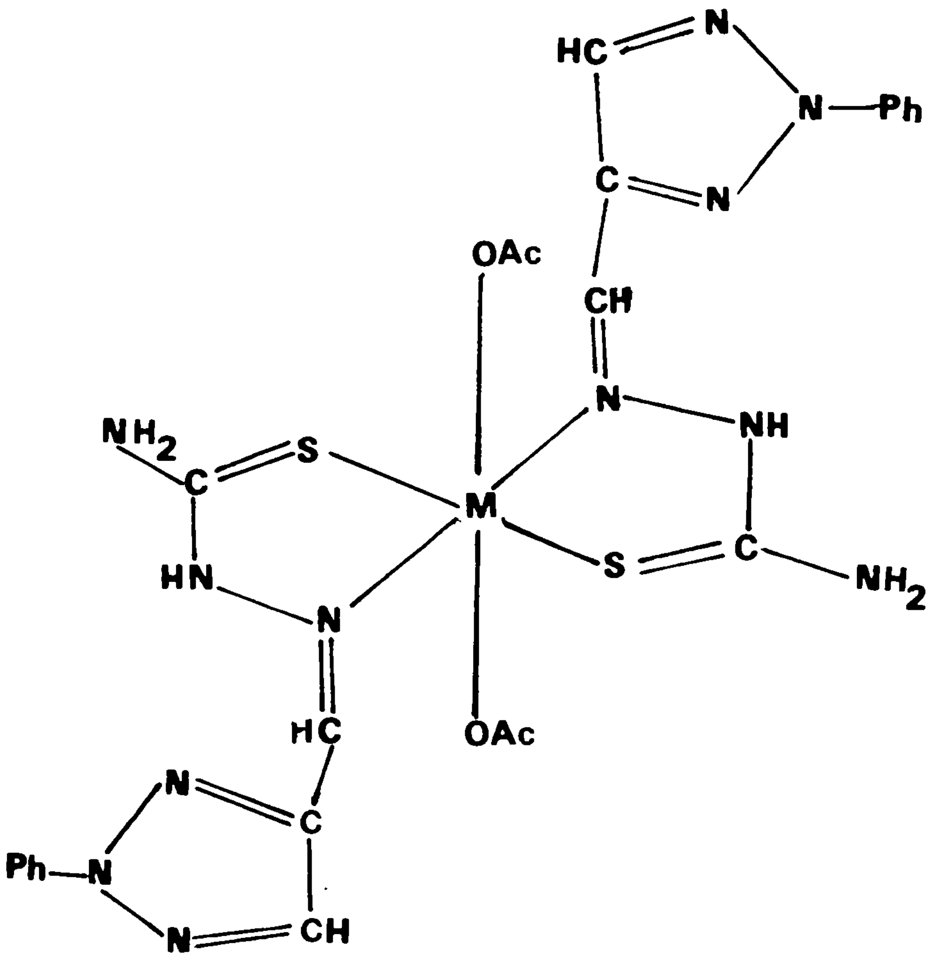


Fig. 4.3 Schematic structure of the complexes. M = Co(II), Ni(II), Cu(II) and Zn(II).

CHAPTER-V

2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALDEHYDE SEMICARBAZONE COMPLEXES OF COBALT(II)

5.1. INTRODUCTION

The coordination chemistry of transition metal complexes of chelating agents with oxygen-nitrogen donor sites have been an area of interest for a number of years. The Schiff base, 2-phenyl-1,2,3-triazole-4-carboxaldehyde semicarbazone (PTCS), is interesting since it contains nitrogen and oxygen as potential donor sites. The complexation behavior of the ligand towards metal ions like cobalt(II), nickel(II), copper(II) and zinc(II) was studied and it was found that only in the case of cobalt, we were able to isolate solid complexes. The results of our studies on the synthesis and characterisation of the Co(II) complexes are described in this chapter.

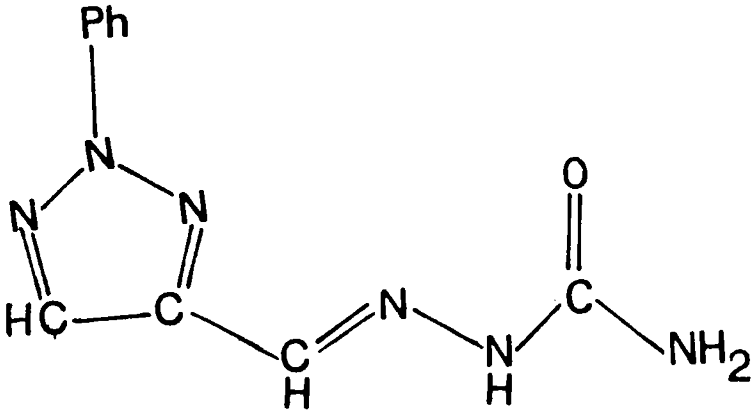


Fig 5.1 Structure of PTCS

5.2 Experimental

5.2.1. Materials

Details regarding the preparation and purification of the ligand are given in Chapter II.

5.2.2. Synthesis of the complexes

The chloro and bromo complexes were prepared by the following general procedure: A solution containing cobalt(II) salt (0.01 mol-2.4 g of $CoCl_2.6H_2O$ or 2.2 g of $CoBr_2$) in glacial acetic acid (150 mL) was added to a solution containing PTCS (0.01 mol, 2.30 g) in glacial acetic acid (150 mL). The mixture was heated on a water bath for 2-3 h. The complexes separated out on cooling were filtered, washed with chloroform and dried *in vacuo* over anhydrous $CaCl_2$. (Yield 60%)

For the synthesis of iodo and thiocyanato complexes, the following procedure was used: First, $Co(NO_3)_2.6H_2O$ (0.005 mol, 1.45 g) and KSCN/KI(0.01 mol - 0.97 g of KSCN or 1.66 g of KI) were separately dissolved in minimum quantity of ethanol and mixed. The precipitated KNO_3 was filtered off. The filtrate was concentrated to a very small volume and then added to a solution containing PTCS (0.01 mol, 2.30 g) in glacial acetic acid (150 mL). The mixture was heated on a water bath for 2-3 h. The complexes separated out on cooling were filtered, washed with chloroform and dried *in vacuo* over anhydrous $CaCl_2$. (Yield 60%).

5.2.3 Analytical methods

Details regarding the analytical methods and other characterisation techniques are given in Chapter II.

5.3 RESULTS AND DISCUSSION

All the complexes are crystalline, non-hygroscopic and are stable to atmospheric oxidation. The complexes are soluble only in DMF and DMSO . The analytical data of the complexes are given in Table V.1. The molar conductance values (Table V.2) show that these complexes are non-electrolytes in DMF. The analytical and molar conductance data show that the complexes have the general empirical formula $[Co(PTCS)X_2]$ (where X = Cl, Br, I or SCN).

5.3.1. Magnetic Susceptibility Measurements

Tetrahedral complexes of cobalt(II) can be distinguished from octahedral complexes using the magnetic susceptibility measurements. Generally tetrahedral cobalt(II) complexes have magnetic moment values in the range 4.1-4.8 BM. All the complexes exhibit μ_{eff} values in this range (Table V.2) suggesting a

Table V.1

Physical and Analytical data

Substance	% Yield	C (%) Found (Calc.)	H (%) Found (Calc.)	N (%) Found (Calc.)	Anion (%) Found (Calc.)	Metal Found (%) (Calc.)
1. $[Co(PTCS)Cl_2]$	60	33.10	2.8	23.30	19.70	16.36
$[CoC_{10}H_{10}N_6OCl_2]$		(33.43)	(2.78)	(23.40)	(19.75)	(16.41)
2. $[Co(PTCS)Br_2]$	60	26.85	2.10	18.85	35.80	13.00
$[CoC_{10}H_{10}N_6OBr_2]$		(26.74)	(2.22)	(18.71)	(35.61)	(13.13)
3. $[Co(PTCS)I_2]$	60	22.50	1.90	15.50	46.80	10.75
$[CoC_{10}H_{10}N_6OI_2]$		(22.11)	(1.84)	(15.48)	(46.76)	(10.85)
4. $[Co(PTCS)(SCN)_2]$	60	35.48	2.90	20.65	14.20	14.45
$[CoC_{12}H_{10}N_8OS_2]$		(35.56)	(2.96)	(20.75)	(14.32)	(14.55)

Table V.2

Molar conductance and magnetic moment data

Compound	Molar conductance (ohm^{-1} cm^2 $mole^{-1}$)	Magnetic moment(BM)
$[Co(PTCS)Cl_2]$	7.65	4.2
$[Co(PTCS)Br_2]$	5.85	4.3
$[Co(PTCS)I_2]$	7.21	4.5
$[Co(PTCS)(SCN)_2]$	8.81	4.2

tetrahedral structure for these complexes[121].

5.3.2 Infrared spectra

The ligand exhibits bands around 1699 cm^{-1}, 1670 cm^{-1}, 1601 cm^{-1} which might be due to the ν(C=O), ν(C=N) of the azomethine group and ν(C=N) of the triazole ring[122] respectively. In the spectra of the chloro and bromo complexes, the azomethine band and the ν(C=N) band of triazole ring appear at 1659 cm^{-1} and 1585 cm^{-1} respectively, indicating the participation of these nitrogen atoms in coordination to the metal atom[122-125]. The ν(C=O) band at 1699 cm^{-1} does not undergo any shift which shows that the carbonyl oxygen is not involved in coordination. However, there is a definite indication that the carbonyl oxygen is involved in bonding of the iodo and thiocyanato complexes. In these cases the ν(C=O) band shifts to a lower frequency (1685 cm^{-1})[103,126]. Furthermore, non involvement of the ring nitrogen in bonding is indicated by the retention of band at 1601 cm^{-1}. The thiocyanato complex shows a strong band at 2100 cm^{-1} which can be assigned to ν(C-N) of the thiocyanate group[103]. A band at 490 cm^{-1} is also seen in the spectra of the thiocyanate complex, which is usually exhibited by complexes in which the NCS group is bonded through nitrogen. This band may be assigned to NCS deformation[127]. Thus PTCS acts as a bidentate ligand in these complexes. In chloro and bromo complexes, azomethine nitrogen and ring nitrogen have been used for

Table V.3

Infrared absorption frequencies (cm^{-1}).

L	I	II	III	IV	Assignment
2365 m	2360 m	2360 m	2365 m	2360 m	
2350 m	2350 m	2350 m	2350 m	2350 m	
-----	-----	-----	------	2100 s	ν(C-N) (thiocyanate)
1895 w	1890 w	1895 w	1890 w	1890 w	
1815 w	1815 w	1815 w	1815 w	1815 w	
1755 w	1755 w	1755 w	1780 w	1755 w	
1710 w	1710 w	1710 w	1710 w	1710 w	
1699 w	1699 w	1699 w	1685 w	1685 w	ν(C=O)
1670 s	1655 s	1660 s	1660 s	1655 s	ν(C=N) (azomethine)
1650 w	1650	1650 w	1650 w	1650 w	
1601 s	1585 s	1580 s	1601 s	1601 s	ν(C=N) ring
1520 s	1520 s	1520 s	1520 s	1520 s	
1500 s	1500 s	1505 s	1500 s	1505 s	
1470 m	1480 m	1470 m	1475 m	1480 m	
1455 m	1455 m	1465 m	1455 m	1455 m	
1435 m	1430 m	1430 m	1430 m	1430 m	
1370 s	1360 s	1370 s	1360 s	1360 s	
1348 w	1345 w	1340 w	1345 w	1345 w	
1310 s	1305 s	1305 s	1305 s	1305 s	
1250 m	1250 m	1250 m	1250 m	1250 m	
1205 m	1205 m	1210 m	1205 m	1205 m	
1180 w	1180 w	1185 w	1180 w	1185 w	
1150 w	1150 w	1150 w	1150 w	1150 w	
1105 w	1100 w	1105 w	1100 w	1105 w	
1040 s	1040 s	1040 s	1040 s	1040 s	
1030 m	1025 m	1030 m	1025 m	1025 m	
965 w	965 w	965 w	965 w	965 w	
860 s	860 s	860 s	860 s	860 s	

Table V.3 (continued)

L	I	II	III	IV	Assignment
790 m	785 m	785 m	790 m	785 m	
770 s	770 s	770 s	770 s	770 s	
700 s	700 s	700 s	705 s	700 s	
690 s	690 s	690 s	690 s	690 s	
665 s	665 s	665 s	665 s	665 s	
620 w	620 w	620 w	625 w	620 w	
----	----	----	-----	490 m	δ(NCS)
420 w	425 w	420 w	420 w	420 w	

Abbreviations : s = strong, m = medium, w = weak

L. PTCS, I. $[Co(PTCS)Cl_2]$, II. $[Co(PTCS)Br_2]$,

III. $[Co(PTCS)I_2]$, IV. $[Co(PTCS)(SCN)_2]$.

coordination while in the iodo and the thiocyanato complexes the azomethine nitrogen and carbonyl oxygen have been used.

5.3.3 Electronic spectra

The electronic spectral data are given in Table-V.4. All the complexes exhibit an absorption band with hyperfine structure in the region 14000 — 19000 cm^{-1} and can be assigned to $^4A_2 \longrightarrow {}^4T_1(P)$ electronic transition. The fine structure observed for the complexes in this region is characteristic of the tetrahedral complexes and arise due to spin orbit coupling of the T state[128]. The broad absorption in the region 6000 — 8000 cm^{-1} is assigned to $^4A_2 \longrightarrow {}^4T_1(F)$ transition. The low energy band expected for the tetrahedral complexes is seen around 5000 cm^{-1} in the spectra of the complexes and is due to the $^4A_2 \longrightarrow {}^4T_2$ transition. The higher intensity of band observed at 32720 cm^{-1} in the spectra of the complexes may be due to intraligand transition. Based on the information the structures shown in Fig-5.5 may be assigned for the complexes.

