SYNTHESIS, CHARACTERISATION AND CATALYTIC ACTIVITY STUDIES OF SOME NEW TRANSITION METAL CHELATES OF THE SCHIFF BASES DERIVED FROM 3-HYDROXYQUINOXALINE-2-CARBOXALDEHYDE

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JOSE MATHEW

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022

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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.

K.K.

Kochi
7-11-1995

Dr. K. K. Mohammed Yusuff
(Supervising Teacher)

PREFACE

The thesis deals with our studies on synthesis, characterisation and catalytic activity studies of metal complexes of Schiff bases, N,N'bis-(3-hydroxyquinoxaline-2-carboxalidene)-ethylenediamine (QED), N,N'bis-(3-hydroxyquinoxaline-2-carboxalidene)-*o*-phenylenediamine (QPD) 3-hydroxyquinoxaline hydrazone (QHD) and N,N'bis-(3-hydroxyquinoxaline-2-carboxalidene)diethylenetriamine (QDT). The phenolic oxygens and azomethine nitrogen are the main donor atoms of the multidentate ligands. As these atoms are attached to the electron deficient positions of the quinoxaline ring, the ligand field strength of these Schiff bases would be weaker, when compare to that of Schiff bases derived from salicylaldehyde. The complexes of these ligands are found to be interesting from structural point of view and exhibit anomalous magnetic behavior.

The thesis is divided into 11 chapters; Chapter I presents a brief introduction to the coordination chemistry of Schiff bases with special emphasis on tetradentate Schiff base complexes.

The details of the preparation and purification of the ligands are given in Chapter II. Furthermore, the various characterisation techniques employed are also described in this chapter. These techniques include elemental analysis, magnetic and conductance measurements and techniques like IR. UV-Vis., ESR and Mossbauer spectroscopy.

Chapters III to VII deal with the synthesis and characterisation of the complexes of these ligands with manganese(II), iron(III), cobalt(II), nickel(II) and copper(II). To explore the possibility of using these complexes as catalysts, we have studied their catalytic activity in some selected reactions. The catalytic activity of manganese(II) complexes towards the hydrogen peroxide decomposition was studied and the details are presented in Chapter VIII. Cobalt(II) and copper(II) complexes were screened for their catalytic activity in the oxidation of 3,5-di-tert-butylcatechol to quinone and our findings are given in Chapter IX.

In an attempt to heterogenise these systems we have supported Fe(III) complexes on Seralite SRC 120 resin and cobalt(II) complexes on activated charcoal. These supported complexes were tested for their catalytic activity in the oxidation of ascorbic acid and p-thiocresol respectively and the experimental methods and conclusions are described in Chapter X and Chapter XI respectively.

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CHAPTER III STUDIES ON MANGANESE(II) COMPLEXES

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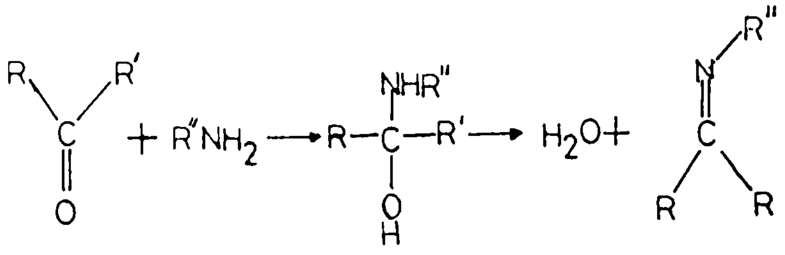
CHAPTER I

INTRODUCTION

Easy design and synthesis of ligands containing the azomethine group provide ample scope for the fabrication of specifically designed complexes for an inorganic chemist. The compounds containing this group are widely known as Schiff bases since the synthesis of this kind of compounds was first reported by Schiff[1]. Different methods for the synthesis of these ligands have been reviewed by Dayagi and Dagani[2]. Schiff base complexes can generally be prepared by the interaction of metal ions and concerned Schiff bases in suitable solvents. However, in some cases the complexes were prepared by reacting the metal ions, aldehydes and amines[3-6].

The most common method for obtaining a Schiff base (4) is straight forward, as indicated in the condensation reaction between (1) and (2) with the formation of an intermediate hemiaminal (3).



(1) (2) (3) (4)

The basic strength of C=N group is insufficient by itself in some cases to permit the formation of stable complexes. Therefore, it is necessary that the Schiff base ligand should have one more coordination site so that it can form a five or six membered ring and thus increase the stability of the complex by chelate effect. Among the compounds which meet this requirement are salicylaldimine, its N-hydroxy derivative, *i.e.*, salicylaldoxime, Schiff bases derived from β-ketoamines, *o*-hydroxynaphthaldehyde etc. Information on the structure and properties of some of the complexes formed by such Schiff base ligands has been brought out in an excellent review written by Holm, Everett and Chakravorthy[7].

Schiff bases derived from salicylaldehyde, substituted salicylaldehyde and *o*-hydroxynaphthaldehyde show enol-imine and keto-amine tautomerism in solution[8]. In the case of salicylaldimines, the enol-imine form predominates in solution; while the keto-amine predominance is usually observed in the case of 2-hydroxy-1-naphthaldimines. 2-Hydroxynaphthaldimines exist almost exclusively as the enol-imine form in solution[9].

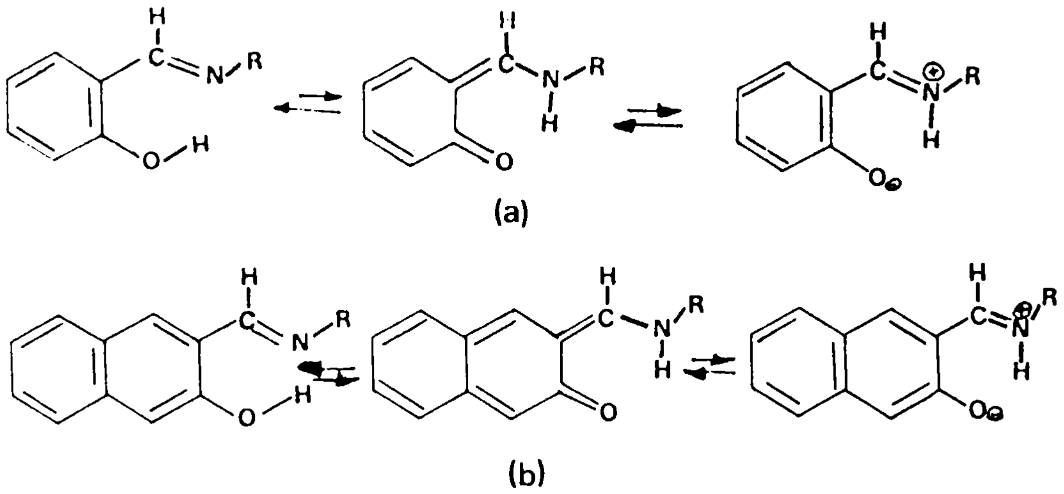


Fig. 1.1 Keto-amine/enol-imine tautomeric equilibria

(a) salicylaldimines (b) 2-hydroxy-1-naphthaldimines.

During the last few years a significant amount of information on the synthesis and characterisation of transition metal complexes of the Schiff bases has appeared in the literature, and this has resulted in the flow of useful ideas between inorganic chemists and biochemists[10-13]. The model complexes derived from specially designed and synthesised Schiff bases help us to understand the chemistry of biological systems, particularly, enzymes and proteins. About 30 percent of enzymes are metalloenzymes and they are involved in acid-catalysed hydrolysis, redox reactions, decarboxylation and processes that rearrange carbon-carbon bonds[14-23]. The role of a metal ion in such reactions are found to depend upon the nature of its coordination sphere[24-26]. It is possible through studies on manipulated Schiff base complexes to obtain better knowledge of the factors that modify the coordination sphere and the electronic properties of the central metal atom and thus get more insight into the behaviour of the complexes in biological systems. The events happening at the metal centre of a biological system and its synthetic model need not essentially be the same. However, the model studies help in explaining the role of the metal site and its coordination environment to bring out a particular function by undergoing a formal or partial reversible oxidation state change. The redox property of some biologically important systems have been studied by Lovecchio *et al.*[27]. Electrochemical studies of acyclic Schiff base complexes have been carried out to understand the behaviour of such systems[28.29].

The stereo and shape selectivity of natural systems can be imposed on its synthetic model by adequate modification of the ligand. Metal complexes with chiral Schiff base ligands are able to catalyse a reaction in a stereo selective manner. Chiral Mn(III) Salen complexes catalyse the epoxidation of olefin in this manner in the presence of stoichiometric oxidants[30-34]. Asymmetric catalysis using transition metal complexes is considered as a thrust programme for research support[35]. It would be difficult to discuss all the aspects of Schiff base complexes here. So further discussions will be limited to the structural aspects of Schiff base complexes with multidentate ligands.

Bidentate Schiff base complexes

Bidentate Schiff bases are usually N,N, N,S or N,O donor set ligands. Majority of bidentate ligands utilised for the synthesis of Schiff bases belong to the N,O donor set and these ligands generally act as chelating mono anions.

Bidentate Schiff bases derived from salicylaldehyde can form bis- or tris- chelates with M(II) and M(III) metal ions respectively. The bis-chelates are of considerable interest as they vary in structure from coplanar to tetrahedral, depending upon the nature of the metal ion and the nature of the ligand. Usually the coordination of phenolic oxygen and azomethine nitrogen induces a low spin configuration at the metal centre.

The magnetic susceptibility measurements are used as a simple excellent method to resolve the geometry of the complexes. N-Aryl substituted salicylaldimine Co(II) complexes have magnetic moment values ranging from 4.36 to 4.45 BM suggesting a tetrahedral structure for these complexes. It was thought that the bulky substituents have forced a tetrahedral configuration around the metal ions.

The Cu(II) complexes of bidentate salicylaldimine derivatives have been found to have planar structure isomorphous with corresponding Ni(II) complexes. However, Sacconi *et al.* have shown that the phenolic oxygen atom under certain circumstances may bridge two metal atoms, forming binuclear complexes[36,37]. In such a case the Schiff base should be considered as a tridentate ligand.

Tridentate Schiff base complexes

Usually tridentate Schiff bases have N_2O, NO_2, N_2S and NSO donor sets[38-41]. They usually form mononuclear complexes with Ni(II), Cu(II), VO and UO_2. The vacant coordination sites have been found to be taken up by solvent molecules. These types of Schiff bases can form binuclear or polymeric complexes using bridging donor atoms. Indications about the structure of these complexes would be easily obtained by the measurement of magnetic moments. The dimeric structure gives an abnormal magnetic moment to the complexes due to the spin exchange between the metal centers. The Schiff bases derived from the condensation of salicylaldehyde with o-aminophenol and 2-aminopyridine are prototype ligands of this kind; while the former gives dimeric or polymeric structure, the latter leads to octahedral complexes[42-44].

Tetradentate Schiff base complexes

Tetradentate Schiff bases with an N_2O_2 donor set have been widely studied for their ability to coordinate metal ions. The properties of these complexes are determined by the electronic nature of the ligand as well as its conformational behavior. In 1933, Pfeiffer *et al.* have noted that bis(salicylaldehyde)ethylenediiminecobalt(II), now commonly called as CoSalen has an unusual property of absorbing molecular oxygen from atmosphere leading to subsequent darkening of the complex[45]. This phenomenon was later studied thoroughly and a significant amount of information is now available in the literature[46-51]. The importance of tetradentate Schiff base complexes in modelling oxygenase enzymes has been widely discussed[52]. Such complexes are interesting in view of catalysis also. As the dibasic ligand can form neutral complexes with vacant coordination sites, their potential in catalysis is being explored by many workers.

One of the most studied Mn(II) tetradentate Schiff base complexes is Mn(II)Salen. After its synthesis by Pfeiffer *et al.*[53] considerable amount of work has been done on the system, especially on its magnetic properties[54-56]. These studies revealed the existence of strong antiferromagnetic exchange interactions. The dimeric structure proposed for this system was further supported by powder X-ray diffraction studies. Though Mn(II) tetradentate Schiff base complexes are air stable, they have a tendency to undergo oxidation in solution. Three kinds of oxidation products are possible from Mn(II) Schiff base complexes: MnSalen-O_2-MnSalen, $[Mn(Salen)O]_n$, a polymeric complex, and another species which can be considered as an intermediate in the formation of polymeric complexes of the type $[Mn(Salen)O]_n$. Similar manganese(II) Schiff base complexes with substituent groups in the phenyl rings were assumed to have a binuclear or a linear chain structure.

Iron(III) Schiff base complexes generally form spin-free paramagnetic and weakly coupled antiferromagnetic systems. [Fe(Salen)Cl] was found to be dimeric in structure. Again the structure was confirmed by magnetic and X-ray diffraction techniques[57-59]. The temperature dependent asymmetry observed in the Mössbauer spectra of dimeric [Fe(Salen)Cl] has been explained in terms of a spin-spin relaxation effect[60]. The nitromethane solvate of [Fe(Salen)Cl] reveals a five coordinated monomeric structure. Not much information about the structure of the iron(III) complexes could be obtained, as electronic transitions are forbidden. The low energy absorptions shown by some dimeric Schiff base Fe(III) complexes have been explained in terms of forbidden transition with increased intensity due to simultaneous electron pair excitation[61].

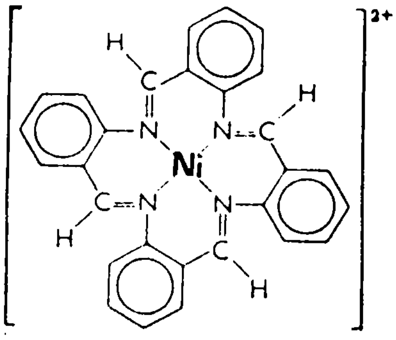
The Co(II) complexes of tetradentate Schiff bases have received great deal of attention owing to their ability to undergo reversible adduct formation with molecular oxygen. Different crystalline and solvate forms have been found with differing capacity of oxygenation, including one inactive form for CoSalen. The inactive form was found to be a dimeric species. In this form the cobalt becomes five coordinated with a rectangular based pyramid. The close packing of the dimeric units may be the reason for oxygenation inactivity.

Pyridine adduct of the CoSalen in solution undergoes oxygenation readily. The axially bonded ligands may be capable of influencing the electron distribution in the equatorial ligand. Polarographic studies and studies on steric effects of axially bonded ligands reveal that, though the packing effects are the major factor which determine the oxygenation activity, electronic effects of the substituent groups are also important. Co(II) planar Schiff base complexes are normally low-spin in nature, with magnetic moment values in the range 2.1-2.9 BM.

A great deal of confusion arose in the early development of the chemistry of Schiff base complexes of nickel. This has been mainly due to the ability of the compounds, particularly bidentate complexes, to aggregate to various degrees in solid state, to undergo conformational change in solution and to coordinate additional water molecules. NiSalen was found to exist as centrosymmetric dimers in the solid state, incorporating approximately planar NiSalen units.

The nickel(II) Schiff base complexes derived from salicylaldehydes and o-hydroxynaphthaldehydes show interesting ligand effects. It has been shown that the substituent effect causes nickel(II) complexes to change their geometry in going from solution to solid state[62-64]. This change also depends on the donor character and polarity of the solvent.

The self condensation of aminobenzaldehyde in the presence of Ni(II) and Cu(II) ions give products, isolated as salts, with the following structure:



The perchlorate, tetrafluoroborate and tetraphenylborate of nickel(II) complexes are all diamagnetic whereas iodide, nitrate and thiocyanate are all fully paramagnetic with magnetic moment values around 3.2 BM. The chloride and bromide complexes, on the other hand, have the intermediate magnetic moment of 1.68 and 1.47 BM respectively at room temperature. The magnetic susceptibilities of the latter two salts and their variations with temperature have been interpreted in terms of a thermal distribution between a singlet ground state with no unpaired electrons and triplet excited state with two unpaired electrons[65].

Copper(II) Schiff base complexes are also interesting due to their spectral, magnetic and structural properties. The colour of the copper Schiff base complexes was earlier used to distinguish their geometries. Waters *et al.*[66] proposed that the green complexes have coordination number exceeding four and brown or violet complexes have four coordinate copper.

The CuSalen was shown to have a dimeric structure using X-ray diffraction methods. However, the magnetic moment values reported are in the range 1.8 - 2.0 BM, indicating the absence of antiferromagnetic interactions, despite the known dimeric nature of these compounds. This was suggested to result from copper-oxygen bond lengths and angles involved between the metal centers.

The electronic spectra of Cu(II) tetradentate Schiff base complexes have been extensively studied. Three or four transitions are possible for such systems depending on the symmetry involved[67,68].

The electrochemical studies of the complexes as well as the NMR spectral pattern of the ligands prove that the substitution of a suitable substituent like halogen, nitro group etc. on the Schiff base chelate greatly influences the electron density distribution in the ligand and the redox potentials of the chelate[69-71]. The substituent effects and donor properties of the ligand will be reflected in the classical spectroscopic properties of the chelate like IR, UV-VIS, EPR etc.

Scope of the present study

From the foregoing account, it is clear that the composition, symmetry, chemical, physical and electronic properties of compounds with tetradentate Schiff bases are controlled by the effect of the ligands themselves. By introducing electron releasing or electron withdrawing substituents, by incorporating an aromatic ring as an integral part of the chelate to stiffen the ligand, or by attaching a group which can provide a fifth coordination etc., one can `tune' the electronic and magnetic properties of a metal chelate derived from planar quadridentate Schiff bases.

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

- To synthesise Schiff bases which can force a particular geometry for the metal complexes and thus alter the electronic nature of the chelate.
- To investigate the nature of coordination of such Schiff base ligands with metal ions like manganese(II), iron(III), cobalt(II), nickel(II) and copper(II).
- To undertake a qualitative study of the catalytic activity of such complexes in some selected reactions.

Schiff bases with an electron withdrawing heterocyclic ring system derived from 3-hydroxyquinoxaline-2-carboxaldehyde would be interesting, as their ligand field strengths are expected to be weaker than the Schiff bases derived from salicylaldehyde.

Four Schiff bases have been synthesised by the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde with

a) ethylenediamine	(QED)
b) *o*-phenylenediamine	(QPD)
c) hydrazine hydrate	(QHD) &
d) diethylenetriamine	(QDT).

