STUDIES ON SOME NEW METAL COMPLEXES OF QUINOXALINE BASED LIGANDS

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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 Dr. K. K. Mohammed Yusuff

20-4-1996 (Supervising Teacher)

PREFACE

This thesis deals with the synthesis, characterisation and catalytic activity studies of some new metal complexes derived from quinoxaline based ligands. Structural elucidation is done using conductance, magnetic susceptibility measurements, infrared, UV-Vis., EPR, Mössbauer and XRD studies.

The thesis is divided into nine chapters. Chapter I of the thesis presents an introduction of the metal complexes of aromatic nitrogen heterocyclic ligands.

Chapter II gives details of the preparation and purification of the ligands. It also gives various characterization techniques employed which include elemental analyses, magnetic and conductance measurements, and IR, UV-Vis., ESR, Mössbauer, and XRD spectral studies.

Chapters III to VII deal with synthesis and characterization of some new metal complexes of the ligands 2,3-bis-hydrazinoquinoxaline (BHQ), 3-hydroxyquinoxaline-2-carboxalidene-o-aminophenol (QHA), 3-hydroxyquinoxaline-2-carboxalidene-2-furfurylamine (QHF), 3-hydroxyquinoxaline-2-carboxaldehyde semicarbazone (QHS), and 3-hydroxyquinoxaline-2-carboxaldehyde thiosemicarbazone (QHT)

Chapter VIII presents our attempts to synthesise some cobalt(II) and copper(II) complexes of the ligands QHA, QHF, QHS and QHT in the supercage of zeolite Y and characterise such complexes. Chapter IX deals with the catalytic activity studies of the synthesised complexes in the oxidation of 3,5-ditert-butylcatechol to corresponding quinone.

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CHAPTER I

INTRODUCTION

The development of coordination chemistry indeed occurs through the innovative design and synthesis of new ligands and their complexes[1,2]. For the sake of simplicity, a ligand system can be considered as a collection of many adjustable components such as,

a) The donor atoms and their basicities
b) The functional groups and their spatial orientation
c) Ring substituents and their steric and electronic effects etc.

The quest of a coordination chemist is directed at acquiring a deeper understanding of the natural processes in which metal ions act as catalysts as well as at acquiring the competence to design more effective catalysts for a variety of metal catalyzed ligand reactions.

A strategically crafted ligand can hold the metal ion in a pre-determined manner with desired properties, which forms the basis of biomimetic chemistry. Biomimetic chemistry is mainly concerned with the study of synthetic models of biological metal complexes such as enzymes, haemoglobin, etc. The model complexes need not necessarily follow exactly what we learn from enzymes. Enzymes generally bind their substrates in a specific manner to achieve substrate selectivity, reaction selectivity and stereo selectivity. Binding can be achieved by metal coordination, ion pairing, Lewis acid-base coordination or hydrogen bonding.

The properties of the model complexes can be changed or controlled using modified ligands. In this regard aromatic nitrogen heterocycles provide an important class of ligands in coordination chemistry. Monodentate ligands such as pyridine, and chelating ligands such as 2,2'-bipyridine readily form stable complexes with most transition metal ions and have long been extensively used in both analytical and preparative coordination chemistry. Six membered aromatic nitrogen heterocycles (azines) have relatively low π^* orbitals which act as good acceptors of metal d-orbital density[3,4]. The metal ligand interactions are governed by the specific metal and ligand involved.

As our present investigation is confined to the studies on some metal complexes of quinoxaline based ligands, a brief discussion on such heterocyclic systems and its derivatives is presented here. The uses of heterocycles as bridging ligands have been reviewed by Steel[5]. The complexes of quinoxaline with several transition metal salts have been studied by various workers[6-10].

Of the diazanaphthalenes, quinoxaline has frequently been employed as a bridging ligand in both homobimetallic and heterobimetallic complexes[11]. In general, it behaves in a similar manner to pyrazine to which it is structurally related. The X-ray structures of polymeric copper[12] and silver[13] complexes containing bridging quinoxalines have been reported.

A number of recent studies of the physicochemical properties of transition metal complexes of nitrogen heterocycles, in combination with theoretical calculations have greatly improved our understanding of the nature of metal-ligand interactions[5]. Consequently, it is now becoming possible to predict accurately the physical properties of new metal ligand combinations and to tune these properties by subtle changes in the ligand structure. Thus many new heterocyclic ligands are expected to be synthesized in the future which are specifically designed to impart specially desired features in the properties of their metal complexes. Such ligands offer exciting new possibilities for the preparation of new binuclear and polynuclear complexes with potential applications as catalysts, photosensitizers or low dimensional conducting polymers.

Since the seminal work by Schiff and coworkers, metal chelate Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility, diversity and structural variability[14,15]. The coordination chemistry of Schiff bases is of considerable interest due to their biological and catalytic applications.

Ligands containing sp^2 hybridised nitrogen atoms, particularly when N-atom is the part of the aromatic system, have a very extensive coordination chemistry. Also for donors of this type, a much more extensive and useful coordination chemistry is possible when they are bi or tridentate ligands.

Iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base derived from quinoxaline-2-carboxaldehyde and 2-aminocyclopent-1-ene-1-dithiocarboxylic acid have been reported[16]. The complexes have the general formula [MLCl] for the cobalt(II), nickel(II) and copper(II) complexes and $[FeLCl(OH)(H_2O)]$ for the iron(III) complex. Octahedral and tetrahedral structures have been assigned for the iron(III) and cobalt(II) complexes respectively, while nickel(II) and copper(II) complexes have square planar geometry. The ligand acts as a tridentate ligand coordinating through one of the sulphur atoms, the azomethine nitrogen atom and also through nitrogen atom of the quinoxaline ring.

Iron(III), cobalt(II), nickel(II) and copper(II) complexes of another Schiff base ligand derived from quinoxaline-2-carboxaldehyde and amino group supported on crosslinked polystyrene have been reported[16]. The empirical formula for the iron(III) complex is $[FeL(OAc)_3(H_2O)_2]$ and that for Co(II), Ni(II) and Cu(II) complexes is $[ML(OAc)_2(H_2O)]$ where OAc represents an acetate group. Infrared spectra indicate that in all the complexes bonding of Schiff base unit is through the azomethine nitrogen atom and not through the nitrogen atom of the quinoxaline ring. Based on the electronic spectra and magnetic behaviour, octahedral and tetrahedral structures have been assigned respectively for the Fe(III) and Co(II) complexes and square planar structures for the Ni(II) and Cu(II) complexes.

Spectral and thermal studies on new complexes of iron(III), cobalt(II), nickel(II) and copper(II) with a Schiff base derived from quinoxaline-2-carboxaldehyde and glycine have been reported. A dimeric octahedral structure involving Cl and OH bridges has been proposed for these complexes[17]. The complexes were subjected to a systematic TG/DTG analysis. The decomposition process consists of two stages for all these complexes. Kinetic parameters were evaluated for each of these stages using the Coats-Redfern equation. The rate of decomposition at the second stage seems to have a bearing on the catalytic effect of the metal oxides formed during this stage[18].

The sulphur containing heterocyclic thiosemicarbazones are proven to have considerable biological action. Many of these are active against influenza, protozoa, smallpox and certain kinds of tumours[19,20]. Heterocyclic thiosemicarbazones exercise their beneficial therapeutic values in mammalian cells by inhibiting ribonucleotide reductase, a key enzyme in the synthesis of DNA precursors. Their ability to provide this inhibitory action is thought to be due to the coordination of iron via their NNS tridentate ligating system. A large number of transition metal complexes of 2-heterocyclic thiosemicarbazones as well as the related S-alkyl thiosemicarbazates have been synthesized and studied[21-23].

The attachment of thiosemicarbazone to the metal atoms is usually through the thione\thiol S atom and hydrazine N atom in a bidentate manner. Thiosemicarbazones are not so strong as other soft base ligands like cyanide, diarsine and certain charged S^- ligands. The thione form cannot cause any spin pairing in the metal complexes but thiol form can lead to low spin complexes of cobalt and nickel, however, they are not capable of causing spin pairing in the iron complexes[24].

Synthesis, characterization and cytotoxicity of new quinoxaline-2-carboxaldehyde thiosemicarbazone (QTSC) complexes of Co(III), Ni(II) and Cu(II) have been studied[25]. The complexes have the empirical formulae, $[Co(QTSC)_2]X_2$, $[Ni(QTSC)_2(OAc)X]$ and $[Cu(QTSC)(OAc)(H_2O)]_2$ where X = Cl/Br and OAc = acetate group. The magnetic and spectral data suggest a distorted octahedral geometry for the complexes. The copper complex appears to be dimeric with bridging acetate groups. The ligand acts as a uninegative tridentate NNS donor in the cobalt and copper complexes, while it acts as a neutral bidentate NS donor in the nickel complexes. The cytotoxicity of the cobalt(III) complexes were determined *in vitro* as well as in tissue culture. The chloro complex was found to have greater cytotoxic activity than the bromo complex.

The replacement of the sulphur atom of the thiocarbonyl group by oxygen, selenium, an imine, an oxime etc, modification of the sulphur center by alkylation, changing thiosemicarbazone's point of attachment on the heterocyclic ring, the substitution on the terminal nitrogen atom and the variation of the nature of the aldehyde and ketone are known to have great influence in the biological activity. As the chelating ability of the thiosemicarbazones is vital in this regard, thiosemicarbazones having a third potential binding site may have considerable biological activity[26,27].

The most prominent application of complexes containing nitrogen donors is in the field of catalysis. Catalysis is now a relatively mature field with numerous and diverse reactions being explored along with informative studies of mechanism and theory. Relationships to important areas such as heterogeneous catalysis, organometallic chemistry and biocatalysis have been firmly established. Many Schiff base metal chelates catalyse reactions like hydrolysis, carboxylation, decarboxylation, elimination, aldol condensation and redox reactions[28-30]. The metal chelate catalysis is considered to include any reaction that is altered or modified by metal ions through chelate ring formation as well as reaction of metal ions themselves. From a mechanistic point of view, metal ions may be considered to have the following effects on a coordinated ligand.

1. *Electronic*: Electrons are shifted toward the metal ion, either partially in ionic reaction or completely in redox reactions,
2. *Steric*: The metal ion will generally impose steric requirement on ligand reaction due to metal chelate ring formation and to the geometry of the "Coordination sphere" of the metal atom.
3. *Equilibrium*: The formation of the metal chelate compound is favoured by strong entropy effects in dilute solution, thus increasing the probability of forming a reactive species, or increasing the probability of an activated complex containing metal chelate rings.

Many copper(II) and cobalt(II) Schiff base complexes were found to cause oxidative coupling of phenols. The chelate with vacant coordination site are capable of forming oxygenated complexes at low temperatures in solution. Such synthetic oxygen carriers have received much attention and many Co(II) and Fe(II) complexes have this property[31-33].

The epoxidation reactions of olefins using tris and tetradentate Schiff base complexes of Fe(III) as catalysts and iodosyl benzene as oxidant have been studied. Cyclohexene give cyclohexene oxide, cyclohexanol and cyclohexanone as products[32]. Many manganese(II) Schiff base complexes have also been employed as catalysts for epoxidation of olefins[34].

The heterocyclic ligand moiety is capable of inducing electron distribution changes at the metal center and this will considerably influence the catalytic properties of the system. Further, the presence of an sp^3 hybridised carbon at the vicinity of the metal center in the Schiff base metal complexes gives ample scope for the derivation of asymmetric catalysts. Such metal complexes with an asymmetric group attached to the carbons which are two bond lengths away from the metal centre are capable of bringing out chemical reactions in a stereoselective manner and many research groups are working in this area[35,36].

Catalysis remains a relatively untapped resource whose importance cannot be overestimated. As industry becomes more oriented toward speciality chemicals, methods to catalyze functional group transformations, polymerisations and inductions of asymmetry will be increasingly in demand.

One way to enhance the catalytic activity of metal complexes is to anchor them on a suitable support. Silica, alumina and polymers are commonly used to support complex catalysts. Several reviews on formation, characterization and catalytic activities of polymer-metal complexes have appeared[37,38]. An ideally supported complex catalyst should combine the advantages of both homogeneous and heterogeneous catalysts. In this regard zeolites seem promising due to the large cages and channels present in them. Zeolites are a novel class of catalysts well known for their shape selective catalytic properties. The possibility to incorporate certain transition metal ions, with redox characteristics, in zeolite silicate network provides an opportunity to carry out selective oxidation reactions in a confined zeolite microenvironment around catalytically active sites. One way to explore this structure is to encapsulate complex catalyst within the large zeolite cage. The structural specialities and electric field gradient present within the cage can alter the reactivity and thus enable the catalyst to perform in a size and shape selective manner, of course, leading to better enzyme mimics.

Intra zeolite synthesis of organometallic compounds such as metal carbonyl clusters has been of great interest[39,40] recently because of the promise for rational preparation of tailor-made catalysts derived from the homometallic/bimetallic cluster compounds which are entrapped inside zeolite pores as the ultimate "nanometer size-vessels". Ichikawa et al have performed a so-called "ship-in-bottle" technique to synthesise bulky metal carbonyl clusters inside Na-Y and Na-X zeolite micropores[41,42].

Hybrid catalysts of this type might be viewed as heterogeneous but with retention of some of the solution properties of the metal complexes. The advantages of shape selectivity and site isolation inside the zeolite might also be realized. For example, the inclusion of iron-phthalocyanine in Y-type zeolites results in a catalyst which is 10^3 times more active than the homogeneous catalyst[43].

Synthetic faujasite type zeolites have been modified with cobalt(II) and copper(II) hexadecafluorophthalocyanines by the template synthesis of the complexes inside Na-Y zeolites ion exchanged with Co^{+2} and Cu^{+2}. FT-IR and UV-Vis spectroscopy as well as X-ray powder diffraction and elemental analysis provide evidence for the encapsulation of the complexes inside the zeolites. The redox properties of the intrazeolite metal complexes were investigated by cyclic voltammetry[44].

Iron(III) exchanged A and X type crystalline zeolites in hydrated form have been investigated by Ermiridis using ESR techniques[45].

Copper-salen complex encapsulated in zeolite Y is characterized by various physicochemical techniques and is shown to be a catalyst for the selective oxidation of cyclohexanol to cyclohexanone in the presence of H_2O_2 under much milder conditions (80^oC) than those in current practice[46].

Zeolite encapsulated manganese complex of the salen ligand was synthesized by Bowers and Dutta, and its catalytic activity toward various olefins was examined. Iodosyl benzene was chosen to be terminal oxidant. Oxidation products which included the epoxide, alcohol and aldehyde are formed from cyclohexene, styrene and *trans*- and *cis*-stilbene. In comparison with catalysis by Mn-salen complexes in solution, encapsulation lowers the rate of reaction considerably, but provides for selective oxidation based on olefin size and ability to penetrate the zeolite cage[47].

Synthesis of modified metal complexes to achieve desired catalytic properties is still one of the intruiging area of coordination chemistry.

Scope of the present study

From the forgoing discussion it is clear that the complexes of heterocycle based ligands can have potential pharmaceutical and catalytic properties. The presence of the heterocyclic rings as an integral part of the ligand system can influence the nature and electronic properties of the metal ion in the complex. A literature survey revealed that there have not been much work done on quinoxaline based oxygen and nitrogen donor ligands, especially with the Schiff bases derived from 3-hydroxy quinoxaline-2-carboxaldehyde.

The present work have been taken up with the following objectives:

- To synthesise some new quinoxaline based ligands capable of providing oxygen, nitrogen and sulphur as donor atoms.
- To investigate the nature of coordination of such ligands with metal ions like manganese(II), iron(III), cobalt(II), nickel(II) and copper(II).
- To undertake a qualitative study of the synthesised complexes in the activation of molecular oxygen.
- To synthesise some new metal complexes in the supercage of zeolite Y and study their catalytic activity.

The ligands chosen for the present study are the following:

1) 2,3-Bishydrazinoquinoxaline(BHQ)
2) 3-Hydroxyquinoxaline-2-carboxalidene-*o*-aminophenol(QHA)
3) 3-Hydroxyquinoxaline-2-carboxalidenefurfurylamine(QHF)
4) 3-Hydroxyquinoxaline-2-carboxaldehyde semicarbazone(QHS)
5) 3-Hydroxyquinoxaline-2-carboxaldehyde thiosemicarbazone(QHT)

New complexes of Mn, Fe, Co, Ni and Cu with the above mentioned ligands have been synthesised. The synthesised complexes have been screened for the catalytic activity in the oxidation of 3,5-ditertiarybutylcatechol to the corresponding quinone using molecular oxygen as the oxidant. The new zeolite encapsulated metal complexes synthesised have also been tested for their catalytic activity in the above oxidation.

Scope of the application of zeolite encapsulated complexes in industrial catalysis as well as in biomimetic chemistry is quite promising. The complexes reported herein may find application as catalysts and also, may find application in the field of medicine.

CHAPTER II

EXPERIMENTAL TECHNIQUES

Details of the general reagents used, the preparation of the ligands and the various analytical and physical methods employed in the characterisation of the metal complexes are presented in this chapter.

2.1 REAGENTS

The following metal salts were used:

$MnCl_2.4H_2O$ (E. Merck), anhydrous $FeCl_3$ (Aldrich, 98%), $CoCl_2$. $6H_2O$ (E. Merck), $NiCl_2.6H_2O$ (Qualigens), $CuCl_2.2H_2O$ (BDH) and $ZnCl_2$(Merck).

Oxalic acid (Merck), *o*-phenylenediamine (Merck), sodium pyruvate (E.Merck), 2-furfurylamine (Merck), semicarbazide hydrochloride (Merck), 2-aminophenol (Merck), thiosemicarbazide (E.Merck), 3,5-ditert-butyl catechol (Aldrich), zeolite Y (a gift from United Catalyst India Ltd.) were used for the present work. Unless otherwise specified, all other reagents were of analytical grade purity. Solvents employed were either of 99% purity or purified by known laboratory procedures[48].

2.2 PREPARATION OF LIGANDS

2.2.1 Preparation of 2,3-bishydrazinoquinoxaline

2.2.1.1 2,3-Dihydroxyquinoxaline (I)

A mixture of oxalic acid (0.05 mol, 6.3 g) and *o*-phenylenediamine (0.05 mol, 5.4 g) in 3N HCl (25 mL) was heated on a boiling water bath for 1h. The mixture was cooled, and the crystals of 2,3-dihydroxyquinoxaline separated out were filtered, and washed repeatedly with water and dried. Yield : 95%, m.p.: 260°C. (lit[49]. m.p.: 300°C)

2.2.1.2 2,3-Dichloroquinoxaline (II)

2,3-Dihydroxyquinoxaline (0.025 mol, 4.05 g) along with a slight excess of phosphorous oxychloride (6 mL) and a catalytic amount of DMF (2 mL) was heated over a water bath for 3h. The solution was cooled and poured into crushed ice with vigorous stirring. The precipitate that separated out was filtered, washed repeatedly with water and dried. The product was recrystallized from hexane to give pure 2,3-dicholoroquinoxaline. (Yield: 91%, m.p.: 151°C- lit[50].m.p.152°C)

2.2.1.3 2,3-Bishydrazinoquinoxaline (III)

The ligand was synthesized by adopting the following procedure:

A solution of 2,3-dichloroquinoxaline (0.02 mol, 3.96 *g*) in methanol (250 mL) was treated with 80% hydrazine hydrate in methanol (5 mL) and 5 drops of triethylamine. The mixture was heated over a boiling water bath for 30 minutes. When the reaction was completed, the mixture was cooled and filtered. The product was recrystallized from methanol to give 2,3-bishydrazinoquinoxaline. (Yield: 92%, m.p.: 278°C - lit[51] m.p.: 280°C)

2.2.2 Synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde

A procedure, different from that reported by Ohle *et.al.*[52] was used to synthesise 3-hydroxyquinoxaline-2-carboxaldehyde, as it would give sufficiently pure ligands which can be directly used without further purification.

2.2.2.1 3-Hydroxy-2-methylquinoxaline (IV)

o-Phenylenediamine (0.1 mol, 10.8 *g*) and sodium pyruvate (0.1 mol, 11 *g*) were dissolved in 250 mL water. A slight excess of conc. HCl than needed to convert sodium pyruvate to pyruvic acid was added to the pyruvate solution. The solutions were then mixed and stirred for 30 minutes. The precipitated yellow compound was then filtered and dried over anhydrous calcium chloride. (Yield: 90%, m.p.: 255°C).

2.2.2.2 3-Hydroxy-2-dibromomethylquinoxaline (V)

3-Hydroxy-2-methylquinoxaline (0.1 mol, 16.2 g) was dissolved in glacial acetic acid (200 mL). To this, 10% (v/v) bromine in acetic acid (110 mL) was added and kept in sunlight for 1 h with occasional stirring. The solution was then diluted to 1 L with water and the precipitated dibromo derivative was filtered and purified by recrystallization from 50% alcohol. (Yield: 95%, m.p.: 246°C).

2.2.2.3 3-Hydroxyquinoxaline-2-carboxaldehyde (VI)

The dibromo compound (0.0157 mol, 5 g) was thoroughly mixed with 20 g of precipitated calcium carbonate. This was taken in a 3L RB flask with water (1.5 L). The solution was kept on a water bath with timely shaking for 3 h. The aldehyde formed will remain in water and the yellow solution was collected by filtration. The aqueous solution thus obtained is very stable and this can be used to prepare the Schiff bases.

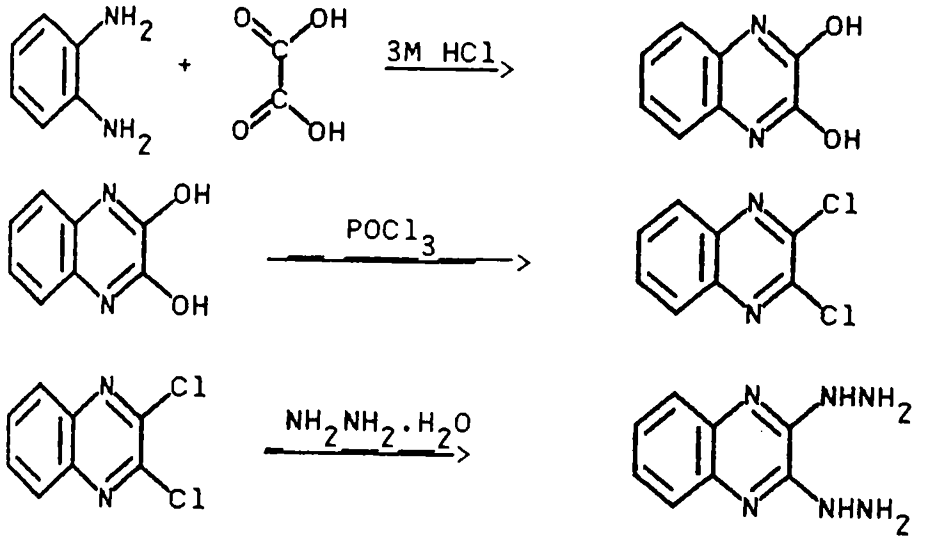
2.2.3 Preparation of Schiff Bases

2.2.3.1 Synthesis of 3-hydroxyquinoxaline-2- carboxalidine-*o*-aminophenol (QHA)

To the solution containing 3-hydroxyquinoxaline-2-carboxaldehyde (obtained by starting with 5 g of 3-hydroxy-2-dibromomethylquinoxaline), an aqueous solution of o-aminophenol (1.6 g in 20 mL water) was added drop by drop while

Synthesis of 2,3-bishydrazinoquinoxaline

The procedure consists of three synthetic steps as shown below:



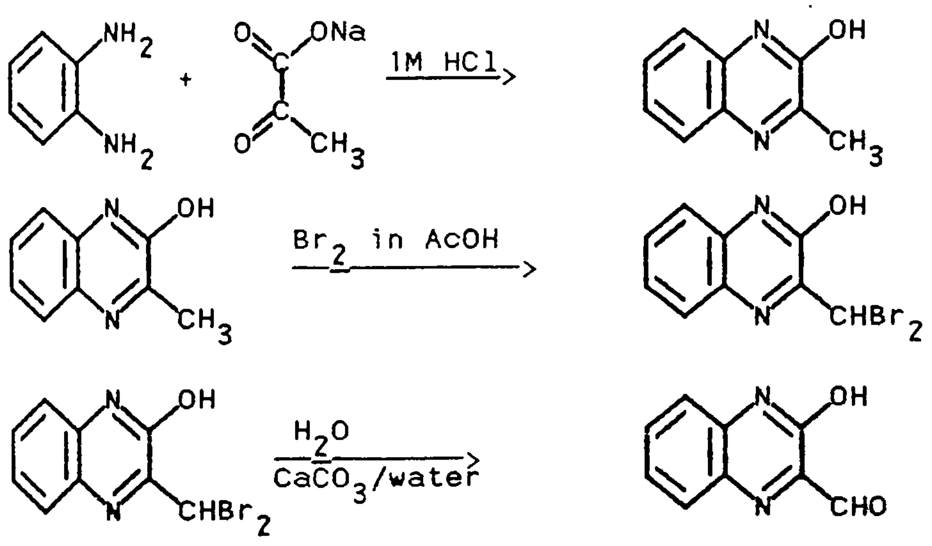
I

II

III

Synthesis of 3-hydroxyquinoxaline -2-carboxaldehyde

A new procedure adopted consists of three synthetic steps as shown below:



IV

V

VI

stirring the solution. The amine solution was added till the precipitation of the Schiff base was complete. The yellow compound thus obtained was filtered and washed with methanol and dried *in vacuo* over anhydrous calcium chloride. (Yield: 60%, m.p.: 225°C).

2.2.3.2 Synthesis of 3-hydroxyquinoxaline-2-carboxalidene-2-furfurylamine (QHF)

This compound was prepared in a similar way as in the case of QHA using a methanolic solution of 2-furfurylamine (1.5mL in 20 mL methanol). The yellow compound separated was washed with methanol and dried *in vacuo* over anhydrous calcium chloride. (Yield: 65%, m.p.: 240°C)

2.2.3.3 Synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde semicarbazone (QHS)

This compound was prepared in the same way as in the case of QHA using an aqueous solution of semicarbazide hydrochloride (1.75 g in 20 mL water). The compound separated out was filtered and washed with methanol. (Yield: 62%, m.p.: 240°C).

2.2.3.4 Synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde thiosemicarbazone (QHT)

In this case also a similar procedure as in the case of QHA was carried out using an ethanolic solution of thiosemicarbazide (1.4 g in 20 mL water). The solution was warmed for half an hour for better yield after the addition of semicarbazide. The compound separated on cooling was filtered and washed with methanol. (Yield:60%, m.p.: 245^{0}C)

Table II.1

Analytical Data of the Ligands

Compound	%Carbon	%Hydrogen	%Nitrogen	Melt. point
	Found(Calculated)			^{0}C
BHQ	50.49 (50.52)	5.20 (5.26)	44.00 (44.2)	205
QHA	67.45 (67.92)	4.01 (4.15)	15.30 (15.84)	225
QHF	66.15 (66.40)	4.18 (4.34)	16.20 (16.6)	240
QHS	51.46 (51.94)	3.65 (3.89)	30.00 (30.3)	240
QHT	48.23 (48.58)	3.23 (3.64)	28.15 (28.34)	245

2.3 ANALYTICAL METHODS

2.3.1 Estimation of Metal Ions

In all cases, the organic part of the metal complexes was completely eliminated before estimation of the metals. The following procedure was used for eliminating the organic part of the sulphur containing complexes. A known weight of the metal complex (0.2-0.3 g) was treated with conc. nitric acid (25 mL) and bromine, and was kept for about 3h. 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 the metal.

A uniform procedure was adopted for eliminating the organic part of all other complexes. 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 the reaction subsided, 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 evaporated to dryness. After cooling, conc. nitric acid (15 mL) was added and evaporated to dryness on a water bath. The residue was dissolved in water and this neutral solution was used for the estimation of the metals.

Manganese and zinc were estimated by EDTA method.Gravimetric procedures were used for the estimation of iron, cobalt and nickel[53]. Iron in the complex was estimated by precipitating the metal with ammonia solution and igniting the resulting hydroxide to ferric oxide. Cobalt was estimated by precipitating it as $[Co(C_5H_5N)_4\ (SCN)_2]$ using ammonium thiocyanate and pyridine. Nickel was precipitated as nickel dimethylglyoximate complex by the addition of an alcoholic solution of dimethylglyoxime and excess of ammonia solution. Iodometric method was employed for the estimation of copper in the copper(II) complex.

2.3.2 CHN Analyses

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

2.3.3 Estimation of Sulphur

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 were determined at ~ 28°C in DMF using a conductivity bridge (Century 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) on a simple Gouy-type magnetic balance. The Gouy tube was standardised using $Co[Hg(SCN)_4]$ as the standard[54]. The effective magnetic moment was calculated using the equation.