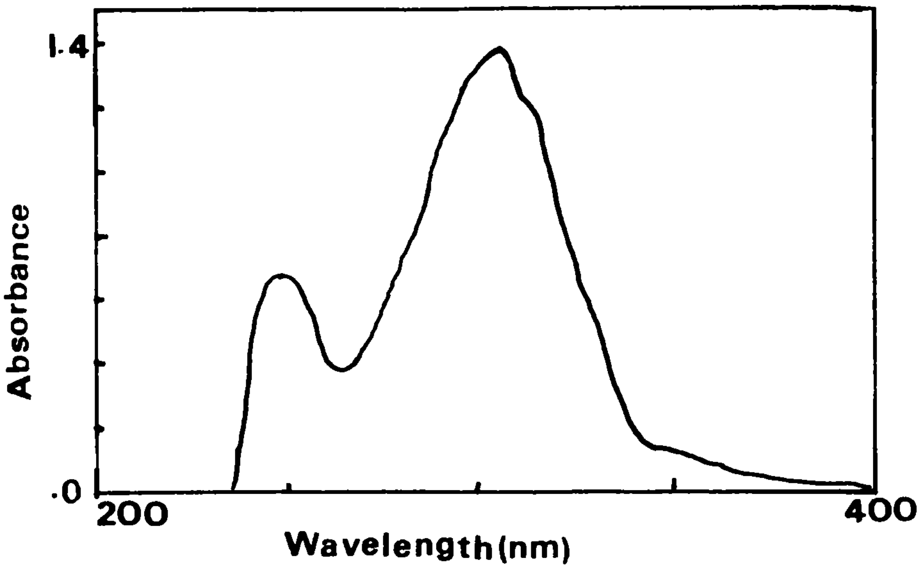


Fig. 5.2 Electronic spectra of [Co(PTCS)Cl_2] in the range 200-400 nm.

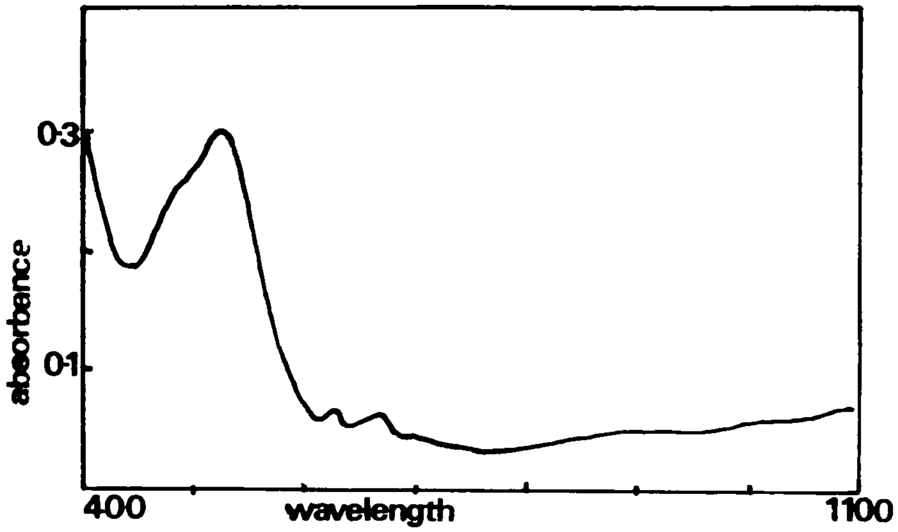


Fig. 5.3 Electronic spectra of [Co(PTCS)Cl_2] in the range 400-1100 nm

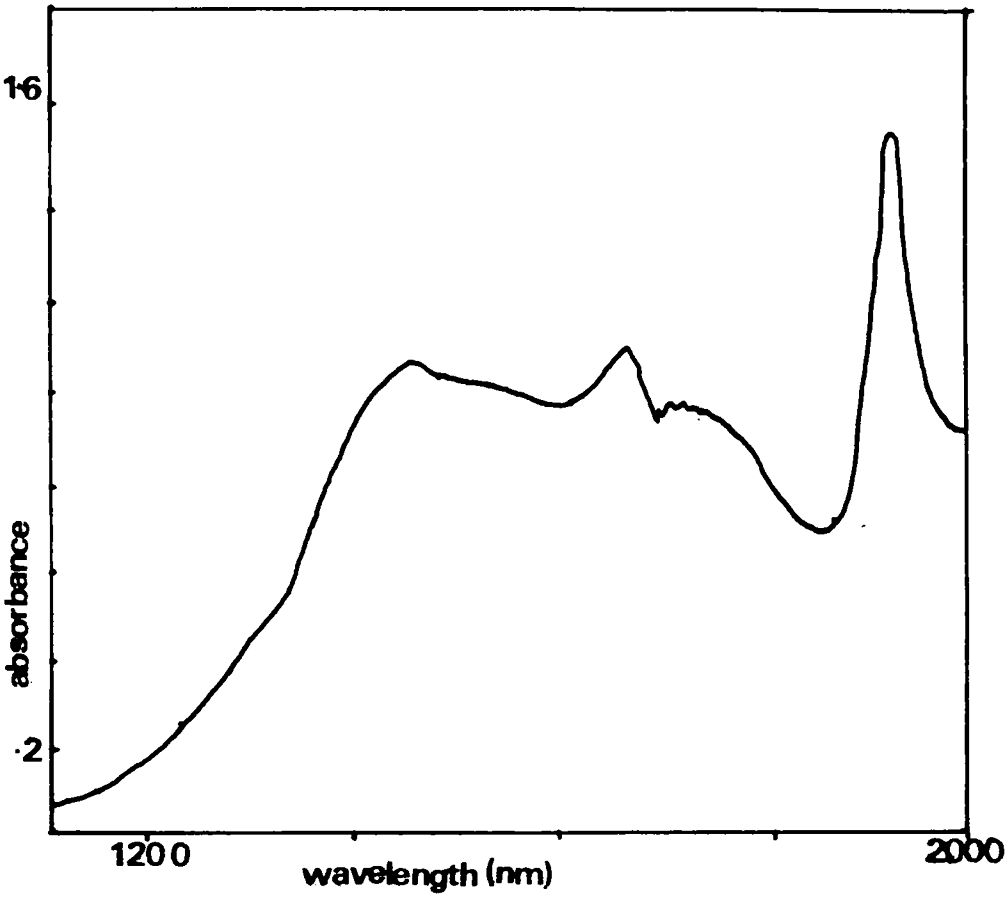


Fig. 5.4 Electronic spectra of $[Co(PTCS)Cl_2]$ in the range 1100-2000 nm

Table V.4
Electronic spectral data

Compound	Absorption Maxima (cm^{-1})	log ε
[Co(PTCS)Cl_2]	5260	1.10
	6070	1.41
	14790	2.62
	16440	2.60
	18900	2.47
	32720	4.10
[Co(PTCS)Br_2]	5210	1.12
	6200	1.43
	14370	2.58
	15600	2.55
	18760	2.49
	32720	4.10
[Co(PTCS)I_2]	5230	1.12
	7840	1.38
	14330	2.66
	15670	2.60
	18210	2.45
	32720	4.10
[Co(PTCS)$(SCN)_2$]	5190	1.10
	7690	1.40
	16050	2.67
	16950	2.60
	19270	2.45
	32720	4.10

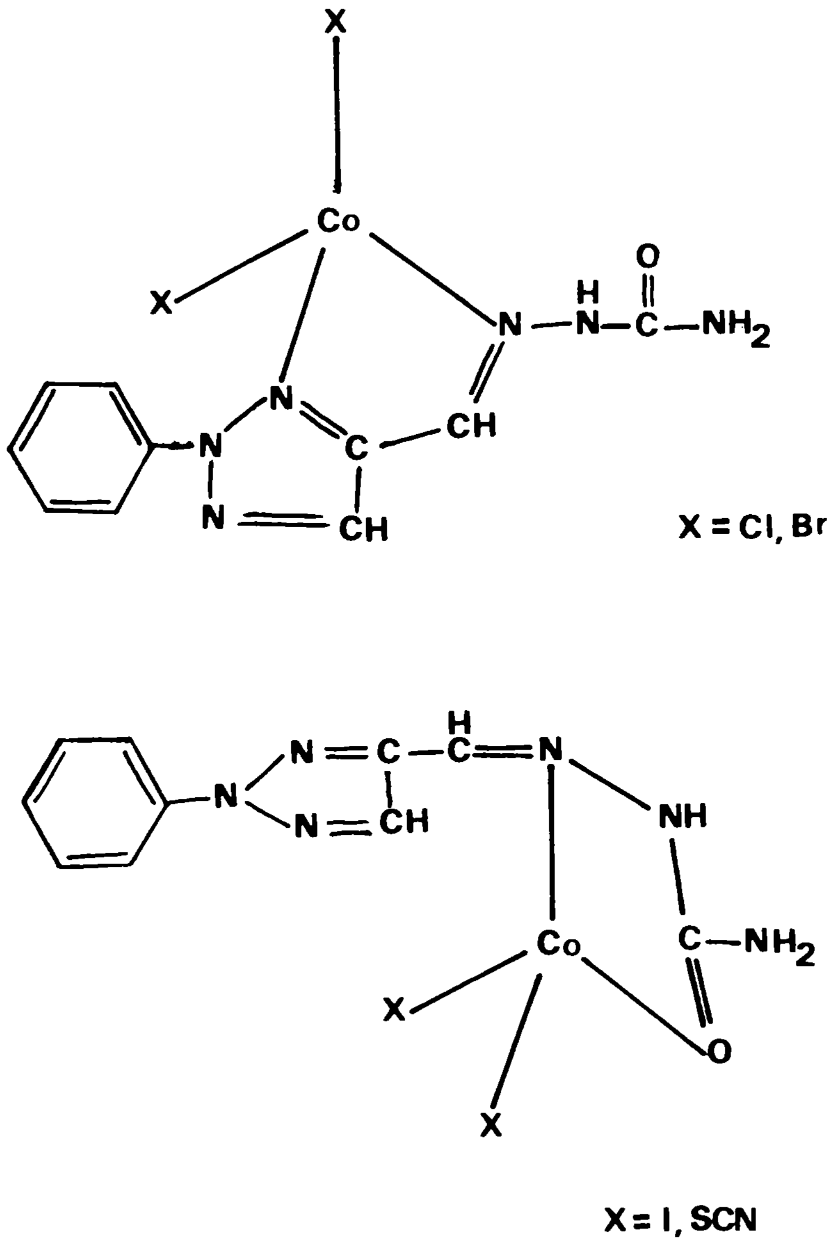


Fig. 5.5 Schematic structures of the complexes

CHAPTER-VI

1-PHENYLFLAVAZOLE-3-CARBOXALDEHYDE THIOSEMICARBAZONE COMPLEXES OF Co(III), Ni(II), Cu(II), AND Zn(II)

6.1 INTRODUCTION

Heterocyclic compounds containing both nitrogen and sulphur atoms find application in many pharmaceutical contexts[129,130]. Recent reports on biological activity of some of the derivatives of 1-phenylflavazole as potential diuretic, anti-inflammatory, analgesic and anti-leukaemic agents[131] have created added interest in synthesising new types of flavazole derivatives, especially its metal complexes. We have synthesised the metal complexes of 1-phenylflavazole-3-carboxaldehyde thiosemicarbazone (FTSC) and the details of our studies on these complexes are presented in this chapter. The ligand has the following structure:

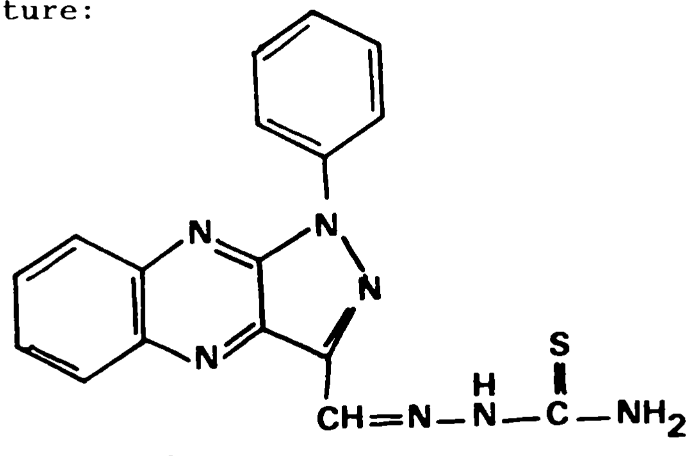


Fig. 6.1 Structure of FTSC

6.2 Experimental

6.2.1 Materials

Details regarding the preparation and purification of the ligand are given in Chapter II.

6.2.2 Synthesis of the complexes

All the complexes were prepared by the following general procedure. The ligand, 1-phenylflavazole-3-carboxaldehyde thiosemicarbazone (FTSC) (0.02 mol, 6.94 g) was dissolved in ethanol (150 mL). To this solution, metal chloride (0.005 mol- 1.19 g of $CoCl_2.6H_2O$, 1.19 g of $NiCl_2.6H_2O$, 0.85 g of $CuCl_2.2H_2O$ or 0.68 g of $ZnCl_2$) in ethanol (150 mL) was added and refluxed on a water bath for 4 h. Sodium acetate (~ 0.25 g) was then added and the reaction mixture was again refluxed for 2 h. The complexes separated out on cooling were filtered, washed with ethanol and dried *in vacuo* over anhydrous $CaCl_2$. (Yield 70-75%)

6.2.3 Analytical methods

Details regarding the analytical methods and other characterisation techniques are given in Chapter II.

6.3 RESULTS AND DISCUSSION

The complexes isolated are non-hygroscopic, crystalline substances and are stable in air. They are soluble in DMF, DMSO and methanol, and insoluble in non-polar solvents like nitrobenzene and toluene . The analytical data (Table VI.1) show that the complexes have the general empirical formulae $[M(FTSC)_2(OAc)_2]$, $[Co(FTSC)_2]OAc$ and $[Cu(FTSC)_2(OAc)_2]_2$(where M = Ni(II) or Zn(II) and OAc represents the acetate group). The molar conductance values (Table-VI.2) show that all the complexes except the cobalt complex are non-electrolytes in methanol. The cobalt complex has a conductance value of 110.3 ohm^{-1} cm^2 mol^{-1} showing that the complex is 1:1 electrolyte in methanol[103].