New complexes of Mn, Fe, Co, Ni and Cu with the above mentioned ligands have been synthesised and characterised. With the limited instrumental facilities available to us, we have been able to explain the vibrational, electronic and magnetic properties of these complexes in some depth and study their catalytic activity in a qualitative manner in some selected reactions.

The complexes reported herein (with or without suitable modification) may find application as industrial catalysts in future. It can also be expected that our results would find use in the promising area of biomimetic chemistry.

CHAPTER II

EXPERIMENTAL TECHNIQUES

Details of the general reagents used, the preparation and characterisation of the ligands and the various analytical and physico-chemical methods employed in the characterisation of the metal complexes are presented in this chapter. Procedural details about the synthesis and catalytic activity studies of the complexes are given in appropriate chapters.

2.1 REAGENTS

The following metal salts were used; $Mn(CH_3COO)_2.4H_2O$ (E. Merck, GR), anhydrous $FeCl_3$ (Aldrich, 98%), $Co(CH_3COO)_2.4H_2O$ (E. Merck, GR), $Ni(CH_3COO)_2.4H_2O$ (Merck, 98%), $Cu(CH_3COO)_2.H_2O$ (E. Merck, GR)

Sodium pyruvate (SRL), *o*-phenylenediamine (Loba Chemie), ethylenediamine (BDH), hydrazine hydrate (SRL), diethylenetriamine (SRL, Technical Grade) and 3,5-di-*tert*-butylcatechol (Aldrich) were used for the present work.

Unless otherwise specified, all the other reagents were of analytical reagent grade. Solvents employed were either of 99% purity or purified by known laboratory procedures[72].

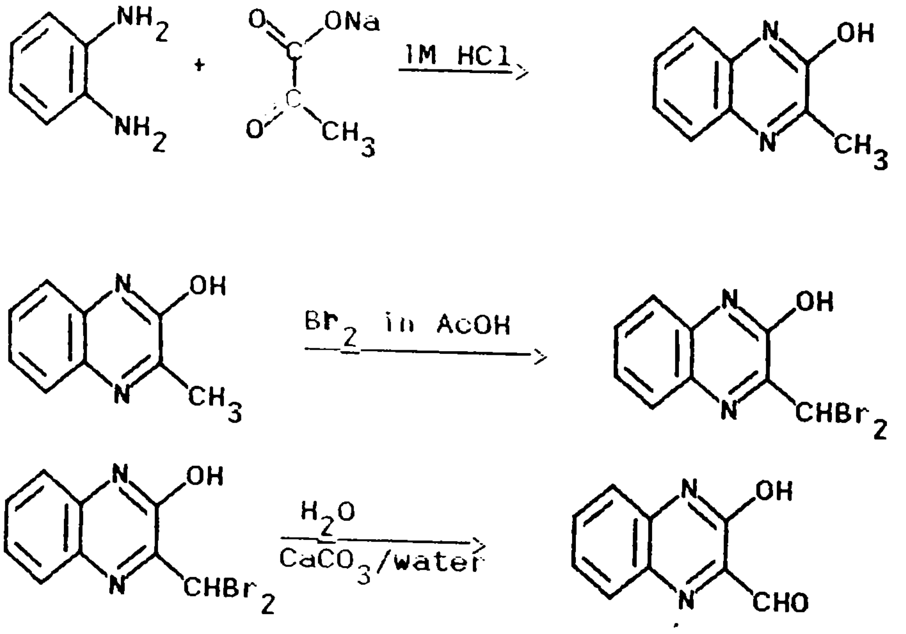
2.2 PREPARATION OF THE LIGANDS

A procedure, different from that reported by Ohle *et al.*[73] was used to synthesise 3-hydroxyquinoxaline-2-carboxaldehyde.

They have prepared this compound from 3-hydroxy-2-(D-arabino)tetrahydroxybutylquinoxaline by oxidation with potassium periodate, either by leaving overnight in the dark at room temperature or by heating at 100°C for 10 minutes in the presence of sodium bicarbonate. This procedure was found to be somewhat inconvenient for our purpose, not only because it could yield the aldehyde only in the hydrated form, but also the compound undergoes some unknown physical changes in presence of light. The following method was found to be suitable, as it would give sufficiently pure ligands which can be directly used without further purification. The aldehyde obtained by the new method has been found to be of spectral grade purity.

Synthesis of the aldehyde

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



I

II

III

3-Hydroxy-2-methylquinoxaline (I)

o-Phenylenediamine (0.1 mol; 10.8 g) and sodium pyruvate (0.1 mol; 11 g) were dissolved in 250 mL water each. A slight excess of con. 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 pale yellow compound was filtered, washed

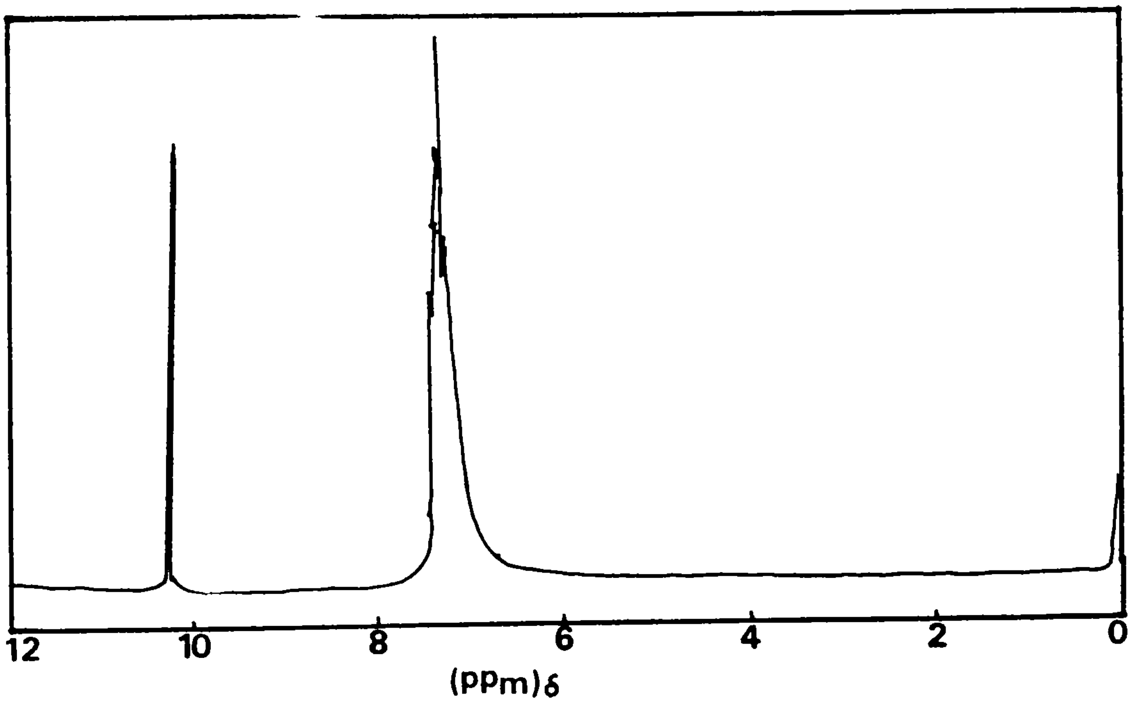


Fig. 2.1 NMR spectrum of 3-hydroxyquinoxaline-2-carboxaldehyde in d^6 DMSO (solvent peaks not shown)

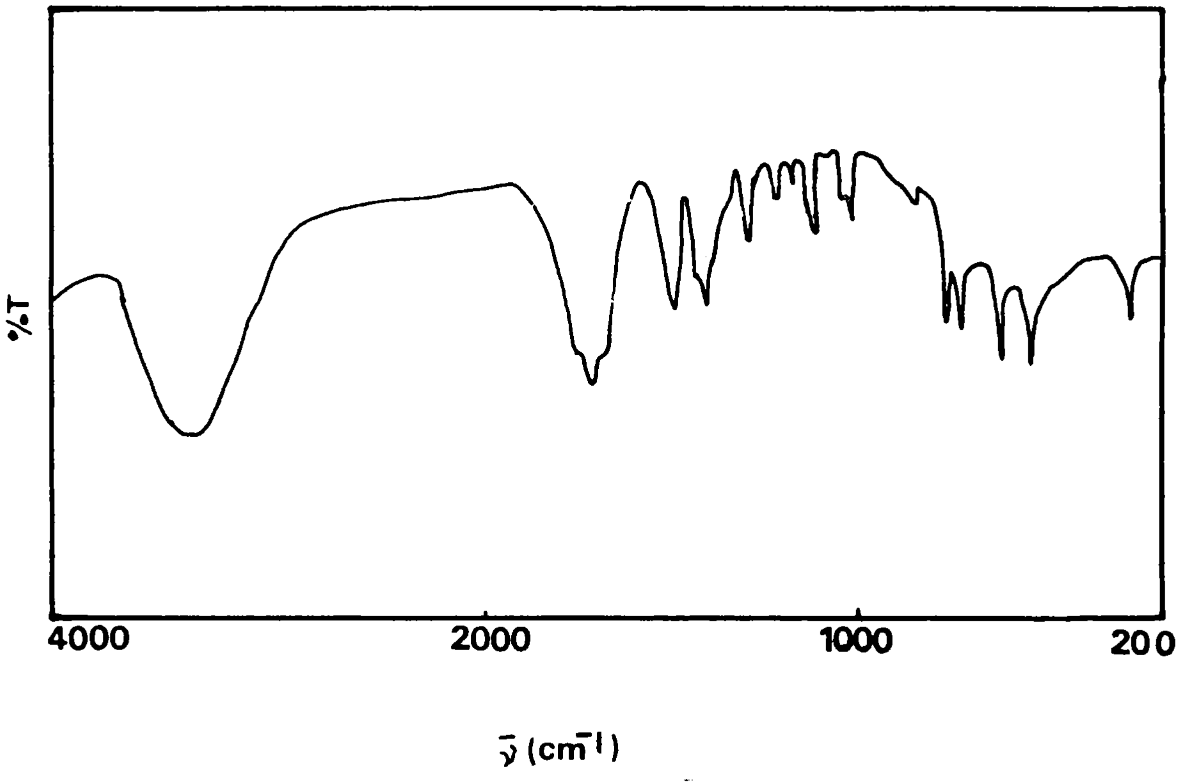


Fig. 2.2 IR spectrum of 3-hydroxyquinoxaline-2-carboxaldehyde

with water, and dried over anhydrous calcium chloride (Yield: 90%, m.p.: 255°C).

3-Hydroxy-2-dibromomethylquinoxaline (II)

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

3-Hydroxyquinoxaline-2-carboxaldehyde (III)

The dibromo compound (5 g) was thoroughly mixed with 20 g of precipitated calcium carbonate. This mixture was treated with water (1.5 L) in a 3 L RB flask and kept over a water bath for 2 h with occasional shaking. The aldehyde formed will remain in water and the solution was collected by filtering hot. The yellow aqueous solution thus obtained is very stable and this can be directly used after cooling, to prepare the Schiff bases.

Preparation of the Schiff bases

2.2.1 N,N'-bis(3-hydroxyquinoxaline-2-carboxalidene)ethylenediamine, (QED)

The aldehyde solution was made 0.025 molar with respect to HCl. An alcoholic solution of ethylenediamine (2 mL in 20 mL alcohol) was added to this drop by drop while the solution was stirred. The amine solution was added till the precipitation of the Schiff base was complete. The yellow compound thus obtained was filtered, washed with methanol and dried *in vacuo* over anhydrous calcium chloride (Yield: 50-60%, m.p.: 260°C).

2.2.2 N,N'-bis(3-hydroxyquinoxaline-2-carboxalidene)-*o*-phenylenediamine, (QPD)

The aldehyde solution was made 0.025 molar with respect to HCl. An aqueous solution of *o*-phenylenediamine (2 g in 20 mL water) was added to this drop by drop while the solution was stirred. The amine solution was added till the precipitation of the Schiff base was completed. The yellow compound thus obtained was filtered, washed with methanol and dried *in vacuo* over anhydrous calcium chloride (Yield: 60-70%, m.p.: 225°C).

2.2.3 3-Hydroxyquinoxaline-2-carboxaldehyde hydrazone, (QHD)

The aqueous solution of the aldehyde was made 0.05 molar with respect to HCl. An aqueous solution of 90% hydrazine hydrate (2 mL in 20 mL water) was added to this drop by drop while the solution was stirred. The amine solution was added till the precipitation of the Schiff base was complete. The yellow compound thus obtained was filtered, washed with methanol and dried *in vacuo* over anhydrous calcium chloride (Yield: 60-70%, m.p.: 200°C). This compound was reported[74] to have resonating structures (Fig. 2.5).

2.2.4 N,N'-bis(3-hydroxyquinoxaline-2-carboxalidene)diethylenetriamine (QDT)

The aldehyde solution was made very feebly acidic with one or two drops of con. HCl and an alcoholic solution of diethylene- triamine (2 mL in 20 mL alcohol) was added to this drop by drop with stirring. The amine solution was added till the precipitation of the Schiff base was complete. The yellow compound thus obtained was filtered, washed with methanol and dried *in vacuo* over anhydrous calcium chloride (Yield: 50-60%, m.p.: 200°C).

The structures of the Schiff bases are given in Fig. 2.5.