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

where, T is the absolute temperature and χ_m' is the molar susceptibility corrected for diamagnetism of all the atoms present in the complex using the Pascal's constants[55,56].

2.4.3 Electronic Spectra

Electronic spectra were taken in solution or in the solid state by mull technique following a procedure recommended by Venanzi[57]. The procedure is as given as 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 160A spectrophotometer.

2.4.4 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 disc on a Shimadzu 8101 FTIR spectrophotometer.

2.4.5 EPR Spectra

The X-band EPR spectra of the manganese(II) and cobalt(II) complexes in DMF were recorded at liquid nitrogen temperature using Varian E-112 X/Q band spectrophotometer. The spectra were calibrated using diphenylpicrylhydrazine(DPPH) as the field marker.

2.4.6 Mössbauer Spectra

Mössbauer spectra were obtained (in zero magnetic field) on a polycrystalline sample at room temperature using a Canberra S100 Mössbauer spectrometer with a ^{57}Co source interfaced to a cryostat. A sodium nitroprusside spectrum collected at room temperature was used as the standard.

2.4.7. X-ray Diffraction

X-ray diffraction pattern were obtained for Y zeolite and the zeolite encapsulated complexes using Philip's Analytical PW 1710 using Ni filtered Cu-Kα radiation (λ = 1.5406 A^{0}).

CHAPTER III

MANGANESE(II), COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES OF 2,3-BISHYDRAZINOQUINOXALINE

3.1 INTRODUCTION

The reaction of heterocyclic aryl substituted hydrazines with transition metal halides is interesting due to the variety of complexes it may yield[58-60]. Most alkyl or aryl substituted hydrazines function as simple monodentate ligand towards non-oxidising transition metal ions[61,62], as such substitution effectively prevents the hydrazine from behaving as a bidentate bridging ligand. However, hydrazines with substituents containing potential donor atoms may act as bidentate ligands and form interesting chelated complexes[63,64]. It was therefore thought worthwhile to synthesise complexes of the latter type of substituted hydrazines. Our studies on some transition metal complexes of 2,3-bishydrazinoquinoxaline (BHQ) are presented in this chapter.

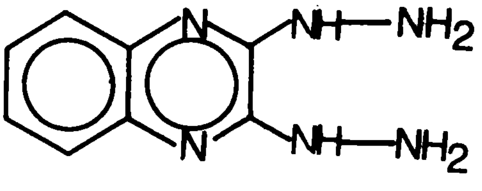


Fig. 3.1 Structure of BHQ

3.2 EXPERIMENTAL

3.2.1 Materials

Details about the preparation and purification of the ligand BHQ is given in Chapter II.

3.2.2 Synthesis of the complexes

All the complexes were prepared by the following general procedure:

The ligand BHQ (0.01 mol, 1.9 g) was dissolved in minimum quantity of glacial acetic acid by heating on a water bath. Metal chloride (0.01 mol; 1.97g of $MnCl_2.6H_2O$, 2.37 g of $CoCl_2.6H_2O$, 2.37g of $NiCl_2.6H_2O$, 1.7 g of $CuCl_2.2H_2O$; or 1.36 g of $ZnCl_2$) was dissolved in minimum quantity of acetic acid (25 mL), and was added to the ligand solution. The mixture was heated for 2h with occasional shaking on a water bath. The resulting solution was cooled to room temperature and the complex separated out was filtered and washed with chloroform. The complexes were recrystallised from ethanol and finally dried *in vacuo* over anhydrous calcium chloride (Yield: 60–70%, m.p.: >260^{0}C).

3.2.3 Analytical methods

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

3.3. RESULTS AND DISCUSSION

The complexes are microcrystalline and are stable in air. They are soluble in DMSO, DMF and methanol, and are found to be insoluble in solvents like ether, chloroform and toluene. The analytical data (Table III.1) show that these complexes have the metal ligand ratio 1:2. The molar conductance values in DMF suggest that all the complexes are non-electrolytes[65]. All the complexes, thus, have the general empirical formula $[M(BHQ)_2Cl_2]$ where, M = manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II).

3.3.1 Magnetic Susceptibility Measurements

Magnetic moment values are given in Table III.2. $[Mn(BHQ)_2Cl_2]$ shows magnetic moment value very close to the spin-only value (5.9 BM), which is as expected for high spin octahedral complex. The magnetic moment value of 5.0 BM for the $[Co(BHQ)_2Cl_2]$ can be due to an octahedral structure. Octahedral structure of $[Ni(BHQ)_2Cl_2]$ is indicated by magnetic moment value of 3.3 BM. The magnetic moment value of 1.9 BM for $[Cu(BHQ)_2Cl_2]$ suggest the absence of any metal-metal interaction in the complexes. It is difficult to get any conclusive evidence regarding the structure of the copper(II) complexes, as the magnetic moment values are generally in the range, 1.73-2.23 BM regardless of stereochemistry. As expected, $[Zn(BHQ)_2Cl_2]$ complex is found to be diamagnetic.

Table III.1

Analytical Data of the Complexes

	Found (calculated)				
Compound	% Carbon	% Hydrogen	%Nitrogen	% Chorine	% Metal
$[Mn(BHQ)_2Cl_2]$	37.80 (38.02)	3.82 (3.96)	33.12 (33.27)	13.74 (13.86)	10.80 (10.88)
$[Co(BHQ)_2Cl_2]$	37.50 (37.65)	3.82 (3.92)	32.65 (32.95)	13.60 (13.90)	11.40 (11.55)
$[Ni(BHQ)_2Cl_2]$	37.68 (37.74)	3.87 (3.93)	32.60 (33.00)	13.68 (13.76)	11.48 (11.53)
$[Cu(BHQ)_2Cl_2]$	29.30 (29.50)	2.98 (3.08)	25.74 (25.89)	21.60 (21.80)	19.30 (19.50)
$[Zn(BHQ)_2Cl_2]$	37.10 (37.25)	3.64 (3.88)	32.51 (32.59)	32.49 (32.59)	13.37 (13.58)

Table III.2

Magnetic and Conductance Data

Compound	Colour	Molar Conductance (ohm^{-1} cm^{2} mol^{-1})	Magnetic moment (BM)
$[Mn(BHQ)_2Cl_2]$	Orange	24	6.1
$[Co(BHQ)_2Cl_2]$	Brown	19	5.0
$[Ni(BHQ)_2Cl_2]$	Green	40	3.3
$[Cu(BHQ)_2Cl_2]$	Brown	43	1.9
$[Zn(BHQ)_2Cl_2]$	Yellow	42	diamagnetic

3.3.2 Electronic Spectra

The electronic absorption spectral data for all the complexes are given in Table III.3.

The electronic spectrum of $[Mn(BHQ)_2Cl_2]$ does not exhibit any d-d transitions. The molar extinction coefficients of d-d transitions of octahedral species and even tetrahedral species of manganese(II) will be usually less than 10 dm^3 mol^{-1} cm^{-1} [66]. It is rarely possible to identify the d-d bands of these complexes, since even the very weak tail of an intraligand band or a charge transfer band appearing in the visible region can obscure them. Therefore, no conclusive evidence can be obtained from the electronic spectra of the manganese(II) complexes regarding their structures.

The visible spectrum of the $[Co(BHQ)_2Cl_2]$ is dominated by the highest energy transition $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ at 22900 cm^{-1}. The fine structure shown by this absorption may be due to spin-orbit coupling or distortion from regular octahedral geometry[67]. The transition $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ is usually very weak for octahedral cobalt(II) complexes and appears as a shoulder band. This band was not observed in the spectrum of $[Co(BHQ)_2Cl_2]$ and the $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ transition appears as a weak band at 7000 cm^{-1}.

The electronic spectrum of the $[Ni(BHQ)_2Cl_2]$ exhibits two d-d bands - one at 18900 cm^{-1} and the other at 22100 cm^{-1}. The positions of these bands are consistent with an octahedral or distorted octahedral environment and are best assigned to the $^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ transitions respectively[68]. A broad d-d absorption band at 13800 cm^{-1} is observed in the case of $[Cu(BHQ)_2Cl_2]$[11]. As expected the $[Zn(BHQ)_2Cl_2]$ does not undergo any characteristic electronic excitation in the visible spectral region.

3.3.3 Infrared Spectra

The important spectral bands and their assignments are shown in Table III.4. Most of the bands due to the free ligand (fig 3.2) are present in the spectra of the complexes. The strong band at 3300 cm^{-1} in the spectrum of the ligand due to the terminal N-H stretching vibration appears at 3240-3250 cm^{-1} in the spectra of the complexes indicating that the coordination occurs through the terminal nitrogen of the ligand. The N-N stretching vibration observed as a shoulder at 1452 cm^{-1} on the $\upsilon(C\overset{\cdots\cdot}{—}C)$ band is resolved and appears as a medium intensity band at 1431 cm^{-1} on complexation. The red-shift of the NH_2 rocking band of the ligand from 540 cm^{-1} to 525 - 530 cm^{-1} on complexation confirms the formation of the metal primary amine bond[69].

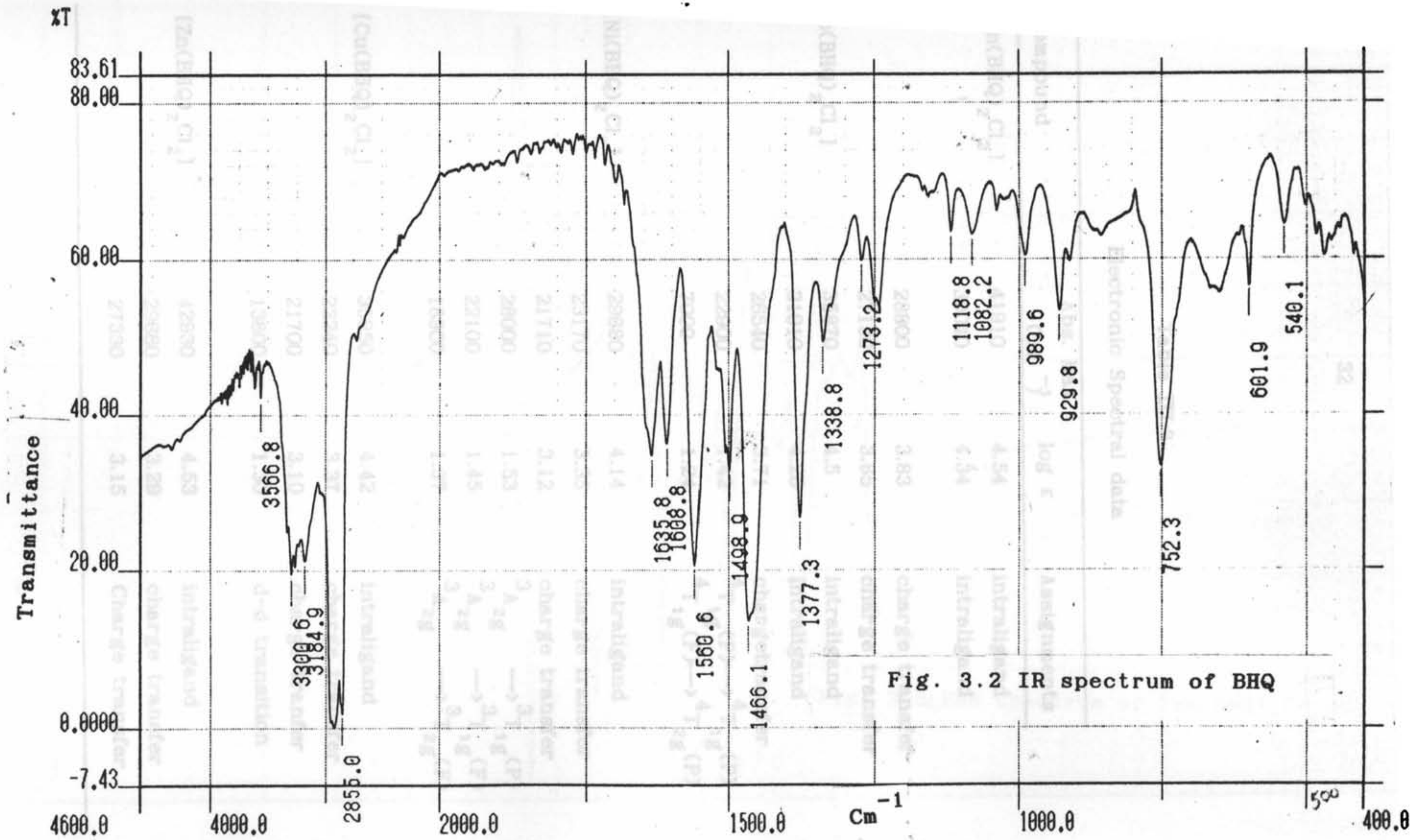


Fig. 3.2 IR spectrum of BHQ

Table III.3

Electronic Spectral data

Compound	Abs. Max. (cm^{-1})	log ε	Assignments
[Mn(BHQ)$_2$Cl$_2$]	41910	4.54	intraligand
	30040	4.34	intraligand
	28800	3.83	charge transfer
	27130	3.65	charge transfer
[Co(BHQ)$_2$Cl$_2$]	35870	4.5	intraligand
	31910	4.26	intraligand
	26540	3.71	chargetransfer
	22900	1.42	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
	7000	1.24	$^4T_{1g}(F) \longrightarrow {}^4T_{2g}(P)$
[Ni(BHQ)$_2$Cl$_2$]	29680	4.14	intraligand
	23170	3.35	charge transfer
	21710	3.12	charge transfer
	28000	1.53	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$
	22100	1.45	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$
	18900	1.37	$^3A_{2g} \longrightarrow {}^3T_{2g}(F)$
[Cu(BHQ)$_2$Cl$_2$]	35950	4.42	intraligand
	23240	3.37	charge transfer
	21700	3.10	charge tranfer
	13800	1.30	d-d transition
[Zn(BHQ)$_2$Cl$_2$]	42930	4.53	intraligand
	29660	3.29	charge transfer
	27330	3.15	Charge transfer

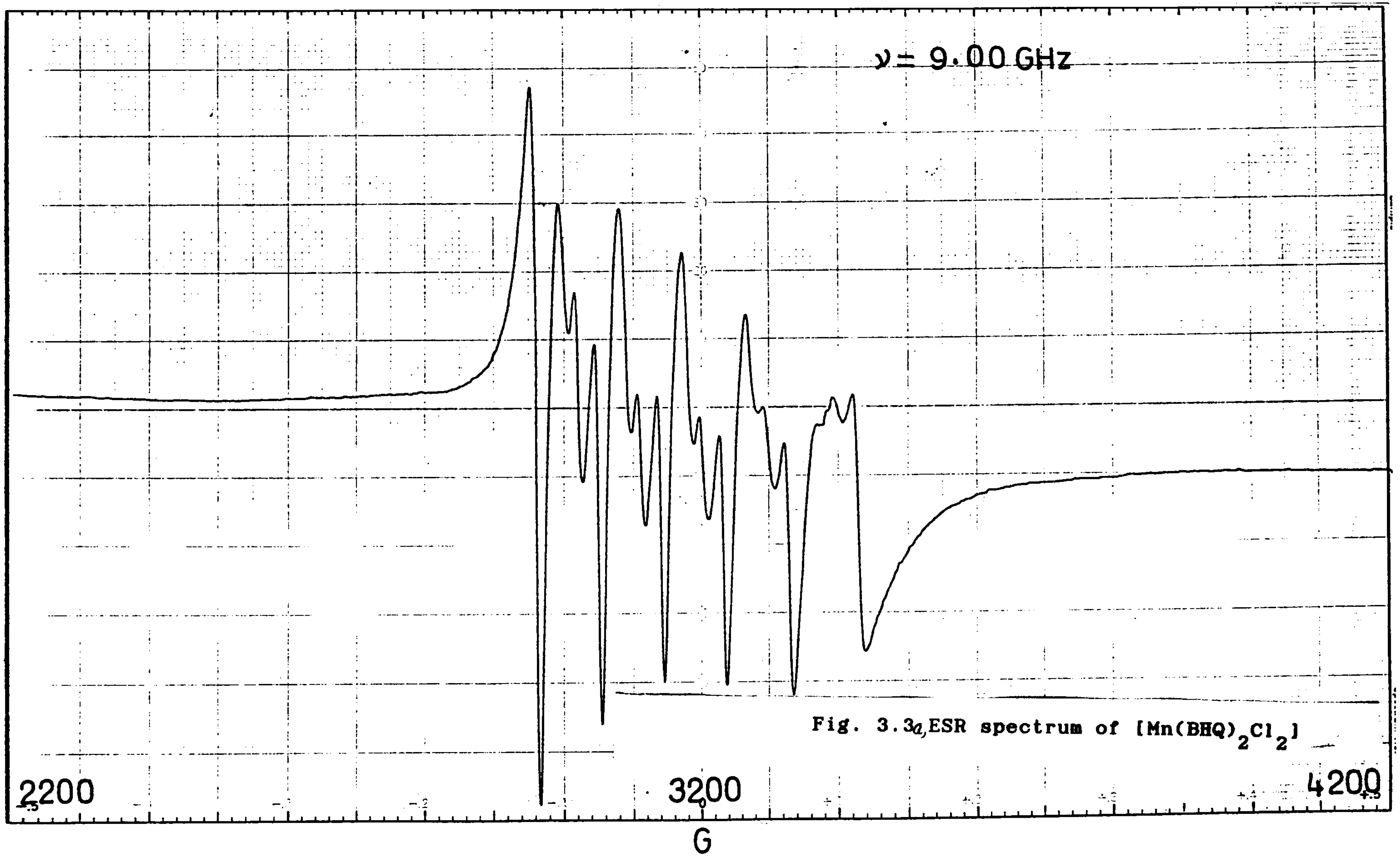


Fig. 3.3a, ESR spectrum of $[Mn(BHQ)_2Cl_2]$

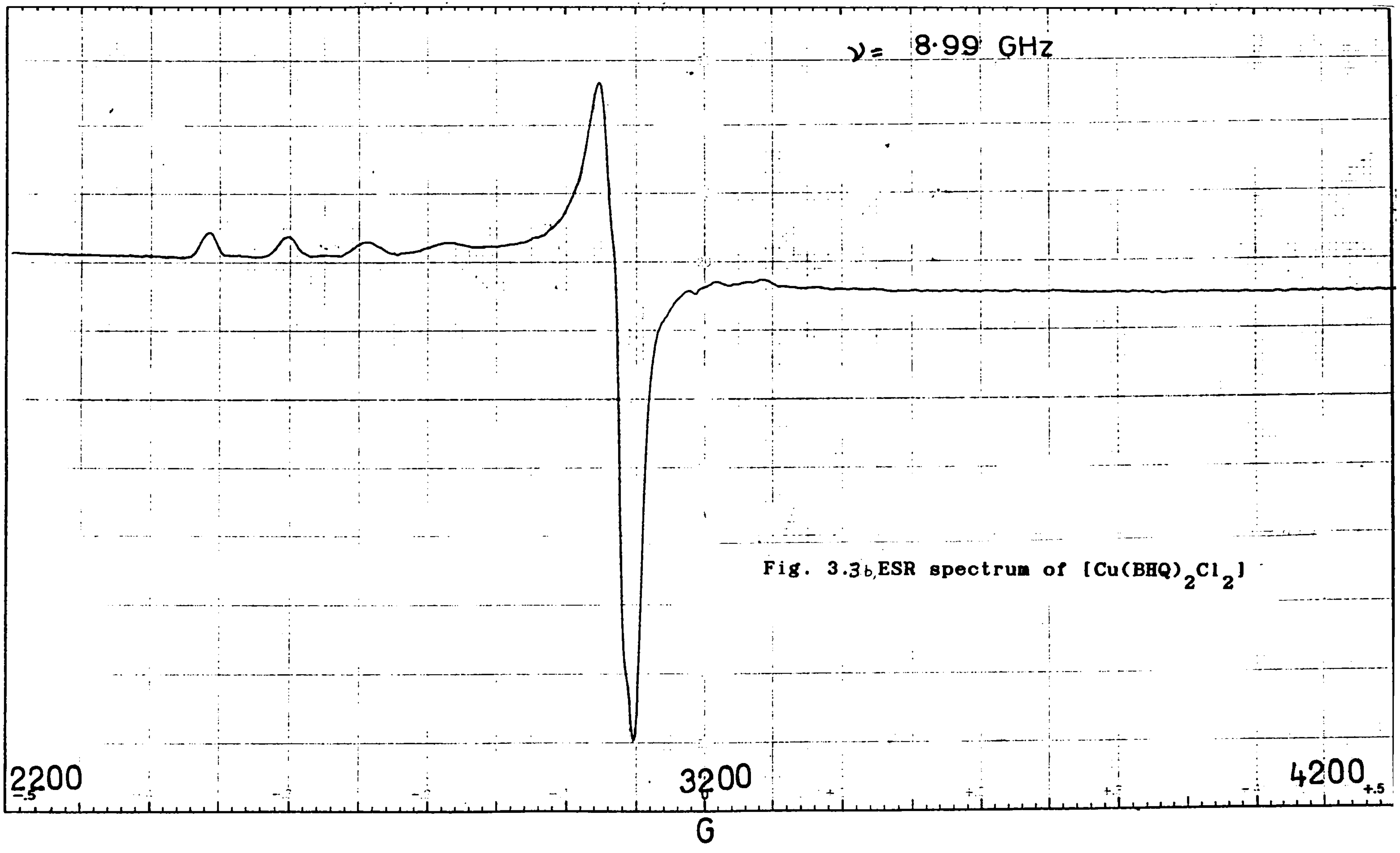


Fig. 3.3b ESR spectrum of [Cu(BHQ)$_2$Cl$_2$]

3.3.4 EPR Spectra

The EPR spectra (Fig 3.3) of $[Mn(BHQ)_2Cl_2]$ and $[Cu(BHQ)_2Cl_2]$ were recorded in DMSO at liquid nitrogen temperature. The *g* and A values are given in Table III.5. Manganese(II) complexes yield a *g* value = 2.0 and this is agreeable with other reported manganese(II) systems[70,71].

The only one *g* value observed for the manganese(II) complex suggests that the structure is almost perfectly octahedral.

Based on the above arguments, the structures shown in Fig. 3.4 are assigned for these complexes.

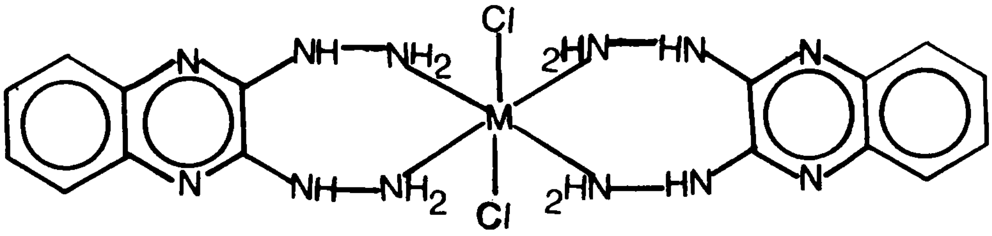


Fig. 3.4 Schematic structure of the complexes

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

Table III.5

EPR Spectral data of the Complexes

Parameters	$[Mn(BHQ)_2Cl_2]$	$[Cu(BHQ)_2Cl_2]$
g_{av}	2.0	——
A_{av}	85.0 G	——
$g_{\parallel}$	——	2.4
$g_{\perp}$	——	2.0
$A_{\parallel}$	——	110.0 G

Table III.4 IR spectral data of the complexes(cm^{-1})

BHQ	I	II	III	IV	V	Assignments of the more relavant bands
3300(m)	3215(m)	3210(m)	3200(m)	3220(m)	3230(m)	ν_{N-H}
2855(s)	2855(s)	2855(s)	2855(s)	2855(s)	2855(s)	
1636(m)	1646(m)	1632(m)	1632(m)	1630(w)	1636(w)	
1609(m)	1615(w)	1602(w)	1608(w)	1612(w)	1610(w)	
1561(s)	1570(m)	1568(m)	1564(m)	1580(m)	1572(m)	
1499(m)	1510(m)	1516(m)	1538(m)	1532(m)	1510(m)	
1466(s)	1458(s)	1460(s)	1482(s)	1493(s)	1458(s)	
1452(sh)	1431(m)	1431(m)	1448(m)	1435(m)	1435(m)	ν_{N-N}
1377(m)	1375(m)	1377(m)	1375(m)	1377(m)	1375(m)	
1339(w)	1339(w)	1344(w)	1350(w)	1338(w)	1339(w)	
1273(w)	1267(w)	1281(m)	1285(m)	1262(w)	1285(m)	
1119(w)	1127(w)	1132(w)	1125(w)	1120(w)	1136(w)	
1082(w)	1048(w)	1079(w)	1076(w)	1080(w)	1074(w)	
1050(w)	1028(w)	1034(w)	1035(w)	1038(w)	1026(w)	
930(w)	928(w)	927(w)	920(w)	930(w)	926(w)	
752(m)	754(m)	752(m)	752(m)	754(m)	754(w)	$\delta_{C-H(Ph)}$
540(w)	528(w)	525(w)	530(w)	535(w)	530(w)	ρ_{N-H}

s = strong, m = medium and w = weak

I = $[Mn(BHQ)_2Cl_2]$, II = $[Co(BHQ)_2Cl_2]$, III = $[Ni(BHQ)_2Cl_2]$,

IV = $[Cu(BHQ)_2Cl_2]$ and V = $[Zn(BHQ)_2Cl_2]$,

CHAPTER IV

MANGANESE(II), IRON(III), COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF 3-HYDROXYQUINOXALINE-2-CARBOXALIDENE-*O*-AMINOPHENOL

4.1 INTRODUCTION

Quinoxalines have been of considerable importance because of their interesting chemical as well as biological properties[72,73]. Reports on the metal complexes of quinoxaline based ligands are scanty. A survey revealed that not much work have been done on the metal complexes of the Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde despite its interesting structure[74]. The following chapters include our studies on these systems, and in this chapter we are presenting our studies on the metal complexes of the Schiff base 3-hydroxyquinoxaline-2-carboxalidene-*o*-aminophenol (QHA) formed by the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde and *o*-aminophenol (QHA)

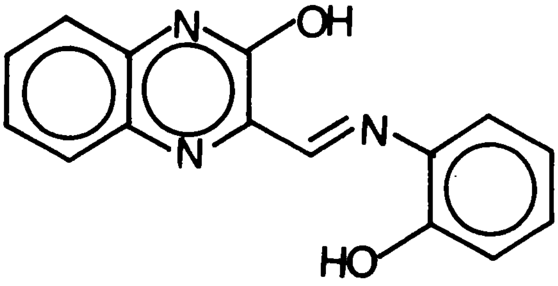


Fig. 4.1 Structure of QHA

4.2 EXPERIMENTAL

4.2.1 Materials

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

4.2.2 Synthesis of the complexes

All the complexes were prepared by the following general procedure.

The ligand QHA (0.02 mol, 5.3 g) was dissolved in ethanol (100 mL). Metal chloride (0.01 mol, 1.97 g of $MnCl_2.6H_2O$, 2.37 g of $CoCl_2.6H_2O$, 2.37 g of $NiCl_2.6H_2O$ or 1.7 g of $CuCl_2.2H_2O$) was dissolved in minimum quantity of ethanol and was added to the ligand solution and refluxed for 2h. In the case of the iron(III) complex, anhydrous iron(III)chloride(0.006 mol, 1.06 g) and QHA (0.02 mol, 5.3 g) were allowed to react in the 1:3 mole ratio. After this, the volume of the solution was reduced to about 1/3 and allowed to cool. The precipitated complexes were collected by filtration and washed with ether and dried *in vacuo* over anhydrous calcium chloride (Yield: 50–60% m.p >270°C).

4.2.3 Analytical methods

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

4.3 RESULTS AND DISCUSSION

All the complexes are microcrystalline and air stable. They were found to be soluble in methanol, DMSO, DMF and in ethanol and insoluble in acetonitrile, acetone, chloroform and water. The analytical data (Table IV.1) show that the complexes have the metal-ligand ratio 1:2 except in the case of Fe(III) complex, for which the metal ligand ratio is 1:3. The low molar conductance values (Table IV.2) in DMF suggest that the complexes are non-electrolytic in nature[75]. The empirical formulae for the complexes may thus be given as $[M(QHA)_2]$ for Mn(II), Co(II), Ni(II) and Cu(II) complexes and $[Fe(QHA)_3]$ for the iron(III) complex.

4.3.1 Magnetic Susceptibility Measurements

The magnetic moment values of the complexes are given in Table IV.2. $[Mn(QHA)_2]$ shows a magnetic moment value very close to the spin-only moment. However, $[Fe(QHA)_3]$ have a little lower value than the spin only value. The values suggest that the manganese and iron complexes have high spin octahedral structures. The magnetic moment value of 4.2 BM for the $[Co(QHA)_2]$ complex indicates a tetrahedral structure[76]. The magnetic moment of $[Ni(QHA)_2]$ is 3.5 B.M which is reasonable for a Ni(II) ion in a tetrahedral environment. The magnetic moment value of 2.0 BM for the $[Cu(QHA)_2]$ indicates the absence of any metal-metal interaction[77].