6.3.1 Magnetic susceptibility measurements

Magnetic moment values of the complexes are given in Table VI.2. The cobalt complex is found to be diamagnetic which indicates that cobalt is in the +3 oxidation state. This further suggests that oxidation of cobalt(II) to cobalt(III) takes place during the preparation of the complex. Such oxidations are reported in the case of reactions involving Co(II) salts and thiosemicarbazones in presence of air[132]. Ni(II)complexe exhibits a magnetic moment value which is in agreement with that for an octahedral complex[133]. The copper complex shows a magnetic moment value of 1.5 BM which may be due to the antiferromagnetic interaction between the neighbouring metal ions. As expcted,

Table VI.1

Physical and Analytical data

Substance	Colour	% Yield	Carbon Found (%) (Calc.)	Hydrogen Found (%) (Calc.)	Nitrogen Found (%) (Calc.)	Sulphur Found (%) (Calc.)	Metal Found (%) (Calc.)
$[Ni(FTSC)_2(OAc)_2]$	Dark brown	65	52.25	3.56	22.43	7.31	6.71
$[NiC_{38}H_{32}N_{14}S_2O_4]$			(52.37)	(3.68)	(22.51)	(7.35)	(6.74)
$[Co(FTSC)_2)]OAc$	Brown	70	53.00	3.48	24.09	7.77	7.19
$[CoC_{36}H_{29}N_{14}S_2O_2]$			(53.20)	(3.57)	(24.14)	(7.88)	(7.26)
$[Cu(FTSC)_2(OAc)_2]_2$	Black	74	52.00	3.61	22.30	7.27	7.21
$[CuC_{76}H_{64}N_{28}S_4O_8]$			(52.08)	(3.65)	(22.38)	(7.3)	(7.25)
$[Zn(FTSC)_2(OAc)_2]$	Brown	65	51.84	3.56	22.31	7.23	7.41
$[ZnC_{38}H_{32}N_{14}S_2O_4]$			(52.08)	(3.65)	(22.38)	(7.3)	(7.45)

Table VI.2

Magnetic moment and conductance data.

Compound	Molar conductance (ohm^{-1} cm^2 $mole^{-1}$)	Magnetic moment(BM)
$[Ni(FTSC)_2(OAc)_2]$	39.5	3.2
$[Co(FTSC)_2)]OAc$	110.3	Diamagnetic
$[Cu(FTSC)_2(OAc)_2]_2$	35.10	1.5
$[Zn(FTSC)_2(OAc)_2]$	30.10	Diamagnetic

Zn(II) complex is found to be diamagnetic. Molecular weight of the complex has been determined using Rast's method[134] and the value observed (~ 1750) indicates a dimeric structure for the copper complex, which is in agreement with the information obtained from magnetic studies.

6.3.2 Infrared spectra

The ir spectral data show that FTSC acts as a uninegative bidentate or tridentate ligand depending on the metal ion and the medium of reaction. Bands due to ν(S-H) is not observed in the free ligand indicating that the ligand exists mainly as thione form in the solid state. The spectra of the ligand and the complexes show two bands in the range 3100- 3300 cm^{-1} which may be assigned to ν(N-H) vibrations[32]. The ligand exhibits bands around 1636 cm^{-1} and 1047 cm^{-1} which might be due to ν(C=N) of the azomethine linkage and ν(N-N') vibrations respectively[103]. Another band at 1602 cm^{-1} is observed which is due to ν(C=N) of the flavazole ring. In the spectra of all the complexes the azomethine band of the ligand shifts to a lower frequency (1620 cm^{-1}), which indicates the involvement of azomethine nitrogen atom in the bonding to the metal atom. In the spectra of the ligand, ν(C=S) appears as a medium band at 780 cm^{-1}. This band also undergoes a red shift to 750 cm^{-1} confirming the involvement of sulphur atom in bonding to the metal atom[103].

Table VI.3

Infrared absorption frequencies (cm^{-1}).

L	I	II	III	IV	Assignment
1720 w	1716 w	1718 w	1716 w	1716 w	
1655 w	1660 w	1655 w	1665 w	1655 w	
1647 s	1650 s	1647 s	1650 s	1647 s	
1636 m	1620 m	1620 m	1620 m	1620 m	ν(C=N) azomethine
-----	1615 m	1615 m	1615 m	1615 m	ν_a(COO)
1602 s	1602 s	1590 s	1590 s	1602 s	ν(C=N) ring
1578 w	1585 w	1578 w	1580 w	1578 w	
-----	-----	------	1558 m	------	ν_s(COO) bridging
1545 w	1541 w	1545 w	1545 w	1541 w	
1500 s	1508 s	1500 s	1505 s	1500 s	
1496 s	1496 s	1496 s	1496 s	1496 s	
1474 w	1475 w	1474 w	1478 w	1478 w	
1470 m	1464 m	1465 m	1464 m	1465 m	
-----	------	------	1456 m	------	ν_a(COO) bridging
1430 m	1427 m	1427 m	1425 m	1430 m	
1358 s	1360 s	1358 s	1360 s	1358 s	
1360 w	1365 w	1360 w	1365 w	1360 w	
-----	1342 m	1340 m	1345 m	1340 m	ν_s(COO)
1250 w	1255 w	1250 w	1250 w	1250 w	
1300 w	1300 w	1300 w	1300 w	1300 w	
1197 m	1196 m	1197 m	1195 m	1190 m	
1126 m	1125 m	1126 m	1130 m	1126 m	
1047 m	1070 m	1070 m	1070 m	1070 m	ν(N-N')
906 w	910 w	906 w	906 w	906 w	
865 w	864 w	864 w	870 w	864 w	
802 m	808 m	802 m	808 m	802 m	
-----	760 m	760 m	760 m	760 m	δ(COO)
780 m	750 m	750 m	750 m	750 m	ν(C=S)

Table VI.3 (continued)

L	I	II	III	IV	Assignment
729 w	729 w	730 w	729 w	729 w	
867 w	867 w	870 w	867 w	865 w	
671 w	675 w	671 w	671 w	675 w	
659 w	659 w	660 w	659 w	659 w	
603 w	603 w	603 w	603 w	603 w	
565 w	565 w	565 w	560 w	565 w	
463 w	465 w	463 w	463 w	463 w	
420 w	420 w	420 w	420 w	420 w	

Abbreviations : s = strong, m = medium, w = weak

L = Ligand, I = $[Ni(FTSC)_2(OAc)_2]$, II = $[Co(FTSC)_2)]OAc$

III = $[Cu(FTSC)_2(OAc)_2]_2$, IV = $[Zn(FTSC)_2(OAc)_2]$

In the spectra of the cobalt complex the band due to ν(C-N) of the flavazole ring shifts to a lower frequency 1590 cm^{-1} (this band is at 1602 cm^{-1} in the spectra of the ligand). This clearly reveals the participation of ring nitrogen in coordination. Further in this complex a blue shift of ν(N-N') band to 1070 cm^{-1} is also observed which suggests the involvement of thiol form of the ligand on coordination[103]. Thus in this complex FTSC acts as a tridentate NNS donor.

In the case of the nickel and zinc complexes, the band at 1602 cm^{-1} is retained indicating the non-coordinating nature of the ring nitrogen. In the spectra of the copper complex two additional bands are seen at 1558 cm^{-1} and 1456 cm^{-1} which may be due to symmetric and asymmetric stretching vibration of the bridging acetate group[135]. The band due to flavazole ring shifts from 1602 cm^{-1} to 1590 cm^{-1}. In this case, FTSC acts as a tridentate ligand coordinating through the azomethine nitrogen, ring nitrogen and thione sulphur. All the complexes show two bands at 1615 cm^{-1} and 1340 cm^{-1} which can be assigned to ν_a(COO) and ν_s(COO) respectively[103]. In addition, they exhibit δ(COO) at 760 cm^{-1} which is unique for the unidentate acetate[103].

6.3.3 Electronic spectra

The electronic spectral data are given in Table VI.4. The cobalt complex shows bands indicative of low spin, distorted octahedral structure. The bands observed around 10330 cm^{-1}, 18180 cm^{-1} and 23530 cm^{-1} may be attributed to $^1A_{1g} \longrightarrow {}^1A_{2g}$, $^1A_{1g} \longrightarrow {}^1E_g$, $^1A_{1g} \longrightarrow {}^1T_{2g}$ respectively[111]. Three spin allowed transitions are expected for Ni(II) octahedral complexes[136]. The absorption band observed around 9190 cm^{-1} for the nickel complex can be attributed to the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition and another band observed around 19460 cm^{-1} can be assigned to $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ transition. The $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transition appears around 25970 cm^{-1}. The band observed in the spectra of the copper(II) complex around 18800 cm^{-1} suggests that it has a tetragonal configuration around copper(II) ion. Tetragonal copper(II) complexes are expected to show the transitions $^2B_{1g} \longrightarrow {}^2A_{1g}$, $^2B_{1g} \longrightarrow {}^2B_{2g}$, $^2B_{1g} \longrightarrow {}^2E_g$, but bands due to these transitions usually overlap to give only one absorption band[137]. Further, the electronic spectra of all the complexes exhibit an intense absorption in the region 28000 — 35100 cm^{-1} which might be due to charge transfer transitions.

6.3.4 EPR spectra

The X band EPR spectrum of $[Cu(FTSC)_2(OAc)_2]_2$ is shown in Fig.6.2. Kneubuhl procedure[111] was used to calculate the

Table VI.4

Electronic spectral data

Compound	Absorption maxima (cm^{-1})	log ε
[Ni(FTSC)$_2$(OAc)$_2$]	9190	1.22
	19460	1.77
	25970	2.27
	32250	4.38
[Co(FTSC)$_2$)]OAc	10330	1.22
	18180	2.32
	23530	1.67
	28990	4.03
[Cu(FTSC)$_2$(OAc)$_2$]$_2$	18800	1.60
	29760	4.07

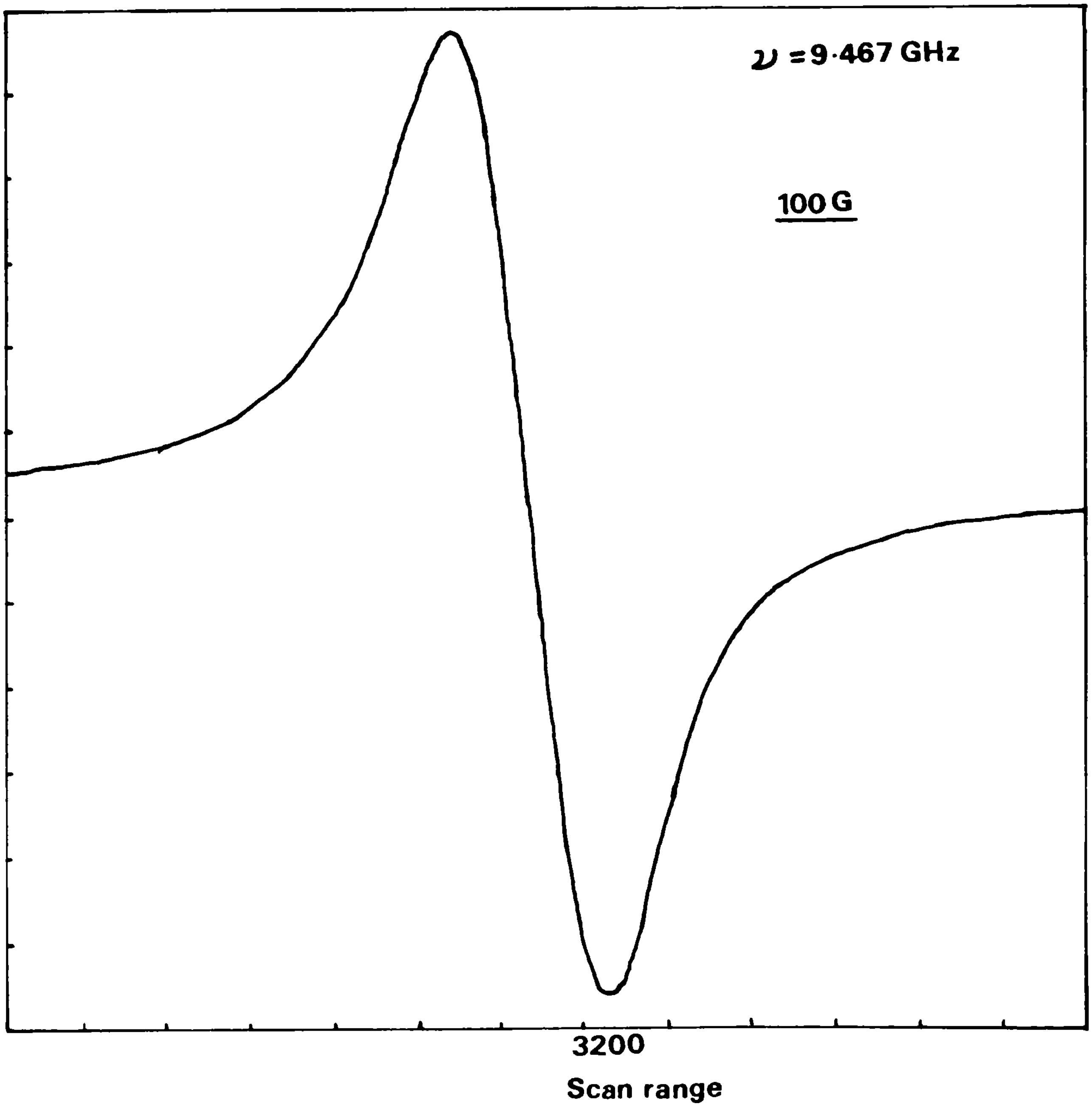


Fig. 6.2 EPR spectrm of $[Cu(FTSC)_2(OAc)_2]_2$ at liquid nitrogen temperature.

g-values. The complex yields two g values ($g_{\parallel} = 2.225$, $g_{\perp} = 2.094$). The greater $g_{\parallel}$ value compared to the $g_{\perp}$ value indicate that the complex has an elongated octahedral structure and also that the unpaired electron is in the $d_{x^2-y^2}$ giving $^2B_{1g}$ as the ground state.[113] However, the $g_{\parallel}$ value is found to be less than 2.3 suggesting covalent character of the metal ligand bond[114]. Based on the above information the complexes have been assigned the following structure. (Fig 6.3).