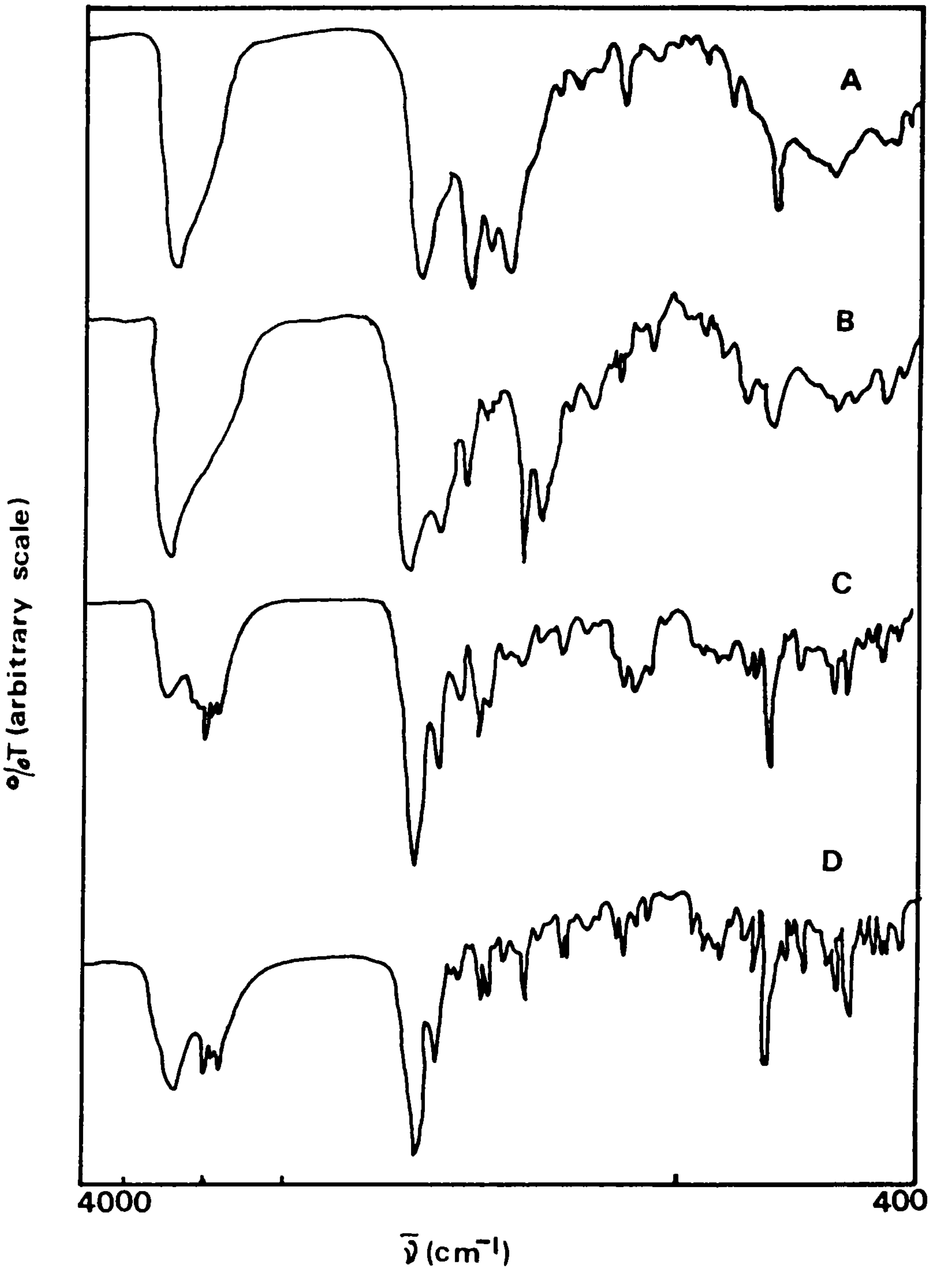


Fig. 2.3 IR spectra of the Schiff bases
A) QED, B) QPD, C) QHD and D) QDT

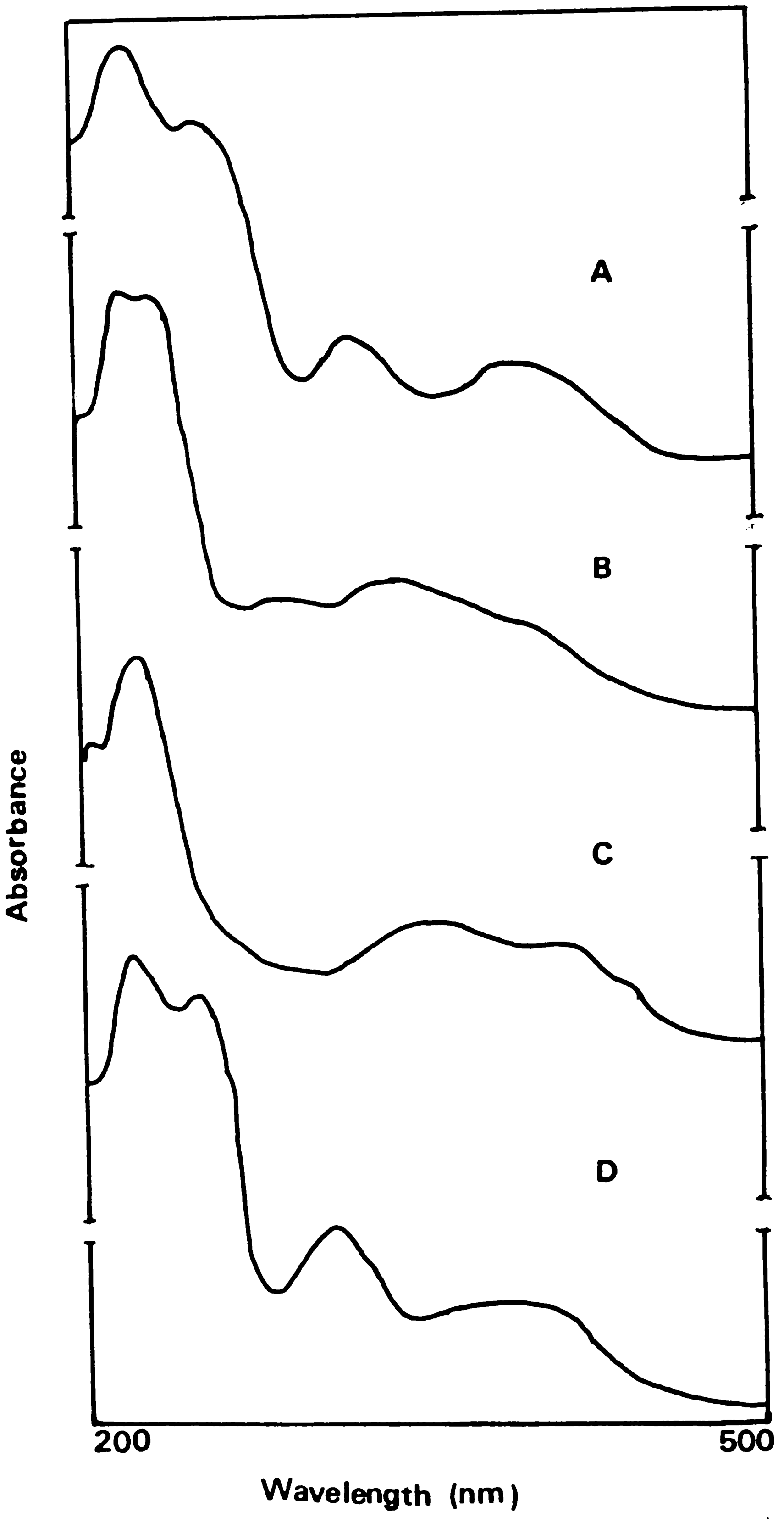


Fig. 2.4 UV-Vis spectra of the Schiff bases A) QED, B) QPD, C) QHD and D) QDT

Table II. 1 Analytical data of the Schiff bases

Compound	Found(calculated) %Carbon	%Hydrogen	%Nitrogen
QED	64.41 (64.52)	4.16 (4.3)	22.63 (22.58)
QPD	68.49 (68.57)	3.68 (3.81)	20.15 (20.00)
QHD	59.47 (59.66)	3.74 (3.86)	23.41 (23.20)
QDT	63.67 (63.77)	4.76 (4.83)	23.80 (23.77)

Table II. 2 Selected IR bands of the Schiff bases (cm^{-1})

Compound	ν_{O-H}	ν_{N-H}	$\nu_{C=N}$	ν_{C-N}	ρ_{C-H}	ν_{C-N}	$\delta_{C-H(Ph)}$
QED	3500s	--	1667s	--	874s	1267m	758s
QPD	3500s	--	1670s	--	--	1271w	760,758s
QHD	3500s	3013s	1667s	1101s	--	1282s	760s
QDT	3500s	3013s	1665s	1130s	875s	1284s	762s

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

2.3 ANALYTICAL METHODS

2.3.1 Estimation of metal ions

In all the cases, the organic part of the metal complexes was completely eliminated before estimation of the

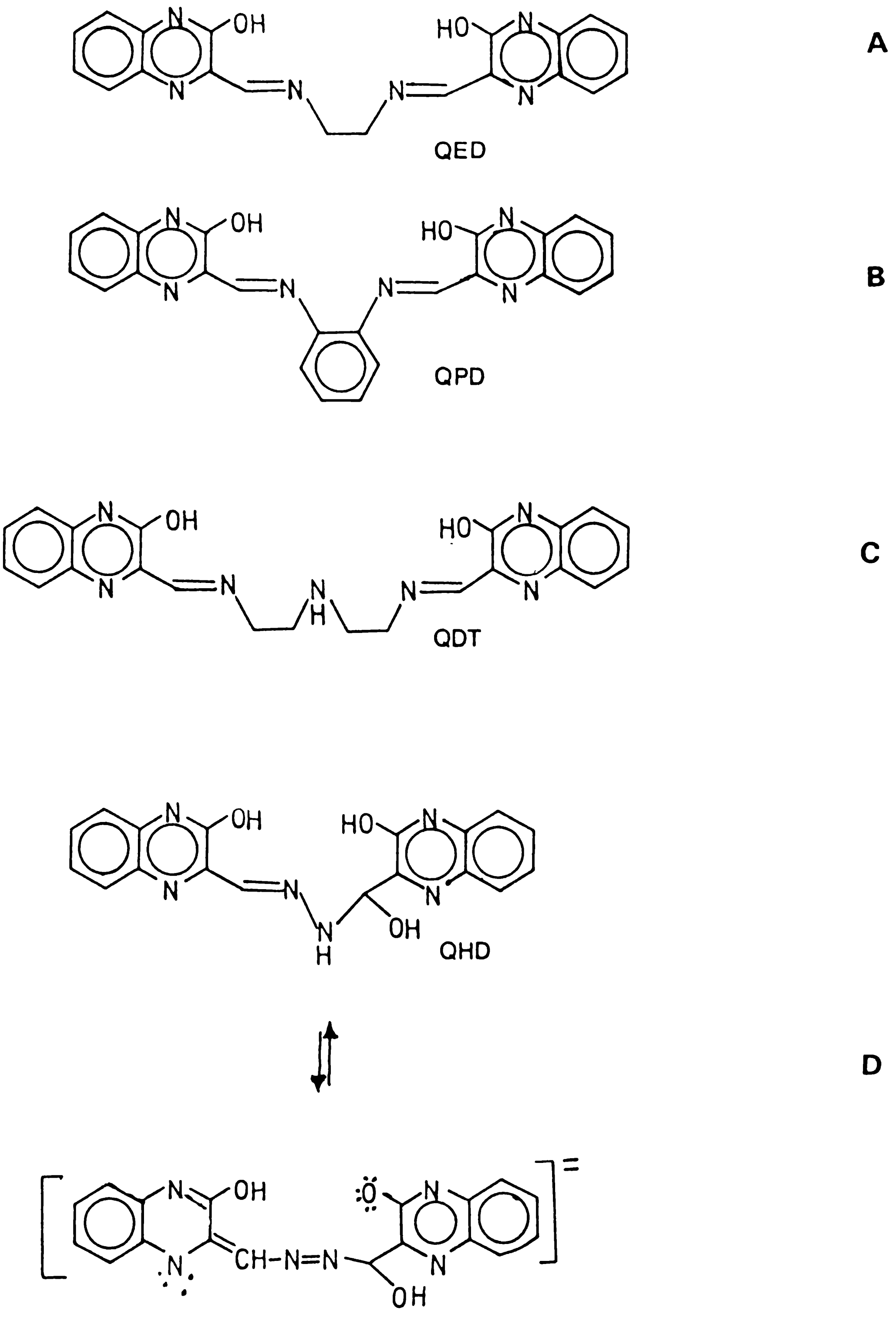


Fig. 2.5 Structures of the Schiff bases
A) QED, B) QPD, C) QDT and D) QHD

metals. The following procedure was used to eliminate the organic part of the complexes. A known weight of the metal complexes (0.2-0.3 g) was treated with con. sulphuric acid (5 mL) followed by con. nitric acid (20 mL). After the completion of the vigorous reaction, perchloric acid (5 mL, 60 %) was added. This mixture was maintained at the boiling temperature for 3 h on a sand bath. The clear solution thus obtained was evaporated to dryness. After cooling concentrated nitric acid (5 mL) was added and evaporated to dryness on a waterbath. The residue was dissolved in water and this solution was used for the estimation of the metals.

Manganese was estimated complexometrically using EDTA. Iron was estimated by titrating against standard potassium dichromate solution after reducing to Fe(II) with $SnCl_2$. Gravimetric procedures[75] were used for the estimation of cobalt and nickel. Cobalt was estimated by precipitating it as $[Co(C_5H_5N)_4](SCN)_2$ using ammonium thiocyanate and pyridine. Nickel was estimated as nickel dimethylglyoximate complex by adding an alcoholic solution of dimethylglyoxime followed by ammonia solution. Iodometric method was employed for the estimation of copper in the complexes.

2.3.2 CHN Analyses

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

2.3.3 Estimation of halogen

Halogen content of the iron complexes was determined by the peroxide fusion of the sample followed by the gravimetric precipitation as AgCl.

2.4 PHYSICO-CHEMICAL METHODS

2.4.1 Conductance measurements

Molar conductances of the complexes were determined at 28 °C using a conductivity bridge (Century CC 601) with a dip type cell and a platinised platinum electrode. The conductance studies were carried out in nitrobenzene as well as in pyridine and no significant differences have been detected. Though most of the complexes prepared have appreciable solubility in nitrobenzene, solutions of some samples were found to be unstable. But, pyridine could be used as a common solvent for all the complexes prepared and the solutions were found to be very stable also. So, the data obtained for the pyridine solutions are given in the text.

2.4.2 Magnetic susceptibility measurements

The magnetic susceptibility measurements were done at room temperature on a simple Gouy-type magnetic balance. The Gouy tube was standardised using $Co[Hg(SCN)_4]$ as the standard[76]. The effective magnetic moment was calculated using the equation,

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

where T is the absolute temperature and X'_m is the molar susceptibility corrected for diamagnetism of all the atoms present in the complex using the Pascal's constants[77-79].

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[80]. The procedure is given below:

Small filter paper strips were impregnated with a paste of the 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 reference. 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, 4600-400 cm^{-1} were taken both as nujol paste and as KBr discs on a Shimadzu 8101 FTIR spectrophotometer.

2.4.5 NMR spectra

NMR spectrum of the aldehyde was recorded on Hitachi R 600 High Resolution NMR spectrometer.

2.4.6 EPR spectra

The X-band EPR spectra of the complexes were taken using Varian E-112 X/Q band spectrometer. For the iron complexes, solid state spectra were recorded using quartz tubes. The spectra of manganese and cobalt complexes were recorded in DMSO at liquid nitrogen temperature. For copper complexes solution spectra in DMF were taken at -140 ^{o}C.

2.4.7 Mössbauer spectra

Mössbauer spectra were obtained (in zero magnetic field) on a polycrystalline sample at room temperature and at liquid nitrogen 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.

CHAPTER III

STUDIES ON MANGANESE(II) COMPLEXES

3.1 INTRODUCTION

Many manganese(II) complexes are known to oxidize alkyl benzenes, alcohols, carboxylic acids, phenols and ethers[81]. Its importance in biological electron transfer reactions have been discussed[82-84]. The redox activity, *i.e.* the capability of a metal ion to change between oxidation states, can be related to metal-metal interactions, the nature and also to the strength of the ligand field around the metal ion. Schiff base type ligands are interesting in this regard and the oxidation state accessibility of manganese has been explored by using large variety of ligands[85,86]. Also, there has been continuing interest in understanding the reaction chemistry of manganese(II) complexes towards oxygen resulting in oxygenated manganese(II) complexes[87-89]. Many manganese(II) complexes were reported to electrocatalyse the epoxidation of olefins[90]. In view of these, we have synthesised manganese(II) complexes of the Schiff base ligands QED, QPD, QHD and QDT and the results of our studies on these complexes are presented in this chapter.

3.2 EXPERIMENTAL

3.2.1 Materials

Details regarding the preparation and purification of the ligands QED, QPD, QHD and QDT are described in Chapter II.

3.2.2 Synthesis of the complexes

All the complexes were prepared by the following general procedure:

Finely powdered ligands (0.01 mol; 3.72 g of QED, 4.18 g of QPD, 3.44 g of QHD or 4.14 g of QDT) were treated with methanol (200 mL) containing NaOH (0.8 g, 0.02 mol). The solution was refluxed for 30 minutes and filtered if necessary. A solution of manganese(II) acetate (2.45 g, 0.01 mol) in deoxygenated methanol (50 mL) was added to the ligand solution and was stirred for 1 h under nitrogen atmosphere. The precipitated complex was collected by filtration through a sintered crucible while maintaining an inert environment. The sample was washed with deoxygenated methanol and dried *in vacuo* over anhydrous calcium chloride (Yield: 50-60%, m.p.: > 250°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 isolated as nonhygroscopic substances and are stable in air in the solid form. They are soluble in DMSO, DMF, nitrobenzene, pyridine and slightly soluble in ethanol and methanol. The analytical data (Table III.1) show that these complexes have the metal-ligand ratio 1:1. The molar conductance values in pyridine suggest that all the complexes are non-electrolytes[91]. The empirical formula of the complexes has been given as [MnL], where, L= QED, QPD, QHD or QDT.

Table III.1 Analytical data of the complexes

	Found (Calculated)			
Compound	% Carbon	% Hydrogen	% Nitrogen	% Manganese
$[Mn(QED)]_2$	56.38 (56,47)	3.74 (3.76)	19.81 (19.76)	13.04 (12.92)
[Mn(QPD)]	60.75 (60.89)	3.35 (3.38)	17.81 (17.76)	11.83 (11.6)
$[Mn(QHD)]_2$	51.98 (52.05)	3.25 (3.32)	20.33 (20.24)	13.34 (13.24)
$[Mn(QDT)]_2$	56.20 (56.4)	4.37 (4.48)	21.10 (20.94)	11.85 (11.74)

3.3.1 Magnetic susceptibility measurements

Magnetic moment values are given in Table III.2. Compounds of high-spin bivalent manganese are expected to show magnetic moments very close to the spin-only value (5.92 BM) irrespective of whether the ligand arrangement is octahedral, tetrahedral or of lower symmetry. Somewhat lower magnetic moment values shown by $[Mn(QED)]_2$, $[Mn(QHD)]_2$ and $[Mn(QDT)]_2$ indicate the presence of metal-metal antiferromagnetic interaction probably propagating through bridging atoms. This shows the dimeric nature of these complexes. [Mn(QPD)] has a magnetic moment close to the spin-only value of a d^5 high-spin system[79,92]. [Mn(QPD)] may have a mononuclear structure as the rigid nature of the ligand does not favour dimerisation or distortion.

Table III.2 Magnetic and Conductance data of the complexes

Compound	Colour	Conductance $ohm^{-1}cm^2mol^{-1}$	Magnetic moment BM
$[Mn(QED)]_2$	Yellow	1.4	4.6
[Mn(QPD)]	Yellow	1.2	5.7
$[Mn(QHD)]_2$	Yellow	1.1	4.5
$[Mn(QDT)]_2$	Yellow	1.4	4.8

3.3.2 Infrared spectra

The important infrared spectral bands and their assignments are shown in Table III.3. The red shift in the C=N stretching frequency in the complexes compared to parent ligands indicates the coordination of the azomethine nitrogen to the metal atom[93]. The υ_{O-H} band is absent in all the complexes except in $[Mn(QHD)]_2$, which evidences the deprotonation as well as coordination of phenolic oxygens.

In $[Mn(QHD)]_2$, the band at 3350 cm^{-1} is due to the presence of the alcoholic OH which does not take part in coordination[94]. In the spectra of free ligands, there is a band at 1282 cm^{-1} which can be assigned to the υ_{C-O} stretching vibration of the phenolic group. The phenolic C-O band of the uncoordinated ligand shifts to higher frequencies during complex formation[95], and appears around 1300 cm^{-1}. Blue shift of this band and the retention of the υ_{O-H} at 3350 cm^{-1} in the spectrum of QHD complex suggest that the ligand is bonded to the metal using phenolic oxygen atoms. The stereochemistry of the ligand QHD is not suitable for the coordination of the two phenolic oxygens and the azomethine nitrogen to the same metal atom. In this case the secondary nitrogen is also coordinating evidenced by the red shift of the N-H stretching frequency. In Mn-QHD complex, the dimerisation probably occurs through the coordination of the azomethine nitrogen of one molecule to the metal center of the neighbouring molecule and *vice versa*, resulting in a square planar arrangement of the donor atoms around both of the metal ions. The C-N band could not be distinguished in the spectrum, probably as a result of coordination. The antiferromagnetism may be operative in this case by a

Table III.3 IR data of the ligands and the complexes (cm^{-1})

Compound	ν_{O-H}	ν_{N-H}	$\nu_{C=N}$	ν_{C-N}	ρ_{C-H}	ν_{C-O}	$\delta_{C-H(Ph)}$
QED	3500s	----	1667s	----	874s	1267m	758s
$[Mn(QED)]_2$	----	----	1649s	----	876s	1280w	758s
QPD	3500s	----	1670s	----	----	1271	760,758s
[Mn(QPD)]	----	----	1657s	----	----	----	756s
QHD	3500s	3013s	1667s	1101s	----	1282s	760s
$[Mn(QHD)]_2$	3350s	2990s	1657s	----	----	1346w	758s
QDT	3500s	3013s	1665s	1130s	875s	1284s	762s
$[Mn(QDT)]_2$	----	2990s	1657s	1150s	873s	1295w	756s

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

superexchange mechanism propagating through two 2-atom bridges. It can be assumed that the phenolic oxygens and the azomethine nitrogens are the binding sites for all of these ligands. In QDT, the amino nitrogen is also coordinating, which makes this ligand capable of binding the metal ions in a pentadentate manner[96].

3.3.3 Electronic spectra

As the transitions in a d^5 system are spin forbidden and the presence of intense charge transfer bands extended to the visible region of the spectra of the ligands themselves, no characteristic d-d transitions are observed in these complexes[97].