Table IV. 1

Analytical Data of the Complexes

Compound	% Carbon	% Hydrogen	% Nitrogen	% Metal
	Found(calculated)			
$[Mn(QHA)_2]$	61.51	3.23	14.10	9.00
	(61.75)	(3.43)	(14.40)	(9.39)
$[Fe(QHA)_3]$	63.57	3.10	14.67	6.32
	(63.69)	(3.50)	(14.86)	(6.58)
$[Co(QHA)_2]$	61.12	3.20	14.12	9.98
	(61.33)	(3.40)	(14.30)	(10.04)
$[Ni(QHA)_2]$	61.06	3.32	14.01	9.79
	(61.36)	(3.40)	(14.30)	(10.00)
$[Cu(QHA)_2]$	60.72	3.14	14.01	10.70
	(60.85)	(3.38)	(14.20)	(10.40)

Table IV.2

Magnetic and Conductance Data

Compound	Colour	Molar Conductance ($Ohm^{-1} mol^{-1} cm^2$)	Magnetic moment (BM)
$[Mn(QHA)_2]$	Dark brown	20	5.8
$[Fe(QHA)_3]$	Black	45	5.6
$[Co(QHA)_2]$	Black	20	4.3
$[Ni(QHA)_2]$	Black	29	3.5
$[Cu(QHA)_2]$	Black	35	2.0

4.3.2 Electronic Spectra

The electronic spectra of all the complexes were recorded in methanol. The observed bands and their assignments are given in Table IV.3. The transitions in the case of $[Mn(QHA)_2]$ and $[Fe(QHA)_3]$ are spin forbidden and were not observed in the spectra. The near UV region in the spectra of all the complexes were masked by $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ transitions of the ligand.

The spectra of $[Co(QHA)_2]$ and $[Ni(QHA)_2]$ suggest a tetrahedral structure for these complexes. The positions of these bands are also consistent with that for a tetrahedral structure[78]. $[Cu(QHA)_2]$ shows a broad d-d absorption at about 19340 cm^{-1} which suggests a square planar structure.

4.3.3 Infrared Spectra

The important infrared spectral bands and their assignments are shown in Table IV.4. Almost all bands due to the free ligand (Fig. 4.2) are present in the spectra of the complexes. The C=N stretching band seen at 1666 cm^{-1} in the spectra of the ligand is shifted to lower frequencies in the spectra of the complexes indicating the coordination of azomethine nitrogen to the metal[79]. The broad OH absorption at 3500 cm^{-1} in the ligand spectrum loses some of its intensity in the spectra of the complexes. It may be drawn that one of the phenolic oxygens deprotonates and involve in bonding to the metal. The phenolic

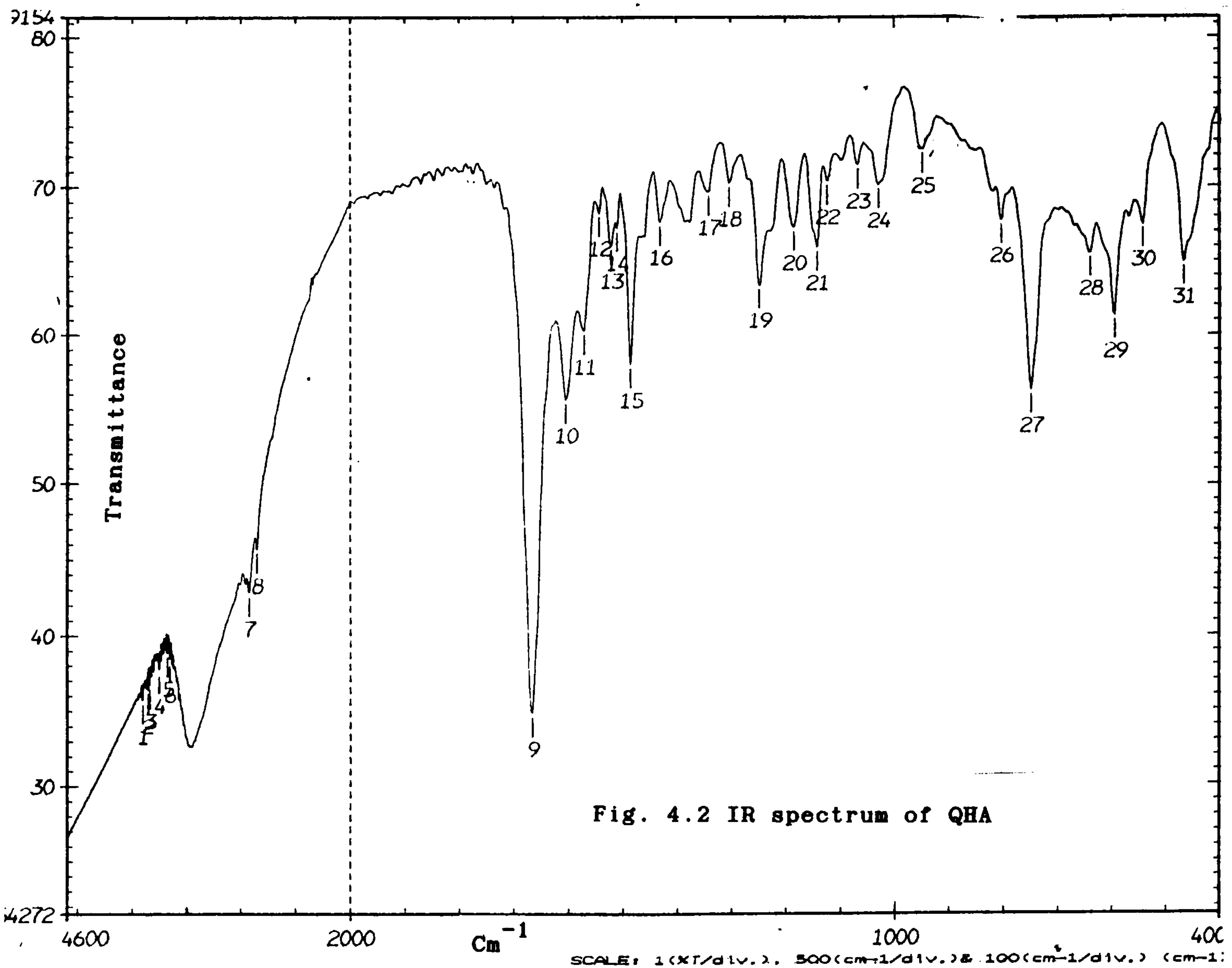


Fig. 4.2 IR spectrum of QHA

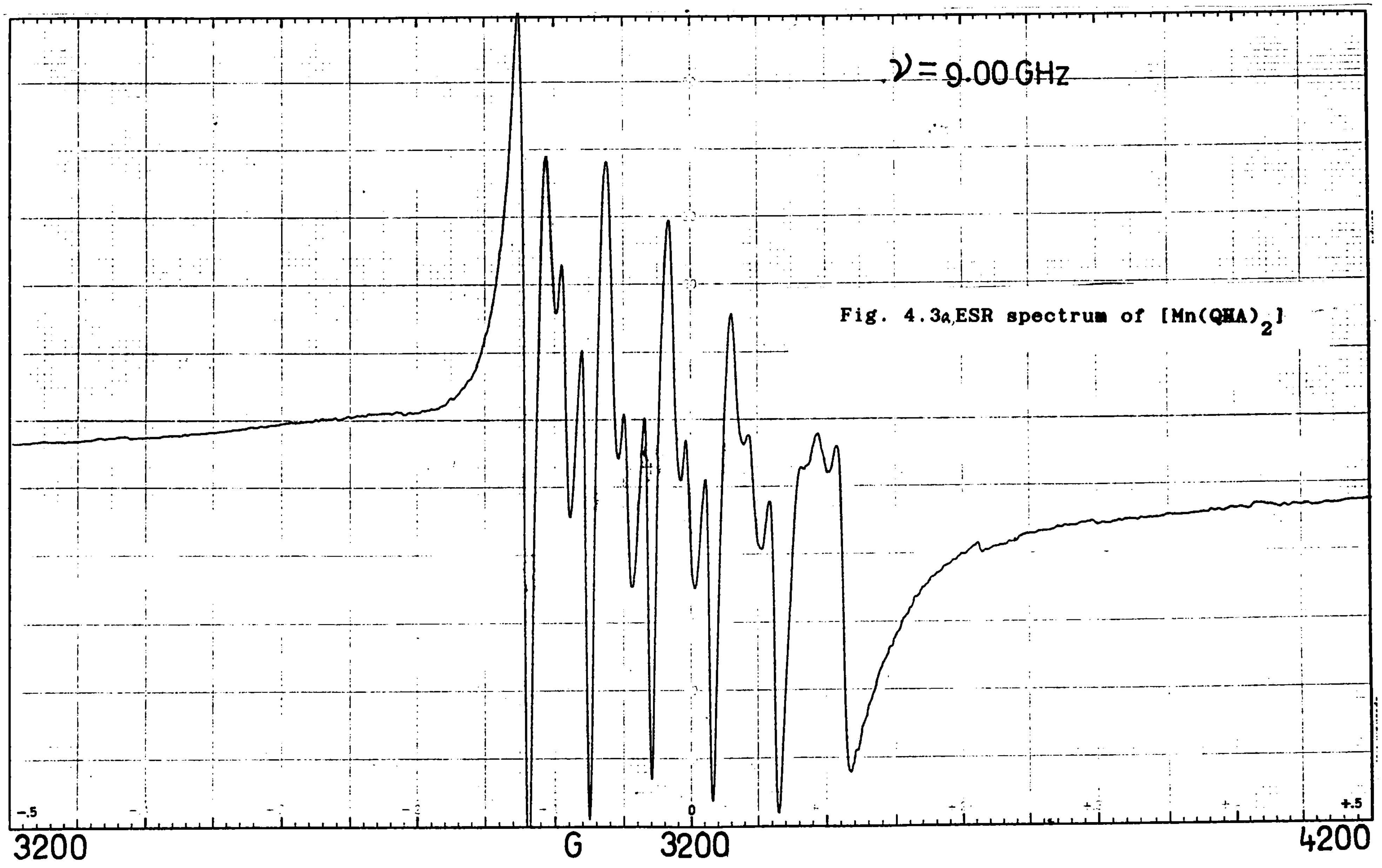


Fig. 4.3a ESR spectrum of [Mn(QHA)$_2$]

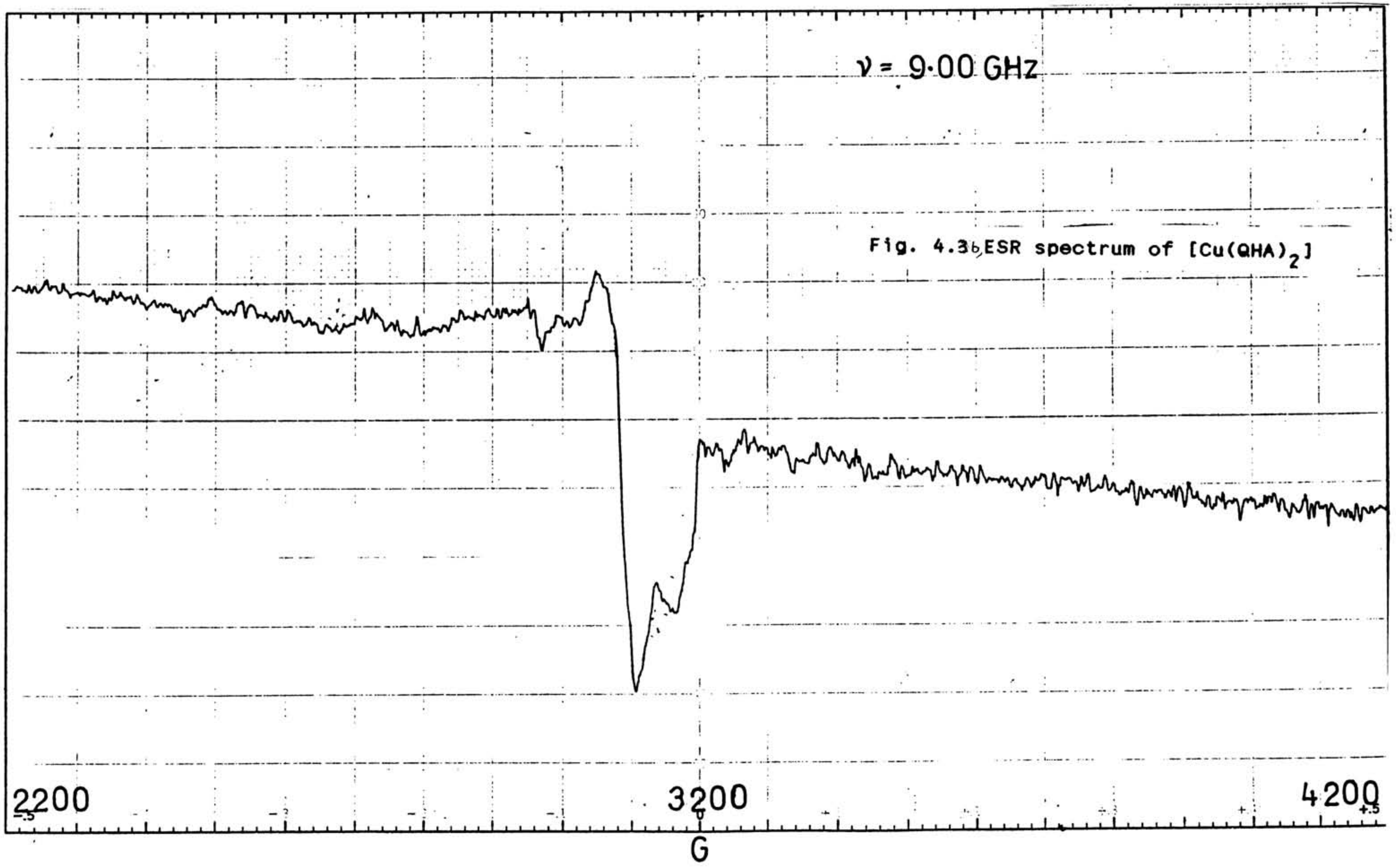
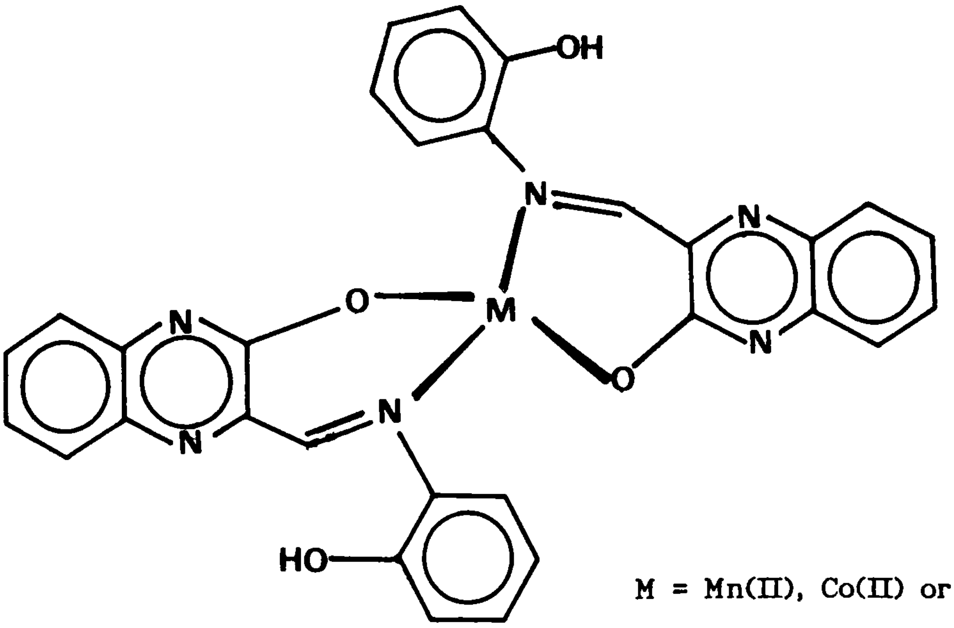


Fig. 4.3b, ESR spectrum of $[Cu(QHA)_2]$

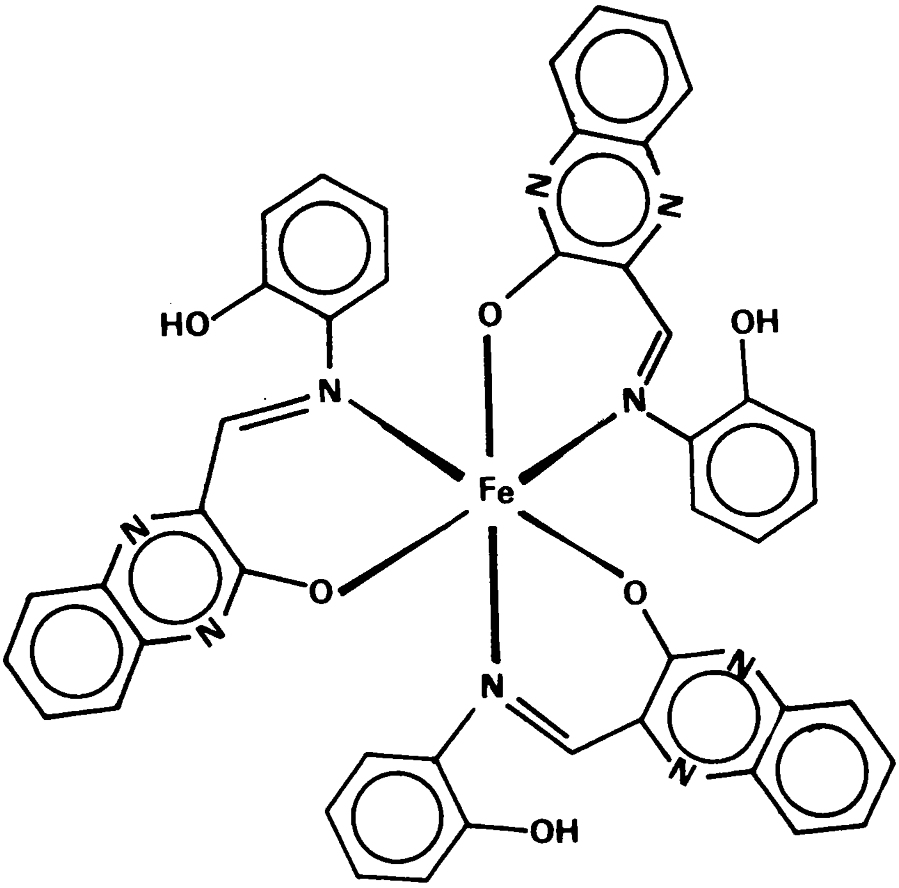
group of the aminophenol part may not be taking part in coordination. The νC—O of the ligand appearing at 1250 cm^{-1} is blue shifted to higher frequencies suggesting the coordination of the phenolic oxygen of the aldehyde[80,69]. The ligand QHA in all the cases act as a bidentate ligand using one of the oxygens and azomethine nitrogen .

4.3.4 EPR Spectra

The EPR spectra (Fig. 4.3) of [Mn(QHA)$_2$] and [Cu(QHA)$_2$] were recorded in DMSO at liquid nitrogen temperature. The g and A values were given in Table IV.5. The g values obtained for [Cu(QHA)$_2$] is in agreement with other square planar complexes.



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



Schematic structure of [Fe(QHA)$_3$]

Fig. 4.4 Schematic structures of the complexes

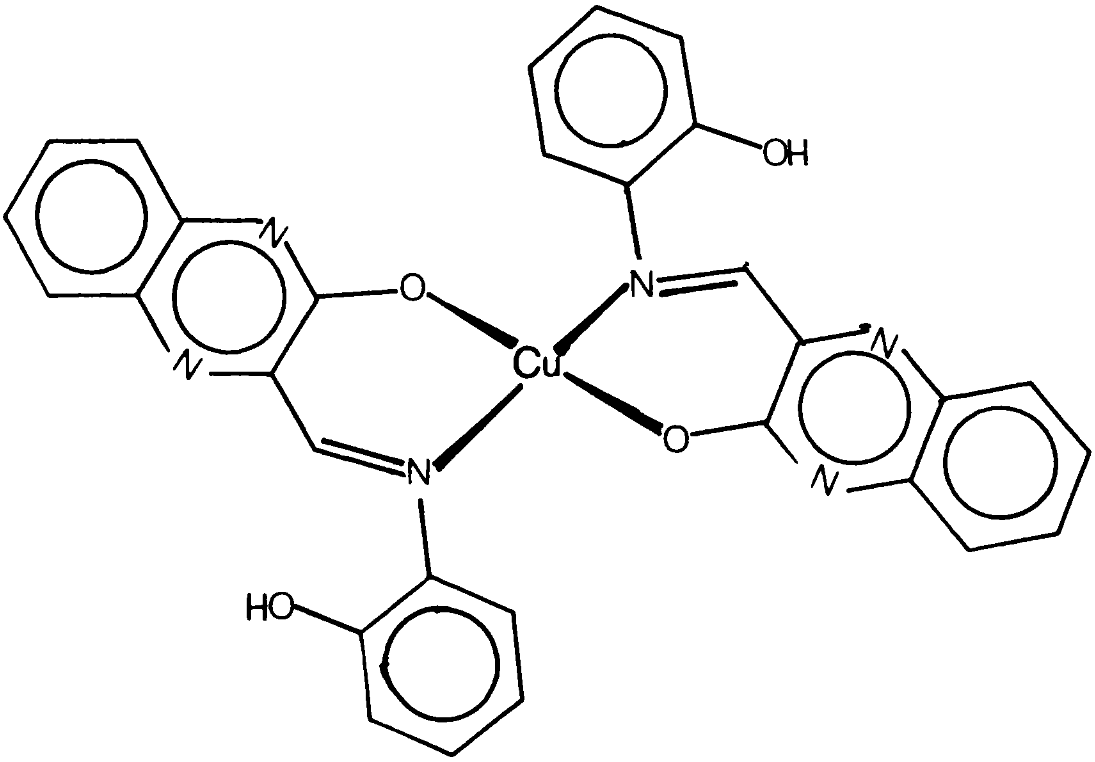


Fig. 4.5 Schematic structure of [Cu(QHA)$_2$]

Table IV.3

Electronic Spectral Data

Compound	Abs. Max. (cm^{-1})	log ε	Assignment
[Mn(QHA)$_2$]	19665	3.65	charge transfer
	25180	3.87	charge transfer
	29200	4.25	intraligand
	36110	4.38	intraligand
[Fe(QHA)$_3$]	26920	3.78	charge transfer
	36100	4.36	intraligand
[Co(QHA)$_2$]	6600	0.74	$^4A_2 \longrightarrow {}^4T_1$ (F)
	20000	1.22	$^4A_2 \longrightarrow {}^4T_1$ (P)
	22880	3.88	charge transfer
	26720	4.03	intraligand
	29170	4.22	intraligand
	36120	4.32	intraligand
[Ni(QHA)$_2$]	6700	0.83	$^3T_1(F) \longrightarrow {}^3A_2(F)$
	18900	1.24	$^3T_1(F) \longrightarrow {}^3T_1(P)$
	19665	2.75	charge transfer
	24650	3.22	charge transfer
	24860	4.03	intraligand
	29660	4.35	intraligand
	36100	4.40	intraligand
[Cu(QHA)$_2$]	19340	0.75	d-d band
	24140	3.27	charge transfer
	28230	4.32	intraligand
	36080	4.36	intraligand

Table IV.4 IR spectral data (cm^{-1})

QHA	I	II	III	IV	V	Assignment of the more relevant band
3500(s)	3500(s)	3500(w)	3500(w)	3500(w)	3500(w)	ν_{OH}
2924(m)	2924(w)	2924(w)	2922(w)	2922(w)	2924(w)	
2855(m)	2855(m)	2852(w)	2855(w)	2854(w)	2855(w)	
1666(s)	1655(s)	1653(s)	1660(s)	1655(s)	1652(s)	$\nu_{C=N}$
1605(m)	1603(w)	1602(w)	1603(w)	1603(sh)	1603(w)	
1572(w)	1570(w)	1568(w)	1571(w)	1570(w)	1572(w)	
1543(w)	1543(w)	1543(w)	1543(w)	1543(w)	1543(w)	
1522(w)	1522(w)	1522(w)	1522(w)	1522(w)	1522(w)	
1510(w)	1510(w)	1510(w)	1510(w)	1510(w)	1508(w)	
1487(m)	1482(w)	1483(w)	1483(w)	1485(sh)	1486(w)	
1431(w)	1429(w)	1430(w)	1431(w)	1431(sh)	1430(w)	
1342(w)	1342(w)	1342(w)	1340(w)	1341(w)	1342(w)	
1304(w)	1304(w)	1304(w)	1304(w)	1304(w)	1304(w)	
1250(w)	1255(m)	1260(m)	1256(m)	1458(w)	1560(m)	ν_{C-O}
1186(w)	1185(w)	1185(w)	1184(w)	1185(w)	1186(w)	
1143(w)	1149(w)	1149(w)	1147(m)	1149(w)	1460(m)	
1124(w)	1123(w)	1124(w)	1122(w)	1123(w)	1124(w)	
1068(w)	1068(w)	1063(w)	1065(w)	1067(w)	1068(w)	
1030(w)	1028(w)	1029(w)	1028(w)	1029(m)	1030(w)	
949(w)	945(w)	947(w)	949(w)	945(w)	942(w)	
804(w)	801(w)	803(w)	804(w)	803(w)	803(w)	
750(m)	756(m)	756(m)	756(m)	756(w)	756(m)	$\delta_{C-H(Ph)}$
640(w)	639(w)	640(w)	638(w)	639(w)	638(w)	
596(m)	594(w)	594(w)	594(m)	594(m)	594(m)	
544(w)	540(w)	542(w)	541(w)	543(m)	544(m)	
468(w)	467(m)	468(w)	464(m)	468(w)	467(m)	

s = strong, m = medium and w = weak
I = [Mn(QHA)$_2$], II = [Fe(QHA)$_3$], III = [Co(QHA)$_2$],
IV = [Ni(QHA)$_2$] and V = [Cu(QHA)$_2$]

Table IV.5

ESR spectral data of the complexes

Parameters	$[Mn(QHA)_2]$	$[Cu(QHA)_2]$
g_{av}	2	---
A_{av}	90 G	---
$g_{\parallel}$	---	2.4
$g_{\perp}$	---	2
$A_{\parallel}$	-	115 G

CHAPTER V

MANGANESE(II), IRON(III), COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF 3-HYDROXYQUINOXALINE-2-CARBOXALIDENE-2-FURFURYLAMINE

5.1 INTRODUCTION

Metal complexes of heterocyclic Schiff bases are well known to possess biological activity. Many such complexes were found to have antibacterial, antifungal, tuberculostatic and anticancerous properties[81]. We thought it would be worthwhile to synthesise a new heterocyclic Schiff base by the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde with another heterocyclic amine namely 2-furfurylamine and its complexes. This chapter describes our studies on the manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of this Schiff base, 3-hydroxyquinoxaline-2-carboxalidene-2-furfurylamine (QHF). Metal complexes of this ligand have not been hitherto reported.

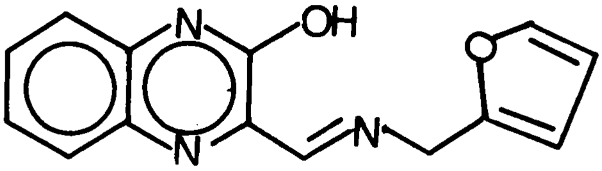


Fig. 5.1 Structure of QHF

5.2 EXPERIMENTAL

5.2.1 Materials

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

5.2.2 Synthesis of the Complexes

The following procedure was adopted to synthesise the manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes.

The ligand QHF (0.02 mol, 5.06 g) was dissolved in ethanol (100 mL). Metal chloride (0.01 mol - 1.97 g of $MnCl_2.6H_2O$; 2.37 g of $CoCl_2.6H_2O$; 2.37 g of $NiCl_2.6H_2O$ or 1.7 g of $CuCl_2.2H_2O$) was dissolved in minimum quantity of ethanol and was added to the ligand solution. The reaction mixture was refluxed for 2h and the volume was reduced to about 1/3. The precipitated complexes were collected by filtration, washed with ether and dried *in vacuo* over anhydrous calcium chloride (Yield: 50-60%, m.p.: >270°C).

The iron complex was prepared in a similar way using the ligand QHF (0.02mol, 5.06 g) and anhydrous ferric chloride (0.0066 mol, 1.06g).