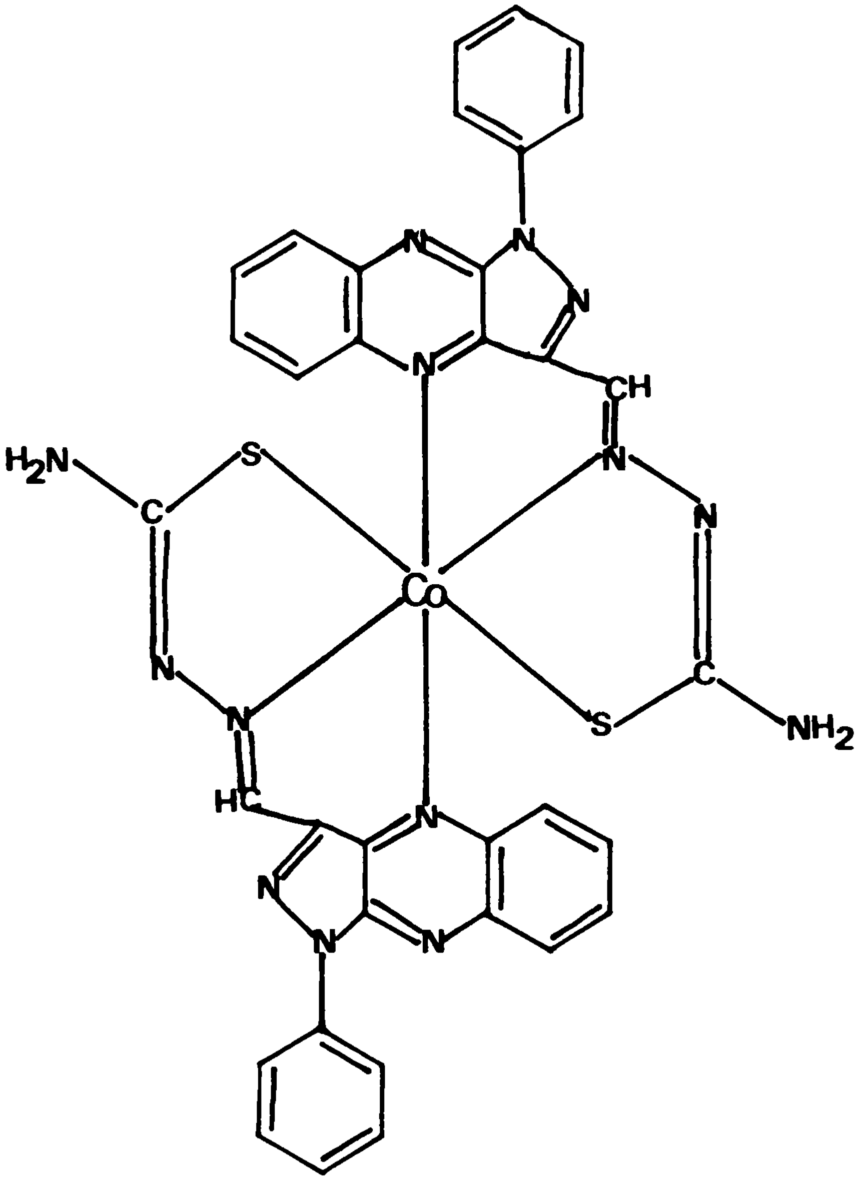
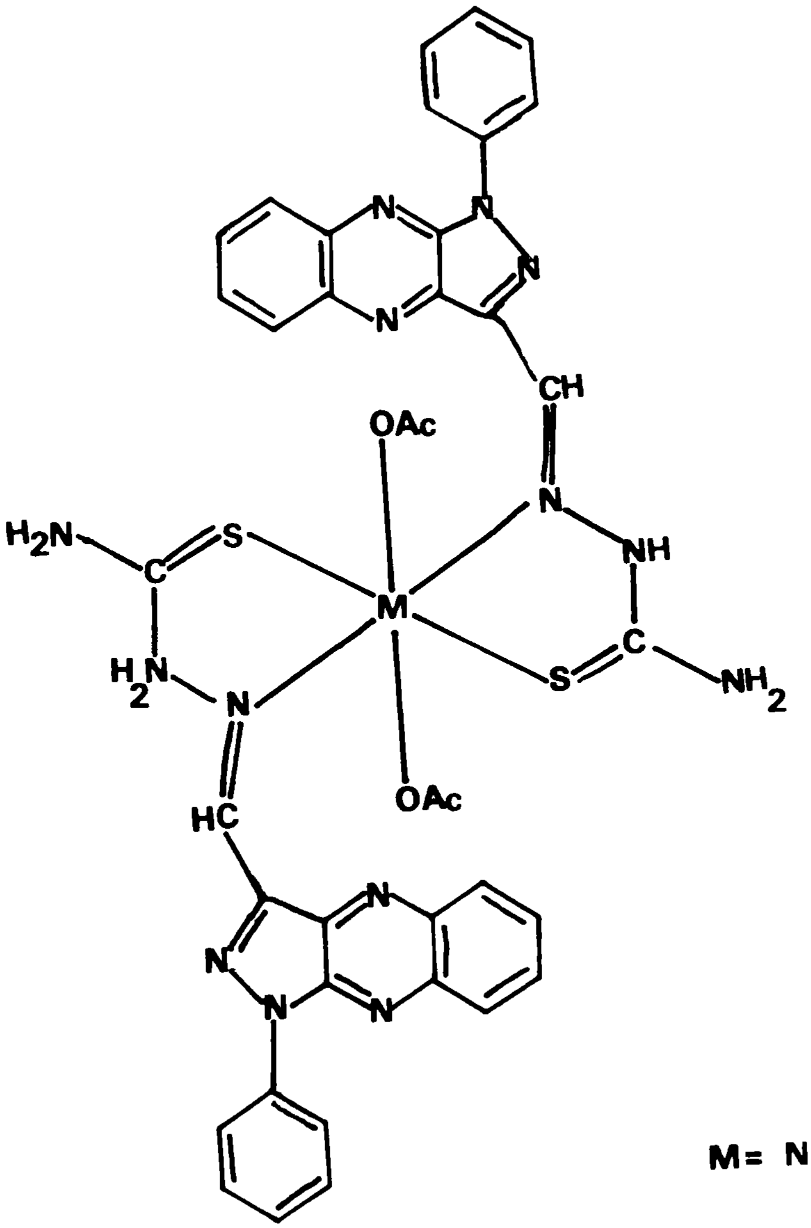


Fig. 6.3 Schematic structure of cobalt complex.



M= Ni(II), Zn(II)

Fig. 6.3 Schematic structures of nickel and zinc complexes.

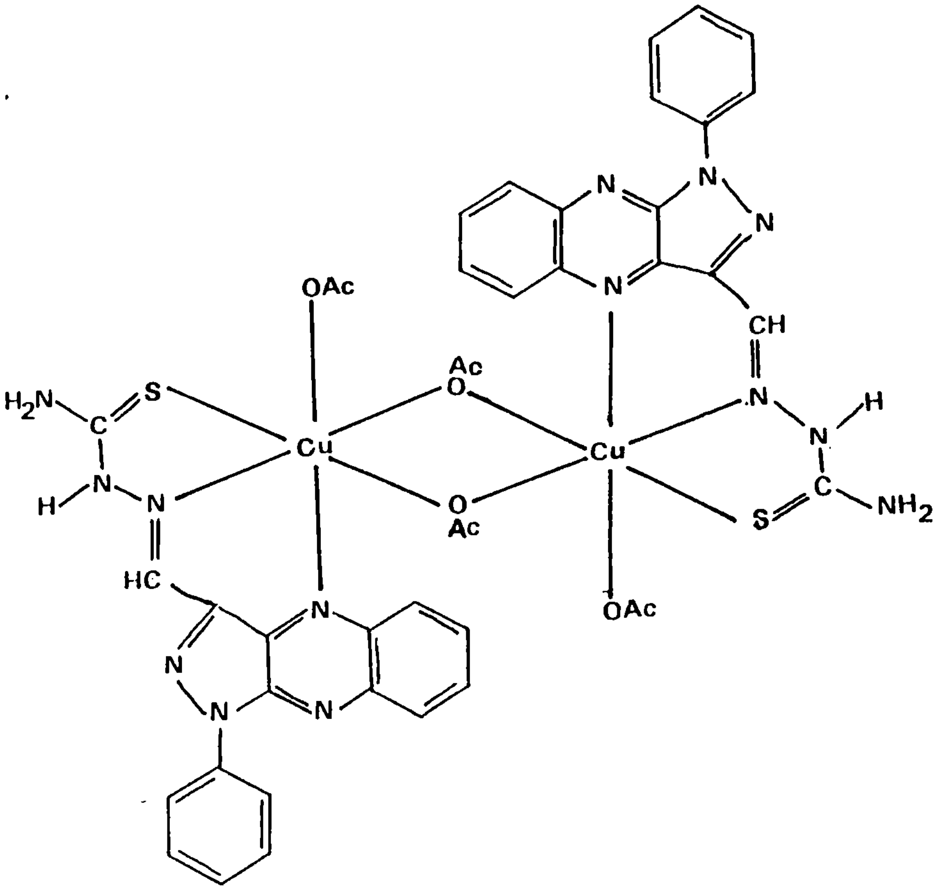


Fig. 6.3 Schematic structure of the copper complex

CHAPTER-VII

1-PHENYLFLAVAZOLE-3-CARBOXALDEHYDE SEMICARBAZONE COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II)

7.1 INTRODUCTION

Transition metal complexes of semicarbazones are of considerable importance not only due to their interesting structures but also due to their possible utility in pharmacology. They act as potential multidentate, oxygen donor ligand. This chapter describes the synthesis and characterisation of some cobalt(II), nickel(II) and copper(II) complexes of the Schiff base, 1-phenyl-flavazole-3-carboxaldehyde semicarbazone (FSE). The ligand has the following structure:

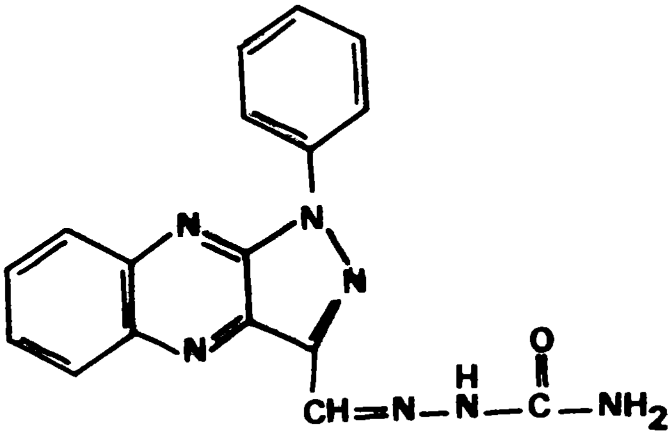


Fig. 7.1 Structure of FSE.

7.2 Experimental

7.2.1. Materials

Details regarding the reagents used and preparation of the ligand are given in Chapter II.

7.2.2. Synthesis of the complexes

All the complexes were prepared by the following general procedure: A solution containing metal salts (0.01 mol-2.37 g of $NiCl_2.6H_2O$, 2.18 g of $NiBr_2$, 2.38 g of $CoCl_2.6H_2O$, 2.18 g of $CoBr_2$, 1.7 g of $CuCl_2.2H_2O$ or 2.23 g of $CuBr_2$) in methanol (100 mL) was added to a solution containing the ligand (0.02 mol, 6.62 g) in methanol (100 mL). The mixture was refluxed on a water bath for 3-4 h. The complexes which separated out on cooling were filtered, washed with chloroform and dried *in vacuo* over anhydrous $CaCl_2$. (Yield 65%)

7.2.3 Analytical methods

Details regarding the analytical methods and other characterisation techniques are given in Chapter II.

7.3 RESULTS AND DISCUSSION

All the complexes are coloured, crystalline and non-hygroscopic substances. They are stable to aerial oxidation. All the complexes except the copper complexes are soluble in DMSO, DMF, acetonitrile and chloroform.Complexes are slightly soluble in methanol and ethanol. The molar conductance values (Table VII.2) reveal that the nickel and the cobalt complexes are 1:2 electrolytes in methanol, while the copper complexes are non-electrolytes. Hence the analytical data together with the information from conductance data show that the nickel(II) and cobalt(II) complexes have the general formula $[M(FSE)_2]X_2$ [where X=Cl or Br and M=Ni(II) or Co(II)] . The copper complexes can be represented as $[M(FSE)_2X_2]$

7.3.1. Magnetic susceptibility measurements

The magnetic moment values of the complexes are presented in Table VII.2. The cobalt and nickel complexes exhibit magnetic moment values which are in agreement with those expected for the octahedral structure[121]. The copper complexes have magnetic moment values around 1.9 BM which indicate the absence of any metal-metal interaction and excludes the possibility of having

Table VII.1

Physical and Analytical data

Substance	Colour	% Yield	Carbon Found (%) (Calc.)	Hydrogen Found (%) Calc.)	Nitrogen Found (%) (calc.)	Halogen Found (%) Calc.)	Metal Found (%) (calc.)
[Ni(FSE)$_2$]Cl$_2$	Yellowish	68	51.20	3.25	24.70	8.90	7.40
[NiC$_{34}$H$_{26}$N$_{14}$O$_2$Cl$_2$]	brown		(51.57)	(3.29)	(24.77)	(8.96)	(7.42)
[Ni(FSE)$_2$]Br$_2$	Yellowish	65	46.30	2.93	22.18	18.00	6.60
[NiC$_{34}$H$_{26}$N$_{14}$O$_2$Br$_2$]	brown		(46.35)	(2.95)	(22.26)	(18.15)	(6.60)
[Co(FSE)$_2$]Cl$_2$	Brown	65	51.20	3.25	24.68	8.92	7.40
[CoC$_{34}$H$_{26}$N$_{14}$O$_2$Cl$_2$]			(51.55)	(3.28)	(24.77)	(8.96)	(7.45)
[Co(FSE)$_2$]Br$_2$	Brown	65	46.00	2.93	22.20	18.10	6.61
[CoC$_{34}$H$_{26}$N$_{14}$O$_2$Br$_2$]			(46.32)	(2.95)	(22.25)	(18.14)	(6.61)
[Cu(FSE)$_2$Cl$_2$]	Black	70	50.90	3.25	24.57	8.90	7.92
[CuC$_{34}$H$_{26}$N$_{14}$O$_2$Cl$_2$]			(51.26)	(3.27)	(24.61)	(8.90)	(7.98)
[Cu(FSE)$_2$Br$_2$]	Black	70	45.95	2.90	22.10	18.00	7.15
[CuC$_{34}$H$_{26}$N$_{14}$O$_2$Br$_2$]			(46.35)	(2.94)	(22.14)	(18.05)	(7.18)

Table VII.2

Magnetic moment and conductance data.