3.3.4 EPR spectra

The EPR spectra (Fig. 3.1) of all the complexes were recorded in DMSO at liquid nitrogen temperature. The g and A values are given in Table III.4. All the complexes yield a g value = 2.0 and this is agreeable with other reported

Table III.4 EPR spectral data of the complexes

Compound	$g_{av.}$	$A_{av.}$ (Gauss)
$[Mn(QED)]_2$	2.0	87
[Mn(QPD)]	2.0	62
$[Mn(QHD)]_2$	2.0	75
$[Mn(QDT)]_2$	2.0	--

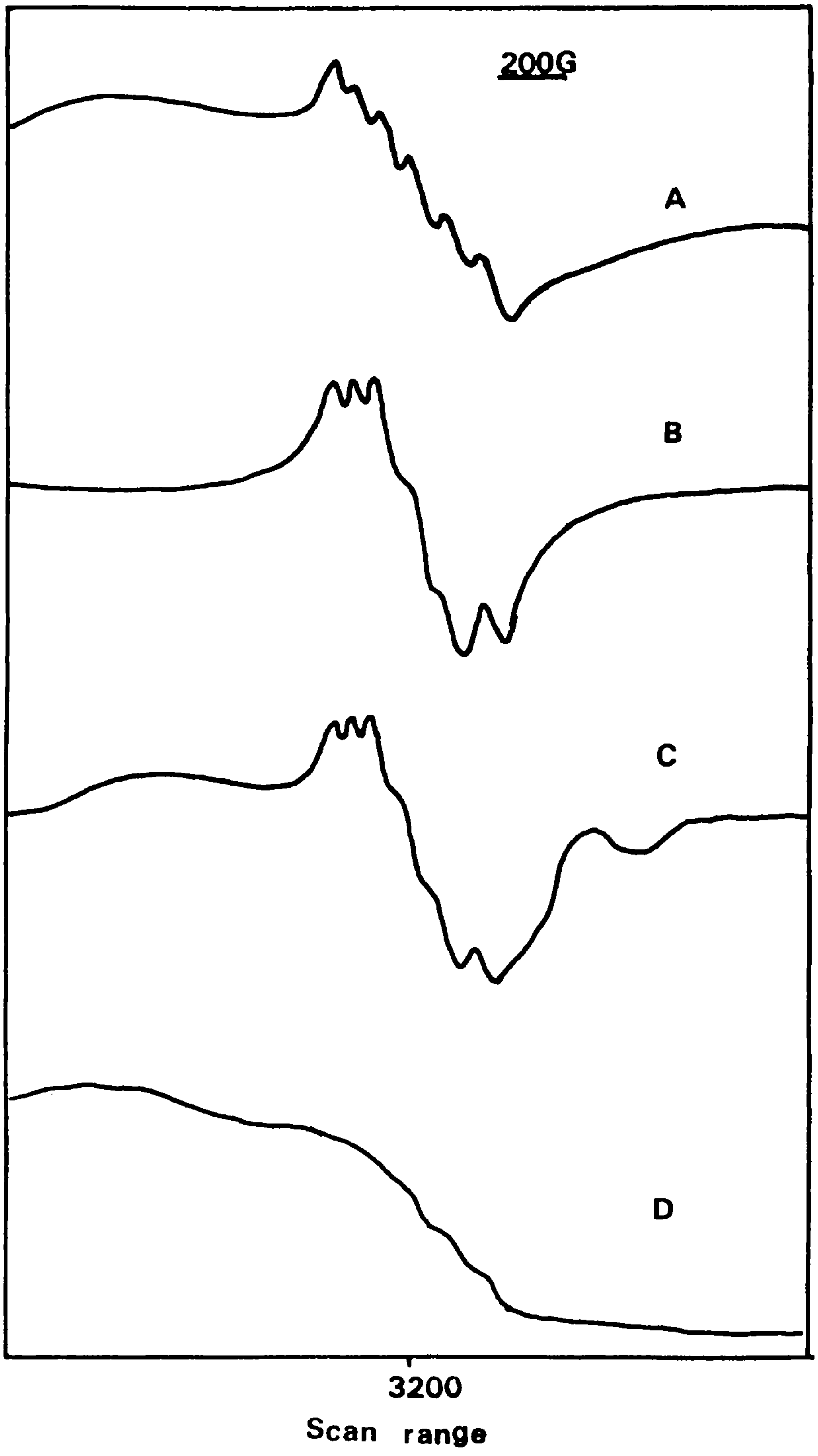


Fig. 3.1 EPR spectra of the complexes in DMSO at LNT
A) $[Mn(QED)]_2$, B) $[Mn(QPD)]$, C) $[Mn(QHD)]_2$ and D) $[Mn(QDT)]_2$

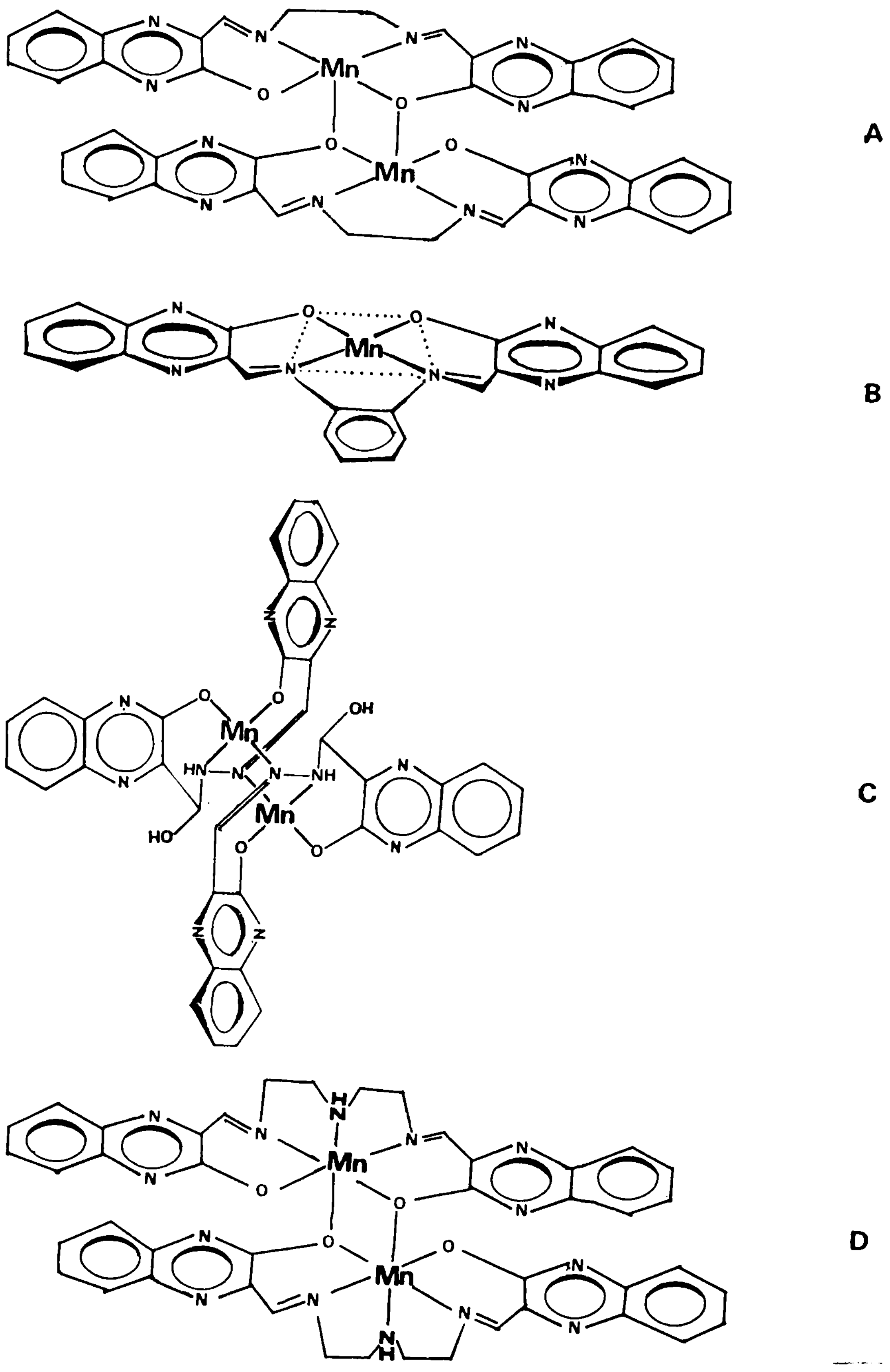


Fig. 3.2 Schematic structures of the complexes

A) $[Mn(QED)]_2$, B) $[Mn(QPD)]$, C) $[Mn(QHD)]_2$ and D) $[Mn(QDT)]_2$

manganese(II) systems[98,99]. It is interesting to note that the spectrum of [Mn(QPD)] and $[Mn(QHD)]_2$ are almost similar in appearance which suggest that the metal ions in both the cases may be in a square planar ligand field[100,101].

Based on the above arguments, the structures shown in Fig.3.2 are assigned for these complexes. A dimeric structure is suggested for all the complexes except [Mn(QPD)], which is thought to be a monomer with a square planar geometry.

CHAPTER IV

STUDIES ON IRON(III) COMPLEXES

4.1 INTRODUCTION

Many Schiff base complexes of Fe(III) have been found to be of biological and industrial importance[102-105]. Fe(III) Salen type complexes can form Lewis-base adducts with bases. Such imidazole and pyrazole adducts were found to exhibit spin crossover phenomena[106,107]. This property was earlier detected in Fe(II) and Fe(III) complexes with sulphur donor ligands and this topic has been reviewed by several workers in this field[108-113]. The variable spin state of iron proteins is believed to be important for the catalytic properties of these bioactive systems. The biological importance of crossover phenomena has been discussed[114-116]. Recently, Conti *et al.* have described why such systems should be studied[117]. Moreover, Fe(III) complexes with Salen type ligands are interesting from the structural point of view also[118]. In this chapter, we describe the studies on the Fe(III) complexes synthesised from the ligands QED, QPD, QHD and QDT.

4.2 EXPERIMENTAL

4.2.1 Materials

Details regarding the preparation and purification of the ligands QED, QPD, QHD and QDT are described in Chapter II.

4.2.2 Synthesis of the complexes

The following general procedure was followed to synthesise the complexes:

Appropriate ligand (0.01 mol; QED. 3.72 g; QPD, 4.18 g; QHD, 3.44 g or QDT, 4.14 g) was finely powdered and taken in a 250 mL RB flask containing dichloromethane (75 mL). Anhydrous ferric chloride (0.01 mol, 1.62 g) in methanol (25 mL) was added to the solution and the mixture was refluxed on a water bath for 1 h. Filtered the solution (to remove any unreacted ligand particles) and the volume of the solution was reduced to half and allowed to cool. The precipitated crystalline complexes were filtered, washed with ether and dried *in vacuo* over anhydrous calcium chloride (Yield: 40-50%, m.p.: > 250 ^{o}C).

4.2.3 Analytical methods

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

4.3 RESULTS AND DISCUSSION

The complexes are crystalline in nature and are stable in air. They are found to be soluble in DMSO, DMF, nitrobenzene, pyridine and partially soluble in ethanol and methanol. The analytical data (Table IV.1) show that these complexes have the general formula, [FeLCl], where L = QED, QPD, QHD or QDT. The molar conductance values (Table IV.2) of the complexes suggest that $[Fe(QED)Cl]_2$, [Fe(QPD)Cl] and $[Fe(QHD)Cl]_2$ are non-electrolytes in pyridine i.e., the chlorine atom is directly attached to the metal. The complex of QDT shows a molar conductance value normally given by a 1:1 electrolyte. In this case, the chloride ion is thought to be out of the coordination sphere[91] and the complex may be formulated as [Fe(QDT)]Cl and probably as a dimer, $[Fe(QDT)]_2Cl_2$.

Table IV.1 Analytical data of the complexes

	Found (Calculated)				
Compound	% Carbon	% Hydrogen	% Nitrogen	% Chlorine	% Iron
$[Fe(QED)Cl]_2$	51.96 (52.02)	3.38 (3.46)	18.31 (18.20)	7.64 (7.68)	12.22 (12.10)
[Fe(QPD)Cl]	56.47 (56.54)	3.09 (3.14)	16.53 (16.49)	7.12 (6.96)	10.85 (10.96)
$[Fe(QHD)Cl]_2$	47.79 (47.86)	3.06 (3.10)	18.74 (18.60)	7.81 (7.86)	10.52 (10.63)
$[Fe(QDT)]_2Cl_2$	52.28 (52.34)	4.05 (4.10)	19.52 (19.43)	7.20 (7.03)	11.00 (11.07)

4.3.1 Magnetic susceptibility measurements

Magnetic moment values are given in Table IV.2. [Fe(QPD)Cl] has a magnetic moment value of 5.87 BM. No orbital contribution can be present in this case and negates the possibility of metal-metal interaction. $[Fe(QED)Cl]_2$ and $[Fe(QHD)Cl]_2$ exhibit a slightly lower value, which may be due to the antiferromagnetic coupling resulting from a dimeric structure[119-122,57].

The magnetic moment value of $[Fe(QDT)]_2Cl_2$ invites special attention. The value is much lower than that expected for a spin free Fe(III) ion. It may be proposed that the Fe(III) center in this complex undergoes spin crossover and at room temperature, the system is a mixture of high-spin and low-spin Fe(III) ions. As the spin crossover phenomena in Fe(III) complexes is seen only with octahedral geometries and keeping in mind that the ligand QDT is capable of forming dimeric octahedral complexes as in the manganese(II) case, it can be assumed that antiferromagnetic coupling can also play a vital role here. To our knowledge, solid state spin transitions of transition metal complexes are cooperative in nature and an interplay of both these effects can give an interesting "antiferromagnetic coupling" *versus* "spin crossover" system[123-125].

Table IV.2 Magnetic and Conductance data of the complexes

Compound	Colour	Conductance $ohm^{-1}cm^2mol^{-1}$	Magnetic moment BM
$[Fe(QED)Cl]_2$	Brown	5	5.27
[Fe(QPD)Cl]	Browm	6	5.87
$[Fe(QHD)Cl]_2$	Brown	4	5.52
$[Fe(QDT)]_2Cl_2$	Yellowish red	113	4.55

4.3.2 Infrared spectra

The important spectral bands and their assignments are given in Table IV.3. It is interesting to note that the C=N stretching frequency do not change appreciably in the complexes when compared to other metal complexes and in fact a broadening of this band was observed. This may be because of the keto-amine tautomeric structure possible for these kinds of ligands. The interaction with a hard Lewis acid like Fe(III) ion can cause a hybridisational change at the sp^2 hybridised azomethine nitrogen by generating a partial sp^3 character in it[126,127]. In the spectra of free ligands, there is a band around 1282 cm^{-1} which can be assigned to the ν_{C-O} stretching vibration of the phenolic group. The phenolic C-O band of the uncoordinated ligand shifts to higher frequencies during complex formation[95],and appears at 1300 cm^{-1}. Blue shift of this band and the retention of the ν_{O-H} at 3350 cm^{-1}in the spectrum of QHD complex suggest that the ligand is bonded to the metal using phenolic oxygen atoms. The change in C-N stretching frequency in $[Fe(QDT)]_2Cl_2$ indicates the coordination of amino group of the ligand QDT to the metal[128]. However, no conclusive evidence could be drawn only from IR spectra in this case.

Table IV.3 Selected IR bands of the complexes (cm^{-1})

Compound	ν_{O-H}	ν_{N-H}	$\nu_{C=N}$	ν_{C-N}	ρ_{CH}	ν_{C-O}	$\delta_{CH(Ph)}$
QED	3500s	---	1667s	----	874s	1267m	758s
$[Fe(QED)Cl]_2$	---	---	1666s	----	872s	1270w	768s
QPD	3500s	---	1670s	----	----	1271w	760,758s
[Fe(QPD)Cl]	---	---	1670s	----	----	1280w	760,758s
QHD	3500s	3013s	1667s	1101s	----	1282s	760s
$[Fe(QHD)Cl]_2$	3350s	3050s	1666s	----	----	1271m	758s
QDT	3500s	3013s	1665s	1130s	875s	1284s	762s
$[Fe(QDT)]_2Cl_2$	----	3057s	1666s	1149s	870s	1310w	762s

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

4.3.3 Electronic spectra

No characteristic d-d bands are observed in the spectra of the complexes as the electronic transitions are spin forbidden. However, $[Fe(QDT)]_2Cl_2$ exhibits an absorption band at 18200 cm^{-1} which may be a spin allowed one. This absorption may be due to the presence of low spin Fe(III) and the band may be assigned to $^2T_{2g} \longrightarrow {}^2E_g$ transition[129]. This further indicates the existence of high-spin <—> low-spin equilibrium in this complex.

4.3.4 EPR spectra

Powder EPR spectra of $[(FeQDT)_2]Cl_2$ at three different temperatures have been taken and are shown in Fig. 4.1. It is not possible to fully explain the EPR spectra of this complex in terms of simple high-spin and low-spin mixtures. In solid state, relaxation, spin-orbit coupling, zero field splitting and strong antiferromagnetic exchange interaction which are expected to be present in this case jeopardize such a simplification.

The room temperature EPR spectrum of $[Fe(QDT)]_2Cl_2$ shows three absorptions. The resonances at $g = 4.8$ and $g = 0.75$ may be due to the high-spin Fe(III) ions present. A low field signal is also expected for a rhombically distorted high-spin Fe(III) center[130]. However, this could not be resolved at room temperature. The broad absorption at $g = 2$ may be due to the low-spin Fe(III) ion present.