5.2.3 Analytical methods

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

5.3 RESULTS AND DISCUSSION

All the complexes were isolated as air stable microcrystalline solids. They were found to be soluble in DMSO, DMF, ethanol and methanol, partially soluble in acetonitrile, acetone and chloroform, and insoluble in water. The analytical data (Table V.1) reveal the empirical formulae of the complexes to be $[M(QHF)_2]$ for manganese(II), cobalt(II), nickel(II) and copper(II) complexes and for the iron complex it corresponds to $[Fe(QHF)_3]$. The molar conductance values suggest that the complexes are non-electrolytes in DMF[82].

5.3.1 Magnetic Susceptibility Measurements

Magnetic moment values of the complexes are given in Table V.2. The magnetic moment values for $[Mn(QHF)_2]$ and $[Fe(QHF)_3]$ complexes reveal the high spin nature of the complexes. The magnetic moment value of 4.1 BM obtained for $[Co(QHF)_2]$ complex and 3.9 BM for the $[Ni(QHF)_2]$ indicate a tetrahedral structure for these complexes. Magnetic moment value of 1.8 BM suggests the absence of any metal-metal interaction and also a square planar structure[83] for the copper(II) complex.

Table V.1

Analytical Data of the Complexes

Compound	found(calculated) % Carbon	% Hydrogen	%Nitrogen	% Metal
$[Mn(QHF)_2]$	60.10	3.15	15.00	9.59
	(60.30)	(3.20)	(15.08)	(9.86)
$[Fe(QHF)_3]$	61.98	3.21	15.23	6.50
	(62.30)	(3.30)	(15.57)	(6.90)
$[Co(QHF)_2]$	59.17	3.12	14.74	10.15
	(59.90)	(3.20)	(14.97)	(10.50)
$[Ni(QHF)_2]$	59.16	3.05	14.76	10.04
	(59.92)	(3.20)	(14.98)	(10.46)
$[Cu(QHF)_2]$	59.10	3.06	14.68	11.10
	(59.40)	(3.18)	(14.85)	(11.23)

Table V.2

Magnetic and Conductance Data

Compound	Colour	Molar conductance ($ohm^{-1}cm^{2}mol^{-1}$)	Magnetic moment (BM)
$[Mn(QHF)_2]$	Yellow	20	5.5
$[Fe(QHF)_3]$	Brown	34	5.6
$[Co(QHF)_2]$	Reddish brown	26	4.1
$[Ni(QHF)_2]$	Reddish brown	35	3.9
$[Cu(QHF)_2]$	Brown	36	1.8

5.3.2 Electronic Spectra

The spectra of the complexes were recorded in methanol. The important spectral bands and their assignments are given in Table V.3. No characteristic d-d bands are observed in the case of $[Mn(QHF)_2]$ and $[Fe(QHF)_3]$ complexes. This may be due to the fact that all the transitions are spin forbidden and may be too weak to be observed. The electronic spectrum of $[Co(QHF)_2]$ shows characteristic absorption due to a tetrahedral cobalt(II) ion. The $^4A_2 \longrightarrow {}^4T_1(P)$ transition appears as multiple absorption in the visible region for the tetrahedral complexes. The two bands appearing at 19400 cm^{-1} and 20390 cm^{-1} in the spectra of $[Co(QHF)_2]$ can be assigned to this transition.

The electronic spectrum of $[Ni(QHF)_2]$ shows $^3T_1(F) \longrightarrow {}^3A_2(F)$ transition at 6900 cm^{-1} [84]. The visible band $^3T_1(F) \longrightarrow {}^3T_1(P)$ show multiple structure comparable to similar complexes of cobalt(II). The two d-d bands observed at 19500 cm^{-1} and 20800 cm^{-1} in the spectrum of $[Ni(QHF)_2]$ may be due to this transition. The positions of these bands are consistent with a tetrahedral nickel(II) structure. In the case of $[Cu(QHF)_2]$, the d-d bands were not observed and these might have been masked by intraligand transitions.

Table V.3

Electronic Spectral Data

Compound	Transition (cm^{-1})	log ε	Assignment
$[Mn(QHF)_2]$	21540	3.32	charge transfer
	22950	3.75	charge transfer
	24560	3.81	charge transfer
	43750	4.40	intraligand
$[Fe(QHF)_3]$	21505	3.30	charge transfer
	24220	3.64	charge transfer
	24220	3.80	intraligand
	43760	4.32	intraligand
$[Co(QHF)_2]$	6700	0.85	$^4A_2 \longrightarrow {}^4T_1$ (F)
	19400, 20390	1.22	$^4A_2 \longrightarrow {}^4T_1$ (P)
	22580	3.35	charge transfer
	24140	3.85	intraligand
	43760	4.32	intraligand
$[Ni(QHF)_2]$	6900	0.88	$^3T_1(F) \longrightarrow {}^3A_2(F)$
	19500, 20800	1.25	$^3T_1(F) \longrightarrow {}^3T_1(P)$
	24220	3.80	charge transfer
	26930	4.19	intraligand
	31345	4.28	intraligand
	38180	4.40	intraligand
$[Cu(QHF)_2]$	22730	3.72	charge transfer
	28925	4.12	intraligand
	32110	4.28	intraligand
	39000	4.35	intraligand

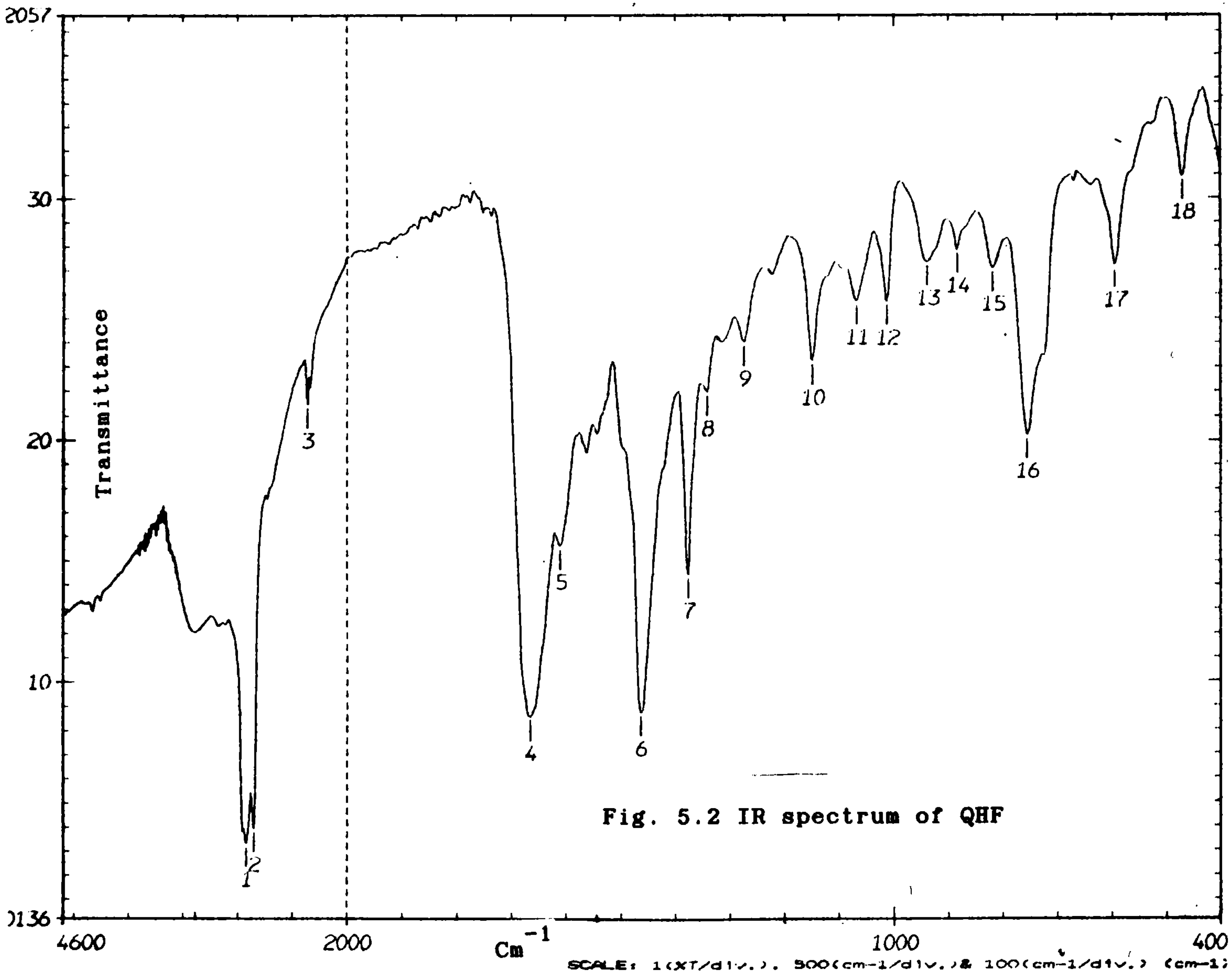


Fig. 5.2 IR spectrum of QHF

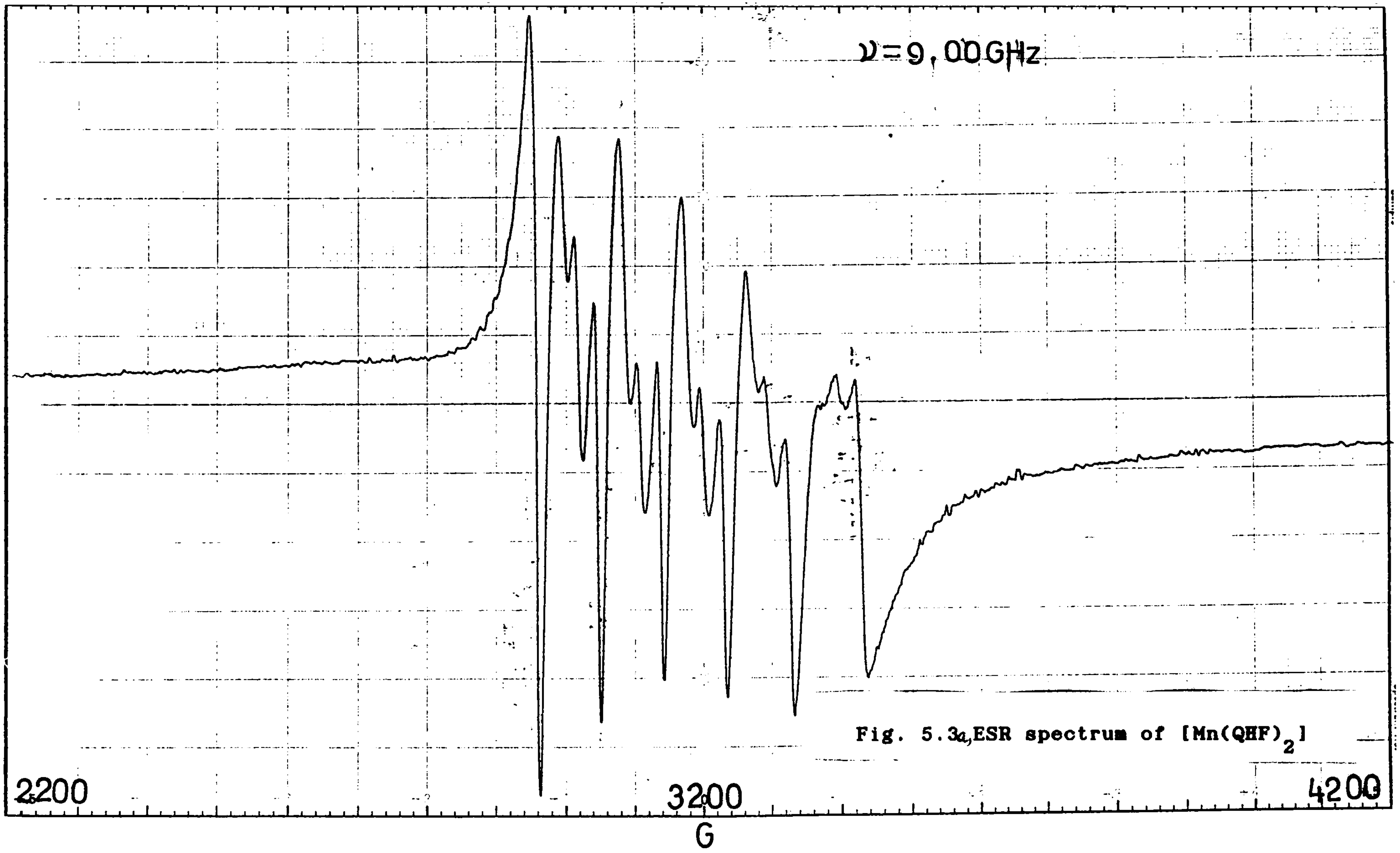


Fig. 5.3a, ESR spectrum of $[Mn(QHF)_2]$

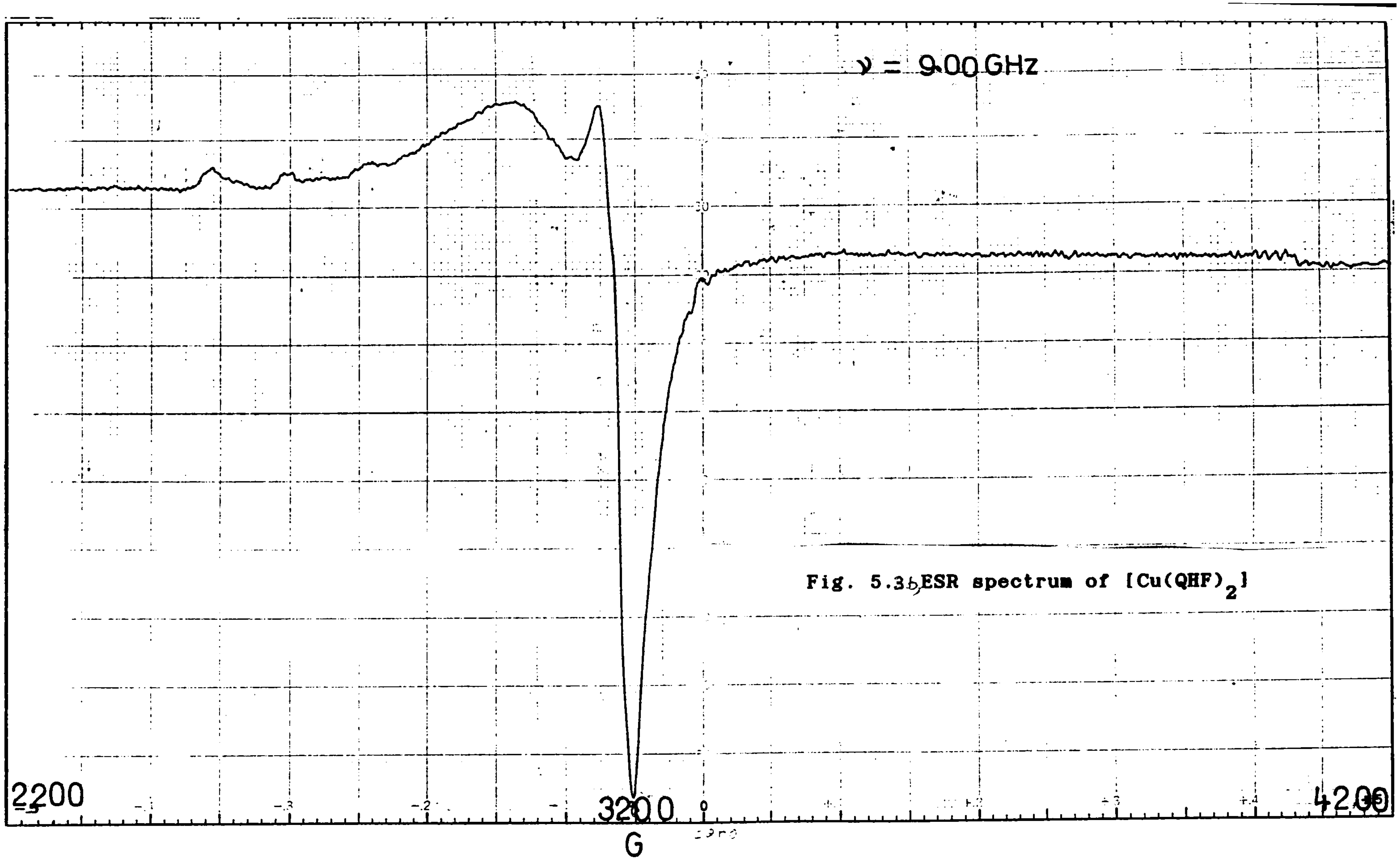


Fig. 5.3b ESR spectrum of $[Cu(QHF)_2]$

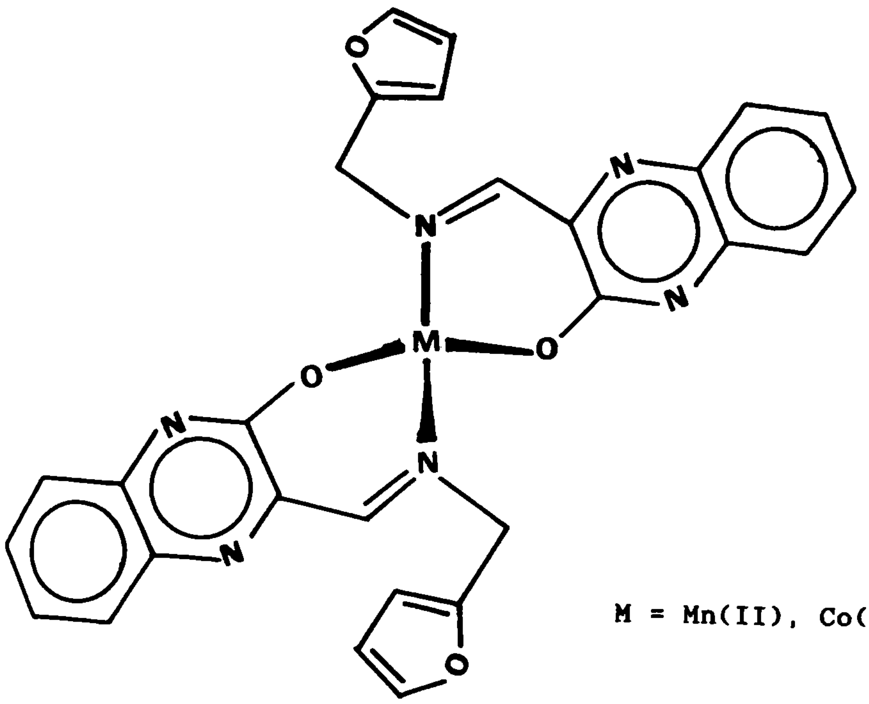
5.3.3 Infrared Spectra

Table V.4 shows important infrared spectral bands and their assignments. The νC=N identified at 1666 cm^{-1} in the infrared of the ligand (Fig. 5.2) was found to undergo a red shift in the complexes indicating the coordination of azomethine nitrogen to the metal ions[85]. The νO–H of the ligand at 3500 cm^{-1} is absent in the spectra of all the complexes suggesting that the phenolic oxygen is taking part in coordination in the ionised form. Further, the νC–O was found to be shifting to higher frequency side in the complexes[86]. The infrared spectral data indicate that the ligand uses its phenolic oxygen and azomethine nitrogen to bind the metal ions.

5.3.4 EPR Spectra

The EPR spectra (Fig. 5.3) of $[Mn(QHF)_2]$ and $[Cu(QHF)_2]$ complexes were recorded in DMSO at liquid nitrogen temperature. The g and A values are given in Table V.5. The $[Cu(QHF)_2]$ shows a spectrum similar to the other copper(II) square planar complexes[87]. The g values also suggest a square planar nature of the Cu(II) complex.

Based on the above arguments, the structure shown in Fig. 5.4 may be assigned for these complexes.



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

Fig. 5.4a Schematic structure of the complexes

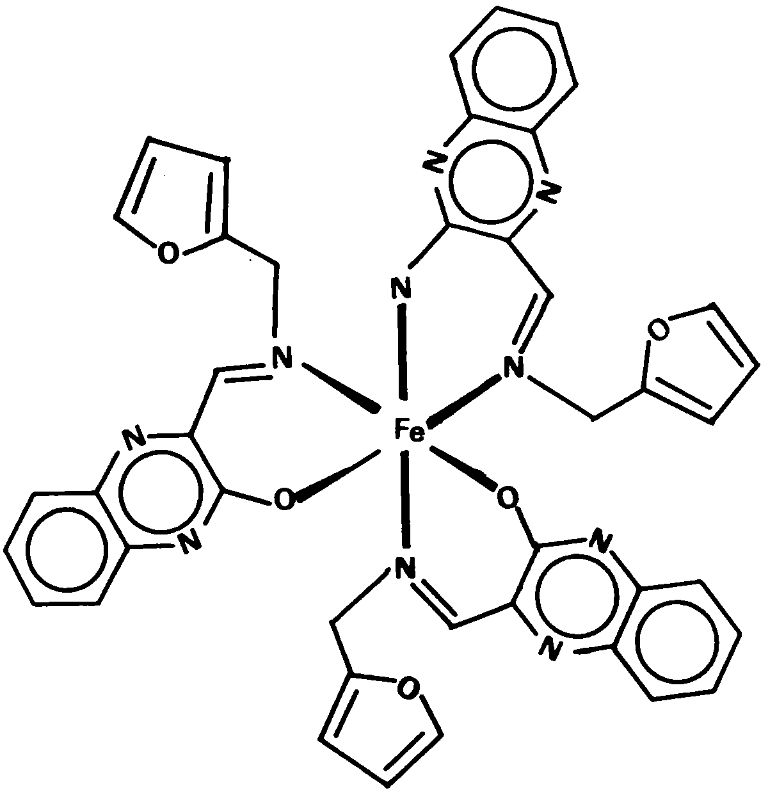


Fig. 5.4b Schematic structure of [Fe(QHF)$_3$]

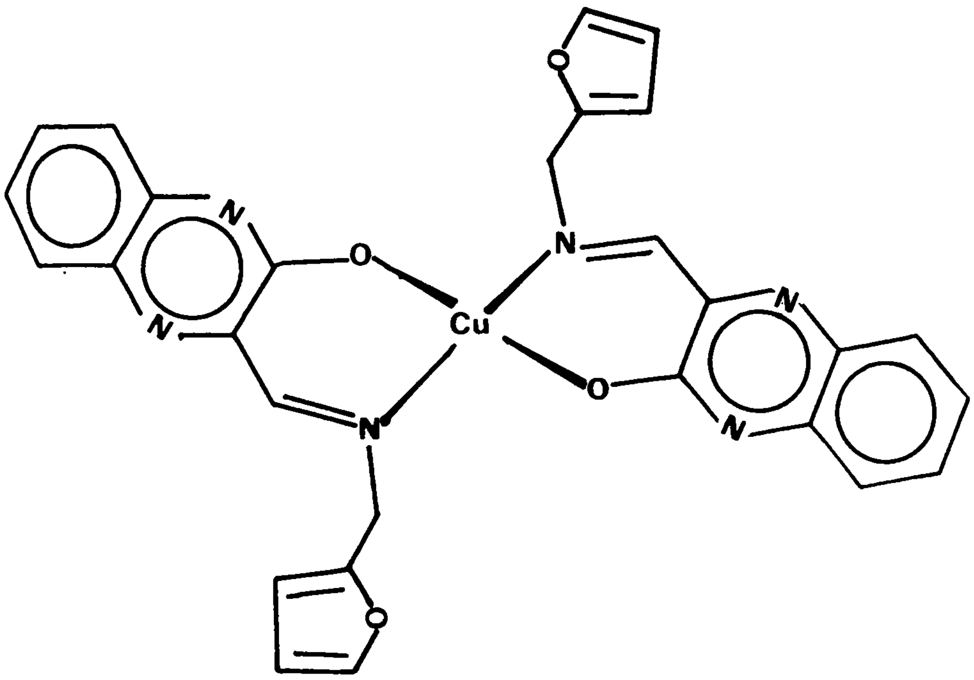


Fig. 5.4c, Schematic structure of $[Cu(QHF)_2]$

Table V.4

IR spectral data (cm^{-1})

QHF	I	II	III	IV	V	Assignments of the more relevant bands
3500(s)	3500(m)	3500(s)	3500(s)	3500(s)	3500(s)	υ_{O-H}
2924(s)	2926(s)	2924(s)	2955(s)	2924(s)	2924(s)	
2855(s)	2855(s)	2855(s)	2855(s)	2855(s)	2855(m)	
2363(m)	2362(m)	2360(m)	2362(w)	2362(m)	2360(m)	
1666(s)	1655(s)	1655(s)	1650(s)	1657(s)	1652(s)	$\upsilon_{C=N}$
1610(sh)	1610(m)	1610(w)	1609(m)	1608(m)	1610(m)	
1544(m)	1525(s)	1523(m)	1520(m)	1525(m)	1525(m)	
1464(s)	1464(m)	1460(m)	1462(s)	1462(s)	1461(m)	
1377(s)	1377(s)	1377(s)	1377(m)	1377(m)	1377(m)	
1342(m)	1340(m)	1342(m)	1340(m)	1340(w)	1341(m)	
1275(w)	1285(m)	1280(m)	1282(m)	1280(m)	1278(m)	$\upsilon_{C=O}$
1149(m)	1153(m)	1153(w)	1151(w)	1151(w)	1149(w)	
1068(w)	1070(w)	1065(w)	1068(w)	1066(w)	1065(w)	
1012(w)	1012(w)	1012(w)	1010(w)	1011(w)	1012(w)	
939(w)	935(w)	938(w)	935(w)	938(w)	935(w)	
883(w)	875(w)	880(w)	880(w)	875(w)	875(w)	
819(w)	819(w)	819(w)	819(w)	819(w)	819(w)	
756(m)	756(m)	756(m)	756(m)	756(m)	756(w)	$\delta_{C-H(Ph)}$
723(w)	723(w)	723(w)	721(w)	721(w)	721(w)	ρ_{CH_2}
470(w)	468(w)	457(w)	463(w)	463(w)	455(w)	

s = strong; m = medium; w = weak.

I = [Mn(QHF)$_2$]; II = [Fe(QHF)$_3$]; III = [Co(QHF)$_2$]; IV = [Ni(QHF)$_2$]; V = [Cu(QHF)$_2$]

Table V.5

EPR Spectral Data of the Complexes

Parameter	$[Mn(QHF)_2]$	$[Cu(QHF)_2]$
g_{av}	2	—
A_{av}	90 G	—
$g_{\parallel}$	—	2.4
$g_{\perp}$	—	2
$A_{\parallel}$	—	135 G

CHAPTER VI

MANGANESE(II), IRON(III), COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF 3-HYDROXYQUINOXALINE-2-CARBOXALDEHYDE SEMICARBAZONE

6.1. INTRODUCTION

Semicarbazones are interesting due to their ability to bind metal ions in various ways. Metal complexes of semicarbazones were found to possess pronounced carcinostatic properties against a wide range of transplanted neoplasm[88-95,24]. In a series of recent papers, the synthetic and structural aspects of a number of transition metal complexes of NS and NO donor ligands have been described[96-102]. There are a large number of reports on the studies on complexes of semicarbazones. However, only very few reports are available on the semicarbazones of quinoxaline derivatives. In this chapter, we present our studies on manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of 3-hydroxyquinoxaline-2- carboxaldehyde semicarbazone (QHS).

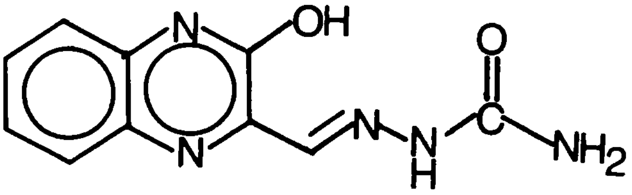


Fig. 6.1 Structure of QHS

6.2. EXPERIMENTAL

6.2.1. Materials

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

6.2.2 Synthesis of the Complexes

The procedure given below was followed to synthesise the manganese(II), cobalt(II), nickel(II) and copper(II) complexes.

The ligand QHS (0.02 mol, 4.62 g) was dissolved in ethanol (100 mL). To this solution, metal chloride (0.01 mol, 1.37 g of $MnCl_2.6H_2O$, 2.37 g of $CoCl_2.6H_2O$, 2.37 g of $NiCl_2.6H_2O$ or 1.7 g of $CuCl_2.2H_2O$) dissolved in minimum quantity of alcohol was added and refluxed for 2h. The volume of the reaction mixture was reduced to 1/3 and allowed to cool. The precipitated complexes were filtered, washed with ether and dried *in vacuo* over anhydrous calcium chloride (Yield: 60–70%; m.p.: 270°C).

Similar procedure is adopted for preparing iron(III) complex using the ligand QHS (0.02 mol, 4.62 g) and anhydrous ferric chloride (0.006 mol, 1.06 g).

6.2.3. Analytical Methods

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

6.3. RESULTS AND DISCUSSION

The isolated complexes are non-hygroscopic, microcrystalline and air stable in nature. They are appreciably soluble in methanol, DMF and DMSO, partially soluble in acetonitrile, acetone and chloroform and insoluble in water. The complexes behave as non-electrolytes in DMF[103] (Table VI.1). Analytical data together with the conductance data suggest that the complexes, except the iron(III) complex have empirical formula $[M(QHS)_2]$ (where, M = manganese(II), cobalt(II), nickel(II) or copper(II) and for the iron(III) complex the empirical formula is $[Fe(QHS)_3]$.