Compound	Molar conductance (ohm^{-1} cm^2 $mole^{-1}$)	Magnetic moment(BM)
$[Ni(FSE)_2]Cl_2$	173	3.02
$[Ni(FSE)_2]Br_2$	178	2.97
$[Co(FSE)_2]Cl_2$	182	4.92
$[Co(FSE)_2]Br_2$	186	5.01
$[Cu(FSE)_2Cl_2]$	20.8	1.8
$[Cu(FSE)_2Br_2]$	21.3	1.9

a tetrahedral structure[133].

7.3.2 Infrared spectra

The infrared spectral bands of the ligand and the complexes are presented in Table VII.3. A comparative study of the spectra of the ligand and complexes show that 1-phenylflavazole-3-carboxaldehyde semicarbazone behaves as a bi or tridentate ligand depending on the nature of the metal ions. The ligand exhibits band around 1696 cm^{-1}, 1636 cm^{-1} and 1602 cm^{-1} which might be due to $\nu(C=O)$, $\nu(C=N)$ of azomethine group and $\nu(C=N)$ of the flavazole ring respectively[103]. In the spectra of the complexes the azomethine band appears at 1620 cm^{-1}. This red shift indicates the participation of azomethine nitrogen in coordination to the metal atom[102-104]. The band at 1696 cm^{-1} is shifted to 1680 cm^{-1} showing the involvement of C=O group in coordination[103]. In the spectra of copper complexes the band due to the flavazole ring remains unaffected showing the non coordinating nature of the ring nitrogen, but in all other cases this band undergoes a red shift to 1590 cm^{-1} showing the participation of ring nitrogen in coordination. The possibility of a bond between the semicarbazone group and metal through the nitrogen atom of the amido group can be excluded, as the frequencies of the N-H stretching vibration in the complexes are

Table VII .3

Infrared absorption frequencies (cm^{-1}).

L	I	II	III	IV	V	VI	Assignment
3040 m	3040 m	3045 m	3040 m	3045 m	3045 m	3045 m	
3020 w	3025 w	3020 w	3027 w	3020 w	3025 w	3020 w	
2855 s	2855 s	2860 s	2855 s	2860 s	2855 s	2860 s	
2840 w	2845 w	2840 w	2845 w	2840 w	2840 w	2845 w	
1696 m	1680 m	1680 m	1680 m	1680 m	1680 m	1680 m	ν(C=O)
1636 s	1620 s	1620 s	1620 s	1620 s	1620 s	1620 s	ν(C=N) azomethine
1602 s	1590 s	1590 s	1590 s	1590 s	1602 s	1602 s	ν(C=N) ring
1568 s	1568 s	1568 s	1568 s	1568 s	1568 s	1568 s	
1504 s	1504 s	1504 s	1504 s	1504 s	1504 s	1504 s	
1450 s	1450 s	1450 s	1450 s	1450 s	1450 s	1450 s	
1431 s	1431 s	1431 s	1431 s	1431 s	1431 s	1431 s	
1373 s	1373 s	1373 s	1373 s	1373 s	1373 s	1373 s	
1334 s	1334 s	1334 s	1334 s	1334 s	1334 s	1334 s	
1286 w	1286 w	1286 w	1286 w	1286 w	1286 w	1286 w	
1250 m	1250 m	1250 m	1250 m	1250 m	1250 m	1250 m	
1246 m	1246 m	1246 m	1246 m	1246 m	1246 m	1246 m	
1204 m	1204 m	1204 m	1204 m	1204 m	1204 m	1204 m	
1160 w	1160 w	1160 w	1160 w	1160 w	1160 w	1160 w	
1140 m	1140 m	1140 m	1140 m	1140 m	1140 m	1140 m	
1070 m	1070 m	1070 m	1070 m	1070 m	1070 m	1070 m	
1032 w	1032 w	1032 w	1032 w	1032 w	1032 w	1032 w	
1000 w	1000 w	1000 w	1000 w	1000 w	1000 w	1000 w	

Table VII.3 (continued)

L	I	II	III	IV	V	VI	Assignment
980 w	980 w	980 w	980 w	980 w	980 w	980 w	
940 w	940 w	940 w	940 w	940 w	940 w	940 w	
918 w	918 w	918 w	918 w	918 w	918 w	918 w	
904 m	904 m	904 m	904 m	904 m	904 m	904 m	
854 m	854 m	854 m	854 m	854 m	854 m	854 m	
821 w	821 w	821 w	821 w	821 w	821 w	821 w	
808 m	808 m	808 m	808 m	808 m	808 m	808 m	
767 s	767 s	767 s	767 s	767 s	767 s	767 s	
753 s	753 s	753 s	753 s	753 s	753 s	753 s	
729 m	729 m	729 m	729 m	729 m	729 m	729 m	
688 s	688 s	688 s	688 s	688 s	688 s	688 s	
679 s	679 s	679 s	679 s	679 s	679 s	679 s	
658 s	658 s	658 s	658 s	658 s	658 s	658 s	
633 w	633 w	633 w	633 w	633 w	633 w	633 w	
603 m	603 m	603 m	603 m	603 m	603 m	603 m	
590 w	590 w	590 w	590 w	590 w	590 w	590 w	
540 w	540 w	540 w	540 w	540 w	540 w	540 w	
507 m	507 m	507 m	507 m	507 m	507 m	507 m	
463 w	463 w	463 w	463 w	463 w	463 w	463 w	
422 s	422 s	422 s	422 s	422 s	422 s	422 s	

Abbreviations : s = strong, m = medium, w = weak

L - ligand, I-$[Ni(FSE)_2]Cl_2$, II-$[Ni(FSE)_2]Br_2$, III-$[Co(FSE)_2]Cl_2$,

IV-$[Co(FSE)_2]Br_2$, V-$[Cu(FSE)Cl_2]$, VI-$[Cu(FSE)Br_2]_2$

slightly greater than the free ligand[137]. Thus, FSE acts as a bidentate ligand in the case of copper complex and tridentate in the case of cobalt and nickel complexes.

7.3.3 Electronic spectra

The electronic spectral data of the complexes in methanol are given in Table VII.4. All the complexes show bands characteristic of high spin octahedral structure[117]. The cobalt complexes show two characteristic bands. The bands around 8000 cm^{-1} and 20100 cm^{-1} can be assigned to ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transitions respectively. The transition to ${}^4A_{2g}(F)$ was not observed, as such a transition is very weak. The bands around 28500 cm^{-1} and 30580 cm^{-1} are due to charge transfer transitions. Three spin allowed transitions are observed for the nickel(II) complex and they are ${}^3A_{2g} \longrightarrow {}^3T_{2g}$, ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$. The absorption maxima of these transitions are observed for the nickel complex around 8450 cm^{-1}, 16600 cm^{-1} and 20410 cm^{-1}, respectively. The intense charge transfer bands are observed around 27400 cm^{-1} and 30670 cm^{-1}. Copper complexes give two absorption maxima, one at 18000 cm^{-1} and another at 28980 cm^{-1}. These can be assigned to d-d and charge transfer transitions respectively. Based on the above information, the following structures have been proposed for the complexes.

Table-VII.4
Electronic spectral data

Compound	Absorption maxima (cm^{-1})	log ε
$[Co(FSE)_2]Cl_2$	8000	1.97
	20080	2.45
	28570	5.16
	30581	5.21
$[Co(FSE)_2]Br_2$	8000	1.92
	20100	2.45
	28470	5.16
	30610	5.20
$[Ni(FSE)_2]Cl_2$	8453	2.10
	20408	2.40
	27397	5.15
	30675	5.17
$[Ni(FSE)_2]Br_2$	8460	2.09
	16600	2.20
	20410	2.36
	27400	5.14
	30620	5.17
$[Cu(FSE)_2Cl_2]$	17860	2.75
	28985	4.94
$[Cu(FSE)_2Br_2]$	18520	2.78
	28409	4.90

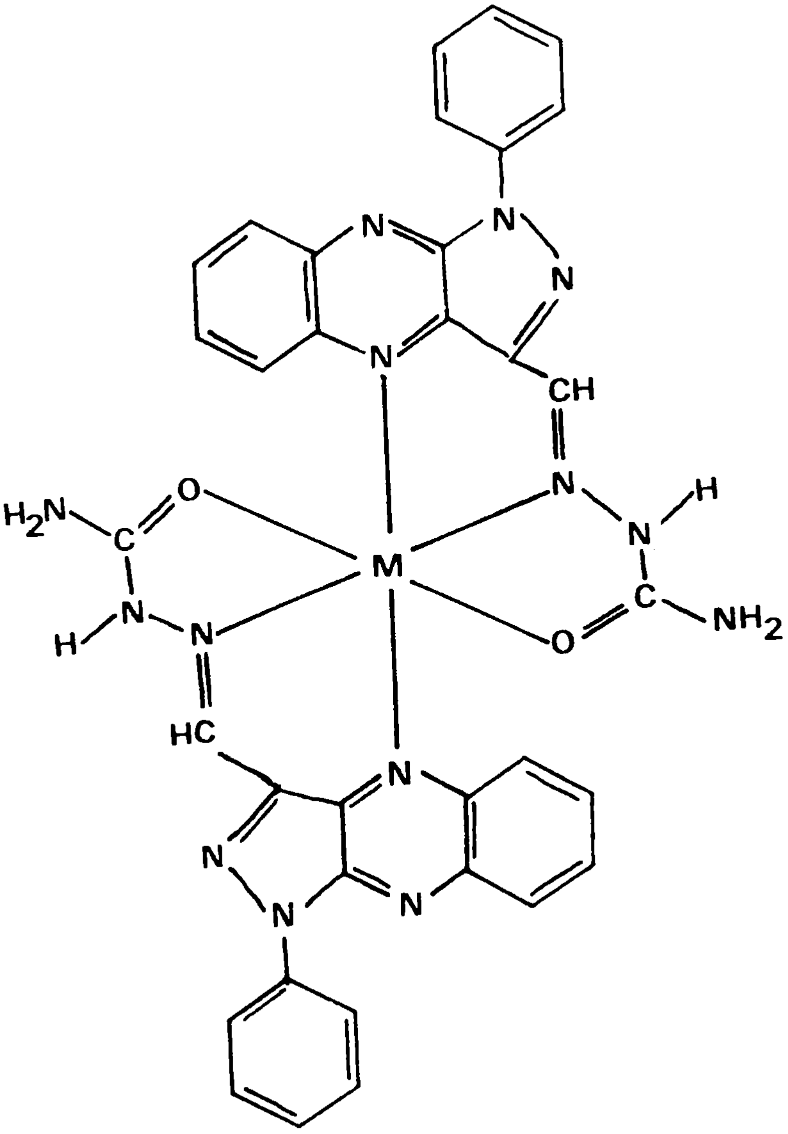


Fig. 7.2 Schematic structures of nickel and cobalt complexes.

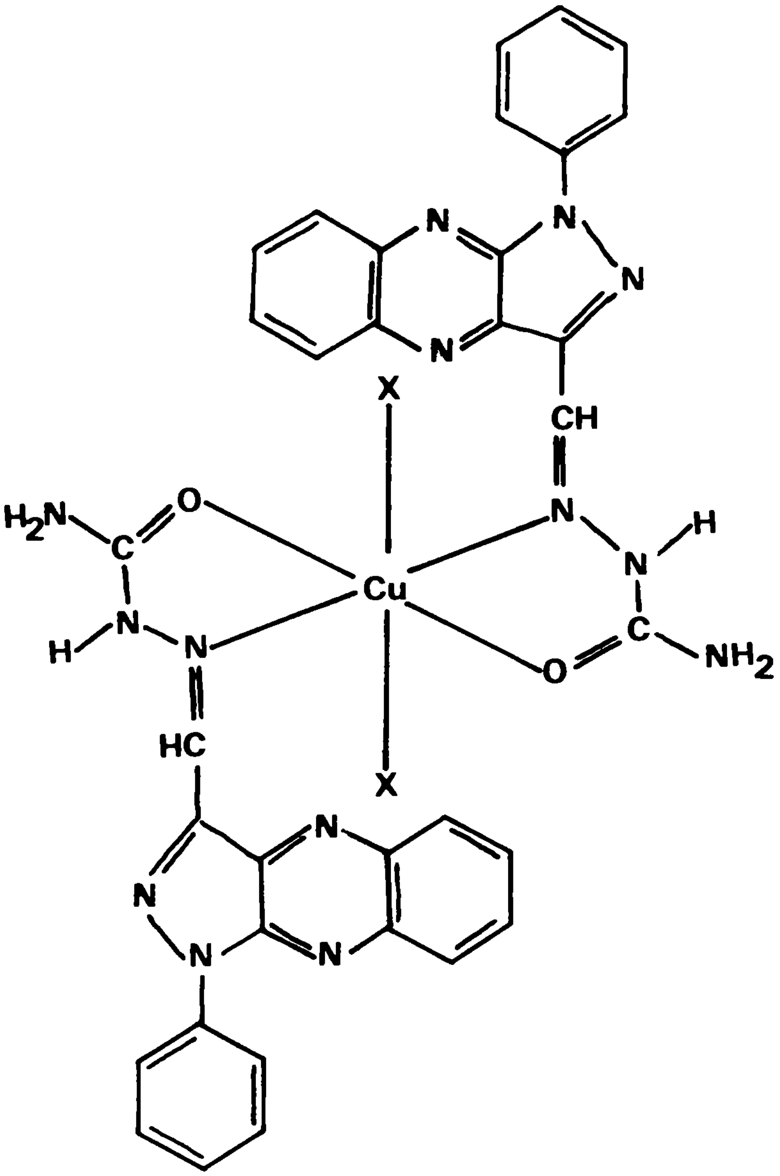


Fig. 7.2 Schematic structure of copper complex.