At lower temperatures the system is expected to undergo transition from high-spin to low-spin state. This probably is accompanied by a geometrical change. The EPR spectrum at 133 K clearly shows the existence of the low-spin Fe(III)

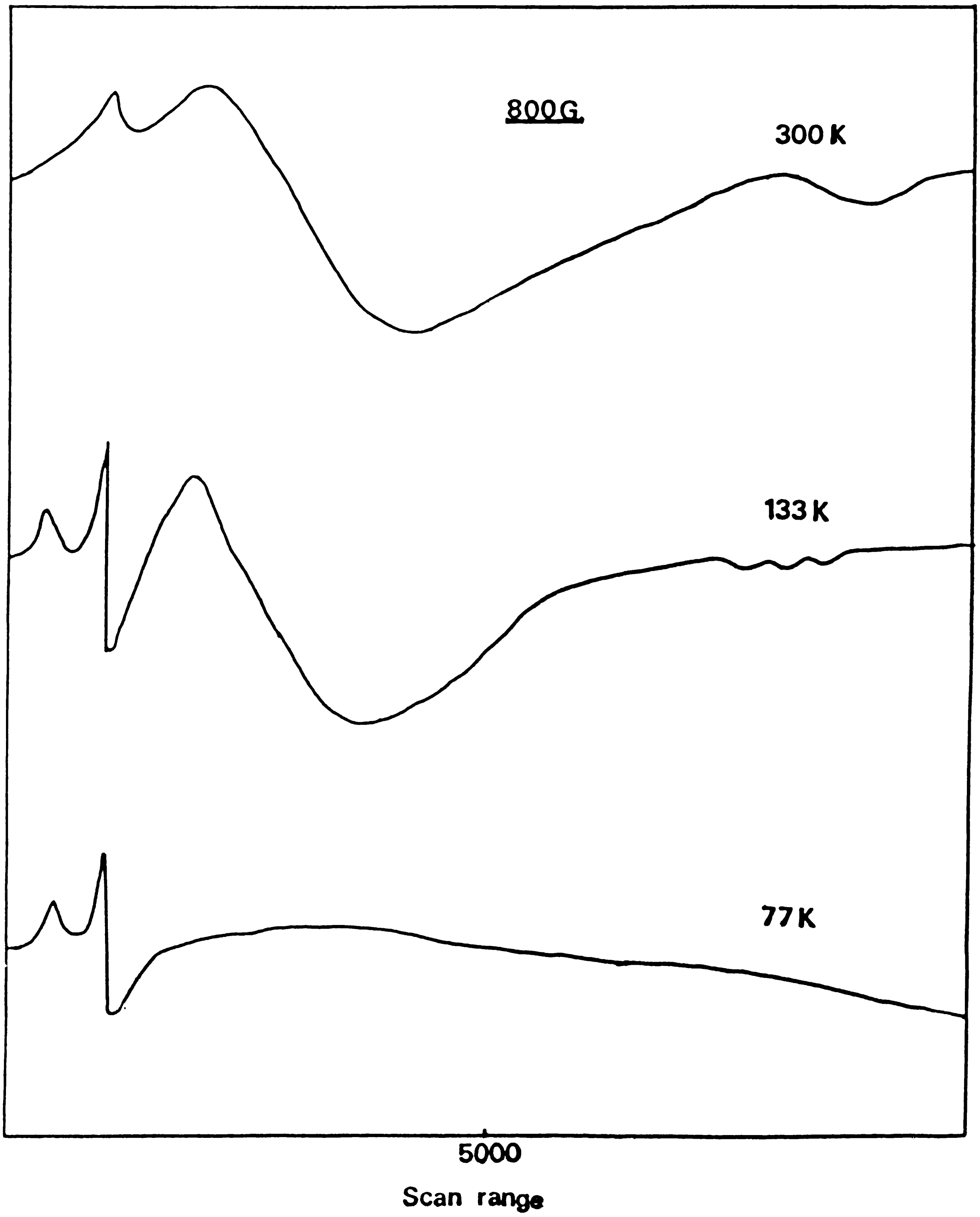


Fig. 4.1 EPR spectra of $[Fe(QDT)]_2Cl_2$ at different temperatures

ion. The absorptions at $g = 9.8$, $g = 5$ and $g = 0.75$ are due to the three Kramers doublet of the rhombic Fe(III) ion. Further, the fine splitting on the high field signal also confirms the rhombic nature. However, the intensity of the high-spin Fe(III) signals at higher fields are seen to decrease. The low-spin signal at $g = 2$ is also weakened at this temperature. In a distorted geometry, low-spin Fe(III) centers suffer large zero field splitting and eventually makes the ground state orbitally and electronically non-degenerate and therefore it would be difficult to observe an EPR spectrum. Furthermore, strongly antiferromagnetically coupled low-spin Fe(III) centers can have an $S = 0$ ground state. This also causes the loss of intensity of the low-spin signal.

At 77 K, the spectrum shows only high-spin signals at $g = 9.8$ and $g = 4.8$. It can be assumed that at this temperature low-spin Fe(III) centres are severely distorted and strongly coupled and were not able to give an EPR spectrum. It is to be noted that even at this temperature some high-spin species are present[131,132].

4.3.5 Mössbauer spectroscopy

To get further information about the antiferromagnetic coupling present in $[Fe(QDT)]_2Cl_2$, the Mössbauer spectrum of this sample was recorded at two different temperatures and are given in Fig. 4.2. The room temperature spectrum shows a quadrupole split doublet with a center shift of 0.62 mm/s. The low-spin and high-spin Fe(III) species could not be distinguished from the spectrum[133,134] and this may be because of the fast relaxation between the electronic spin states relative to the Larmour period of ^{57}Fe, *i.e.* 10^{-9} s. The Mössbauer spectrum at 77 K has interesting features. It shows magnetic hyperfine splitting confirming that the system is antiferromagnetically coupled at this temperature. The low center shift value compared with the room temperature spectrum also supports the dominant low-spin nature of the complex at this temperature.

The spectrum has a large central peak with narrow peak at the left. The large central peak may arise from an $S = 0$ state, as a result of the strong antiferromagnetic coupling of two low-spin Fe(III) centers. The sharp band at the central peak may be arising from the $S = 1$ state. This can

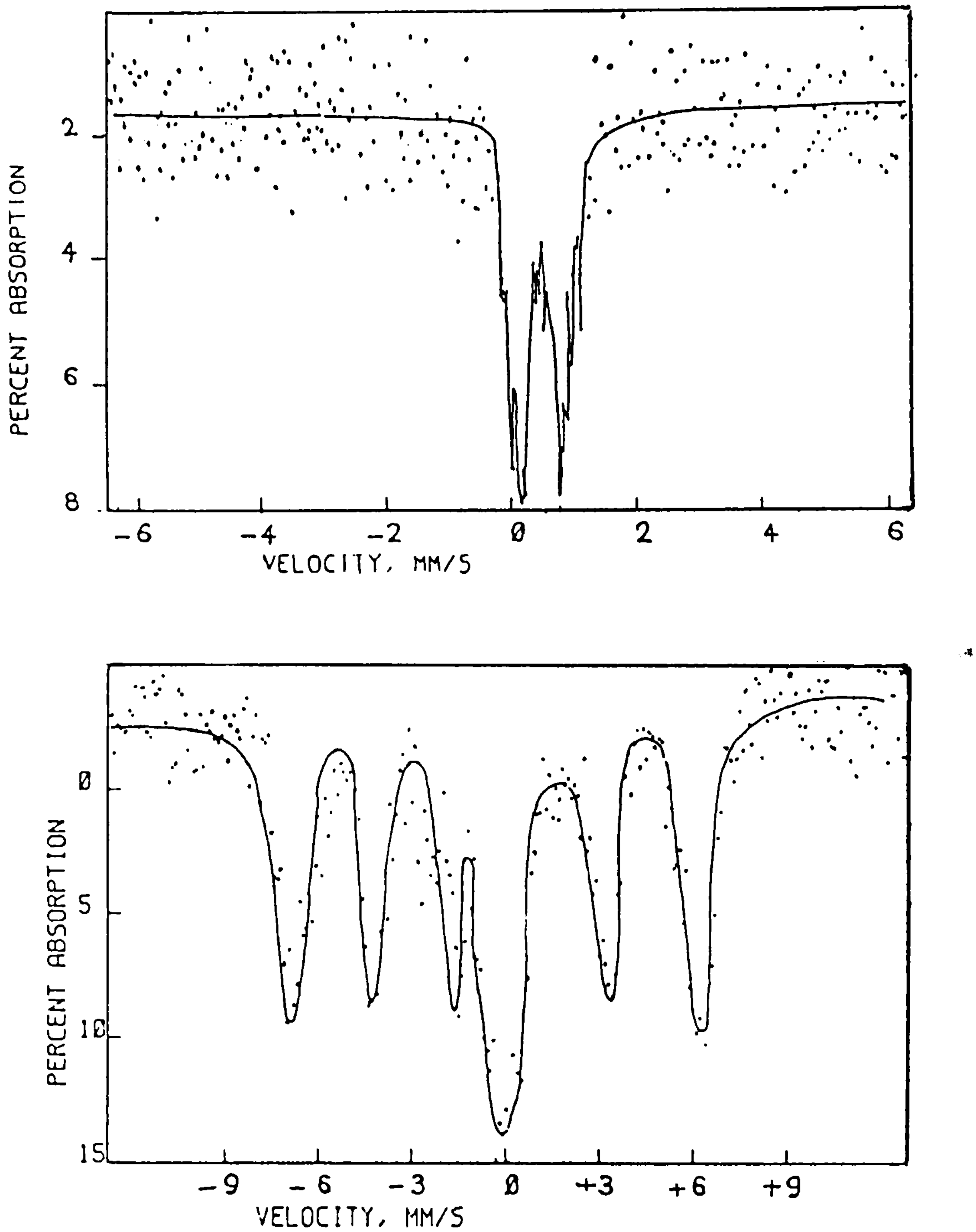


Fig. 4.2 Mössbauer spectra of $[Fe(QDT)]_2Cl_2$ at RT & LNT

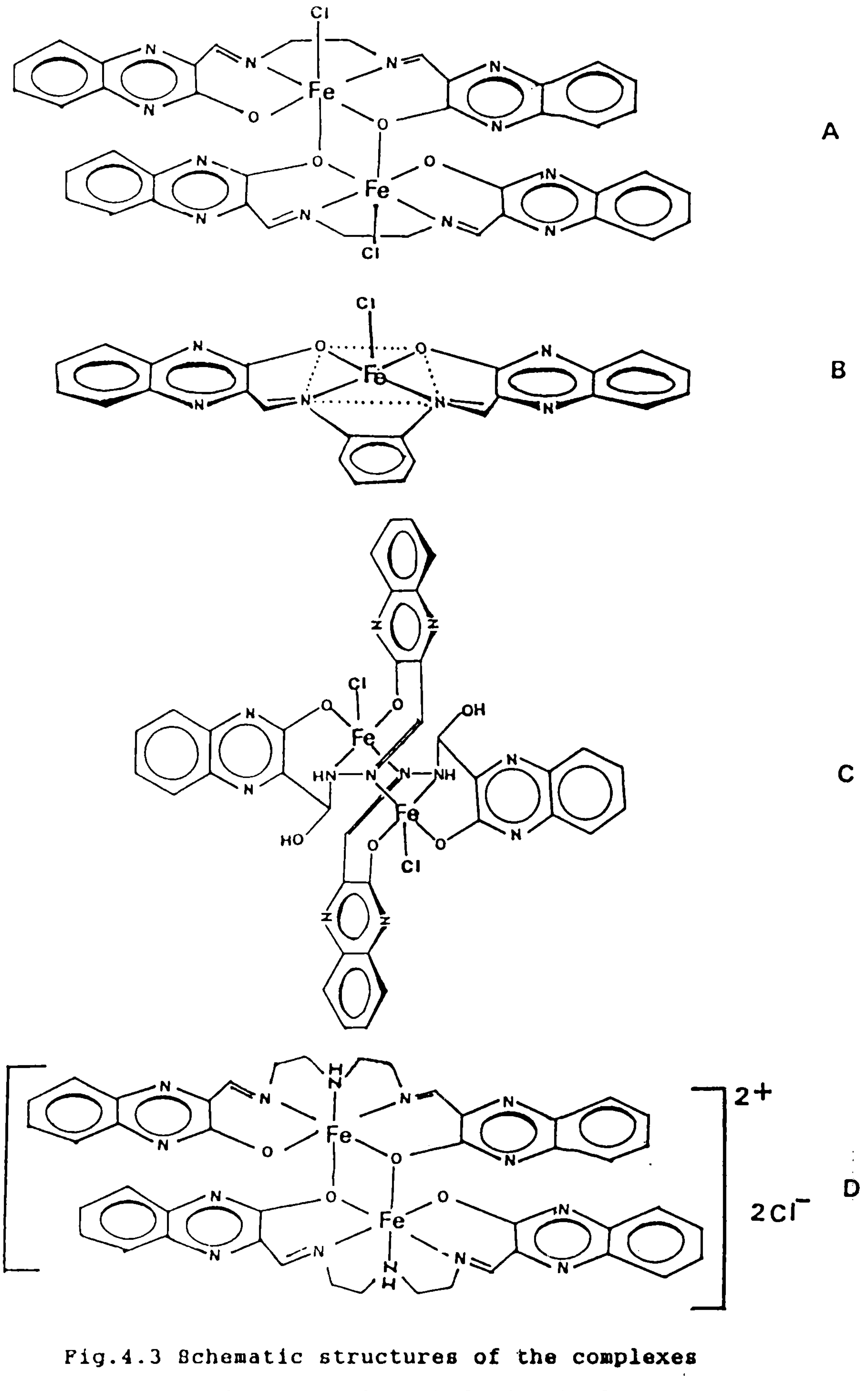


Fig.4.3 Schematic structures of the complexes

A) $[Fe(QED)Cl]_2$, B) $[Fe(QPD)Cl]$,

C) $[Fe(QHD)Cl]_2$ and D) $[Fe(QDT)]_2Cl_2$

also be due to some fast relaxing high-spin species or a ΔMz $\pm$ 2 transition. The appearance of the spectrum confirms that $[Fe(QDT)]_2Cl_2$ is low-spin at 77 K and this strongly antiferromagnetically coupled species undergoes slow relaxation between the spin states[135-140].

Based on the above arguments, a dimeric structure with two chloride ions in the outer sphere has been proposed for $[Fe(QDT)]_2Cl_2$. In $[Fe(QHD)Cl]_2$, the dimerisation is expected to take place by the mutual coordination of the azomethine within the dimer, whereas in $[Fe(QED)Cl]_2$, the dimerisation is through phenolic oxygen atoms. [(Fe(QPD)Cl] may be a monomer with a square pyramidal structure. The schematic diagram of the complexes are given in Fig. 4.3.

CHAPTER V

STUDIES ON COBALT(II) COMPLEXES

5.1 INTRODUCTION

There has been considerable interest in the nature of the tetradentate Schiff base complexes of cobalt(II) owing to the capability of several complexes of this type to undergo reversible oxygenation[141-144]. Such planar Schiff base complexes are important in the catalytic and biochemical perspectives[145-147]. Therefore, the electronic structures of cobalt(II) square planar Schiff base complexes have been extensively studied by electronic and EPR spectroscopy and other methods[148-150]. An excellent review about the electronic structure of the cobalt(II) complexes with tetradentate Schiff bases have been published[151]. In this chapter, we describe our studies on the complexes of Co(II) with QED, QPD, QHD and QDT.

5.2 EXPERIMENTAL

5.2.1 Materials

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

5.2.2 Synthesis of the complexes

The following general procedure was used to synthesise the complexes: Finely powdered ligand (0.01 mol: QED, 3.72 g; QPD, 4.18g; QHD, 3.44 g; QDT, 4.14 g) was added in dichloromethane (75 mL) in a R.B flask. This was mixed with a solution of cobalt(II) acetate (0.01 mol, 2.49 g) in methanol (50 mL) and refluxed for 1.5 h and the solution was filtered, if necessary (normally this step is not necessary, as there would be no undissolved ligand particles). Then the solution was reduced to half its volume and was allowed to cool. The precipitated complexes were filtered, washed with ether and dried *in vacuo* over anhydrous calcium chloride. The complexes obtained were found to contain some methanol trapped in the lattice which can be removed by heating the powdered complex to 100°C under vacuum for 1 h. (Yield: 50-60%; m.p.: > 250°C.)

5.2.3 Analytical methods

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

5.3 RESULTS AND DISCUSSION

The complexes are isolated as non-hygroscopic, microcrystalline substances and are stable in air. They are soluble in chloroform, DMSO, DMF, nitrobenzene and have only partial solubility in ethanol and methanol. The analytical data (Table V.1) show that the complexes have the general empirical formula, [CoL], where L = QED, QPD, QHD or QDT. The molar conductance values (Table V.2) show that these complexes are non-electrolytes in pyridine[91].

Table V.1 Analytical data of the complexes

	Found (Calculated)			
Compound	%Carbon	%Hydrogen	%Nitrogen	%Cobalt
$[Co(QED)]_2$	55.84	3.65	19.61	14.10
	(55.90)	(3.73)	(19.58)	(13.73)
[Co(QPD)]	60.27	3.26	17.74	12.43
	(60.38)	(3 35)	(17.61)	(12.35)
$[Co(QHD)]_2$	51.49	3.27	20.12	14.30
	(51.55)	(3.34)	(20.05)	(14.06)
[Co(QDT)]	55.86	4.29	20.85	12.65
	(55.94)	(4.45)	(20.76)	(12.49)

Table V.2 Magnetic and Conductance data of the complexes

Compound	Colour	Conductance $ohm^{-1}cm^{2}\ mol^{-1}$	Magnetic moment BM
$[Co(QED)]_2$	dark brown	1.8	3.97
[Co(QPD)]	dark brown	1.9	3.89
$[Co(QHD)]_2$	dark brown	1.7	3.95
[Co(QDT)]	dark brown	1.5	4.26

5.3.1 Magnetic susceptibility measurements

The magnetic moment values of the complexes are presented in Table V.2. The magnetic moment values of the complexes necessitate detailed study of these systems. Normally, square planar Schiff base complexes induce a low spin configuration at the Co(II) centre and exhibit a magnetic moment value in the range 2.1 - 2.9 BM. But, a fifth coordination, or a dimeric structure can provide an axial perturbation, and thus bring the excited quartet state closer to the doublet ground state. Such changes have been reported and at higher temperatures anomalous magnetic moment values have been reported in the case of CoSalen complexes[152]. As the ligands QED, QPD, QHD and QDT are derived from electron deficient quinoxaline rings, the ligand field may not be capable of bringing out large 'd' level splitting so that the quartet state becomes very close to the ground state. In such case, the energy difference between these two states would be small, when compared to kT and a Boltzman distribution of the molecules between the $^{2}A_{2}$ and ^{4}E states is possible. In the case of [Co(QDT)] strong axial coordination is also possible which further makes the quartet state closer to the ground doublet state. Such reports about the spin equilibrium of five coordinate Lewis base adducts of Co(II) Schiff base complexes have been appeared in the literature[153-155]. A dimeric structure involving the square planar complex units may also lead to the above situation. The pentacoordinate structure achieved by dimerisation may be the reason for the slightly higher magnetic moment value observed for $[Co(QED)]_2$. Recently, an excellent article discussing effect of the ligand donor strength on the spin state of the Co(II) centre have been published[156] and it was made clear that lower nucleophilicity of the donor atoms favour the formation of high-spin complexes[157]. The anomalous magnetic behaviour observed by cobalt(II) complexes reported herein may be due to the presence of closely lying doublet and quartet energy levels and the consequent thermal equilibrium existing between these two levels.