6.3.1 Magnetic Susceptibility Measurements

Magnetic moment values are given in Table VI.2. $[Mn(QHS)_2]$ shows a magnetic moment value of 5.4 BM. The magnetic moment of $[Fe(QHS)_3]$ is as expected for a d^5 high-spin octahedral complex. The magnetic moment values of $[Co(QHS)_2]$ and $[Ni(QHS)_2]$ suggest an octahedral structure for these complexes[104,105]. $[Cu(QHS)_2]$ shows a magnetic moment of 2.0 BM which indicates an octahedral structure, and further confirms the absence of copper–copper interaction.

Table VI.1

Analytical Data of the Complexes

	found (calculated)			
Compound	% Carbon	% Hydrogen	% Nitrogen	% Metal
[Mn(QHS)$_2$]	46.23	3.81	27.02	10.40
	(46.6)	(3.10)	(27.18)	(10.6)
[Fe(QHS)$_3$]	69.82	4.42	28.08	7.10
	(69.91)	(3.08)	(26.97)	(7.47)
[Co(QHS)$_2$]	46.13	3.00	26.62	11.30
	(46.27)	(3.08)	(26.97)	(11.35)
[Ni(QHS)$_2$]	46.16	3.02	26.87	10.98
	(46.27)	(3.08)	(26.99)	(11.31)
[Cu(QHS)$_2$]	45.80	3.01	26.52	12.09
	(45.84)	(3.05)	(26.74)	(12.13)

Table VI.2

Magnetic and Conductance Data

Compound	Colour	Conductance ($ohm^{-1} cm^{2} mol^{-1}$)	Magnetic moment (BM)
$[Mn(QHS)_2]$	Yellowish	22	5.4
$[Fe(QHS)_3]$	Brown	31	5.6
$[Co(QHS)_2]$	Brown	33	5.2
$[Ni(QHS)_2]$	Brown	35	2.8
$[Cu(QHS)_2]$	Brown	36	2.0

6.3.2 Electronic Spectra

The spectra of all the complexes were taken in methanol (Table VI.3). Strong intraligand transitions mask the uv and near uv region of the spectra, and the forbidden d-d bands could not be observed for $[Mn(QHS)_2]$ and $[Fe(QHS)_3]$. The spectra of $[Co(QHS)_2]$ is found to be almost in agreement with that for an octahedral structure[68].

The band observed at 21300cm^{-1} can be assigned to $^4T_1g \longrightarrow {}^4T_1g(P)$ transition. Other expected bands were not observed due to the very low intensity of these bands.

For $[Ni(QHS)_2]$, the $^3A_2g \longrightarrow {}^3T_2g(F)$ and $^3A_2g \longrightarrow {}^3T_1g(P)$ transitions appear at 20000 cm^{-1} and 24100 cm^{-1} respectively. The $^3A_2g \longrightarrow {}^3T_2g(P)$ transition band was not observed probably because of the very low intensity of the bands[106]. The d-d band of $[Cu(QHS)_2]$ could not be observed, as it might have been masked by the large intense charge transfer bands.

6.3.3 Infrared Spectra

The important infrared spectral bands and their assignments are shown in Table VI.4. Almost all bands present in the spectrum of the ligand (Fig. 6.2) are present in the spectra of the complexes. The υNH_2 observed at 3435 cm^{-1} of the ligand remains unaltered in the spectra of the complexes indicating the non-involvement of NH_2 group in coordination. The C=O and C=N

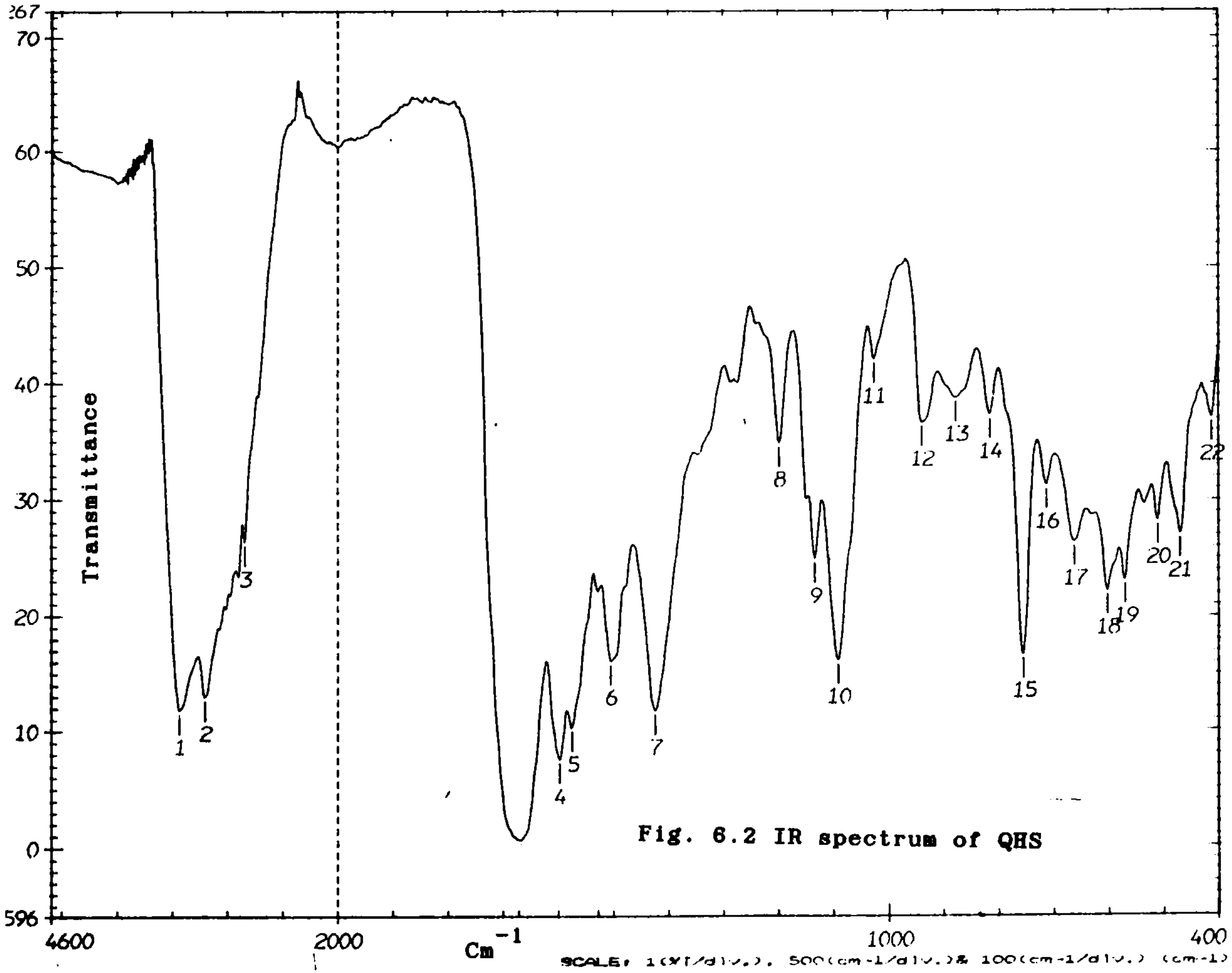


Fig. 6.2 IR spectrum of QHS

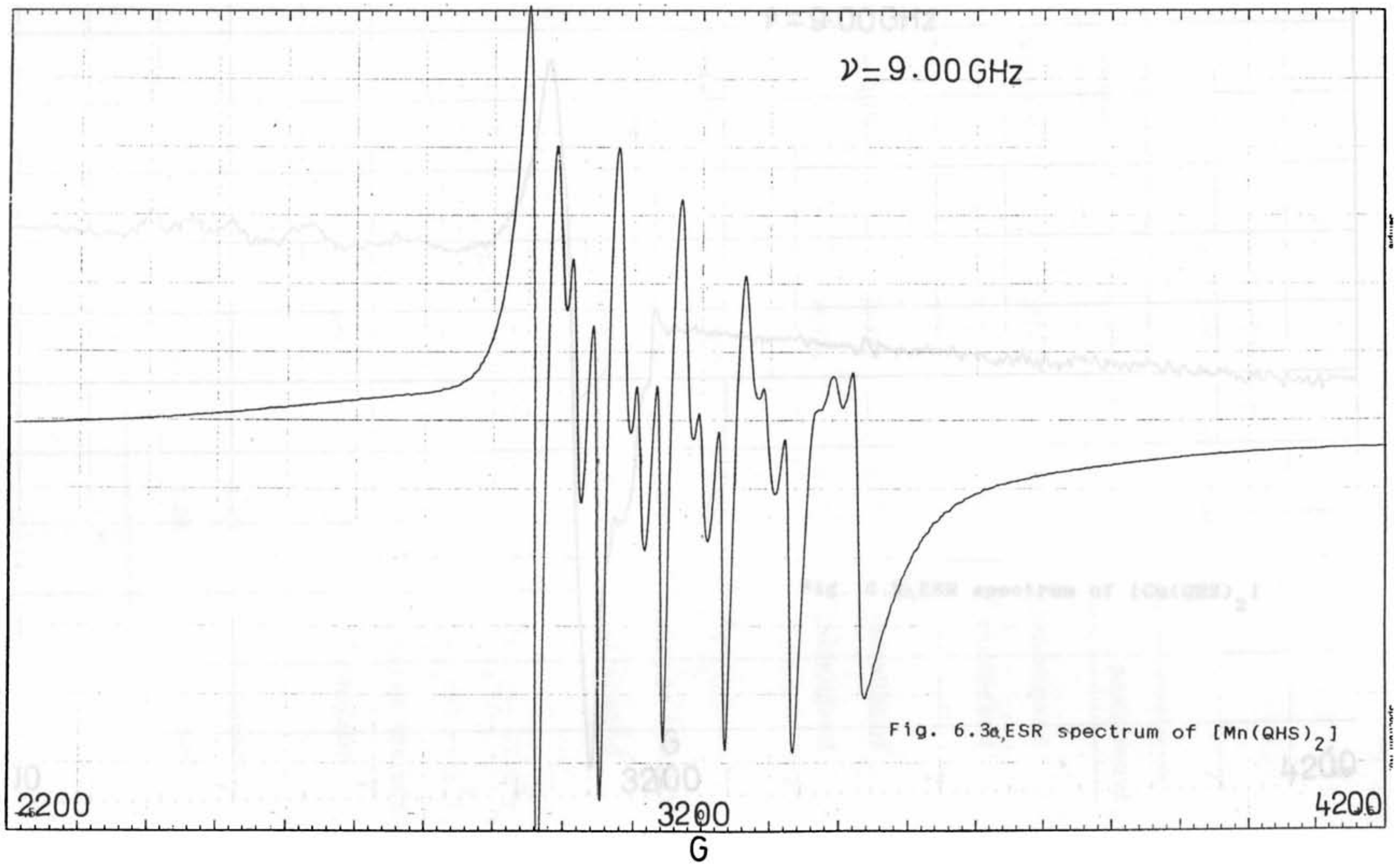


Fig. 6.3a ESR spectrum of [Mn(QHS)$_2$]

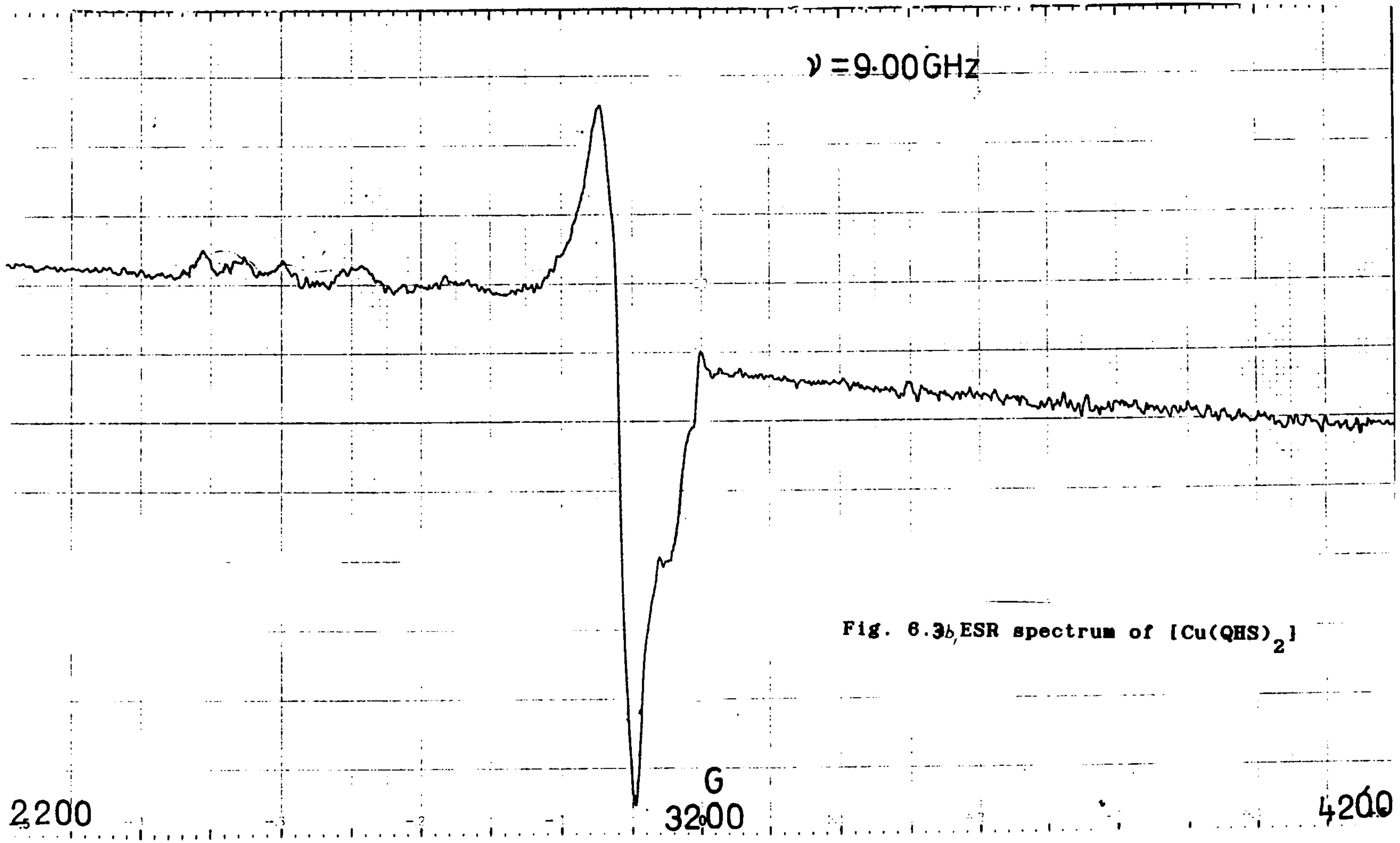


Fig. 6.3b, ESR spectrum of [$Cu(QHS)_2$]

Table VI.3

Electronic Spectral Data

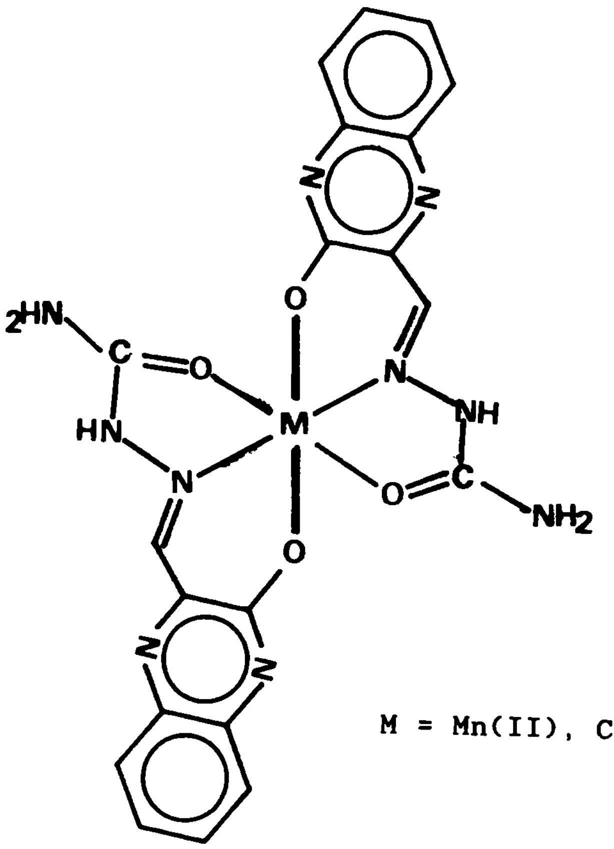
Compound	Abs. max. (cm^{-1})	log ε	Assignemnt
[Mn(QHS)$_2$]	25180	2.53	intraligand
	30435	4.38	intraligand
[Fe(QHS)$_3$]	26320	2.61	intraligand
	28925	4.27	intraligand
[Co(QHS)$_2$]	21300	1.54	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}$ (P)
	25180	3.60	charge transfer
	30435	4.32	intraligand
[Ni(QHS)$_2$]	20000	1.38	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
	24100	1.66	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$
	29000	3.72	charge transfer
	30440	4.30	intraligand
[Cu(QHS)$_2$]	25180	3.25	intraligand
	31260	4.28	intraligand

stretching bands of the ligand appear together as a strong and broad band at 1680 cm^{-1} in spectrum of the ligand. The coordination of the azomethine nitrogen shifts the C=N stretching frequency to lower energy side in all the complexes[107]. The υC=O was also found to decrease in the spectra of the complexes except in the case of $[Fe(QHS)_3]$[108]. The carbonyl oxygen may not be coordinating in $[Fe(QHS)_3]$. The absence of the υO–H band in the complexes and the blue shift of υC–O band confirms the coordination of phenolic oxygen in the deprotonated form.

6.3.4 EPR Spectra

The EPR spectra of $[Mn(QHS)_2]$ and $[Cu(QHS)_2]$ were recorded at LNT in DMSO. The g and A values are given in Table VI.5. The axial symmetry of the spectra suggest an octahedral structure to $[Cu(QHS)_2]$. The g values also support the octahedral nature of the copper(II) complex.

Based on the above facts, structures shown in Fig. 6.4 may be assigned for the complexes.



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

Fig. 6.4a Schematic structure of the complexes

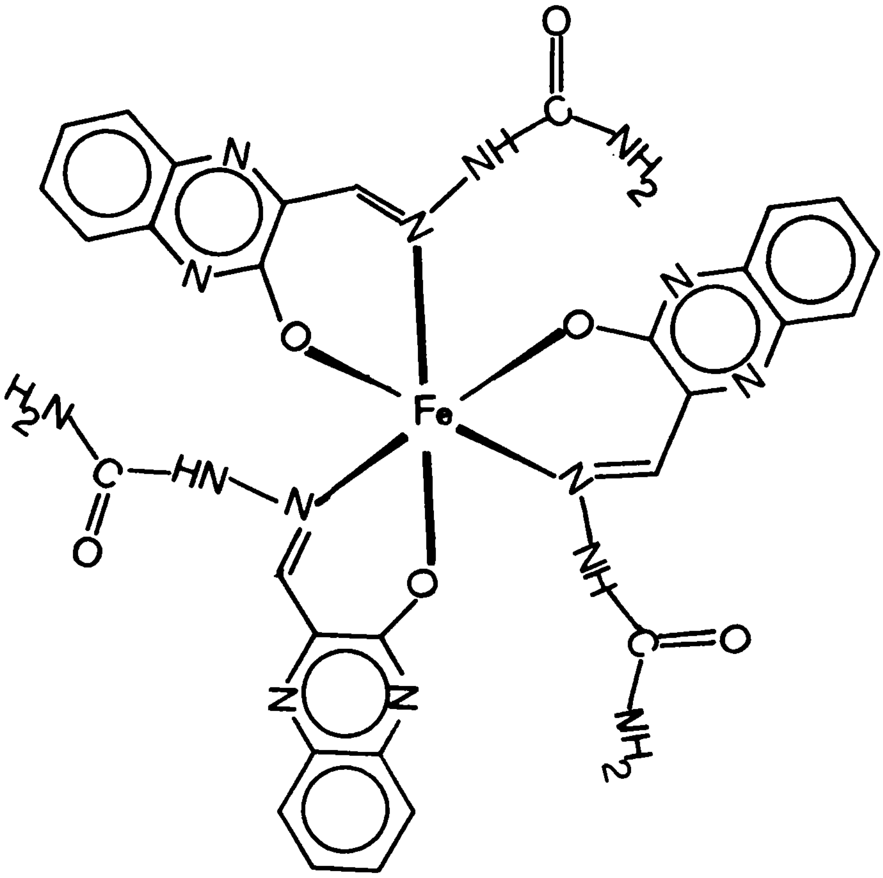


Fig. 6.4b Schematic structure of [Fe(QHS)$_3$]

Table VI.5

EPR Spectral Data of the Complexes

Parameter	$[Mn(QHS)_2]$	$[Cu(QHS)_2]$
g_{av}	2	---
A_{av}	85 G	---
$g_{\parallel}$	---	2.2
$g_{\perp}$	---	2
$A_{\parallel}$	---	100 G

Table VI.4 Infrared spectral data(cm^{-1})

QHS	I	II	III	IV	V	Assignments of relevant bands
3500(s)	———	———	———	———	———	ν_{O-H}
3435(s)	3435(s)	3435(s)	3435(s)	3435(s)	3435(s)	ν_{N-H}
2924(s)	3924(s)	2920(s)	2922(s)	2922(s)	2920(s)	
2845(m)	2845(m)	2840(s)	2840(s)	2841(s)	2843(s)	
1680(s)	1678(m)	1680(m)	1670(m)	1672(m)	1674(m)	$\nu_{C=O}$
1680(s)	1662(m)	1664(m)	1660(m)	1662(m)	1664(m)	$\nu_{C=N}$
1599(s)	1547(s)	1545(s)	1562(s)	1565(s)	1565(s)	
1533(sh)	1530(w)	1532(w)	1530(w)	1530(w)	1531(m)	
1506(m)	1500(m)	1504(w)	1500(w)	1502(m)	1503(m)	
1425(s)	1420(s)	1423(s)	1415(s)	1418(s)	1420(s)	
1270(m)	1277(m)	1276(m)	1280(m)	1272(m)	1275(m)	ν_{C-O}
1199(w)	1195(w)	1194(w)	1195(w)	1195(w)	1194(w)	
1136(m)	1134(m)	1130(m)	1130(m)	1133(m)	1134(m)	
1093(m)	1091(m)	1092(w)	1092(w)	1092(m)	1092(w)	
1028(w)	1025(w)	1024(m)	1027(m)	1024(s)	1023(m)	
941(w)	936(w)	935(w)	939(w)	939(w)	935(m)	
879(w)	875(w)	870(w)	874(w)	874(w)	876(w)	
817(w)	817(w)	817(w)	815(w)	817(w)	815(w)	
758(m)	756(m)	756(m)	758(m)	760(m)	756(m)	$\nu_{C-H(Ph)}$
715(w)	710(w)	712(w)	710(w)	712(w)	712(w)	
665(m)	659(w)	654(w)	660(w)	661(w)	660(w)	
605(m)	600(m)	603(m)	603(m)	603(m)	601(w)	
572(m)	570(m)	569(m)	565(m)	565(m)	571(w)	
513(w)	513(w)	511(w)	515(w)	515(w)	515(w)	
472(m)	470(w)	468(w)	468(w)	474(w)	470(w)	
414(w)	414(w)	418(w)	415(w)	413(w)	413(w)	

s = strong, m = medium and w = weak, I = [Mn(QHS)$_2$],

II = [Fe(QHS)$_3$], III = [Co(QHS)$_2$], IV = [Ni(QHS)$_2$]and V = [Cu(QHS)$_2$]

CHAPTER VII

MANGANESE(III), IRON(III), COBALT(III), NICKEL(II) AND COPPER(II) COMPLEXES OF 3-HYDROXYQUINOXALINE-2-CARBOXALDEHYDE THIOSEMICARBAZONE

7.1 INTRODUCTION

Many "classical" complexes containing thiosemicarbazones as coordinated ligands with bidentate coordination through the sulphur and hydrazinic nitrogen atoms, have been reported[109-111]. There are also reports of tridentate thiosemicarbazones where atoms such as nitrogen and oxygen become the part of the aromatic ring[112]. Thiosemicarbazones have a wide range of pharmacological activity. Their biological activity has been thought to improve selectively on certain biological systems, due to their ability to chelate with trace metals[113,114]. Several metal complexes of thiosemicarbazone derivatives are reported to possess activity against viruses, tumours and fungi[115,116]. Many thiosemicarbazide derivatives and their complexes have been extensively reported[117-121]. However, no work has been done on the thiosemicarbazones of 3-hydroxyquinoxaline-2-carboxaldehyde. We have prepared manganese(III), iron(III), cobalt(III), nickel(II) and copper(II) complexes of 3-hydroxyquinoxaline-2-carboxaldehyde thiosemicarbazone (QHT) and the results of our studies on these complexes are presented in this chapter.

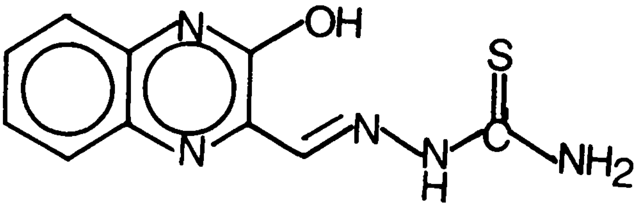


Fig. 7.1 Structure of QHT

7.2 EXPERIMENTAL

7.2.1 Materials

Details regarding the preparations and purification of the ligand QHT is given in Chapter II.

7.2.2 Synthesis of the Complexes

The following procedure was used to prepare the complexes.

The ligand QHT (0.02 mol, 4.94 g) was dissolved in ethanol(100 mL). Metal chloride (0.01 mol, 1.97 g of $MnCl_2.6H_2O$; 2.37 g of $CoCl_2.6H_2O$; 2.37 g of $NiCl_2.6H_2O$ or 1.7 g of $CuCl_2.2H_2O$) was dissolved in minimum quantity of ethanol and added to the ligand solution. The reaction mixture was refluxed for 5h and the volume was reduced to about 1/2. Allowed to cool. The precipitated complexes were collected by filtration, washed with ether and dried *in vacuo* over anhydrous calcium chloride (Yield: 50–60%, m.p.: >270°C).

Iron complex was prepared in a similar way using the ligand QHT (0.02 mol, 4.94g) and anhydrous ferric chloride (0.006 mol, 1.06 g).

7.2.3 Analytical Methods

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

7.3 Results and Discussion

All the complexes are crystalline, nonhygroscopic and are quite stable to aerial oxidation. The complexes are soluble in methanol, DMF and DMSO, partially soluble in acetonitrile, chloroform and insoluble in water. Based on the analytical data (Table VII.I) and low molar conductance values, the empirical formula $[M(QHT)_3]$ has been suggested for the manganese, iron and cobalt complexes and $[M(QHT)_2]$ for the nickel and copper complexes.

7.3.1 Magnetic Susceptibility Measurements

Magnetic moment values are given in Table VII.2. The $[Mn(QHT)_3]$ have a magnetic moment 4.27 BM, which suggests that the complex is high-spin octahedral complex in the +3 oxidation state. $[Fe(QHT)_3]$ has a magnetic moment 5.4 BM which is slightly lower than what is expected for a high-spin iron(III) ion. This may either be due to the presence of spin crossover equilibria or be due to antiferromagnetic coupling.

Table VII.1

Analytical Data of the Complexes

Compound	% Carbon	% Hydrogen	%Nitrogen	% Sulphur	% Metal
	found (calculated)				
[Mn(QHT)$_3$]	45.20 (46.4)	3.01 (3.02)	26.26 (26.48)	8.01 (8.07)	6.90 (6.92)
[Fe(QHT)$_3$]	45.18 (45.34)	3.00 (3.02)	26.38 (26.45)	7.98 (8.06)	6.70 (7.03)
[Co(QHT)$_3$]	45.08 (45.17)	2.98 (3.01)	26.12 (26.35)	8.00 (8.03)	7.10 (7.39)
[Ni(QHT)$_2$]	43.46 (43.58)	2.45 (2.90)	25.31 (25.42)	11.56 (11.62)	10.18 (10.65)
[Cu(QHT)$_2$]	43.15 (43.20)	2.67 (2.88)	25.08 (25.20)	11.40 (11.52)	11.10 (11.43)

Table VII.2

Magnetic and Conductance Data

Compound	Colour	Conductance (Ohm^{-1} cm^{2} mol^{-1})	Magnetic moment BM
[Mn(QHT)$_3$]	Brown	14	4.27
[Fe(QHT)$_3$]	Brown	48	5.41
[Co(QHT)$_3$]	Brown	36	Diamagnetic
[Ni(QHT)$_2$]	Brown	45	3.28
[Cu(QHT)$_2$]	Brown	28	1.78

Oxidation of the metal ion happens in the case of cobalt complexes also. The diamagnetic nature of the cobalt complex shows that cobalt(II) ion gets oxidised to cobalt(III) during the formation of the complex, resulting in a low spin octahedral cobalt(III) complex[122]. Eventhough (for the synthesis of manganese and cobalt complexes) the metal salts in +2 oxidation state were used, complexes in the +3 oxidation state were obtained. Similar observations were made earlier in the case of thiosemicarbazone ligands.