CHAPTER-VIII

1-PHENYLFLAVAZOLE-3-CARBOXALIDENE-2-AMINOPHENOL COMPLEXES OF Co(II), Ni(II), Cu(II) AND Zn(II)

8.1 INTRODUCTION

In this chapter, the results of our studies on transition metal complexes of the Schiff base derived from 2-aminophenol and 1-phenylflavazole-3-carboxaldehyde (PFCA) are presented. The complexes may be of biological interest since it contains the flavazole residue.[139] This ligand comprises chelation sites which include phenolic oxygen, azomethine nitrogen and ring nitrogen. The ligand has the structure given below:

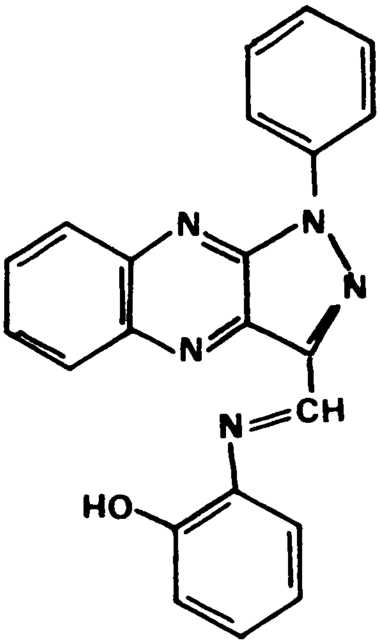


Fig.8.1 Structure of PFCA

8.2 Experimental

8.2.1. Materials

Details regarding the preparation and purification of the ligand are given in Chapter II.

8.2.2. Synthesis of the complexes

The complexes were prepared by the following general procedure: A solution containing metal acetates(0.01 mol, 2.48 g of $(CH_3COO)_2Ni.4H_2O$, 2.49 g of $(CH_3COO)_2Co.4H_2O$, 1.81 g of $(CH_3COO)_2Cu$ or 2.19 g of $(CH_3COO)_2Zn.2H_2O$) in ethanol (100 mL) was added to a solution of the ligand (0.02 mol, 7.3 g) in ethanol (100 mL). The mixture was refluxed for 4 h and allowed to cool. The complexes separated out were filtered, washed with methanol and dried *in vacuo* over anhydrous $CaCl_2$.(Yield : 60%).

8.2.3 Analytical methods

Details regarding the analytical methods and other characterisation techniques are given in Chapter II.

8.3 RESULTS AND DISCUSSION

The complexes isolated are non-hygroscopic, crystalline substances and are stable in air. They are soluble in chloroform, DMSO, DMF, nitrobenzene, acetonitrile, ethanol and methanol and partially soluble in benzene and hexane . The analytical data (Table VIII.1) show that the complexes have the general formula $[M(PFCA)_2]$ (where M=Co(II), Ni(II), Cu(II) and Zn(II). The molar conductance values (Table VIII.2) show that these complexes are non-electrolytes in methanol[103].

8.3.1. Magnetic susceptibility measurements

The magnetic moment values of the complexes are presented in Table VIII.2. The nickel and cobalt complexes exhibit magnetic moment values which are in agreement with an octahedral structure[133]. In the case of the copper complex the prediction of structure using the magnetic moment data is very difficult, as the magnetic moment values of the simple Cu(II) complexes usually are in the range 1.73 - 2.2 BM regardless of stereochemistry. However the magnetic moment value for the copper complex excludes the possibility of a tetrahedral structure and any antiferromagnetic interaction between neighbouring Cu(II) centres[133].

Table-VIII.1

Physical and Analytical data

Substance	Colour	% Yield	Carbon Found (%) (Calc.)	Hydrogen Found (%) (Calc.)	Nitrogen Found (%) (Calc.)	Metal Found (%) (Calc.)
Ni(PFCA)$_2$]	Brown	60	66.89	3.78	17.68	7.38
[$NiC_{44}H_{30}N_{10}O_2$]			(66.95)	(3.80)	(17.75)	(7.44)
[Co(PFCA)$_2$]	brown	60	66.88	3.78	17.70	7.39
[$CoC_{44}H_{30}N_{10}O_2$]			(66.92)	(3.80)	(17.74)	(7.47)
[Cu(PFCA)$_2$]	Black	60	66.89	3.76	17.61	8.10
[$CuC_{44}H_{30}N_{10}O_2$]			(66.54)	(3.78)	(17.64)	(8.00)
[Zn(PFCA)$_2$]	Pale brown	60	66.35	3.78	17.60	8.19
[$ZnC_{44}H_{30}N_{10}O_2$]			(66.38)	(3.77)	(17.60)	(8.22)

Table VIII.2

Molar conductance and magnetic moment data

Substance	Molar conductance (ohm^{-1} cm^2 $mole^{-1}$)	Magnetic moment(BM)
[Ni(PFCA)$_2$]	0.02	3.2
[Co(PFCA)$_2$]	0.02	5.1
[Cu(PFCA)$_2$]	0.02	1.9
[Zn(PFCA)$_2$]	0.02	Diamagnetic

8.3.2. Infrared spectra

The characteristic absorption frequencies of the ligand and the complexes are summarized in Table VIII.3. The ligand exhibit a broad band at 3300 cm^{-1} which may be due to O-H stretching vibration[103]. Further the ligand shows bands at 1630 cm^{-1} and 1599 cm^{-1} which are assigned to ν(C=N) of the azomethine and ν(C=N) of the flavazole ring respectively. In the spectra of the complexes the ν(C=N) band of the azomethine undergoes a red shift to 1620 cm^{-1}. This indicates the participation of azomethine nitrogen and ring nitrogen in bonding to the metal atom[103]. The retention of band at 1599 cm^{-1} and formation of a new band at 1580 cm^{-1} show that only one of the ring nitrogen atoms is involved in the bond formation. The phenolic ν(C-O) found around 1257 cm^{-1} in the spectra of the Schiff base shows a slight shift towards higher frequency and appears at 1270 cm^{-1} in the spectra of the complexes. Such shifts towards higher frequencies have been noted in the case of phenolic ligands on coordination[140,141]. The disappearance of band due to the phenolic -OH of the ligand at 3300 cm^{-1} in the spectra of the complexes shows the deprotonation of the ligand. Thus PFCA acts as a tridentate ligand coordinating through azomethine nitrogen, ring nitrogen and phenolic oxygen.

Table-VIII.3

Infrared absorption frequencies (cm^{-1}).

L	I	II	III	IV	Assignment
3300 s	------	------	------	------	ν(O-H)
2855 s	2855 s	2855 s	2855 s	2855 s	
2100 w	2100 w	2100 w	2100 w	2100 w	
2020 w	2020 w	2020 w	2020 w	2020 w	
1630 m	1620 m	1620 m	1620 m	1620 m	ν(C=N) azomethine
1599 m	1599 m	1599 m	1599 m	1599 m	ν(C=N) ring
------	1579 m	1579 m	1579 m	1578 m	ν(C=N) ring
1506 s	1506 s	1506 s	1506 s	1506 s	
1485 s	1485 s	1485 s	1485 s	1485 s	
1435 s	1435 s	1435 s	1435 s	1435 s	
1373 s	1373 s	1373 s	1373 s	1373 s	
1350 m	1350 m	1350 m	1350 m	1350 m	
1257 s	1270 s	1270 s	1270 s	1270 s	ν(C-O) phenolic
1207 m	1207 m	1207 m	1207 m	1207 m	
1180 m	1180 m	1180 m	1180 m	1180 m	
1140 s	1140 s	1140 s	1140 s	1140 s	
1100 w	1100 w	1100 w	1100 w	1100 w	
1050 w	1050 w	1050 w	1050 w	1050 w	
945 m	945 m	945 m	945 m	945 m	
900 m	900 m	900 m	900 m	900 m	
852 m	852 m	852 m	852 m	852 m	
812 m	812 m	812 m	812 m	812 m	
762 s	762 s	762 s	762 s	762 s	
744 s	744 s	744 s	744 s	744 s	

Table VIII.3 (continued)

L	I	II	III	IV	Assignment
715 w	715 w	715 w	715 w	715 w	
685 m	685 m	685 m	685 m	685 m	
660 m	660 m	660 m	660 m	660 m	
605 m	605 m	605 m	605 m	605 m	
585 w	585 w	585 w	585 w	585 w	
550 w	550 w	550 w	550 w	550 w	
507 m	507 m	507 m	507 m	507 m	
424 m	424 m	424 m	424 m	424 m	

Abbreviations: s = strong, m = medium and w = weak.

L-PFCA, I-$[Co(PFCA)_2]$, II-$[Ni(PFCA)_2]$, III-$[Cu(PFCA)_2]$,

V $[Zn(PFCA)_2]$

8.3.3 Electronic spectra

The electronic spectral data are given in Table VIII.4. All the complexes exhibit a broad band with high intensity in the region 28900-39900 cm^{-1} and this band can be assigned to charge transfer transition[122].

The Co(II) complex shows three bands indicative of high spin octahedral structure[133]. The absorption bands observed at 8000 cm^{-1} and 19570 cm^{-1} for this complex can be attributed to ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ and ${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ transitions respectively. Further, a weak shoulder band observed at 25640 cm^{-1} is due to ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition. Three spin allowed transitions are expected for octahedral Ni(II) complexes[111]. The spectrum of the present complex exhibits bands at 8330 cm^{-1}, 19570 cm^{-1} and 26040 cm^{-1}, which are attributed to ${}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$, ${}^3A_{2g} \longrightarrow T_{1g}(F)$ and ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transitions respectively. The Cu(II) complex shows a broad band at 18220 cm^{-1} which is due to d-d transition. Based on the above information, structure given in Fig 8.2 can be assigned for the complexes.

Table-VIII.4

Electronic spectral data

Compound	Absorption Maxima (cm^{-1})	log ε
$[Co(PFCA)_2]$	8000	1.05
	19570	1.62
	25640	1.84
	39840	5.03
$[Ni(PFCA)_2]$	8330	1.19
	19570	1.58
	26040	1.92
	38460	5.29
$[Cu(PFCA)_2]$	18220	1.66
	28990	5.01

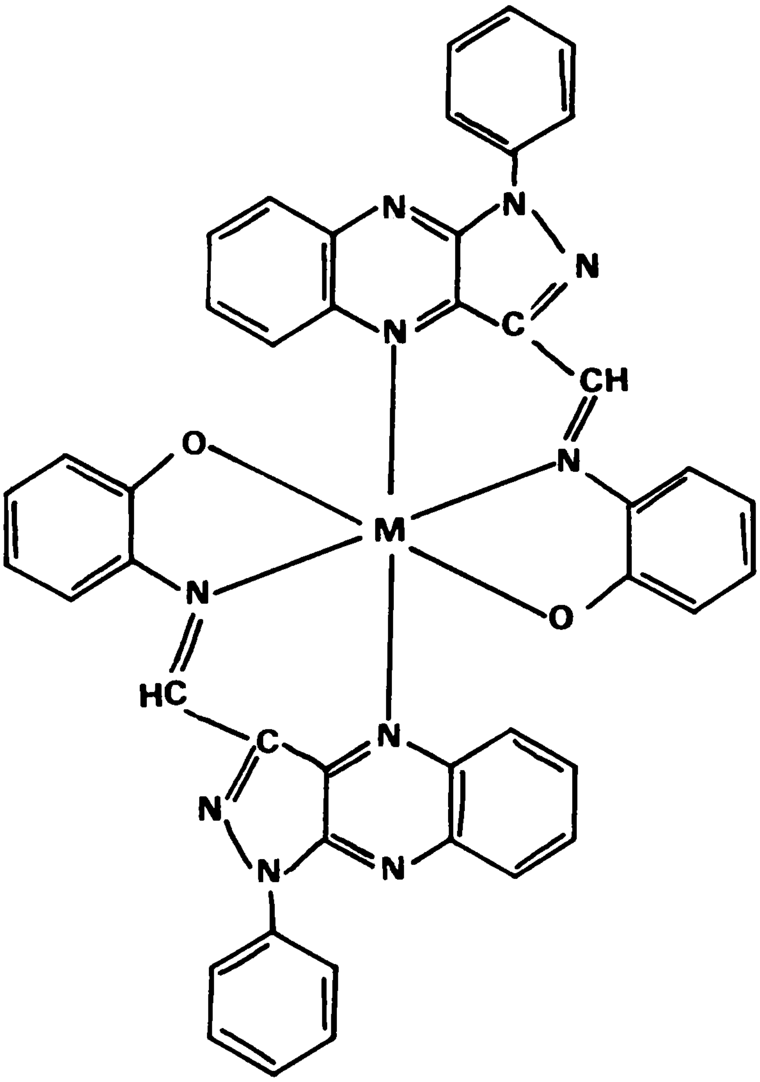


Fig. 8.2 Schematic structure of $[M(PFCA)_2]$ where M = Co(II), Ni(II) Cu(II) and Zn(II).

CHAPTER-IX

THERMAL AND CATALYTIC ACTIVITY STUDIES OF SOME OF THE SCHIFF BASE COMPLEXES DERIVED FROM 2-PHENYL-1,2,3-TRIAZOLE-4-CARBOXALDEHYDE AND 1-PHENYLFLAVAZOLE-3-CARBOXALDEHYDE

9.1. INTRODUCTION

Much effort has been devoted to develop useful catalytic system for mild and selective oxidations of organic compounds with the aid of molecular oxygen[142,143]. Selective oxidation or oxygenation of organic substances is important in chemical and petrochemical industries due to the wide variety of products synthesised in this route. The important oxygen sources at the moment are dioxygen, hydrogen peroxide, alkyl peroxides, hypochlorate anion and iodosobenzene. Among these, dioxygen is very attractive due to its low cost and availability from liquid air; however, it usually reacts with organic substrates only in the presence of a catalyst.