5.3.2 Infrared spectra

The important bands and their tentative assignments are shown in Table V.3. The red shift of the C=N stretching frequencies indicate the coordination of azomethine nitrogen to cobalt.

Table V.3 Selected IR bands of the complexes (cm^{-1})

Compound	υ_{O-H}	υ_{N-H}	$\upsilon_{C=N}$	υ_{C-N}	ρ_{C-H}	υ_{C-O}	$\delta_{C-H(Ph)}$
QED	3500s	----	1667s	----	874s	1267m	758s
$[Co(QED)]_2$	----	----	1664	----	825	1280w	760
QPD	3500s	----	1670s	----	----	1271w	760,758s
[Co(QPD)]	----		1660	----	----	1278w	760,758
QHD	3500s	3013s	1667s	1101s	----	1282s	760s
$[Co(QHD)]_2$	3500	masked by OHstr	1663	1153	----	1290w	760
QDT	3500s	3013s	1665s	1130s	875s	1284s	762s
[Co(QDT)]	----	----	1663	1154	873	1305w	762

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

The absence of the υ_{O-H} in all cases shows that phenolic oxygen atoms are coordinated in the deprotonated form. The alcoholic OH group in QHD gives a band at 3350 cm^{-1}. In

$[Co(QHD)]_2$, the azomethine nitrogen of the ligand is thought to be coordinated to the neighbouring cobalt center acquiring a dimeric molecule with square planar geometry around the metal ions. In the spectra of free ligands, there is a band around 1282 cm^{-1} which can be assigned to the υ_{C-O} stretching vibration of the phenolic group. The phenolic C-O band of the uncoordinated ligand shifts to higher frequencies during complex formation[95], and appears at 1300 cm^{-1}. Blue shift of this band and the retention of the υ_{O-H} at 3350 cm^{-1} in the spectrum of QHD complex suggest that the ligand is bonded to the metal using phenolic oxygen atoms. The change in the C—N stretching frequency in $[Co(QHD)]_2$ and [Co(QDT)] indicate the participation of the secondary nitrogen of QHD and the amino nitrogen of QDT in bonding[158].

5.3.3 Electronic spectra

The solid state electronic spectra of all the complexes were recorded at room temperature . At this temperature it is supposed that the ^2A and ^4E states are populated and molecular system is in dynamic equilibrium between these states. So the assignment of the transitions becomes difficult. The spectra of all the samples show a broad weak absorption at the tail end of the intraligand bands and are assigned to d-d transitions[159]. This consists of two absorptions at 19000 cm^{-1} and 17400 cm^{-1}. An intense $^4A_2 \longrightarrow {}^4T_1(P)$ absorption at ~ 15000 cm^{-1} with fine splitting due to spin-orbit coupling is characteristic of all Co(II) ions in tetrahedral geometry[129]. However, the absence of such an absorption at this wavelength denies the possibility of tetrahedral geometry for these complexes.

5.3.4 EPR spectra

The frozen EPR spectra of the complexes in DMSO at 77 K are given in Fig. 5.1. The solution spectrum of [Co(QPD)] at room temperature is also given in the figure. At room temperature [Co(QPD)] does not yield any sharp signal, instead shows a weak and a very broad band. This may be due to the spin transitions[160] or due to thermal vibrations which decrease the life time of the excited states. But, on cooling to 77 K all the complexes gave good spectrum corresponding to a single unpaired electron. The hyperfine splitting due to S=7/2 Co nuclei could also be observed[161] and all the complexes give a g value 2 which is almost in agreement with the g values observed for other Co(II) low-spin systems. The g and A values are given in Table V.4. From the EPR behaviour, it can be assumed that all the

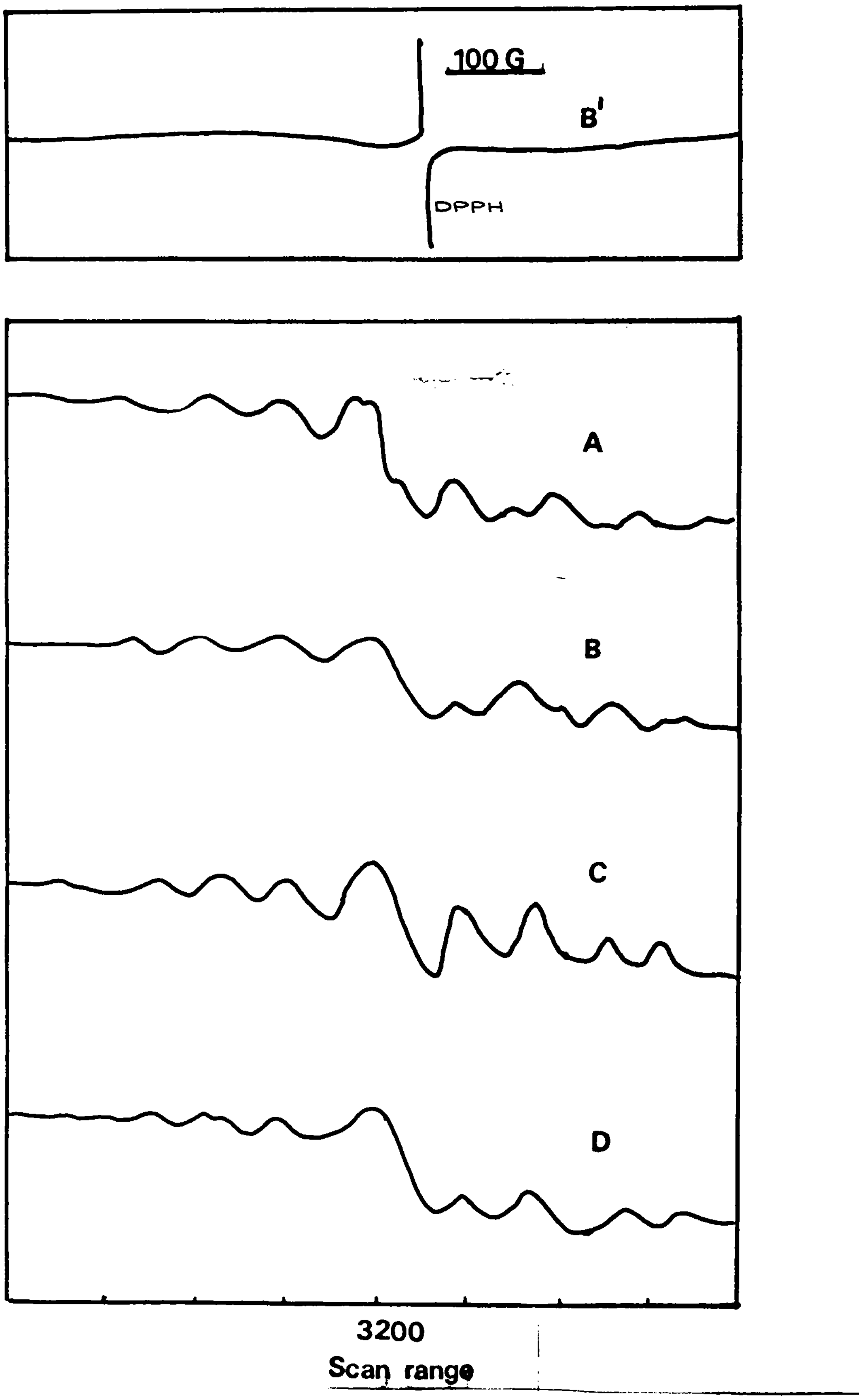


Fig. 5.1 EPR spectra of the complexes in DMSO

(B') [Co(QPD)] at RT

(A) [Co(QED)]$_2$, (B) [Co(QPD)], (C) [Co(QHD)]$_2$ and

(D) [Co(QDT)] at LNT

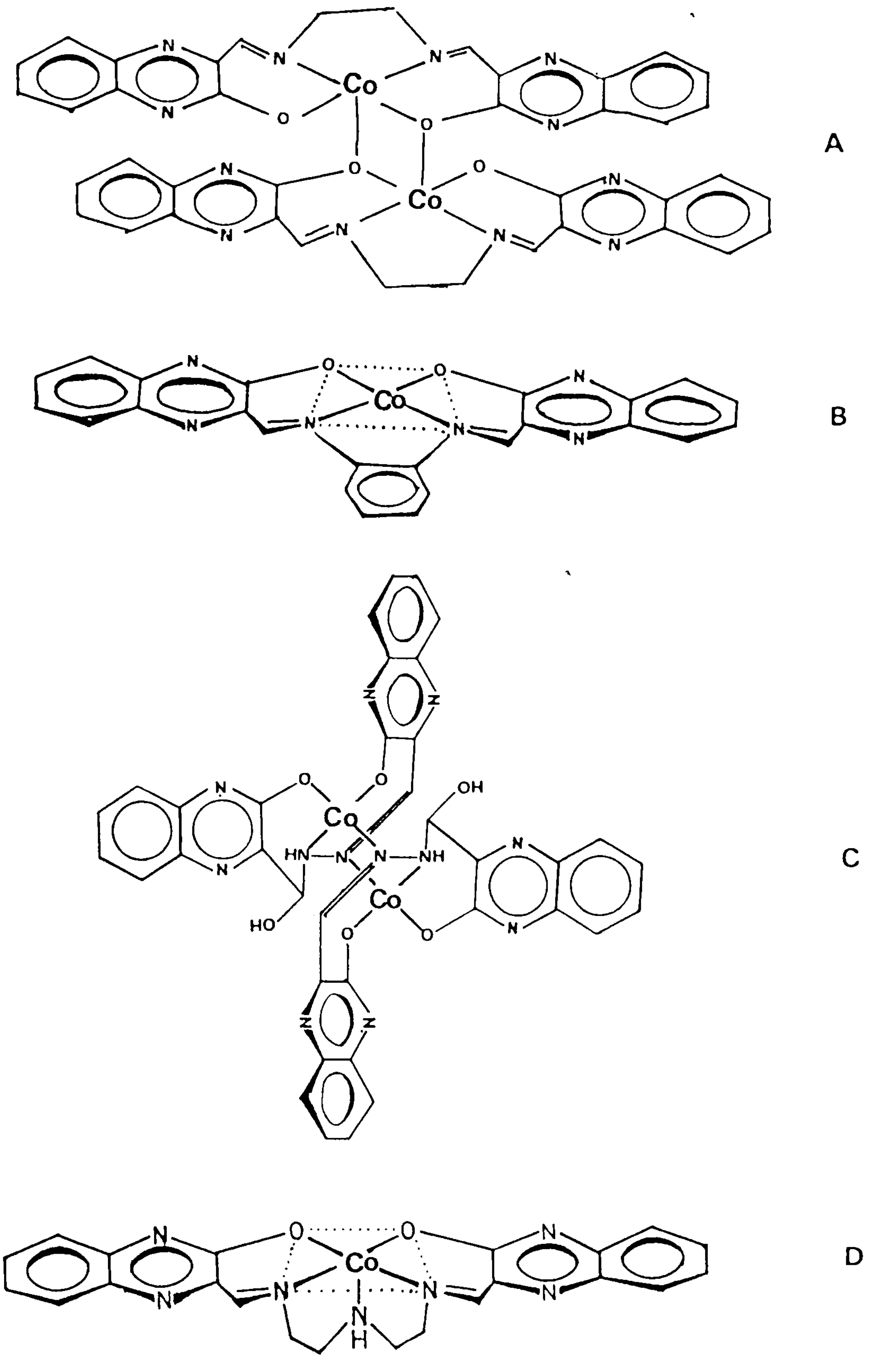


Fig. 5.2 Scematic structu~~t~~res of the complexes

A) $[Co(QED)]_2$, B) $[Co(QPD)]$, C) $[Co(QHD)]_2$ and D) $[Co(QDT)]$

complexes are in $^2A \rightleftharpoons {}^4E$ equilibrium at room temperature, and at 77 K all the complexes exist in a low spin state with one unpaired electron.

Table.V.4 EPR spectral data of the complexes

Compound	g_{av}	A_{av} (Gauss)
$[Co(QED)]_2$	2.0	74
[Co(QPD)]	2.0	76
$[Co(QHD)]_2$	2.0	70
[Co(QDT)]	2.0	70

On the basis of the above arguments, structures shown in Fig. 5.2 may be assigned to the complexes.

CHAPTER VI

STUDIES ON NICKEL(II) COMPLEXES

6.1 INTRODUCTION

Nickel(II) salicylaldimine complexes were extensively studied due to their anomalous magnetic properties[162-165]. Many nickel(II) square planar complexes with Schiff bases were known to develop paramagnetism in solution or on heating the solid either alone or in an inert medium[166-169]. This phenomenon was explained on the basis of a planar-tetrahedral equilibrium[170-173] or as occuring due to a geometrical change to a higher coordination state through polymerisation[174-178]. Alternative theories were also suggested for this on the basis of crystal field theory[179] and our understanding in this area is not yet complete[180]. In this chapter, we describe our studies on the synthesis and characterisation of nickel(II) complexes of the ligands QED, QPD, QHD and QDT.

6.2 EXPERIMENTAL

6.2.1 Materials

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

6.2.2 Synthesis of the complexes

All the complexes were prepared by the following general procedure:

The finely powdered ligands (0.01 mol; QED, 3.72 g; QPD, 4.18 g; QHD, 3.44 g and QDT, 4.14 g) and nickel(II) acetate tetrahydrate (0.01 mol; 2.48 g) were refluxed in ethanol for 1 h. Filtered the solution to remove the unreacted ligand, if any, and the volume was reduced to 1/3. The complex separated on cooling was collected by filtration and washed twice with ether and dried *in vacuo* over anhydrous calcium chloride (Yield: 50-60%, m.p.: > 250 ^{o}C).

6.2.3 Analytical methods

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

6.3 RESULTS AND DISCUSSION

The analytical data (Table VI.1) show that the complexes have the general empirical formula, [NiL] where, L = QED, QPD, QHD or QDT. The complexes [Ni(QPD)] and $[Ni(QHD)]_2$ are obtained as red and dark brown crystalline substances respectively. The $[Ni(QED)]_2$ is a buff coloured amorphous powder. [Ni(QDT)] is yellow in colour. All the complexes are moderately soluble in DMF, pyridine and DMSO, and partially soluble in methanol and ethanol. They are insoluble in water, ether, acetone and acetonitrile. The molar conductance values suggest that they are non-electrolytes in pyridine[91].

Table VI.1 Analytical data of the complexes

	Found (Calculated)			
Compound	% Carbon	% Hydrogen	% Nitrogen	% Nickel
$[Ni(QED)]_2$	55.87 (55.98)	3.61 (3.70)	19.62 (19.58)	13.70 (13.68)
[Ni(QPD)]	60.31 (60.42)	3.25 (3.36)	17.72 (17.62)	12.35 (12.31)
$[Ni(QHD)]_2$	51.48 (51.58)	3.29 (3.34)	20.11 (20.06)	14.08 (14.03)
[Ni(QDT)]	55.87 (55.96)	4.39 (4.45)	20.81 (20.74)	12.48 (12.44)

6.3.1 Magnetic susceptibility measurements

The magnetic moment values of the complexes are shown in Table VI.2. Only [Ni(QDT)] shows a reasonable value for two unpaired electrons. The other three complexes show intermediate magnetic moment values. This problem can be approached by the assumption that the decrease in the effective ligand field or a distortion from the strict square planar structure can reduce the energy difference (ΔE) between the singlet and triplet states, so that, ΔE will be comparable with thermal energy, kT. There is little chance for the rigid QPD ligand to deviate from the square planar geometry in its complex. Therefore, the paramagnetism shown by this complex cannot be due to the planar-tetrahedral equilibrium. Here, the partial paramagnetism shown by the [Ni(QPD)] can be better attributed to the decreased singlet-triplet separation[181-183]. The magnetic moment value for [Ni(QDT)] is agreeable for a square pyramidal Ni(II) complex and the ligand QDT is capable of coordinating in a square pyramidal fashion. The $[Ni(QED)]_2$ shows a slightly higher value than that for [Ni(QPD)] and $[Ni(QHD)]_2$, and this may be due to the presence of a dimeric form of the complex or a paramagnetic form of the compound as an impurity. Similar observations have been made for the metal complexes with terdentate Schiff base ligands[184,185].

Table VI.2 Magnetic and Conductance data of the complexes

Compound	Colour	Conductance ($ohm^{-1}cm^{2}mol^{-1}$)	Magnetic moment (BM)
$[Ni(QED)]_2$	Buff colour	2.10	2.30
[Ni(QPD)]	Dark red	4.40	2.10
$[Ni(QHD)]_2$	Dark brown	1.80	1.90
[Ni(QDT)]	Yellow	1.70	2.70

Slightly lower value for the $[Ni(QHD)]_2$ can be attributed to the strong antiferromagnetism operative between the metal centres, and this value in a way supports the dimeric structure of the complex.