The magnetic moment value of $[Ni(QHT)_2]$ is 3.28, which support an octahedral geometry for the Ni(II) complex[123]. As the metal ligand ratio in the nickel complex is 1:2, the QHT may be acting as a tridentate ligand in this complex. The $[Cu(QHT)_2]$ complex exhibits a magnetic moment value of 1.78 BM[124], which indicates a square planar structure for the complex.

7.3.2 Electronic Spectra

The electronic spectra of all the complexes are taken in methanol. The observed bands and assignments are given in Table VII.3. In the case of $[Mn(QHT)_3]$, the d-d absorptions are not seen probably it might have been masked by the charge transfer absorptions. The spectra of $[Fe(QHT)_3]$ does not exhibit any characteristic d-d absorption. For the $[Co(QHT)_3]$, the transitions $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$ were observed at 21500 cm^{-1} and 35900 cm^{-1} respectively[125]. The three transitions

Table VII.3

Electronic Spectral Data

Compound	Band position (cm^{-1})	log ε	Assignment
$[Mn(QHT)_3]$	24330	3.87	intraligand transition
	31350	4.12	intraligand transition
	40650	4.32	intraligand transition
$[Fe(QHT)_3]$	17300	3.69	charge transfer
	25005	3.90	intraligand transition
$[Co(QHT)_3]$	21500	1.28	$^1A_{1g} \longrightarrow {}^1T_{1g}$
	18200	1.82	charge transfer
	18800	1.94	charge transfer
	35980	4.28	intraligand transition
	35900	4.10	$^1A_{1g} \longrightarrow {}^1T_{2g}$
	45270	4.37	intraligand transition
$[Ni(QHT)_2]$	19720	1.25	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$
	24220	3.58	intraligand transition
	42700	4.29	intraligand transition
	46460	4.41	intraligand transition
$[Cu(QHT)_2]$	16390	1.79	d-d transition
	26460	3.84	intraligand transition
	46880	4.56	intraligand transition

expected for an octahedral [Ni(QHT)$_2$] could be identified in the spectra of nickel(II) complex[126]. A broad d–d absorption was observed at about 16390 cm^{-1} observed for [Cu(QHT)$_3$] complex[127] which further indicates the square planar nature of the complex.

7.3.3 Infrared Spectra

The important infrared spectral bands of the ligands and the complexes are given in Table VII.4. Almost all of the bands due to the free ligand (Fig. 7.2) are present in the spectra of the complexes. The νOH band seen at about 3500 cm^{-1} is absent in the spectra of the complexes, which suggests the coordination of the phenolic oxygen in the deprotonated form. Also the νC–O band has undergone a blueshift from 1280 cm^{-1} to higher frequencies in the spectra of the complexes[128]. The azomethine stretching frequency observed at 1659 cm^{-1} is seen to be shifted during the complex formation. In the case of [Mn(QHT)$_3$], [Fe(QHT)$_3$] and [CoQHT)$_3$] complexes this band is observed at higher frequencies[129]. This may be due to the hybridisation change induced on the nitrogen by the interaction with the metals in the +3 oxidation state. But in the case of [Ni(QHT)$_2$] and [Cu(QHT)$_2$] this band is observed at lower frequencies[130]. The νC=S band observed at 1082 cm^{-1} remain unaltered except in the case of [Ni(QHT)$_2$][131]. The sulphur atom may be taking part in coordination in the case of Ni(II) complex only. Besides, no new band at about 660 cm^{-1} due to νC–S is observed suggesting that

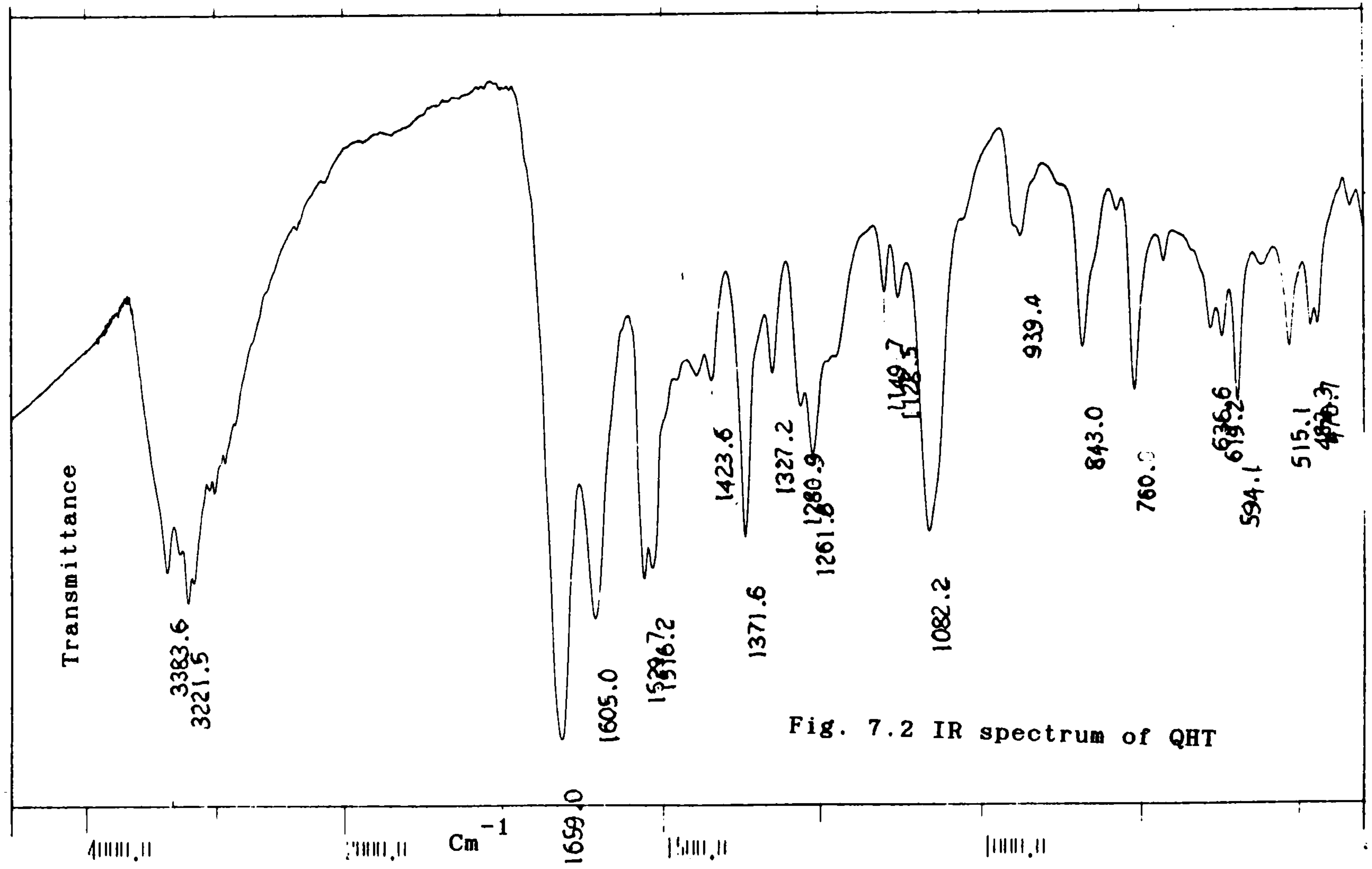


Fig. 7.2 IR spectrum of QHT

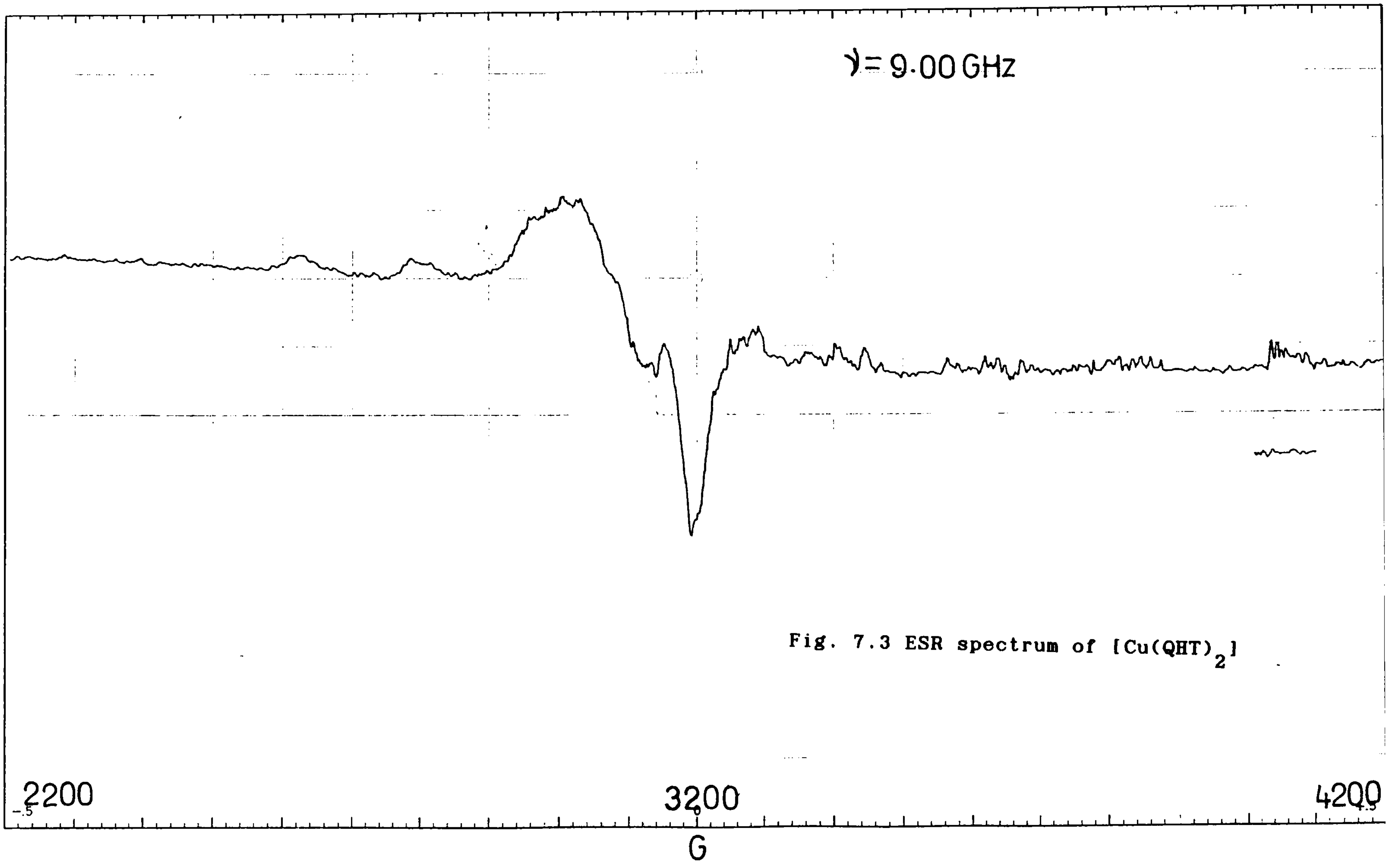


Fig. 7.3 ESR spectrum of $[Cu(QHT)_2]$

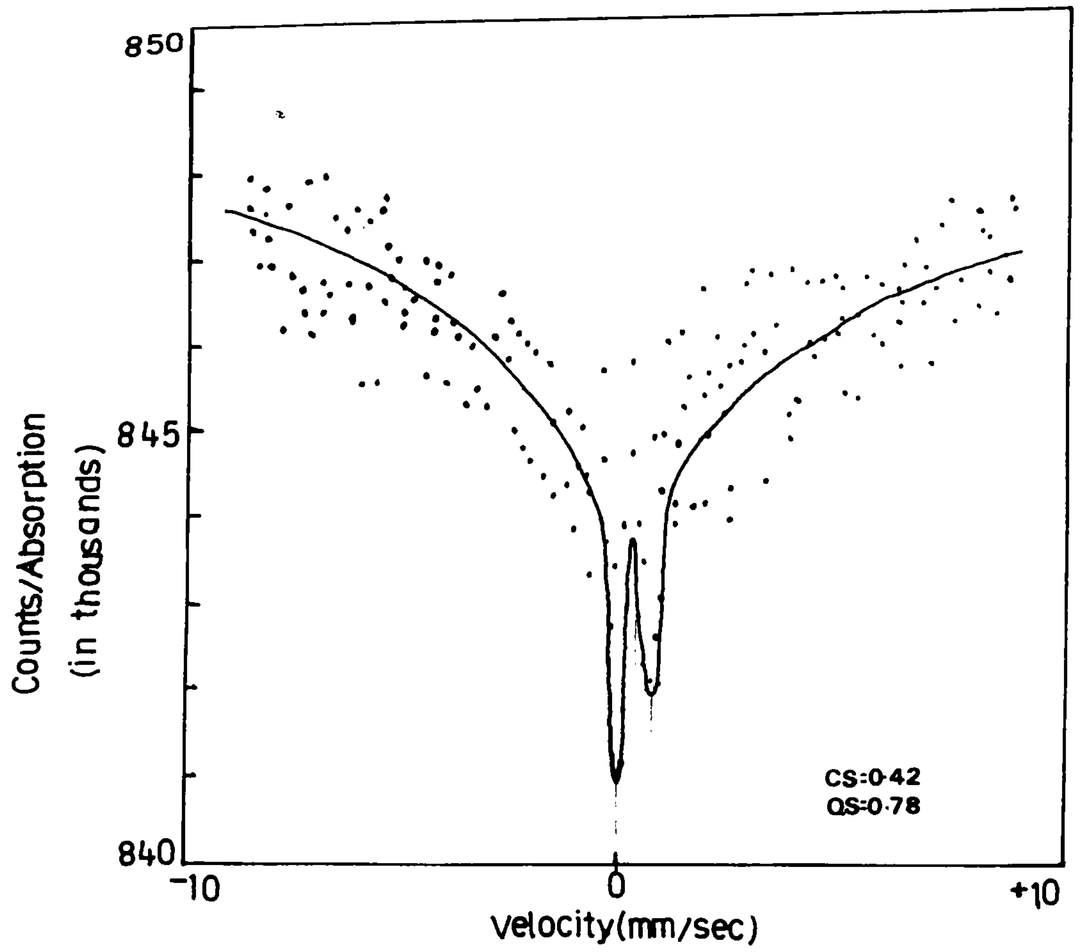


Fig. 7.4 Mössbauer spectrum of [Fe(QHT)$_3$]

the ligands coordinates in the thione form[132]. The retention of the NH_2 stretching frequencies prove that this nitrogen is not used for metal ligand bonding. QHT thus behaves as a bidentate ligand in the case of $[Mn(QHT)_3]$, $[Fe(QHT)_3]$, $[Co(QHT)_3]$ and $[Cu(QHT)_2]$ and tridentate using phenolic oxygens, azomethine nitrogen and sulfur atom only in the case of $[Ni(QHT)_2]$.

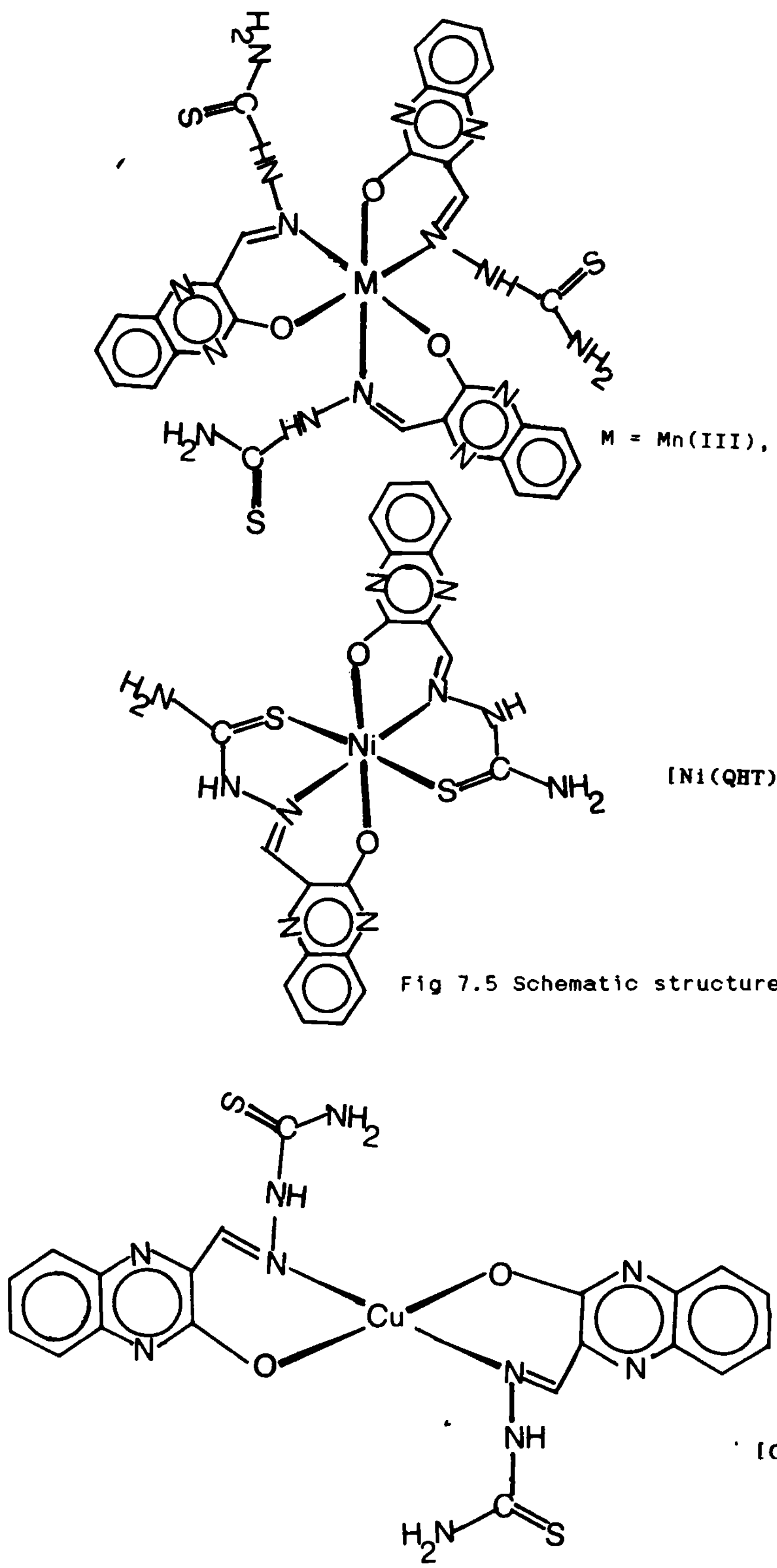
7.3.4 EPR Spectra

EPR spectrum of $[Cu(QHT)_2]$ was recorded in DMSO at liquid nitrogen temperature. The $g_{\parallel}$ value 2.2 and and $g_{\perp}$ value of 2.0 are reasonable for a square planar Cu(II) complex. The EPR spectrum given an A value of 160 for $[Cu(QHT)_2]$. Similar results have been obtained for many square planar copper(II) complexes[133].

7.3.5. Mössbauer spectra

The Mössbauer spectrum recorded at room temperature shows a quadrupole split doublet with centre shift of 0.42 mm s^{-1} and quadrupole splitting of 0.78 mm s^{-1}. The low centre shift values shows that the iron atom is in +3 oxidation state The quadrupole splitting is in agreement with the high-spin iron(III) complex. Further, the spectrum does not give evidence for the presence of low-spin iron(III) complexes.

Based on the above arguments the following structures may be assigned for the complexes.



M = Mn(III), Fe(III) or Co(III)

$[Ni(QHT)_2]$

Fig 7.5 Schematic structures of the complexes

$[Cu(QHT)_2]$

Table VII.4 IR spectral data(cm^{-1})

QHT	I	II	III	IV	V	Assignments of the more relevant bands
3500(s)	———	———	———	———	———	υ_{O-H}
3380(s)	3380(s)	3380(s)	3380(s)	3380(s)	3380(s)	υ_{N-H}
3221(s)	3220(s)	3218(m)	3220(m)	3218(m)	3219(m)	
1659(m)	1668(m)	1668(m)	1672(m)	1628(m)	1647(m)	$\upsilon_{C=N}$
1605(s)	1601(s)	1606(m)	1605(m)	1604(m)	1601(s)	
1529(s)	1522(m)	1525(s)	1525(s)	1520(m)	1521(m)	
1516(s)	1510(m)	1510(m)	1512(w)	1514(m)	1513(m)	
1423(m)	1420(m)	1416(m)	1418(m)	1415(s)	1419(m)	
1371(s)	1377(s)	1373(m)	1373(m)	1373(m)	1371(m)	
1327(m)	1325(m)	1321(m)	1321(m)	1323(s)	1326(m)	
1280(w)	1288(w)	1289(w)	1285(w)	1282(w)	1280(w)	υ_{C-O}
1261(m)	1256(m)	1260(m)	1265(m)	1255(m)	1269(w)	
1149(w)	1151(m)	1149(m)	1149(s)	1149(m)	1151(s)	
1128(w)	1125(m)	1123(m)	1124(m)	1124(m)	1118(m)	
1082(s)	1082(m)	1080(m)	1080(m)	1066(m)	1080(m)	$\upsilon_{C=S}$
939(w)	933(w)	937(w)	935(w)	936(w)	938(w)	
843(m)	843(w)	843(w)	837(w)	836(w)	836(w)	
760(w)	756(w)	758(w)	758(w)	760(w)	763(w)	$\delta_{C-H(Ph)}$
636(w)	634(w)	635(w)	636(w)	637(w)	639(w)	
619(m)	615(w)	614(w)	618(w)	617(w)	615(w)	
594(w)	594(w)	595(w)	593(w)	590(w)	590(w)	
515(m)	515(m)	510(m)	510(m)	513(m)	514(w)	
482(w)	480(w)	481(w)	482(w)	481(w)	481(w)	
470(w)	470(w)	471(w)	471(w)	472(w)	472(w)	

s = strong, m = medium and w = weak, I = [$Mn(QHT)_3$],
II = [$Fe(QHT)_3$], III = [$Co(QHT)_3$], IV = [$Ni(QHT)_2$] and
V = [$Cu(QHT)_2$]

CHAPTER VIII

SOME NEW ZEOLITE ENCAPSULATED COBALT(II) AND COPPER(II) COMPLEXES

8.1 INTRODUCTION

In the context of catalysis increased efforts have been made in the immobilisation of homogeneous catalyst on solid supports[134]. Under ideal conditions such hybrid catalysts could combine the advantages of both homogeneous and heterogeneous catalysts and minimise the disadvantages of both. In this context zeolites are interesting due to the presence of channels and cages present in these inorganic systems. One way of exploiting the zeolite cage is to introduce a metal complex catalyst in the supercage of zeolite.

Zeolite cage is considered as a molecular-scale microreactor containing a metal complex catalyst. They create within the cage an electric field which modifies the properties of molecules in the cage. They impose steric constraints on an encapsulated molecule, causing it to distort and changing its stability and reactivity[135]. We have used zeolite Y for encapsulating metal complexes.

Zeolite Y is one of the few three dimensional large pore zeolites known, which comes under the group faujasite. In this, the sodalite units are arranged like the carbon atoms in diamond, and generate a large cavity, or supercage, with 12, hexagonal and square faces. Access to the supercage is restricted by a 12 face, or window, which has a free diameter of around 7-8 A^0. The supercage has a diameter of 13A° [136]. The frame work structure of zeolite Y is shown in Fig. 8.1.

The encapsulation of transition metal phthalocyanine complexes (MPc) inside X and Y type zeolites has been well established[137,138]. Such intrazeolite complexes are physically trapped in the zeolite pores and are not necessarily bound to the surface. These encapsulated species have been termed as ship-in-a bottle complexes and could potentially provide new types of reactivity. The advantages of shape selectivity and site isolation inside the zeolite might also be realized[139]. The inclusion of iron phthalocyanine in Y type zeolites results in a catalyst which is 10^3 times more active than the homogeneous catalyst[143] (Fig.8.2). Cobalt and copper phthalocyanine and salen complexes can be incorporated into the zeolite cavity[46,140].

Technically important reaction of carbon monoxide and nitric oxide over zeolite complexes have been explored[141,142]. Mono and polynuclear carbonyl compounds of Rh and Ir have been entrapped in Y-zeolite for vapour phase carbonylation of methanol and aromatic compounds as well as for hydroformylation reactions[143-145]. Oxidation of carbon monoxide by oxygen is more

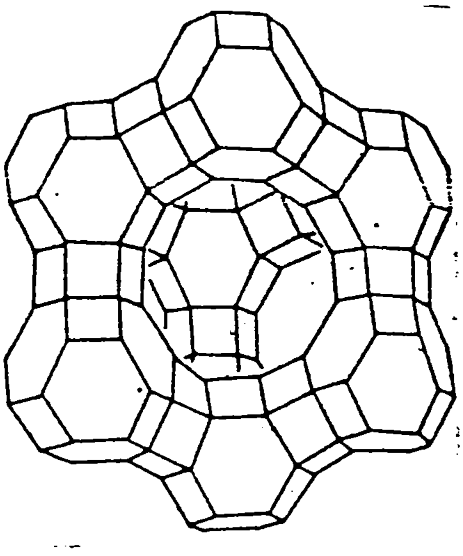


Fig. 8.1 The framework structure of zeolite Y

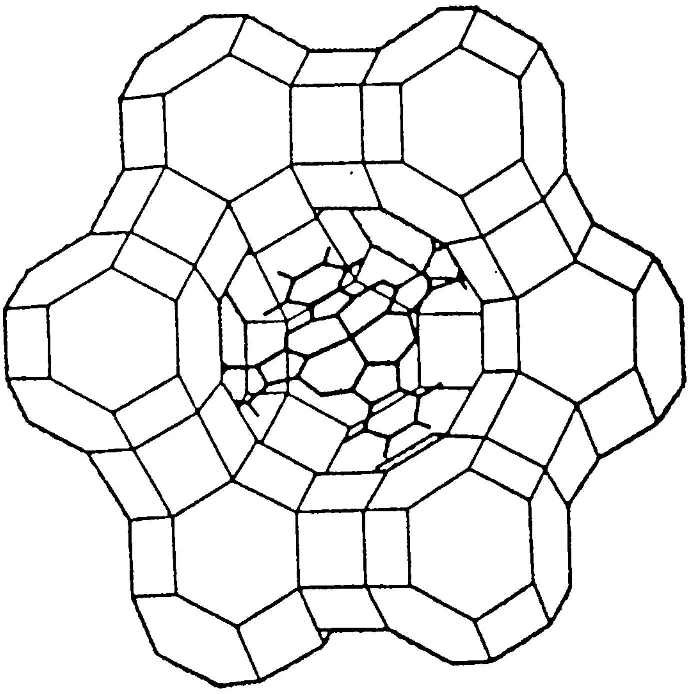


Fig. 8.2 Intrazeolite phthalocyanine complex formation

efficient with cobalt phthalocyanine in NaY than with cobalt phthalocyanine alone[146]. The Pd(salen) complex encapsulated in X or Y zeolite has been found to be an active catalyst for the selective hydrogenation of hex-1-ene in the presence of cyclohexane[147]. We thought it is worthwhile to prepare the complexes of the synthesised ligands in the supercage of zeolite Y, as such an encapsulation may lead us to the generation of potential catalysts.

In this chapter, studies on cobalt(II) and copper(II) complexes of ligand QHA, QHF, QHS and QHT encapsulated inside zeolite Y are presented.

8.2 EXPERIMENTAL

8.2.1 Materials

Zeolite Y (United catalyst India Ltd.) was ion-exchanged with 0.1 M NaCl for 16h prior to use. Details about the preparation and purification of the ligands, QHA, QHF, QHS and QHT are given in Chapter II.

5 g of NaY was shaken with an aqueous solution of cobalt chloride (400 mL, 0.001 M) for 12h. At these low concentration levels it is approximated that all the cobalt ion goes from the solution into the zeolite. The zeolite is then filtered and washed several times with distilled water to remove the chloride ions present.