Catalytic oxidations are of two types: the first type involves the transfer of an electron from the substrate to the oxidant leading to oxidation, and the second type involves the incorporation of oxygen atom by the substrate leading to oxygenation[83]. Metal complexes of planar porphyrins catalyse hydrocarbon oxidation[144,147] but the conversions are found to be too low to have any commercial utility. In recent years there have been several reports of the applications of the Schiff base complexes as oxidation catalyst[146,147]. Schiff base ligands are capable of attaining the planar coordination and are of great importance because of their easy design and simple synthesis. A large number of Schiff base complexes were synthesised and characterised[148,150]. However the catalytic activity of these interesting complexes has been studied only in few cases. It was therefore considered worthwhile to study the catalytic activity of the complexes reported in the thesis in an oxidation reaction: oxidation of hydroquinone to p-bebzoquinone. These complexes were screened for their catalytic activity and pronounced activity was observed only in the case of the copper complexes, therefore, we have restricted catalytic activity studies only to these copper(II) complexes. We have also studied the thermal decomposition kinetics of these complexes and found out a correlation between the thermal and catalytic behaviour of these complexes. Details of these studies are presented in this chapter.

9.2. EXPERIMENTAL

Details regarding the preparation and characterisation of the metal complexes have already been given in the earlier chapters.

Analytical methods

Catalysis experiments were carried out on a Shimadzu UV-Vis. 160 A spectrophotometer using methanol as the solvent. Methanol solutions (25 mL) containing hydroquinone (0.3 mmol) and copper(II) complex (0.003 mmol) were kept under nitrogen. Absorbance of the product at 245 nm (the characteristic absorption band of quinone) was measured at intervals of 10 min after exposing the solution to air[151].

The thermal studies were carried out in a Shimadzu TGA-50 thermal analyser using 5-10 mg samples at a heating rate of 10^{o}C/min. in air using platinum crucible. The evaluation of kinetic parameters, order (n), activation energy (Ea), entropy of activation (ΔS) and the pre-exponential factor (A) using Coats-Redfern equation[152] was based on a computer program which was developed for use on a Busybee, PC/XT computer (HCL.Ltd.), and was used earlier for the determination of kinetic parameters[153-155]. Details about the equation and the evaluation procedures are given in the Appendix of this chapter.

9.3. RESULTS AND DISCUSSION

All the complexes were tested for their catalytic activity in the oxidation of hydroquinone to quinone and pronounced catalytic activity was observed only in the case of the Cu(II) complexes A solution containing hydroquinone and each of the complexes were kept under nitrogen and UV spectrum was recorded [Fig-9.1(m)]. The spectra were again recorded after exposing the solution to air at various time intervals [Fig-9.1(n,o,p,q,r,s,t)]. The characteristic absorption peak due to quinone at 245 nm [156] was absent at the start of the reaction, but it was gradually formed on exposure to air in the presence of the metal complexes. This observation indicates the catalytic activity of these complexes in the oxidation reaction. The absorbance of the solution at 245 nm was noted at an interval of 10 min. (Fig.9.2). The conversion of hydroquinone to quinone is complete within 100 min.. A plot of log ΔA (ΔA = the difference in absorbance at zero and experimental time) versus time gives a straight line showing that the oxidation is first order with respect to the substrate[157].

The catalytic activity was found to be the highest for $[Cu(PFCA)_2]$ next for $[Cu(PTSC)_2(OAc)_2]$ and the least for $[Cu(PTCA)_2(OAc)_2]$. The activity of these complexes may be due to their capability for oxygen chemisorption[158].

Thermal studies of these complexes were also carried out and the thermoanalytical data are presented in Table IX.1. All the complexes follow almost the same pattern of thermal decomposition (Fig.9.3, Fig.9.4 and Fig.3.4). They are stable up

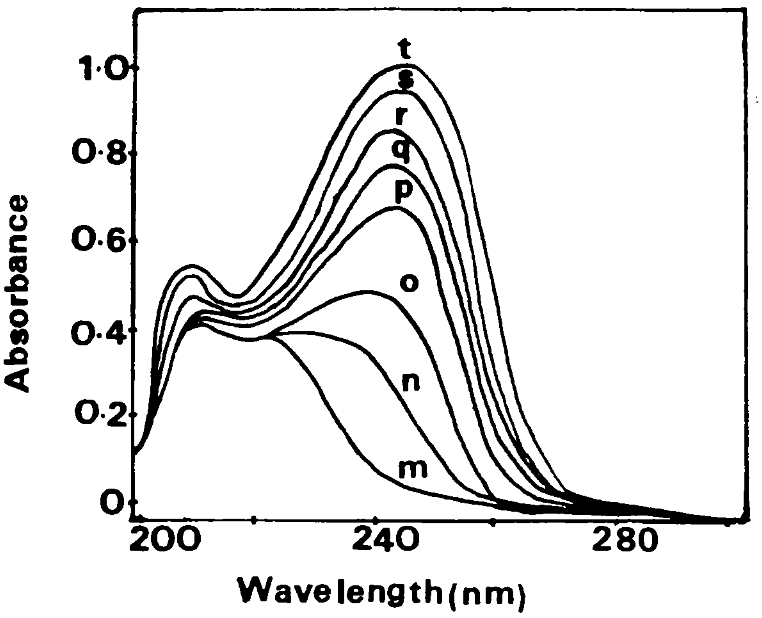


Fig.9.1 Oxidation of hydroquinone in presence of $[Cu(PTCA)_2Br_2]$ n-10 min.,o-20 min.,p-40 min., q-60 min.,r-80 min., and t-100 min.

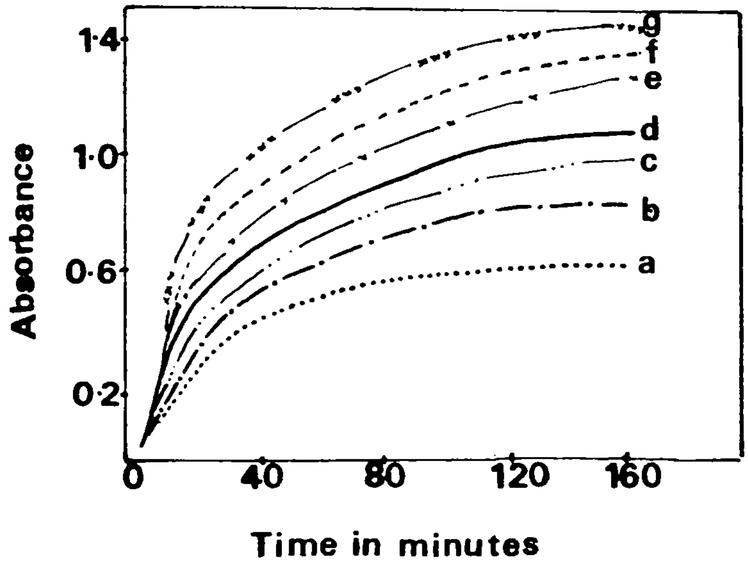


Fig.9.2 Time dependent formation of quinone in presence of

(a) $[Cu(PTCA)_2(OAc)_2]$, (b) $[Cu(PTCA)_2Cl_2]$, (c) $[Cu(PTCA)_2Br_2]$

(d) $[Cu(FTSE)_2(OAc)_2]_2$, (e) $[Cu(FSE)_2Cl_2]$, (f) $[Cu(PTSC)_2(OAc)_2]$

(e)$[Cu(PFCA)_2]$

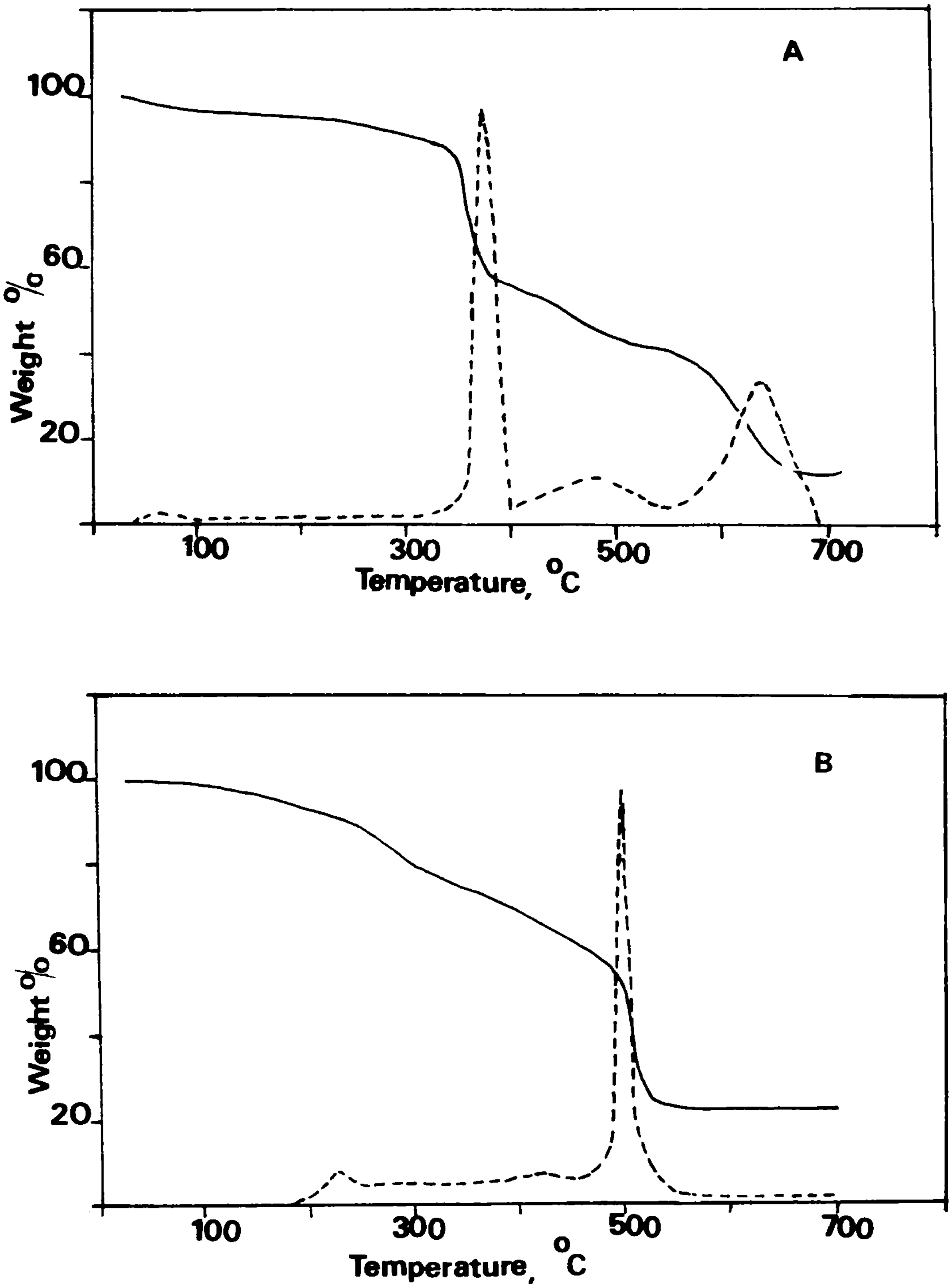


Fig. 9.3 TG/DTG traces of the complexes

A - [Cu(FSE)$_2$X$_2$], B - [Cu(FAMP)$_2$]

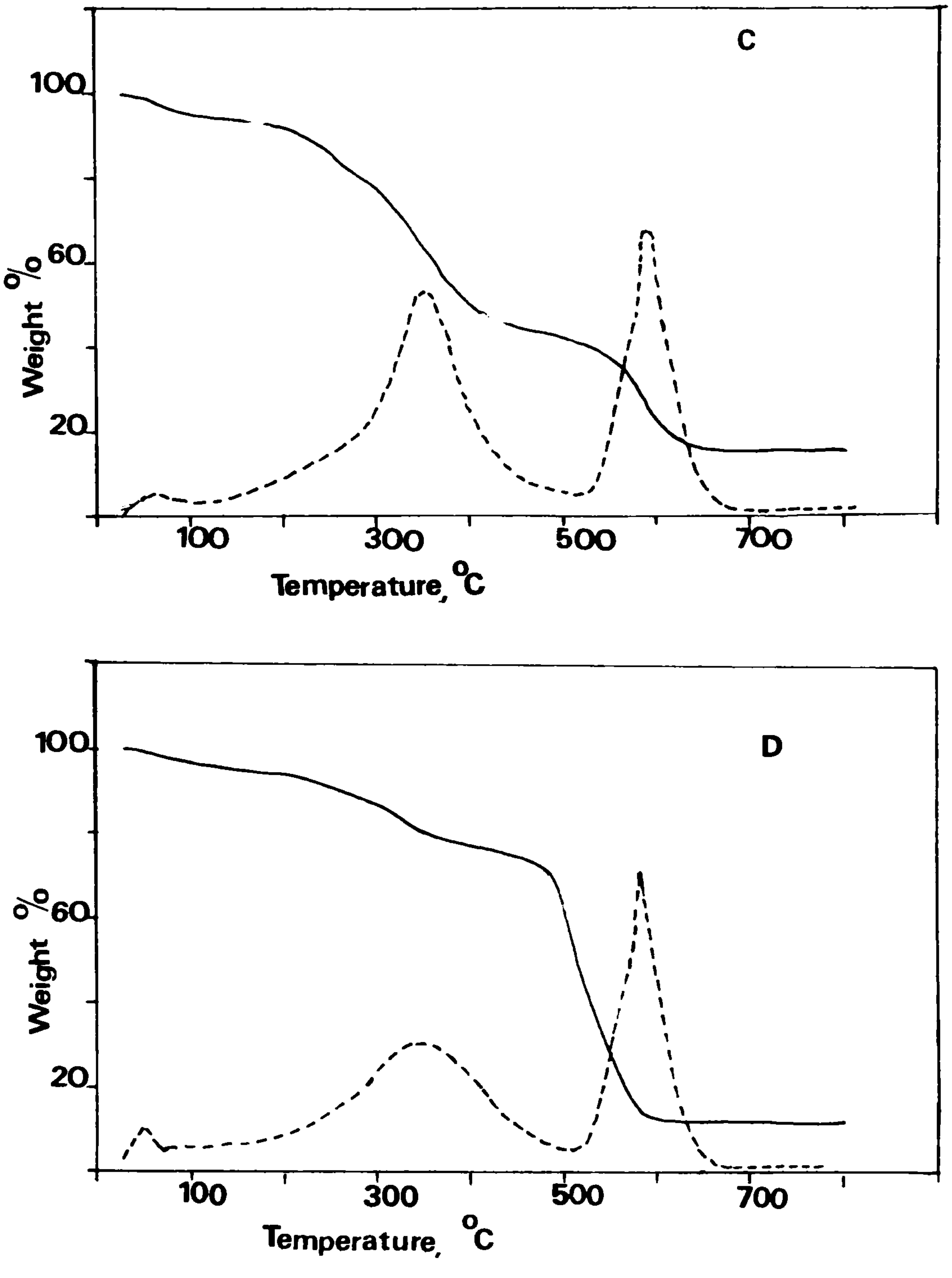


Fig. 9.4 TG/DTG traces of the complexes

C - $[Cu(PTSC)_2(OAc)_2]$, D - $[Cu(FTSC)_2(OAc)_2]_2$

to 120°C and show two DTG peaks. The thermoanalytical and kinetic data are presented in Table IX.1. The kinetic parameters were evaluated for these complexes under the same experimental conditions (same heating rate, furnace atmosphere and sample weight etc.) and have been used for the comparison of the decomposition process[159,160].