6.3.2 Electronic spectra

The electronic spectra of the nickel complexes given in Fig. 6.1 were recorded in solid state as nujol mull to avoid any kind of solvent intervention. The spectra of $[Ni(QED)]_2$, [Ni(QPD)] and $[Ni(QHD)]_2$ show only one d-d absorption around 20000 cm^{-1} as a shoulder band and an absorption around this wavelength is considered to be characteristic of square planar Ni(II) ions[186,187]. The red shift in this absorption when compared to other square planar Schiff base systems can be attributed to the decreased energy level separation or due

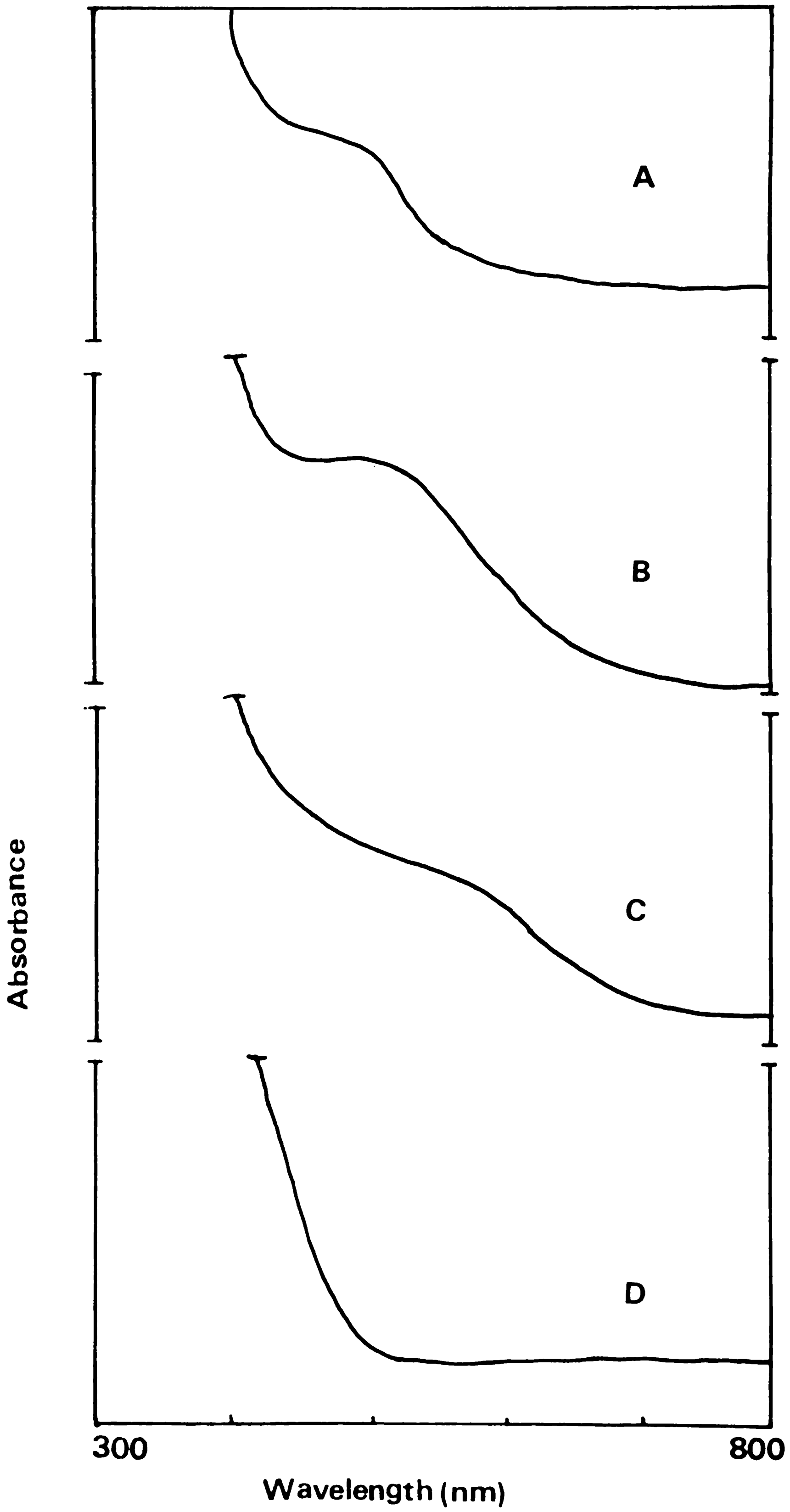


Fig 6.1 UV-Vis. spectra of the complexes
A) $[Ni(QED)]_2$, B) [Ni(QPD)], C) $[Ni(QHD)]_2$ and D) [Ni(QDT)]

to the electron withdrawing nature of the quinoxaline ring system[188]. In [Ni(QDT)], the d-d absorptions are probably masked by charge transfer transitions[189]. However, the lack of any absorptions around or below 10000 cm^{-1} discards the possibility of a tetrahedral or octahedral geometry to these complexes.

6.3.3 Infrared spectra

The more relevant IR bands of the complexes are given in Table VI.3. The ν_{O-H} of the ligands at 3500 cm^{-1} is absent in all the complexes except in $[Ni(QHD)]_2$[127]. Its existence in $[Ni(QHD)]_2$ is due to the presence of an alcoholic OH group in the ligand. Moreover, the $\nu_{C=N}$ is seen to be unshifted in the $[Ni(QHD)]_2$ which indicates that the azomethine nitrogen is not coordinated in this case[96]. In all the other three complexes, considerable shift is seen in C=N stretching indicative of azomethine coordination[190]. The ligands QED, QPD and QDT are almost free from any steric strain for the formation of mononuclear complexes with Ni(II) ions. As the structure of QHD is not suitable for the formation of mononuclear complexes, a dimeric structure with Ni-O-Ni bridging is proposed for this system. In the sepctra of free ligands, there is a band around 1282 cm^{-1} which can be assigned to the ν_{O-H} stretching vibration of the phenolic group. The phenolic ν_{C-O} band of the uncoordinated ligand shifts to higher frequencies during complex formation[95], and appears at 1300 cm^{-1}. Blue shift of this band and the retention of the ν_{O-H} at 3350 cm^{-1} in the spectrum suggest that the ligand is bonded to the metal using phenolic oxygen atoms. The fourth coordination in [Ni(QHD)]$_2$ is provided by one of the phenolic oxygens of the other molecule in the dimer unit. In this case, both the nickel atoms and all the

Table VI.3 IR data of the ligands and the complexes (cm^{-1})

Compound	ν_{O-H}	ν_{N-H}	$\nu_{C=N}$	ν_{C-N}	ρ_{C-H}	ν_{C-O}	δ_{C-H} (Ph)
QED	3500s	----	1667s	----	874s	1267m	758s
[[Ni(QED)]]$_2$	----	----	1642s	----	875s	1280w	758s
QPD	3500s	----	1670s	----	---	1271w	760,758s
[[Ni(QPD)]]	----	----	1644s	----	---	1284s	767,754s
QHD	3500s	3013s	1667s	1101s	---	1282s	760s
[[Ni(QHD)]]$_2$	3500	masked	1670s	1067s	---	1346w	756s
QDT	3500s	3013s	1665s	1130s	875s	1284s	762s
[[Ni(QDT)]]	----	2980s	1611s	1030s	875s	1295w	762s

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

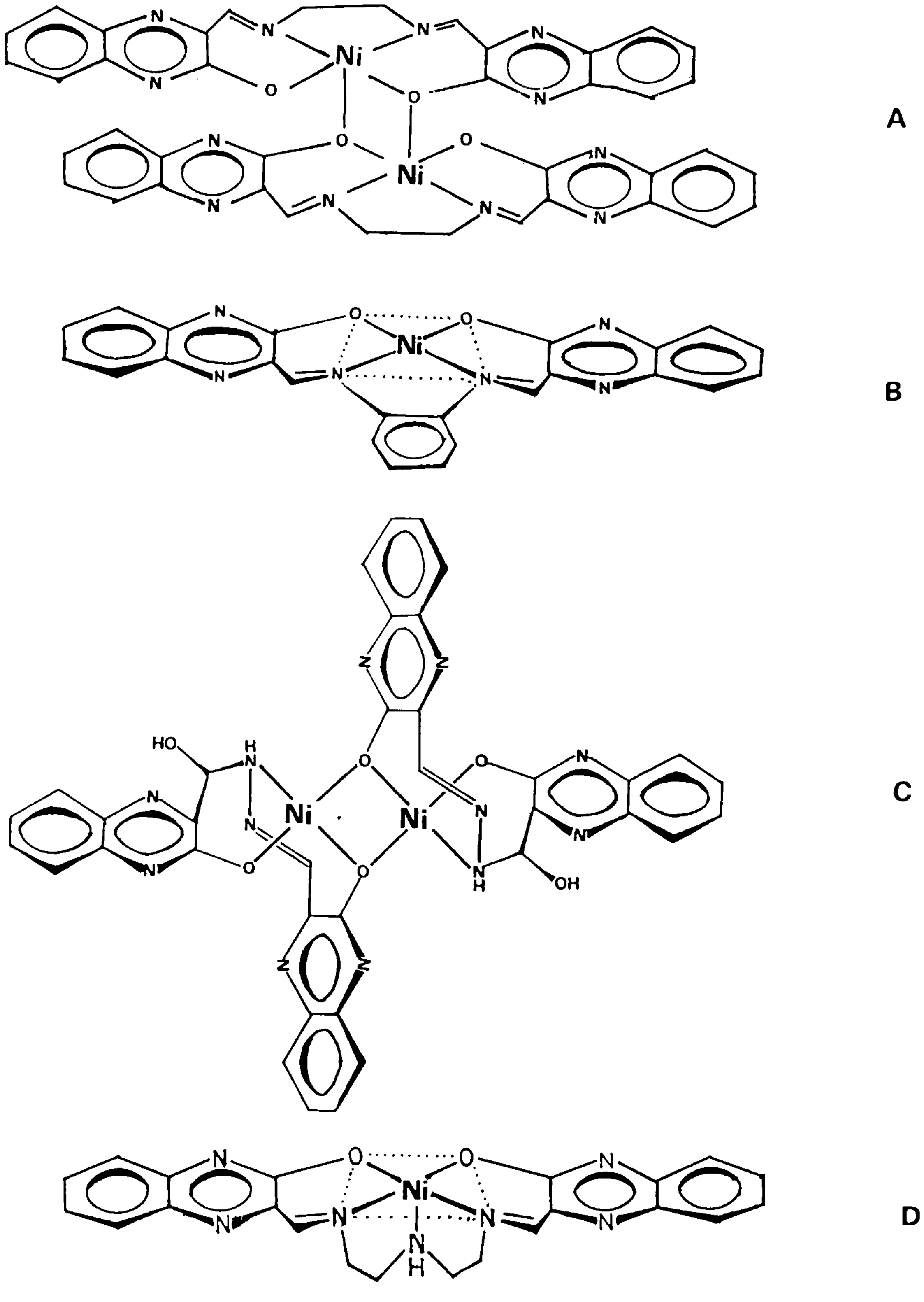


Fig.6.2 Schematic structures of the complexes
A) $[Ni(QED)]_2$, B) $[Ni(QPD)]$, C) $[Ni(QHD)]_2$ and D) $[Ni(QDT)]$

donor atoms lie in one plane. The red shift in the ν_{C-N} indicates the coordination of the secondary nitrogen to the metal in $[Ni(QHD)]_2$. In [Ni(QDT)], the ligand behaves as pentadentate and the coordination of the amino nitrogen is evidenced by the red shift of the C—N stretching frequency.

The EPR spectra obtained for these complexes at 77 K did not give any useful information. The complexes may be EPR silent in nature. The weak signals in the spectra of $[Ni(QED)]_2$ and [Ni(QDT)] may also be due to minor paramagnetic impurities present.

Based on the above arguments, the structures given in Fig. 6.2 can be assigned for these complexes.

CHAPTER VII

STUDIES ON COPPER(II) COMPLEXES

7.1 INTRODUCTION

Copper is of very much biological and catalytic interest[191,192]. A lot of work has been done with designed ligands to mimic both the structure and chemistry of metal ions in biology, especially, copper containing proteins[193-195]. In order to gain a better understanding, many model complexes have been studied for their catalytic activity also[196,197]. Synthesis and characterisation of the copper(II) complexes of the quadridentate ligands QED, QPD, QHD and QDT would be interesting from this point of view. The results of our studies on Cu(II) complexes of these ligands are presented in this chapter.

7.2 EXPERIMENTAL

7.2.1 Materials

Details regarding the preparation and purification of the ligands QED, QPD, QDT and QHD are described in Chapter II.

7.2.2 Synthesis of the complexes

The following general procedure was followed to synthesise the metal complexes:

Finely powdered ligands (0.01 mol; QED, 3.72 g: QPD, 4.18 g: QHD, 3.44 g or QDT, 4.14 g) and copper(II) acetate (0.01 mol, 1.81 g) were dissolved in ethanol (100 mL) and refluxed for 1 h and allowed to cool. The precipitated complexes were filtered, washed with chloroform and dried *in vacuo* over anhydrous calcium chloride (Yield: 50-60%, m.p.: > 250 ^{o}C).

7.2.3 Analytical methods

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

7.3 RESULTS AND DISCUSSION

The complexes are isolated as non-hygroscopic, amorphous substances and are stable in air. They are soluble in DMF, DMSO, nitrobenzene, pyridine and slightly soluble in ethanol and methanol. The analytical data (Table VII.1) show that the complexes have a general formula, [CuL], where L = QED, QPD, QHD or QDT. The molar conductance values in pyridine suggest that all the complexes are non-electrolytes in pyridine.

The colour of the copper Schiff base complexes has been used to distinguish the four coordinated complexes from the five and six coordinated complexes. Waters *et al.* has proposed brown or violet colour for four coordinated systems and green for five or six coordinated systems[66]. The brown colour observed for [Cu(QPD)] and $[Cu(QHD)]_2$ indicates a square planar structure and green colour observed for $[Cu(QED)]_2$ and [Cu(QDT)] indicates the complexes to have a higher coordination number. The QDT ligand forms square

Table VII.1 Analytical data of the complexes

	Found (Calculated)			
Compound	% Carbon	% Hydrogen	% Nitrogen	% Copper
$[Cu(QED)]_2$	55.28 (55.35)	3.61 (3.69)	19.42 (19.37)	14.47 (14.65)
[Cu(QPD)]	59.74 (59.80)	3.30 (3.32)	17.53 (17.40)	13.36 (13.30)
$[Cu(QHD)]_2$	50.85 (50.99)	3.29 (3.30)	19.91 (19.83)	14.87 (15.00)
[Cu(QDT)]	55.32 (55.39)	4.37 (4.40)	20.66 (20.56)	13.27 (13.20)

pyramidal complexes with cobalt(II) and nickel(II). Therefore, in the case of copper also, it might form a square pyramidal geometry can be expected for its copper complex also.

7.3.1 Magnetic susceptibility measurements

Magnetic moment values of the complexes are given in Table VII.2. [Cu(QPD)] shows a magnetic moment agreeable for a Cu(II) ion in a square planar environment. $[Cu(QED)]_2$ has a little higher moment, possibly due to the distortion from a square planar geometry because of its dimeric structure. The low magnetic moment of $[Cu(QHD)]_2$ indicates that strong antiferromagnetic coupling is operative between copper

Table VII.2 Magnetic and Conductance data of the complexes

Compound	Colour	Conductance $ohm^{-1} cm^2 mol^{-1}$	Magnetic moment BM
$[Cu(QED)]_2$	green	3.6	1.95
[Cu(QPD)]	brown	4.0	1.70
$[Cu(QHD)]_2$	brown	3.4	1.40
[Cu(QDT)]	green	4.0	1.96

centres. There is a possibility of direct metal-metal interaction also. The magnetic moment of [Cu(QDT)] is reasonable for a d^9 system where spin-orbit coupling is less, thereby supporting the square pyramidal nature of the complex[198-200].

7.3.2 Infrared spectra

The important IR bands and their tentative assignments are given in Table VII. 3. The coordination of the phenolic oxygen in the deprotonated form is indicated by the absence of the O-H stretching band in the spectra of the complexes. In $[Cu(QHD)]_2$, the appearance of this band may be due to the presence of an alcoholic OH group in the ligand. The $\upsilon_{C=N}$ is found to be unshifted which shows that the azomethine nitrogen is not coordinated in this case, unlike from the other copper(II) complexes reported herein. A dimeric structure with Cu-O-Cu bridging may be proposed for $[Cu(QHD)]_2$. A square planar geometry might be possible in this case with two phenolic oxygens, the secondary nitrogen of the same ligand and a bridging phenolic oxygen as the fourth donor. The QDT ligand in [Cu(QDT)] is expected to behave as an N_3O_2 donor ligand, possibly in a square pyramidal manner[201-205]. In the spectra of free ligands, there is a band around 1282 cm^{-1} which can be assigned to the ν_{O-H} stretching vibration of the phenolic group. The phenolic C-O band of the uncoordinated ligand shifts to higher frequencies during complex formation[95], and appears at 1300 cm^{-1}. Blue shift of this band and the retention of the ν_{O-H} at 3350 cm^{-1} in the spectrum suggests that the ligand is bonded to the metal using phenolic oxygen atoms, N—H stretching band could not be resolved, probably due to the weak coordination of the amino nitrogen.

Table VII.3 IR data of the ligands and the complexes (cm^{-1})

Compound	ν_{O-H}	ν_{N-H}	$\nu_{C=N}$	ν_{C-N}	ρ_{C-H}	ν_{C-O}	δ_{C-H} (Ph)
QED	3500s	----	1667s	----	874s	1267m	758s
$[Cu(QED)]_2$	----	----	1655s	1144s	874s	1280w	758s
QPD	3500s	----	1670s	----	----	1271w	760,758s
[Cu(QPD)]	----	----	1636s	----	----	1288m	758.760s
QHD	3500s	3013s	1667s	1101s	----	1282s	760s
$[Cu(QHD)]_2$	3500s	3000s	1672s	1144s	----	1300m	756s
QDT	3500s	3013s	1665s	1130s	875s	1284s	762s
[Cu(QDT)]	----	3000s	1655s	1146s	879s	1295w	763s

7.3.3 Electronic spectra

The UV-Visible spectra of these complexes did not show any characteristic d-d absorptions. The absorptions may probably be obscured by intraligand or charge transfer transitions[206].

7.3.4 EPR spectra

The EPR spectra of the complexes recorded in DMF solutions at -140^{0}C are given in Fig. 7.1. The g and A values are given in the Table VII.4. The hyperfine splitting due to Cu nuclei is not clearly seen in the spectrum of $[Cu(QED)]_2$. This may be due to magnetic interaction between Cu(II) centers pointing to its dimeric nature[207,208]. The nature of the spectrum of [Cu(QPD)] is as expected for square planar Schiff base Cu(II) complexes[209]. [Cu(QDT)] exhibits a spectrum almost similar to that of the square planar [Cu(QPD)]. The axial coordination in [Cu(QDT)] might be weak and does not severely distorted the in-plane donor atoms, and the geometry of [Cu(QDT)] may be probably square pyramidal. No copper hyperfine splittings are seen in the spectrum of $[Cu(QHD)]_2$ which may be due to the strong exchange coupling between the metal ions[210].