About 200 mg of the ligand (QHA, QHF, QHS or QHT) is dissolved in ethanol (100 mL) and filtered to remove any undissolved particles if present. This solution was taken in 25 mL RB and refluxed with cobalt exchanged zeolite (1 g) for 3h. The colour of the zeolite changed indicating coordination. The zeolite was then filtered and soxhlet extracted with ethanol for 10–12 h to remove any surface bound species that might form during complexation.

Similar procedure was adopted to synthesise copper(II) complexes in the zeolite.

8.2.2 Analytical Methods

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

8.3 RESULTS AND DISCUSSION

The synthesis of zeolite encapsulated complexes were carried out with those ligands having an ionisable proton in order to minimise the chance for the formation of surface bound metal complexes. The metal ions adsorbed on the surface will react with the ligands to form neutral complexes and thereby remain in solution or can be easily washed away by soxhlet extraction. The metal ion present in these complexes was found to be in the range, 0.55 to 0.70%. As we could not get the other analyses

(C,H,N, etc.) of these samples, stoichiometry of the complexes could not be determined.

The type of ligands used have large size so that it is reasonable to assume that only one ligand molecule will be capable of interacting with the metal ion situated within the supercage of zeolite Y. Such a conclusion was arrived at in the case of zeolite encapsulated Salen complexes[46,148]. The remaining coordination sites may be occupied by the oxide ions or water molecules. We hope that the vacant coordination sites or positions with labile solvent molecules make such zeolite encapsulated complexes catalytically more efficient.

8.3.1 Electronic Spectra

The electronic spectra of all the complexes were taken as solid state spectra. The observed bands and their assignments are given in Table VIII.1. In these complexes, the d-d bands were difficult to be observed because the complexes were situated within the cage and the absorptions may be very weak.

8.3.2 IR Spectra

The infrared spectral data of the zeolite encapsulated complexes are given in Tables VIII.2a & 2b. The Spectra show the prominent bands of the complexes in the region 1000–2000 cm^{-1} (Fig.8.3). The C–N stretching band clearly indicates the coordination of the ligand with the metal ion inside the zeolite cage.

Table VIII.1 Electronic Spectral Data

Sample	Absorptions (cm^{-1})	Assignment
CuQHAY	39700	intraligand
	33880	intraligand
	27440	charge transfer
	23060	charge transfer
	19025	d-d
CuQHFY	39700	intraligand
	33880	intraligand
	28810	intraligand
	25060	charge transfer
CuQHSY	38380	intraligand
	27440	intraligand
	23060	charge transfer
	18025	d-d transition
CuQHTY	39700	intraligand
	34900	intraligand
	22180	charge transfer
CoQHAY	38380	intraligand
	28810	intraligand
	20160	${}^4A_2 \longrightarrow {}^4T_1(P)$
CoQHFY	30320	intraligand
	24020	intraligand
	23420	charge transfer
CoQHSY	31140	intraligand
	25620	intraligand
CoQHTY	32910	intraligand
	28810	intraligand

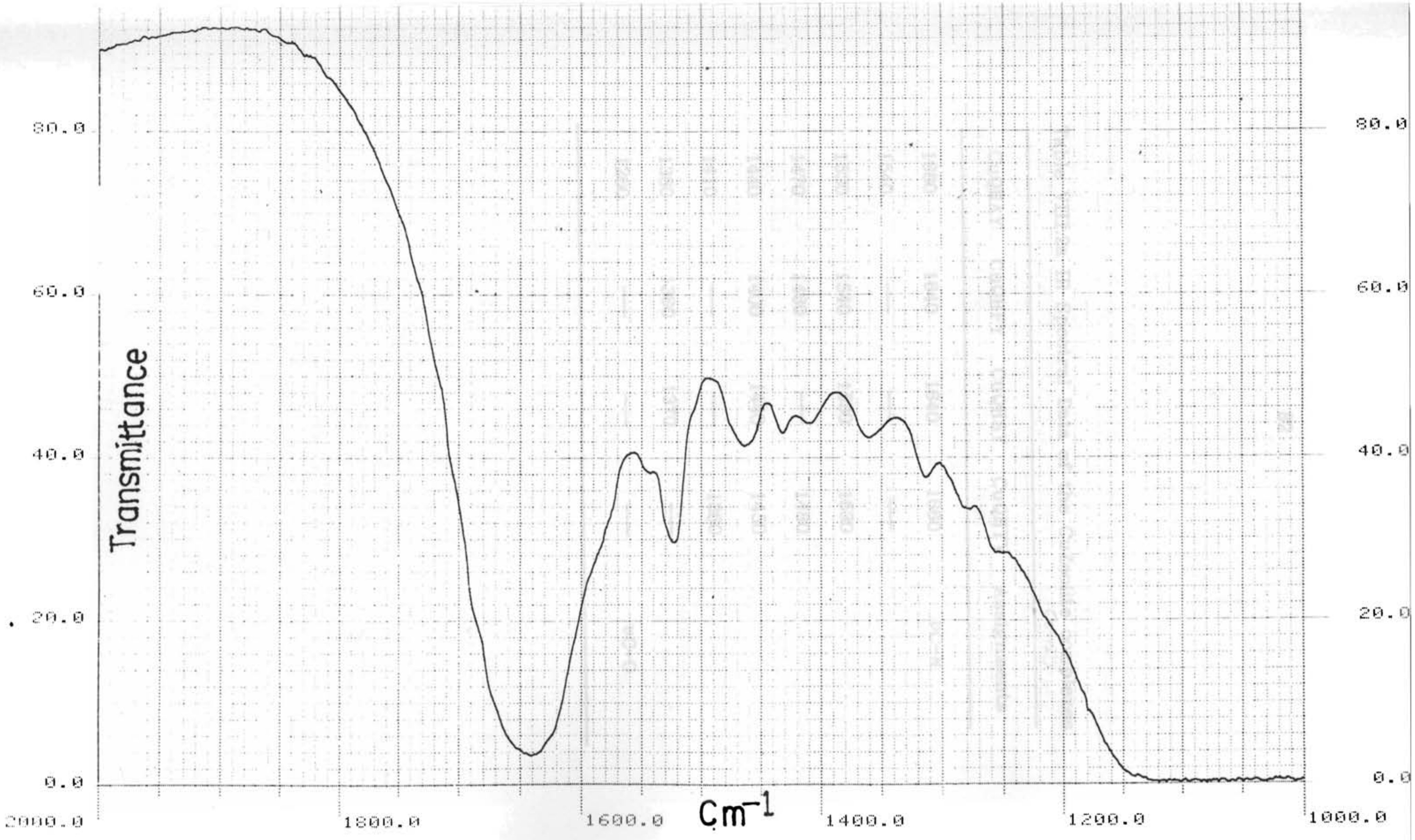


Fig. 8.3 Infrared spectrum of CuQHAY

Table VIII.2a IR Spectral Data of the CuZeolite complexes
(cm^{-1})

CuQHAY	CuQHFY	CuQHSY	CuQHTY	Assignments
1660	1640	1640	1660	υC-N
1540	—	—	—	
1530	1540	1530	1530	
1470	1480	—	1480	
1440	1400	1440	1450	
1410	—	—	1360	
1360	1360	1370	—	
1260	—	—	—	υC-O

Table VIII.2b IR Spectral Data of the CoZeolite complexes

(cm^{-1})

CoQHAY	CoQHFY	CoQHSY	CoQHTY	Assignments
1650	1640	1640	1660	υC-N
1530	1540	1530	—	
1470	1480	—	1480	
1440	1400	1440	1450	
1410	—	—	1360	
1360	1360	1370	—	
1260	—	1260	—	υC-O

8.3.3 X-ray diffraction studies

The results of the X-ray diffraction studies obtained for ZeoliteNaY, CuZeoliteNaY and for the metal complex encapsulated zeolite, CuQHAY are given in Table VIII.3. The peak positions obtained for all the three substances may be seen to be almost identical suggesting them to be isostructural. The strong peak obtained for CuQHAY at 13.65 might be caused by complexation. Similar results have also been observed for the other zeolite encapsulated metal complexes synthesised.

8.3.4 ESR Spectra

The 'g' values for the synthesised zeolite encapsulated complexes are given in Table VIII. 4. The copper complexes show axially symmetric epr indicative of a distorted octahedral geometry. Probably, one ligand and water molecules provide the coordination in these complexes. The spectra of the cobalt complexes recorded at liquid nitrogen temperature show a weak signal at $g \sim 4.3$, which could not be observed at room temperature. This signal may be due to one of the low lying Kramer's doublet of a distorted octahedral cobalt(II) ion.