The activation energy (Ea) for the first stage of decomposition is seen to increase in the following order: $[Cu(PFCA)_2] < [Cu(PTCA)_2Br_2] < [Cu(PTSC)_2(OAc)_2 < [Cu(PTCA)_2Br_2] < [Cu(FSE)_2Cl_2] < [Cu(FTSC)_2(OAc)_2]_2 < [Cu(PTCA)_2(OAc_2)$. The ΔS value for the first stage of decomposition is negative which suggests that the activated complexes have more ordered structure than the reactants[161] and might be due to the chemisorption of oxygen by these complexes during this stage. The Ea value for the second stage of decomposition is found to be smaller than that of the first stage, indicating an increased rate of decomposition during this stage. This might be due to the availability of more vacant coordination sites in the intermediate complex (resulting from the removal of ligands) which can absorb gaseous product and thus catalyse the decomposition reaction[162]. This is further indicated from the more negative ΔS values for this stage. Thus the decomposition at the final stage is seen to have a bearing on the catalytic effect of the oxides formed at this stage. The lower value of Ea at the second stage and the negative ΔS value for the complexes suggest that the oxide formed might be p-type

Table IX.1
Thermal Decomposition Data

Substance	Stage	Temperature Range in DTG	%Loss Found (Calc.)	Composition of expelled group	Order	Ea (kJ mol^{-1})	ΔS (kJ $mol^{-1}K^{-1}$)	A (s^{-1})
$[Cu(PTCA)_2Cl_2]$	I	170-420	77.1 (78.1)	2 PTCA	1.90	43	-96	$0.287x10^2$
	II	420-840	11.0 (11.2)	2 chlorine	1.60	11	-149	$0.221x10^{-4}$
$[Cu(PTCA)_2Br_2]$	I	220-500	67.9 (68.8)	2 PTCA	1.30	28	-113	0.361
	II	500-820	21.8 (22.3)	2 bromine	0.27	16	-133	$0.217x10^{-2}$
$[Cu(PTCA)_2(OAc)_2]$	I	200-500	72.8 (73.1)	2 PTCA	1.8	67	-73	$0.171x10^5$
	II	500-800	17.0 (17.5)	2 acetate	0.64	13	-149	$0.301x10^{-4}$
$[Cu(PTSC)_2(OAc)_2]$	I	200-420	45.0 (45.2)	1 PTSC, 1 OAc	0.79	34	-247	$1.244x10^3$
	II	420-640	44.9 (45.2)	1 PTSC, 1 OAc	0.38	27	-280	0.0427
$[Cu(FTSC)_2(OAc)_2]_2$	I	200-400	13.3 (13.4)	4 OAc	1.3	65	-186	2.465
	II	400-600	39.0 (39.6)	2 FTSC	0.38	59	-233	10.86
$[Cu(FSE)_2Cl_2]$	I	220-380	45.8 (46.0)	2 FSC	0.255	63	-203	0.349
	II	380-600	45.5 (46.0)	2 Cl	0.399	24	-288	0.017
$[Cu(PFCA)_2]$	I	250-650	91.7 (92.0)	2 PFCA	0.312	27	-278	0.051

Cu_2O (this will ultimately oxidised to CuO).

It is interesting to note that the increasing order of catalytic activity $[Cu(PTCA)_2(OAc)_2]$ < $[Cu(PTCA)_2Cl_2]$ < $[Cu(PTCA)_2Br_2]$ < $[Cu(FTSE)_2(OAc)_2]_2$ < $[Cu(FSE)_2Cl_2]$ < $[Cu(PTSC)_2(OAc)_2]$ < $[Cu(PFCA)_2]$ is same as their decreasing order of entropy of activation for the first stage of thermal decomposition (Table-IX.1). Thus the catalytic studies further strengthen our suggestion that the decrease in ΔS values for the first stage is mainly due to oxygen chemisorption[163].

APPENDIX

KINETIC PARAMETERS FROM NONISOTHERMAL THERMOGRAVIMERTY

The specific rate equation for the thermal decomposition of a single solid giving another solid and a volatile product:

$$\text{A (Solid)} \longrightarrow \text{B (Solid)} + \text{C (Gas)} \qquad (A.1)$$

can be written in the form,

$$d\alpha/dt = kf(\alpha)$$

where α is the fraction decomposed at time t, $f(\alpha)$ is a function of α and can have various forms; k is the specific reaction rate. In the derivation of almost all the well known kinetic equations developed for evaluating kinetic parameters, simplified form of $f(\alpha)$; $f(\alpha) = (1-\alpha)^n$ is used. Eventhough, n can be usually identified as the order of the reaction, it does not have much physical significance in solid state reactions, which are usaually heterogeneous[164-167].

For the decomposition reaction with a constant linear heating rate, Φ, (where $\Phi = dT/dt$) equation (A.1) may be rewritten as,

$$d\alpha/dT = (k/\Phi)\ f(\alpha) = (k/\Phi)\ (1-\alpha)^n \qquad (A.2)$$

Invoking the Arrhenius equation, ie.,

$$k = A\ e^{-Ea/RT} \qquad (A.3)$$

into the equation (A.2), we get an equation, which is the fundamental equation employed in non-isothermal TG.

$$d\alpha/dT = (A/\Phi)\ e^{-Ea/RT}\ (1-\alpha)^n \qquad (A.4)$$

where A is the pre-exponential factor and E_a is the energy of activation.

The method for evaluting the kinetic parameters using the equation (A.4) can be broadly classified into three groups[168]. (1) differential methods; (2) approximation methods and (3) integral methods. Integral methods are considered to be most accurate and give quite reliable values[169,170]. Among them, Coats-Redfern method is the most reliable one and in the present investigation this method has been used for the evalution of kinetic papameters. Therefore, only details about the Coats-Redfern method are included here.

The Coats-Redfern Method

This method employs the integrated form of the equation (A.4) in the following form:

$$d\alpha/(1-\alpha)^n = (A/\Phi)\ e^{-Ea/RT}\ dT \qquad (A.5)$$

The integration of the left hand side (LHS) of equation (A.5) with limits 0 to Ø is easy, but the integration of the right hand side (RHS) with limits 0 to T poses some difficulty, as it has no exact solution. The integral of LHS, denoted by the function $g(\alpha)$, can be written as,

$$g(\alpha) = [1-(1-\alpha)^{1-n}]/(1-n) \qquad (A.6)$$

when $n \neq 1$, and

$$g(\alpha) = -\ln(1-\alpha) \qquad (A.7)$$

when $n = 1$. Coats and Redfern evaluated the RHS of equation (A.5), ie, the temperature integral, with the aid of the Rainville function[171]. The final form of the equation derived by them was,

$$\log g(\alpha)/T^2 = (\log AR/\Phi Ea)\ (1-2RT/Ea) - Ea/2.303\ RT \qquad (A.8)$$

The term 2RT/Ea is negligible in comparison with unity and can therefore be neglected. Therefore equation (A.8) can be written in the form,

$$\log g(\alpha)/T^2 = \log AR/\Phi Ea - Ea/2.303\ RT \qquad (A.9)$$

The $g(\alpha)$ values can be calculated only if the value of n is known. For the determination of the best value of n, the following procedure is adopted: first a value of n is selected and $g(\alpha)$ values are calculated. The best values of intercept (a) and slope (b) of the equation (A.9) for this value of n are found out by the method of least squares. Using these values of a and b, the $g(\alpha)$ values are calculated employing the equation (A.9). Then, the sum of the squares of deviation of these values from the $g(\alpha)$ values, S, is calculated and the whole procedure is repeated for various of n until S is a minimum. The value of n which gives the minimum value of S is taken as the best value.

A plot of $\log g(\alpha)/T^2$ *vs.* $1/T$ will be linear and the slope of this plot will give the value of $-Ea/2.303\ R$ from which activation energy value (Ea) can be calculated. Knowing Ea, the value of pre-exponential factor (A) can be found out from the intercept.

The entropy of activation, ΔS, is calculated using the relation, $A = (kT/h)\ e^{\Delta S/R}$, where k is the Boltzmann constant, h is the Plank's constant and R is the gas constant. The DTG peak temperature is usually taken as the value of temperature term T in the above equation.

SUMMARY

The thesis deals with the synthesis, characterisation and catalytic activity studies of some new Schiff base complexes derived from 2-phenyl-1,2,3-triazole-4-carboxaldehyde and 1-phenylflavazole-3-carboxaldehyde.

The thesis is divided into nine chapters . Chapter I of the thesis presents an introduction to the coordination chemistry of Schiff base ligands, with emphasis on thiosemicarbazones and semicarbazones. Application of Schiff base complexes as catalysts for various oxidation reactions and the scope of the present investigation are also outlined in this chapter. In Chapter II, informations on the preparation and purification of the ligands and physico-chemical techniques employed in the characterisation of metal complexes are given. Chapter III deals with the synthesis and characterisation of 2-phenyl-1,2,3-triazole-4-carboxalidene-aniline(PTCA) complexes of copper(II). All the complexes except the perchlorate complex are non-electrolytes in nitrobenzene. The complexes have the general formula $[Cu(PTCA)_2X_2]$ (where X = Cl, Br or acetate group) and $[Cu(PCTA)_2X]X$ (where X = ClO_4). PTCA acts as a bidentate ligand coordinating through the azomethine nitrogen and one of the ring nitrogen atoms. Based on the spectral studies, a distorted octahedral structure has been assigned for the complexes.

Chapter IV deals with the synthesis and characterisation of some cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 2-phenyl-1,2,3-triazole-4-carboxaldehyde and thiosemicarbazone (PTSC). The complexes are non-hygroscopic and are non-electrolytes in nitrobenzene. This can be represented by the formula $[M(PTSC)_2(OAc)_2]$, (where M is the metal atom and OAc represents an acetate group). The bonding of the PTSC ligand in these complexes is through the thione sulphur and azomethine nitrogen. A distorted octahedral structure has been assigned for these complexes.

Chapter V gives details about the synthesis and characterisation of complexes of the type $[Co(PTCS)X_2]$ (where PTCS = 2-phenyl-1,2,3-triazole-4- carboxaldehyde semicarbazone and X = Cl, Br, I and SCN). The ligand PTCS in these complexes act as a bidentate ligand bonding through azomethine nitrogen and oxygen. Magnetic moment data together with electronic spectral data suggest a tetrahedral structure for the complexes.

Chapter VI deals with 1-phenylflavazole-3-carboxaldehyde thiosemicarbazone (FTSC) complexes of cobalt(III), nickel(II), copper(II) and zinc (II). All the complexes except the cobalt complex are non-electrolytes in methanol. Cobalt complex is found to be 1:1 electrolyte in methanol. The complexes have the general empirical formula $[M(FTSC)_2(OAc)_2]$ for nickel and zinc complexes, $[Co(FTSC)_2]OAc$ for the cobalt complex and $[Cu(FTSC)_2(OAc)_2]_2$ for the copper complex. The ligand FTSC acts as a bidentate ligand in the case of nickel and zinc complexes and as a tridentate ligand in the case of cobalt and copper complexes. Based on the magnetic and spectral studies, an octahedral structure has been assigned for all the complexes. Molecular weight and magnetic moment value of (1.5 BM) for the copper complex indicate a dimeric structure.

Chapter VII deals with complexes of cobalt(II), nickel(II) and copper(II) with the Schiff base 1-phenylflavazole-3-carboxaldehyde semicarbazone (FSE). All the complexes except the copper complexes are 1:2 electrolytes in nitrobenzene. Cobalt(II) and nickel(II) complexes have the general formula $[M(FSE)_2]X_2$ and the copper complexes can be represented as $[M(FSE)_2X_2]$ (where X = Cl or Br). This ligand acts as a tridentate ligand in the case of nickel and cobalt complexes and bidentate in the copper complexes.

Chapter VIII deals with the synthesis and characterization of nickel(II), cobalt(II), copper(II) ad zinc(II) complexes of the Schiff base derived from 1-phenylflavazole-3-carboxaldehyde and 2-aminophenol(PFCA). The complexes are non-electrolytes in methanol. All the complexes have the general empirical formula $[M(PFCA)_2]$. The ligand, acts as a tridentate ligand coordinating through azomethine nitrogen, phenolic oxygen and ring nitrogen. An octahedral structure has been assigned for these complexes.

Chapter IX deals with the thermal and catalytic activity studies of the complexes reported in this thesis. The activity of the complexes was tested in the oxidation of hydroquinone to *p*-benzoquinone. Pronounced catalytic activity was observed only in the case of the copper(II) complexes. Catalytic activity was found to be the highest for $[Cu(PFCA)_2]$ and the least for $[Cu(PTCA)_2(OAc)_2]_2$. We have also studied the thermal decomposition kinetics of some of these complexes and found a correlation between the thermal and catalytic activity.

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