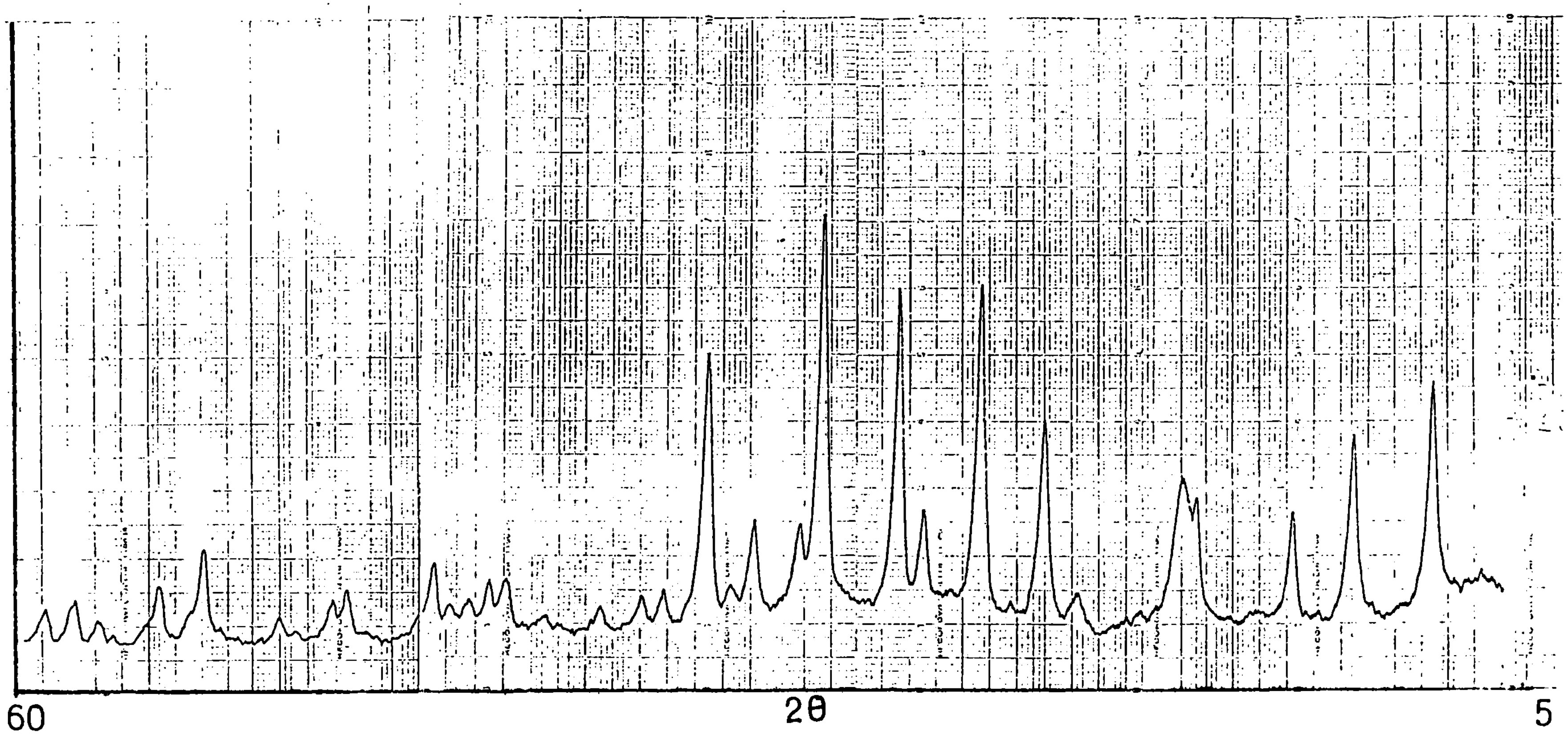


Fig. 8.4 XRD pattern of zeolite Nay

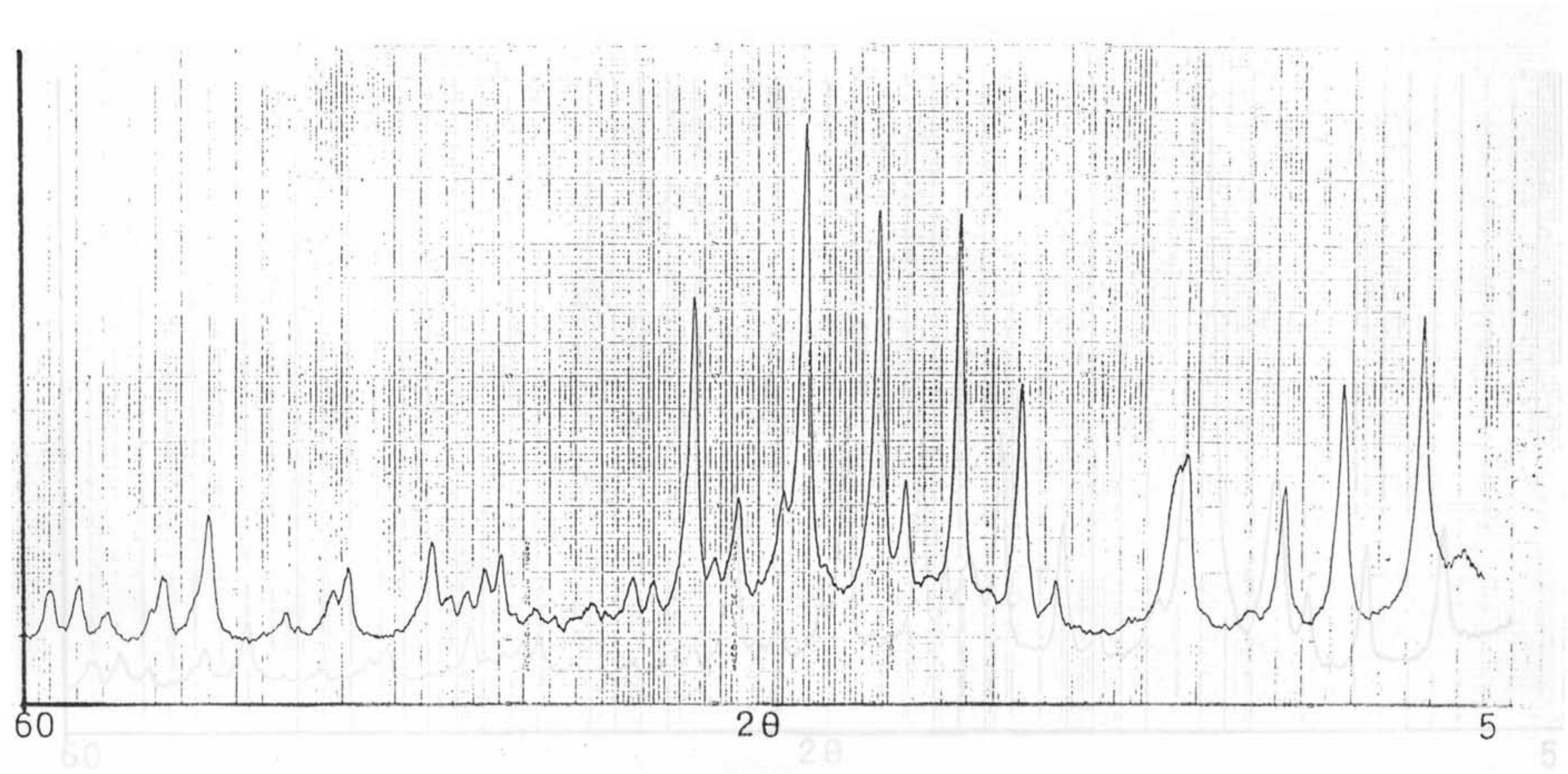


Fig. 8.5 XRD pattern of CuNay

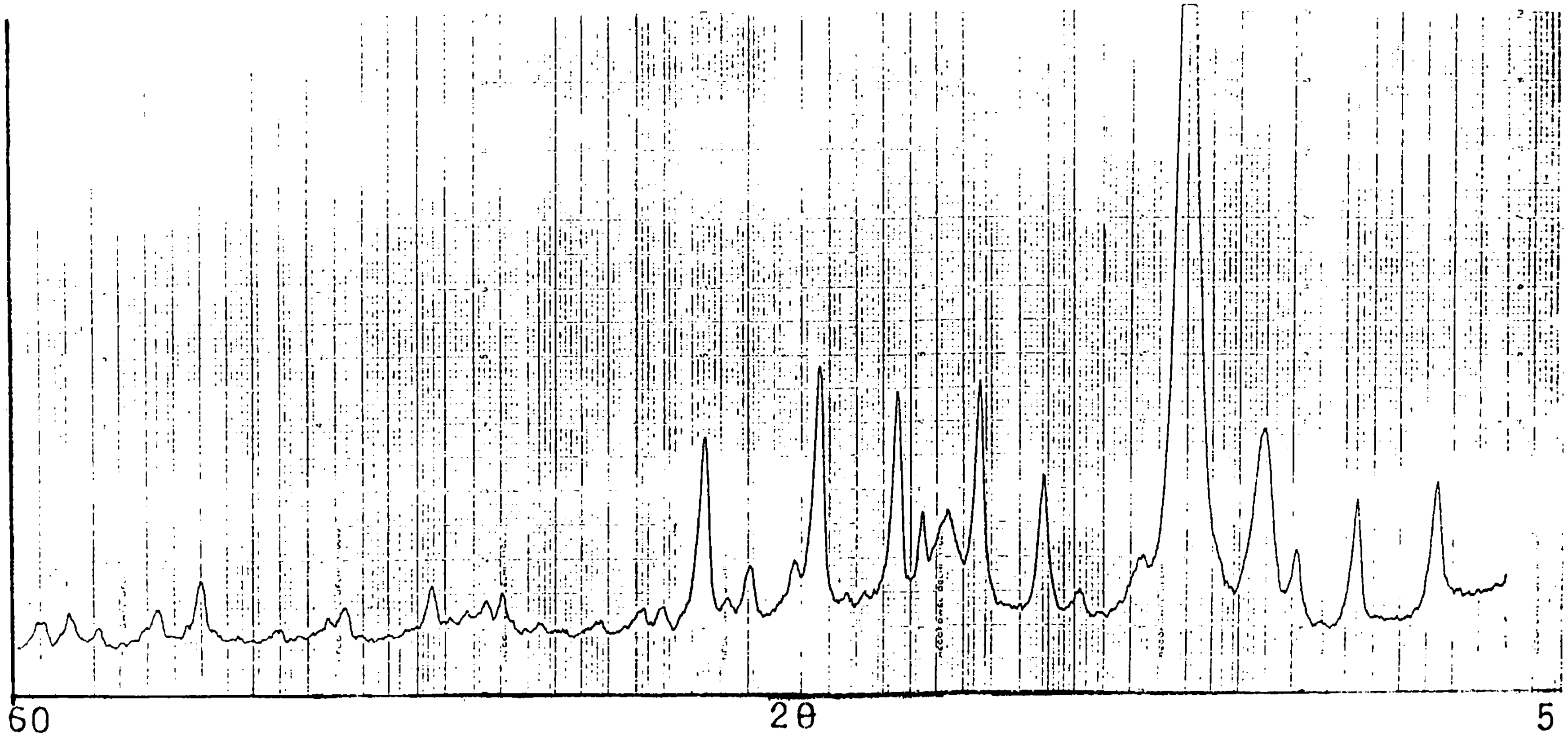


Fig. 8.6 XRD pattern of CuQHAY

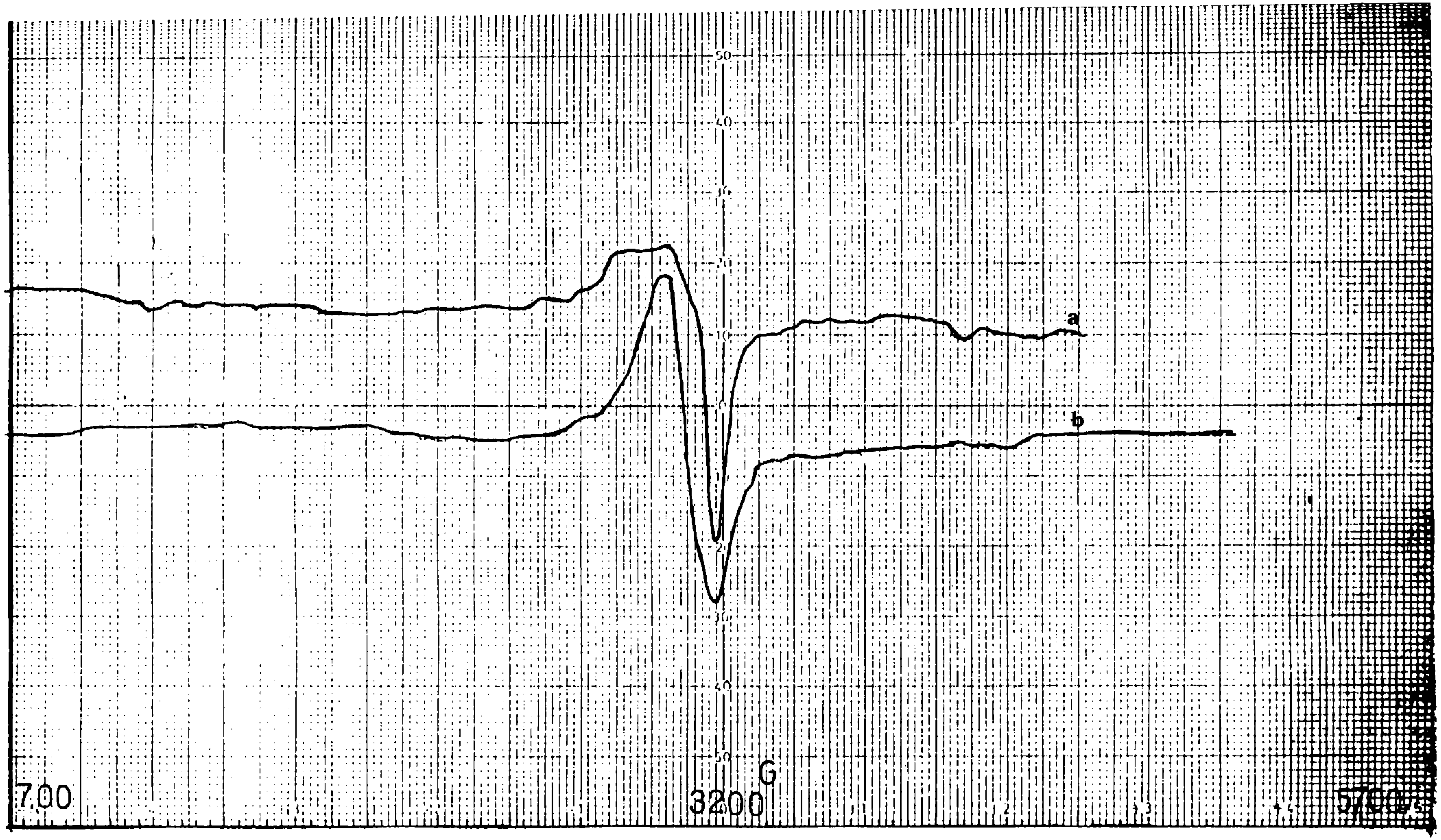


Fig. 8.7 ESR spectra of

a, CuNaY b, CuQHAY

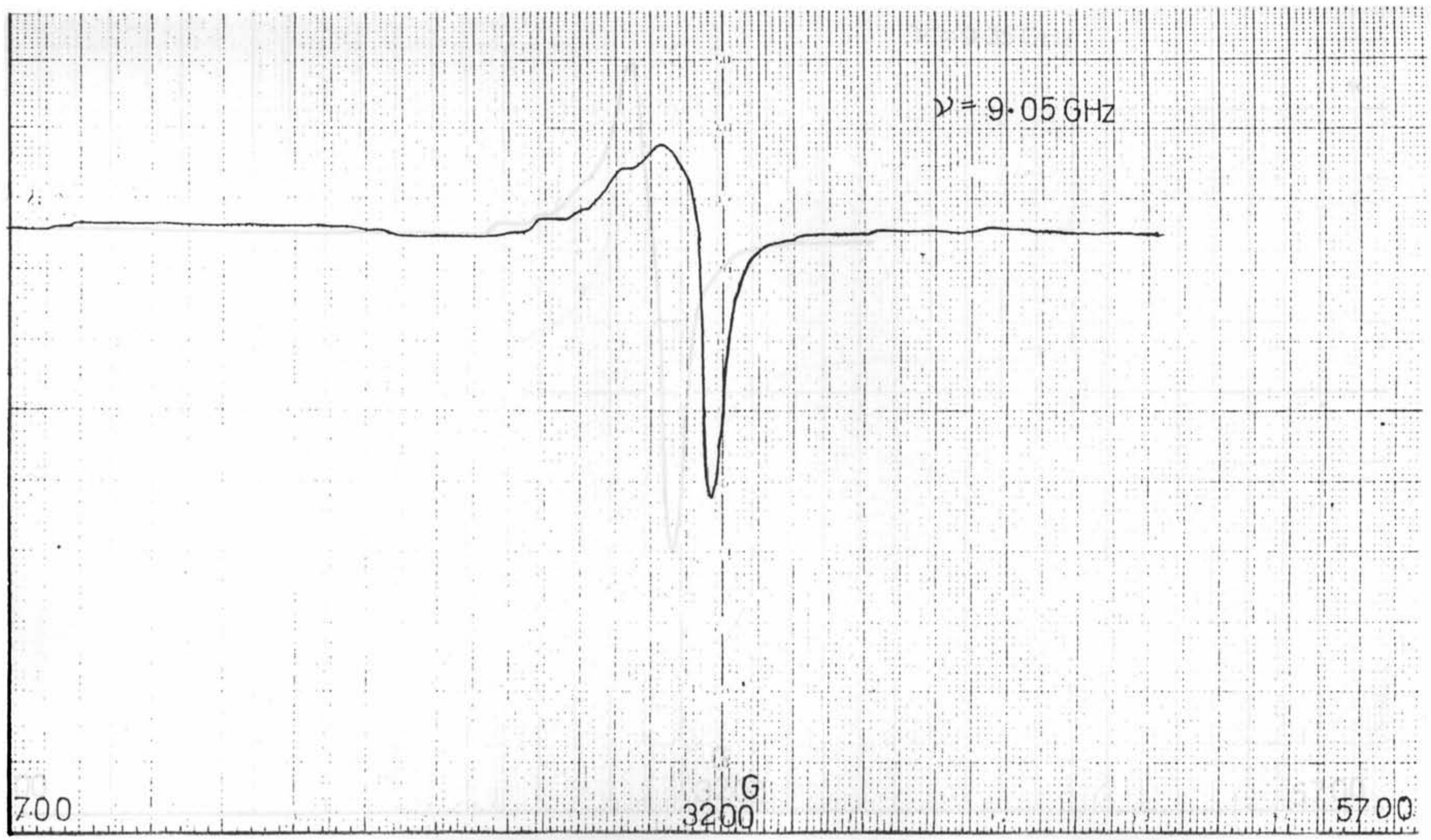


Fig. 8.8 ESR spectrum of CuQHFY

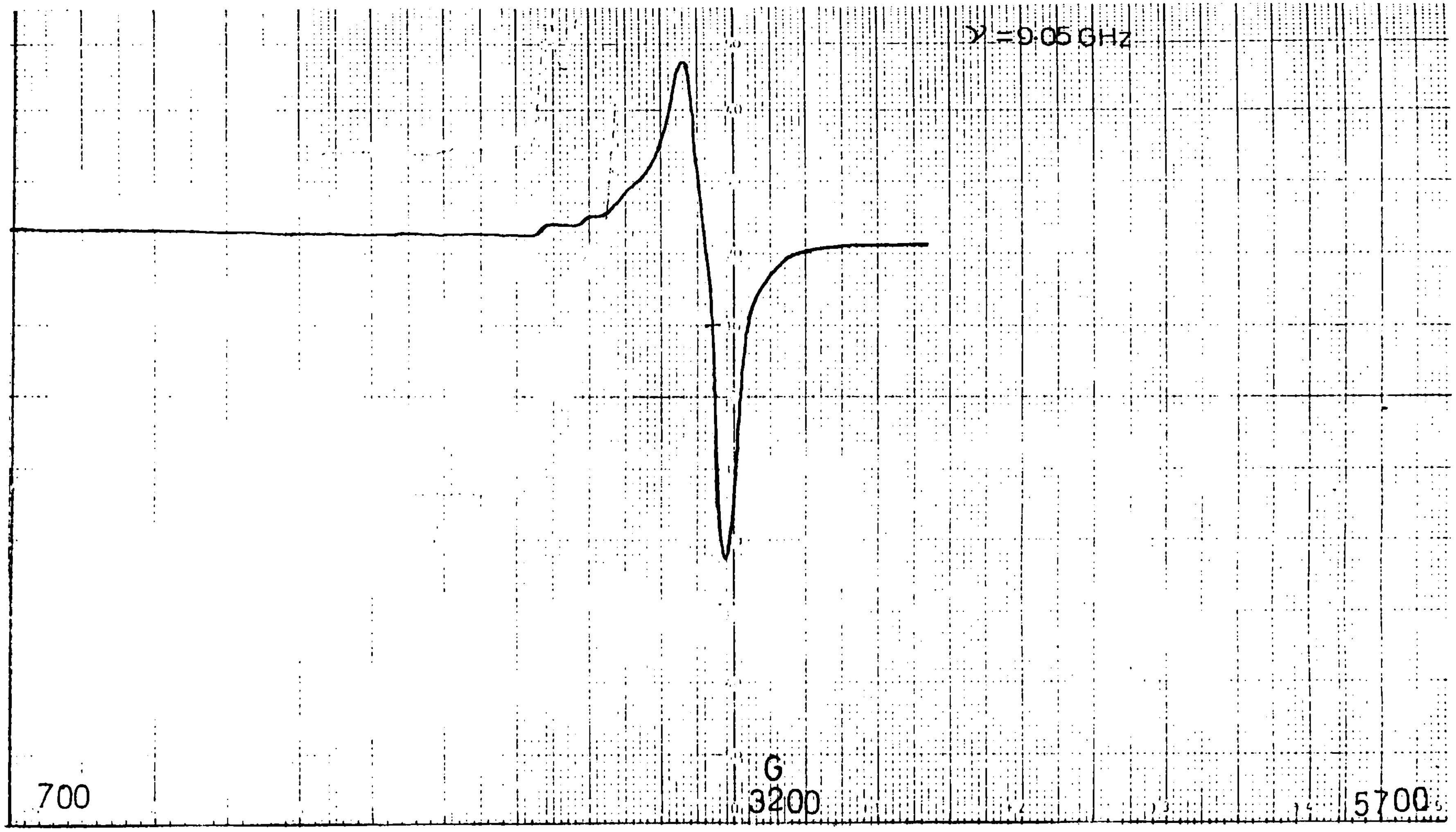


Fig. 8.9 ESR spectrum of CuQHSY

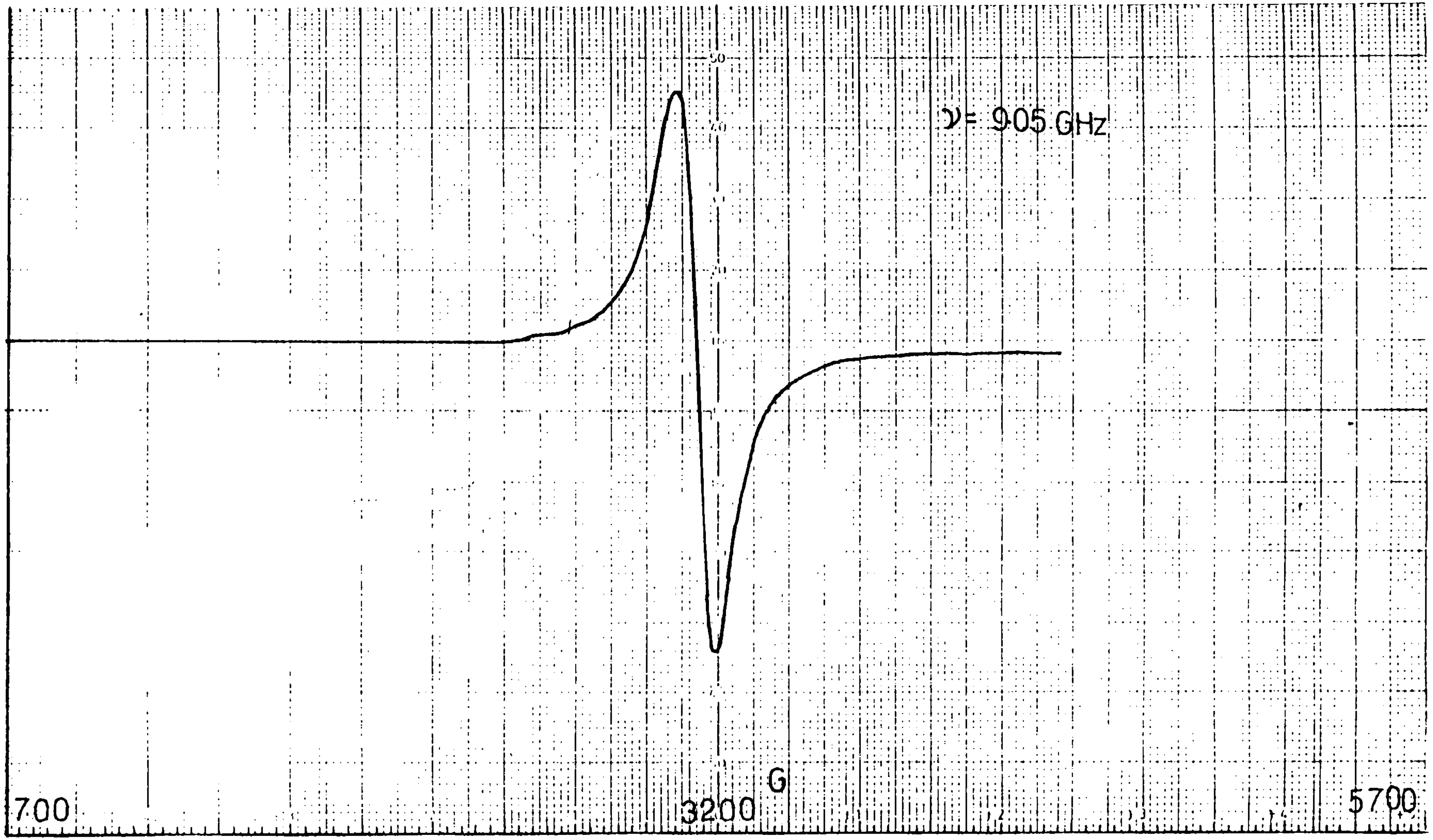


Fig. 8.10 ESR spectrum of CuQHTY

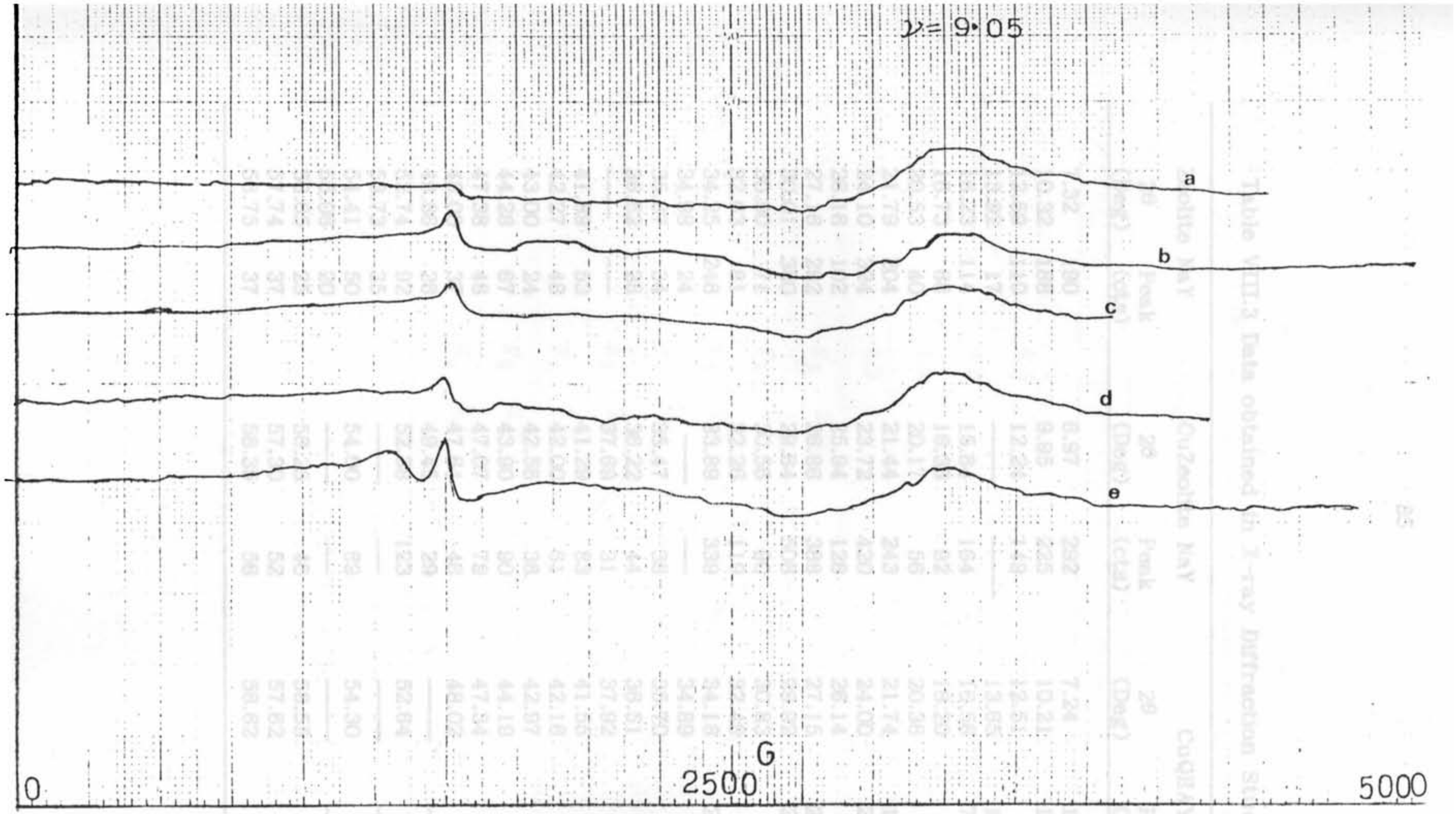


Fig. 8.11 ESR spectra of

a, CoNaY b, CoQHAY c, CoQHFY d, CoQHSY e, CoQHTY

Table VIII.3 Data obtained in X-ray Diffraction Studies

Zeolite NaY		CuZeolite NaY		CuQHAY	
2θ (Deg)	Peak (cts)	2θ (Deg)	Peak (cts)	2θ (Deg)	Peak (cts)
7.32	190	6.97	292	7.24	146
10.32	188	9.95	225	10.21	139
12.59	110	12.24	149	12.51	85
13.92	17	——	——	13.65	169
16.23	114	15.84	164	16.56	734
16.73	88	16.36	92	18.20	46
20.53	40	20.17	56	20.36	31
21.79	204	21.44	243	21.74	161
24.10	324	23.72	420	24.00	262
26.18	102	25.94	128	26.14	98
27.16	292	26.86	388	27.15	246
30.01	380	29.64	506	29.92	296
30.90	71	30.56	90	30.83	55
32.63	81	32.26	119	32.49	61
34.25	246	33.89	339	34.18	202
34.98	24	——	——	34.89	40
35.87	34	35.47	38	35.70	27
36.62	28	36.22	44	36.51	24
——	——	37.69	31	37.92	34
41.69	53	41.29	83	41.55	55
42.27	48	42.00	61	42.16	37
43.00	24	42.58	38	42.97	45
44.28	67	43.90	90	44.19	61
47.38	48	47.07	79	47.34	45
48.00	37	47.64	46	48.02	29
49.86	26	49.45	29	——	——
52.74	92	52.38	123	52.64	74
53.73	35	——	——	——	——
54.41	50	54.00	69	54.30	44
55.06	20	——	——	——	——
56.65	25	56.25	40	56.55	28
57.74	37	57.30	52	57.62	34
58.75	37	58.35	56	58.62	32

Table VIII.4. EPR Spectra of the Zeolite encapsulated Metal Complexes

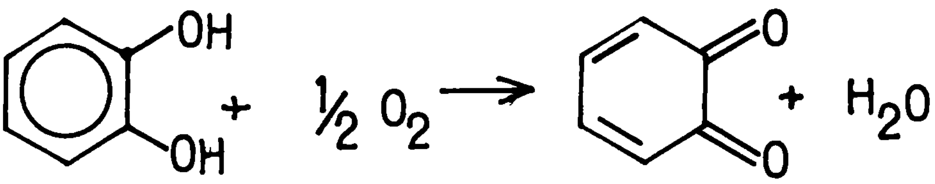
Compound	g		A(Gauss)
CoQHAY	4.3		---
CoQHFY	4.3		---
CoQHSY	4.3		---
CoQHTY	4.3		---
CuQHAY	$g_{\parallel}$	2.48	150
	$g_{\perp}$	2.1	
CuQHFY	$g_{\parallel}$	2.2	150
	$g_{\perp}$	2.01	
CuQHSY	$g_{\parallel}$	2.5	125
	$g_{\perp}$	2.0	
CuQHTY	$g_{\parallel}$	2.2	125
	$g_{\perp}$	2.0	

CHAPTER IX

CATALYTIC ACTIVITY STUDIES IN THE OXIDATION OF 3,5-DITERTIARYBUTYLCATECHOL TO QUINONE

9.1 INTRODUCTION

Catalysis by transition metal complexes is one of the frontier areas of chemistry. At present many valuable organic compounds are prepared in this route. This includes stereo and shape selective synthesis of drugs in small quantity to bulk preparation of chemicals. Liquid phase oxidation of catechol and its derivatives catalyzed by metal complexes like copper(II), iron(III), ruthenium(II) and vanadium(II) complexes have been reported[149-152]. The metal ion catalyzed oxidation of 3,5-ditert-butylcatechol by oxygen has been carried out in the presence of metal salts in slightly alkaline aqueous methanol in which the main product was 3,5-ditert-butyl-o-benzoquinone[153]. Studies of metal chelate catalysed oxidation of pyrocatechol to o-benzoquinone using bidentate chelating agents such as 4-nitrocatechol and tetrabromocatechol as auxilliary ligands have been reported[154,155]. The metal chelate catalyzed oxidations of catechol derivatives have been compared to free manganese(II) ion and base catalysed auto-oxidations. Such a study would provide new information on the activation of oxygen by metal ions, a subject of interest to synthetic organic chemists[156]. In this chapter, we present our studies on the catalytic activity of the metal complexes of BHQ, QHA, QHF, QHS and QHT in the oxidation of 3,5-ditert-butyl catechol (DTBC) to corresponding quinone (DTBQ). This reaction is chosen because it is easy to follow the formation of product, quinone, which has a characteristic absorption at 400 nm.



9.2 EXPERIMENTAL

9.2.1 Materials and methods

The catalytic oxidation of DTBC to the corresponding quinone has been studied in the presence of the manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 2,3- bishydrazinoquinoxaline (BHQ) and manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of 3-hydroxyquinoxaline-2-carboxalidine-*o*-aminophenol (QHA), and manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of 3-hydroxyquinoxaline-2-carboxalidenefurfurylamine (QHF), and manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of 3-hydroxyquinoxaline-2-carboxaldehyde semicarbazone (QHS), and manganese(III), iron(III), cobalt(III), nickel(II) and copper(II) complexes of 3-hydroxyquinoxaline-2-

carboxaldehyde thiosemicarbazone (QHT). The catalytic oxidation was also carried out with zeolite encapsulated cobalt(II) and copper(II) complexes of QHA, QHF, QHS and QHT. Details regarding the synthesis of the complexes have been given in the previous chapters.

The catalytic oxidations were carried out in DMF which was made 0.1 M with respect to triethylamine to increase its basicity. The concentration of the catalyst was kept at 1.0×10^{-4} M and the ratio of the concentration of the catalyst to that of the metal complexes was maintained below 1:10. The weights of the complexes employed for the catalytic reactions have been given in Table IX.1. The total volume of the reaction mixture was 100 mL after initiation. The stock solutions of DTBC were prepared afresh before each experiment to avoid change in its concentration due to auto-oxidation.

The following procedure has been employed for determing the rate of conversion of DTBC in the presence of simple metal complex catalysts. The reaction was initiated by adding adequate volume of the stock DTBC solution to the solution containing the appropriate amounts of the catalyst in DMF. The progress of the reaction was monitored by following the absorbance of the product formed at 400 nm against suitable blank. The absorbance measurements were made by extracting about 3 mL of the reaction solutions at an interval of 5 minutes. The concentration of the

Table IX.1 Catalytic oxidation of DTBC using simple complexes

Catalyst	Weight of catalyst taken x 10^3 (g)	Rate of conversion (mol dm^{-3} s^{-1})
$[Mn(QHA)_2]$	2.91	5.8228×10^{-7}
$[Fe(QHA)_3]$	4.23	8.7225×10^{-8}
$[Co(QHA)_2]$	2.93	1.5214×10^{-7}
$[Ni(QHA)_2]$	2.93	3.8813×10^{-8}
$[Cu(QHA)_2]$	2.95	3.3219×10^{-6}
$[Mn(QHS)_2]$	2.57	5.2283×10^{-5}
$[Fe(QHS)_3]$	3.73	2.9410×10^{-8}
$[Co(QHS)_2]$	2.59	1.1525×10^{-6}
$[Ni(QHS)_2]$	2.59	4.3161×10^{-8}
$[Cu(QHS)_2]$	2.61	4.6290×10^{-8}
$[Mn(BHQ)_2Cl_2]$	2.52	6.6746×10^{-7}
$[Co(BHQ)_2Cl_2]$	2.54	6.1664×10^{-7}
$[Ni(BHQ)_2Cl_2]$	2.57	7.9913×10^{-8}
$[Cu(BHQ)_2Cl_2]$	2.57	9.9490×10^{-8}
$[Zn(BHQ)_2Cl_2]$	2.54	3.6135×10^{-8}
$[Mn(QHF)_2]$	2.79	5.1180×10^{-7}
$[Fe(QHF)_3]$	4.05	5.7298×10^{-8}
$[Co(QHF)_2]$	2.81	4.6109×10^{-7}
$[Ni(QHF)_2]$	2.81	4.5910×10^{-8}
$[Cu(QHF)_2]$	2.83	8.6186×10^{-8}

product formed was obtained from the absorbance data using a molar absorption coefficient of 2818 at 400 nm (Fig.9.1).

The initial rates of the reaction were obtained by fitting the concentration versus time data into a polynomial of the form,

$$c = a_1 + a_2t + a_3t^2 + \ldots.$$

and obtaining the slope of the curve[157] at t = 0. A software called "Axum" (Trimetrix, 1989) was used for this purpose. All the kinetic results were found to be reproducible within an error of 2.5%.

For determining the rate of conversion of DTBC in the presence of zeolite encapsulated metal complexes, a slightly different procedure was employed.

For each kinetic run, about 10 identical reaction mixtures were prepared. Each of them was initiated by adding the same amount of zeolite encapsulated metal complex. 3 ml of the reaction solution was carefully withdrawn from each of them successively, after time intervals differing by an increasing time period of 2 minutes, and their absorbance was measured at 400 nm where the product of the reaction has an absorption maxima.

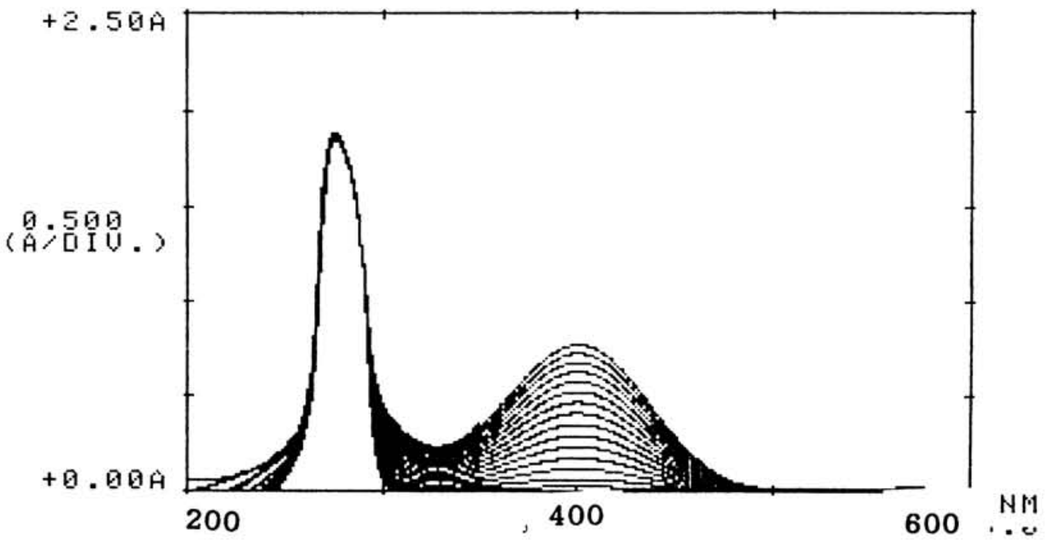


Fig. 3.1 Time dependant formation of quinone, spectra recorded at an interval of 300 secs in the absence of any catalyst

9.3 RESULTS AND DISCUSSION

9.3.1. Catalytic activity studies of simple complexes

The oxidation reaction of DTBC was found to be very slow even in presence of the metal complex catalyst. However, on adding the amine, the reactions acquired a measurable rate. Therefore in all experiments, triethylamine was added. DTBC may partially be dissociated in the presence of amine so that it can easily interact with the metal complexes.

The results of these studies are given in Table IX.1. The data clearly indicate that most of the synthesised complexes have appreciable catalytic activity. However, the complexes with ligand QHT were found to be almost catalytically inactive.

The reaction mechanism assumed here includes associative oxygen species absorbed on metal ion. Generally the manganese and cobalt complexes are found to be with higher activity. The greater dioxygen affinities of these metals may be the reason for this observation. In the catalytic reaction, the first step may be the interaction between DTBC and the metal centres of the catalyst.

The intermolecular electron transfer within the ternary complex (DTBC-CoL-0_2) generates corresponding quinone. In order to form the ternary complex, the prerequisite is that the catalyst should have vacant coordination sites. Surprisingly even the octahedral complexes show some activity in the reaction. It may be proposed that on the approach of DTBC molecule some of the labile metal ligand bond dissociates and give way to the formation of the ternary complex. However, for arriving at real mechanism of these catalytic reactions, detailed kinetic studies are required.

Even the cobalt and manganese complexes of QHT did not show catalytic activity. The cobalt complexes of QHT are in the +3 oxidation state and are inert complexes. Hence, there is not much possibility of dissociation of the metal-ligand bond and interacting with DTBC.

9.3.2. Catalytic activity studies of the zeolite encapsulated metal complexes.

The Table IX.2 shows the results of the catalytic activity studies of zeolite encapsulated cobalt(II) and copper(II) complexes of QHA, QHF, QHS and QHT. Even though the amount of the metal ions contained in the zeolite encapsulated complexes (less than 3.0×10^{-4} g) is smaller than that in the simple complexes, ($\sim$ 0.064 g), the rate of conversion is found to be greater in the case of the zeolite encapsulated complexes. This may be due to the restrictions imposed with regard to the number of ligands that can be accommodated in the zeolite cage resulting in an increase in the number of vacant coordination sites around the metal ions.

Table IX.2 Catalytic oxidation of DTBC using zeolite encapsulated complexes.

Catalyst	Weight of catalyst taken x 10^2 (g)	Rate of conversion (mol dm^{-3} s^{-1})
CoQHAY	5.0	1.042×10^{-6}
CoQHFY	5.0	4.070×10^{-7}
CoQHSY	5.0	9.550×10^{-7}
CoQHTY	5.0	6.150×10^{-7}
CuQHAY	5.0	7.130×10^{-7}
CuQHFY	5.0	2.980×10^{-7}
CuQHSY	5.0	5.690×10^{-7}
CuQHTY	5.0	7.920×10^{-7}

SUMMARY

The thesis deals with the synthesis, characterization and catalytic activity studies of some new metal complexes of the ligands having a quinoxaline ring as the integral part. The thesis is divided into nine chapters. Chapter I of the thesis presents an introduction to the synthetic, structural, bonding and applications of interesting metal complexes of heterocyclic ligands. The scope of the present investigation is also outlined in this chapter. Chapter II gives the procedures for the synthesis of the ligands, purification methods adopted, and various techniques employed for the characterization of the metal complexes.

Chapter III deals with the synthesis and characterization of the manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of the ligand 2,3-bishydrazinoquinoxaline (BHQ). All the complexes are non-electrolytes in DMF. The complexes have the general formula $[M(BHQ)_2Cl_2]$, where, M = manganese(II), cobalt(II), nickel(II), copper(II) or zinc(II). The IR spectra of the complexes indicate that the ligand binds the metal through the nitrogen atom of the primary amino group. From the magnetic moment measurements and UV-Visible spectral studies, an octahedral structure has been assigned for the complexes.

In Chapter IV studies on the synthesis and characterization of manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base derived from the condensation of 3-hydroxyquinoxaline-2-carboxalidene-*o*-aminophenol (QHA) are presented. All the complexes are microcrystalline and are stable in air. Conductivity measurements reveal that all these complexes are non-electrolytes in DMF. The empirical formula for the manganese(II), cobalt(II), nickel(II) or copper(II) complex is found to be $[M(QHA)_2]$, where M represents the metal ion, and for the iron(III) complex, it is found to be $[Fe(QHA)_3]$. The IR spectra of the complexes indicate that the ligand QHA acts as a bidentalte ligand using its azomethine nitrogen and one of the phenolic oxygens. The magnetic and electronic spectral data suggest a high-spin octahedral structure for the manganese(II) and iron(III) complexes, tetrahedral structure for the cobalt(II) and nickel(II), and a square planar structure for the copper(II) complex. The EPR spectrum of the copper complex reveals a square planar structure.

Chapter V deals with studies on the manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of 3-hydroxyquinoxaline-2-carboxalidene-2-furfurylamine (QHF). Conductivity measurements indicate that all the complexes are non-electrolytes in DMF. The empirical formula for the complexes is found to be $[M(QHF)_2]$, where, M = manganese(II), cobalt(II), nickel(II) or copper(II), and for the iron(III) complex, it corresponds to [Fe(QHF)$_3$]. The infrared spectral data indicate that the ligand uses its phenolic oxygen and azomethine nitrogen to bind the metal ions. Magnetic moment measurements and UV-Visible spectral studies suggest that a tetrahedral structure has been assigned for the manganese(II), cobalt(II) and nickel(II) complexes, an octahedral structure for the iron(III) complex and a square planar structure for the copper(II) complex. Appearance of the EPR spectrum of the copper(II) complex is similar to that of a square planar complex.

Synthesis and characterization of manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of 3-hydroxyquinoxaline-2-carboxaldehyde semicarbazone (QHS) are presented in chapter VI. Conductivity measurements in DMF indicate the non-electrolytic nature of the complexes. The empirical formula for the complexes is found to be [M(QHS)$_2$], where M = manganese(II), cobalt(II), nickel(II) or copper(II), while that for the iron(III) complex is [Fe(QHS)$_3$]. The IR spectral data suggest that the ligand coordinate in a tridentate manner in the case of manganese(II), cobalt(II), nickel(II) and copper(II) complexes using phenolic oxygen, azomethine nitrogen and carbonyl oxygen and in the iron(III) complex, the QHS is bidentate with azomethine nitrogen and phenolic oxygen donors. Magnetic moment value and UV-Visible data suggest an octahedral structure for the complexes.

Chapter VII gives details about the synthesis and characterization of manganese(III), iron(III), cobalt(III), nickel(II) or copper(II) complexes of 3-hydroxyquinoxaline-2- carboxaldehyde thiosemicarbazone (QHT). All the complexes are found to be non-electrolytes in DMF. The general empirical formula for the complexes is found to be $[M(QHT)_2]$, where, M = nickel(II) or copper(II). For the other three complexes, this corresponds to $[M(QHT)_3]$. Magnetic moment measurements reveal that manganese and cobalt are in the +3 oxidation state in these complexes despite the fact that metal(II) salts were employed for the synthesis. An octahedral structure is assigned for all the complexes except copper(II) complex which is found to have a square planar structure. EPR spectral data also agree with the above observation.

Chapter VIII presents our attempts to explore the possibility of using some of the complexes as size and shape selective catalysts. Cobalt(II) and copper(II) complexes of the ligands QHA, QHF, QHS and QHT were synthesised in the supercage of zeolite Y. The results obtained from the IR, UV-Visible and ESR spectroscopic studies and XRD methods are presented in this chapter.

Chapter IX of the thesis deals with the catalytic activity studies of the synthesised complexes in the oxidation of 3,5-ditert-butylcatechol to the corresponding quinone by molecular oxygen. The progress of the reaction was followed by noting the absorbance at an interval of 300 seconds at 400 nm which is characteristic of the quinone. Most of the complexes prepared were found to have good catalytic activity. The activity of the zeolite encapsulated complexes were found to be greater than that of the simple complexes.

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