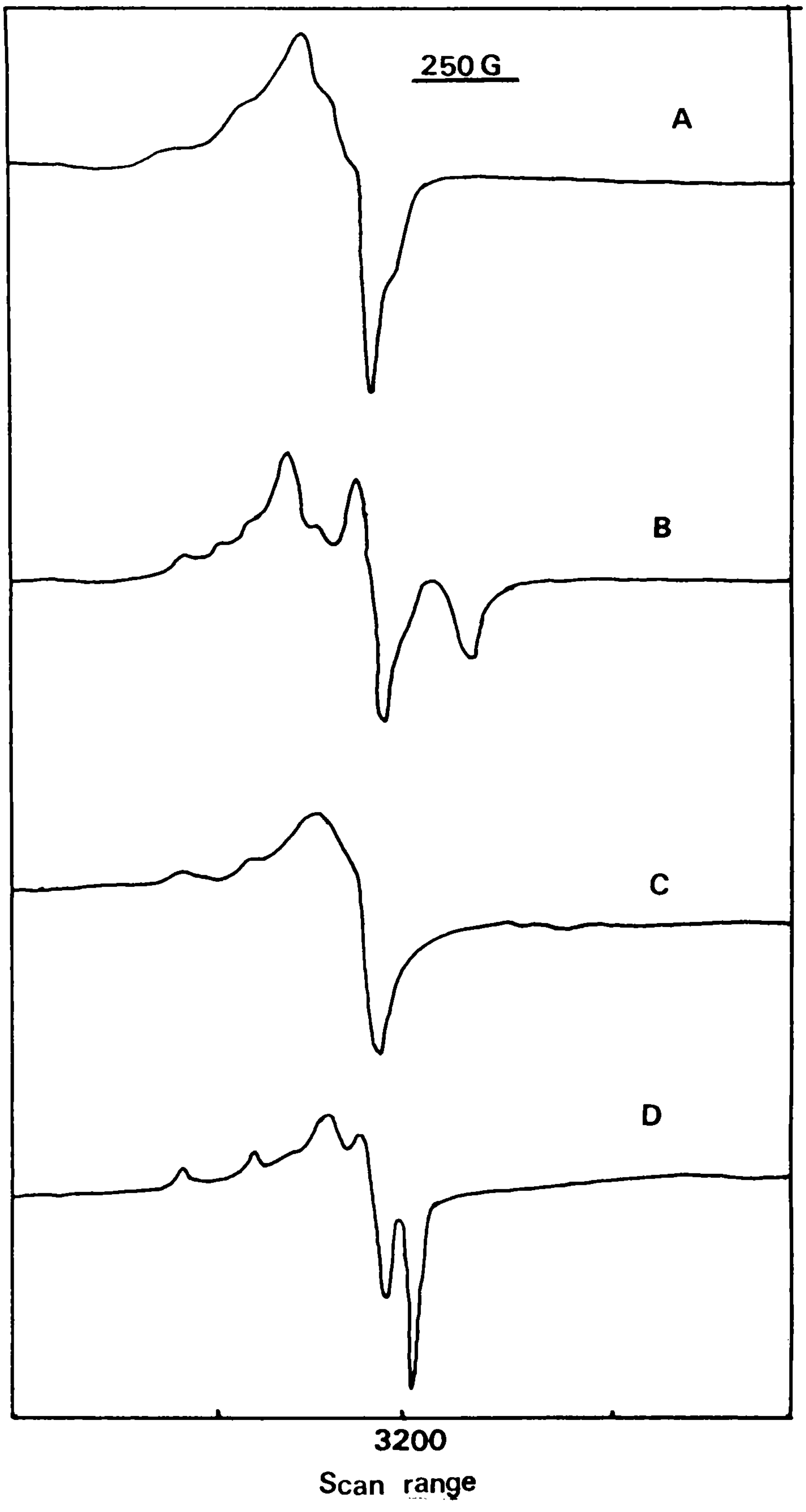


Fig. 7.1 EPR spectra of the complexes in DMF at 133 K
A) $[Cu(QED)]_2$ B) [Cu(QPD)], C) $[Cu(QHD)]_2$ and D) [Cu(QDT)]

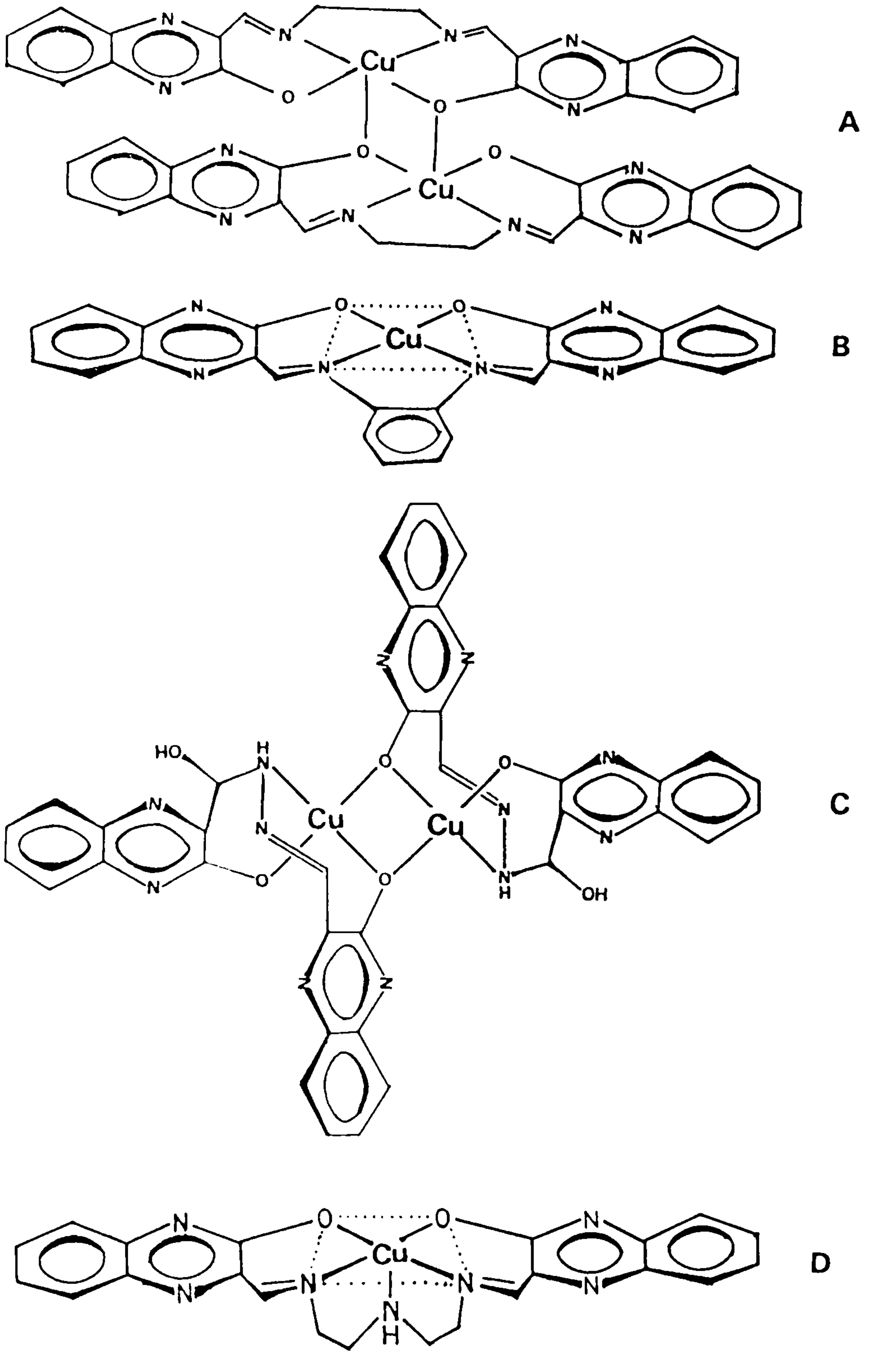


Fig. 7.2 Schematic structures of the complexes
A) [Cu(QED)]$_2$ B) [Cu(QPD)], C) [Cu(QHD)]$_2$ and D) [Cu(QDT)]

Table VII.4 ESR spectral data of the complexes

Sample	$g_{\parallel}$	$g_{\perp}$	A (Gauss)
$[Cu(QED)]_2$	2.29	2.09	160
$[Cu(QPD)]$	2.37	2.04	160
$[Cu(QHD)]_2$	2.30	2.09	---
$[Cu(QDT)]$	2.30	2.06	166

Based on the above arguments, the structures shown in the Fig. 7.2 can be assigned for the complexes.

CHAPTER VIII

CATALYTIC ACTIVITY OF MANGANESE(II) COMPLEXES IN THE DECOMPOSITION OF HYDROGEN PEROXIDE

8.1 INTRODUCTION

The metal chelate catalysed disproportionation of hydrogen peroxide has received much attention due to its relevance in bioinorganic chemistry *i.e.* mimicking the catalytic activity of enzymes[211]. In the biological systems, hydrogen peroxide is most effectively decomposed by the enzyme, catalase. The presence of metal ions has been found to considerably enhance the oxidising action of hydrogen peroxide[212-214]. Sigel *et al.* studied the catalytic action of copper(II) ethylenediamine complexes on the decomposition of hydrogen peroxide, and proposed a binuclear model as an intermediate complex[215]. The use of metal Schiff base complexes as catalysts towards the decomposition of hydrogen peroxide are scanty[216]. Recently, Oishi *et al.* have studied the catalytic effect of some planar Schiff base complexes of copper(II)[217]. In this chapter, we present our studies on the catalytic activity of the manganese complexes

($[Mn(QED)]_2$, $[Mn(QPD)]$, $[Mn(QHD)]_2$, $[Mn(QDT)]_2$) in the decomposition of hydrogen peroxide.

8.2 EXPERIMENTAL

8.2.1 Materials

The syntheses of the manganese(II) complexes are already described in Chapter II. Hydrogen peroxide (E. Merck, 6% purified) was made to 0.5% with ion free water and the concentration was determined by potassium permanganate method[75].

8.2.2 Catalytic experiments

The experimental set up is as shown in Fig.8.1. The following procedure was adopted to study the decomposition of hydrogen peroxide.

The reaction vessel containing hydrogen peroxide solution (0.5 %, 30 mL) and magnetic fish was kept on a water bath maintained at room temperature (28 ± 1 ^{o}C). The manganese complex (2.5×10^{-5} mol; MnQED, 0.0106 g; MnQPD, 0.0118 g; MnQHD 0.0097 g or MnQDT 0.01105 g) was taken in a plastic float and was placed over the solution. The gas burette was

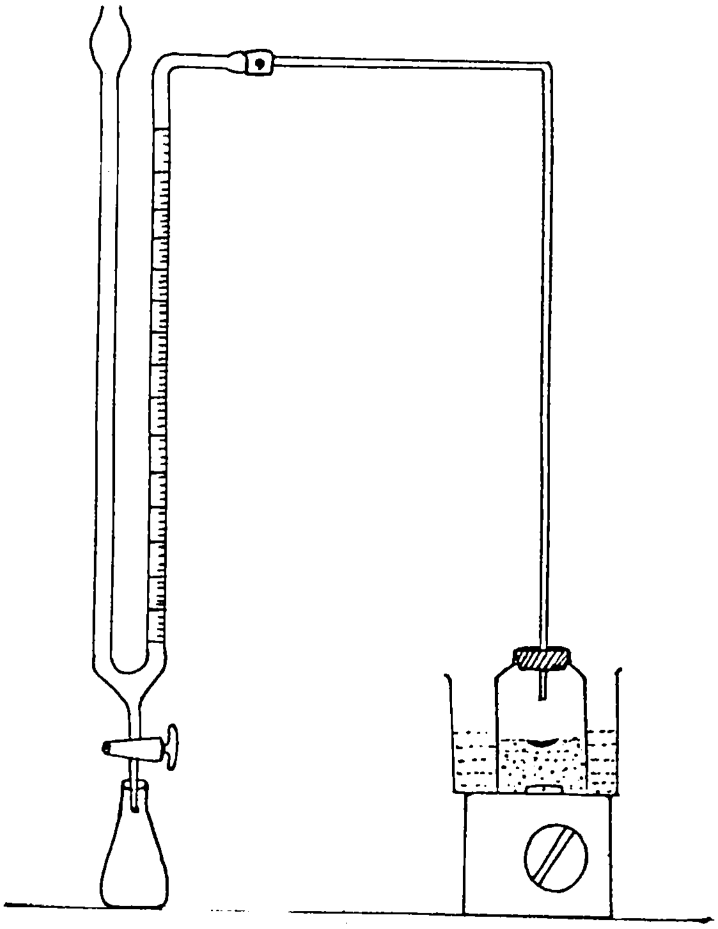


Fig. 8.1 Experimental set up for H_2O_2 decomposition study

filled with dichromate solution for easy detection of the levels, and was attached to the reaction vessel. Then the vessel was tightly closed and the levels in the two arms of the gas burette were made equal and the reading was noted. A stop watch was started at the moment when the complex was introduced into the solution by magnetic stirring. As reaction proceeds, oxygen is produced and the level in the right arm is lowered. This was balanced by running away the solution through the tap. Readings were noted at an interval of 300 seconds after making the levels in the two arms equal. The process was continued until 50 mL oxygen was collected in the burette. A computerised technique was used to find the rate of the reaction[218].

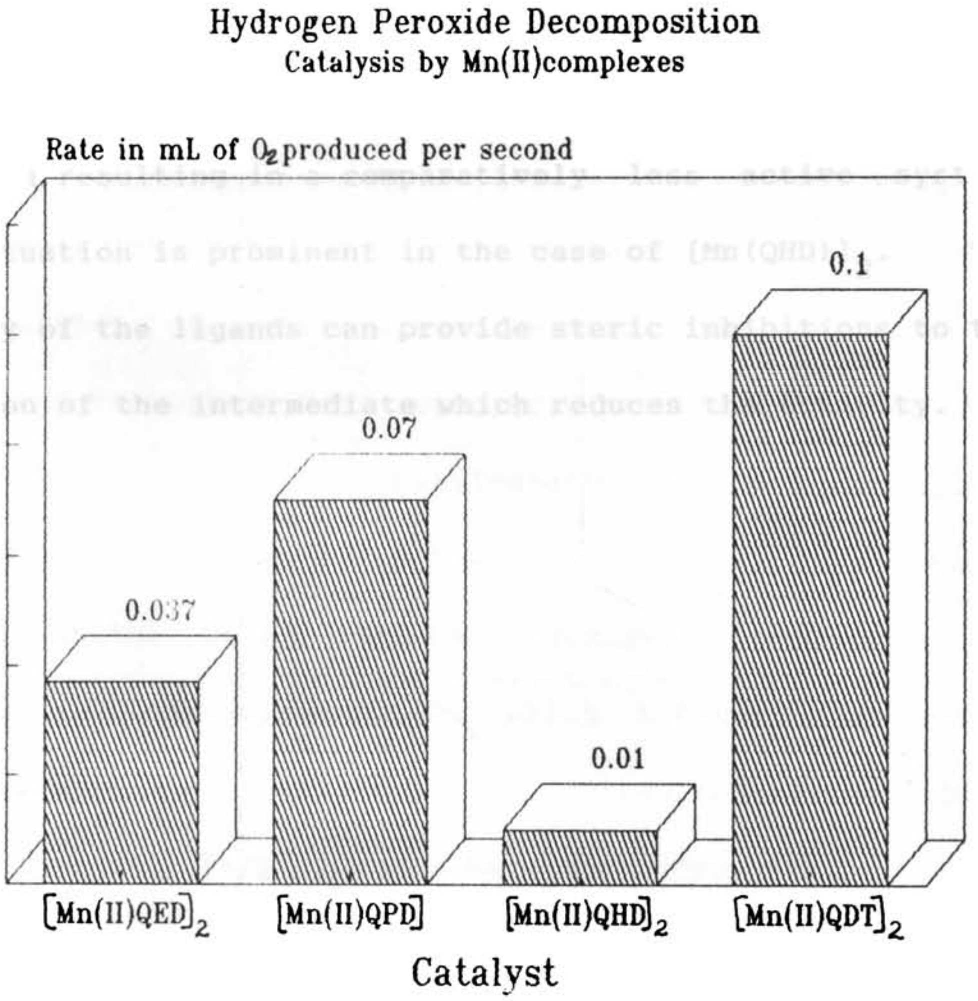
8.3 RESULTS AND DISCUSSION

The results of decomposition studies carried out by different Mn(II) complexes are presented in the Table VIII.1. The catalytic activity behaviour is well portrayed in the present series of complexes. The aim of the catalytic activity study was to test the prepared complexes for their ability to interact with another molecules, as this is considered as the single prime quality of a complex catalyst. After the reaction, the solution was seen to be coloured, which may be due to the formation of any water soluble Mn(III) species.

TABLE VIII.1

Catalyst	Rate of O_2 evolved per sec (in mL)
$[Mn(QED)]_2$	3.7×10^{-2}
$[Mn(QPD)]$	7.3×10^{-2}
$[Mn(QHD)]_2$	1.0×10^{-2}
$[Mn(QDT)]_2$	12.8×10^{-2}

As the reaction is between the aqueous solution of H_2O_2 and the solid manganese complexes (which are hydrophobic in nature), the physical nature of the complex can also affect the activity. Neglecting this aspect for the sake of comparing the results it was found that the catalytic activity increases in the following order: $[Mn(QHD)]_2$ < $[Mn(QED)]_2$ < $[Mn(QPD)]$ < $[Mn(QDT)]_2$. As the system is heterogeneous, it would be difficult to give a proper explanation in these cases. The vacant coordination site might have been formed in the case of $[Mn(QDT)]_2$ through the oxidative dissociation of the dimeric complex. Furthermore, the pentadentate ligand QDT may favour the formation of H_2O_2 adduct with the five coordinate complex formed and this may be one of the reasons for the high activity exhibited by


Hydrogen Peroxide Decomposition
Catalysis by Mn(II)complexes
Rate in mL of O2 produced per second
0.037
0.07
0.01
0.1
[Mn(II)QED]2
[Mn(II)QPD]
[Mn(II)QHD]2
[Mn(II)QDT]2
Catalyst

[Mn(QDT)]$_2$. In the case of the [Mn(QPD)] complex, the square planar nature of complex can facilitate easy interaction with hydrogen peroxide which might be the reason for the greater activity of this complex. The case of [Mn(QED)]$_2$ cannot be explained easily, probably the dimer is stable towards adduct formation resulting in a comparatively less active system. This situation is prominent in the case of [Mn(QHD)]$_2$. The geometry of the ligands can provide steric inhibitions to the formation of the intermediate which reduces the activity.

CHAPTER IX

CATALYTIC ACTIVITY OF COBALT(II) AND COPPER(II) SCHIFF BASE COMPLEXES IN THE OXIDATION OF 3,5-DI-TERTIARY BUTYLCATECHOL

9.1 INTRODUCTION

Liquid phase oxidation of catechol and its derivatives catalysed by metal complexes has been the subject of considerable interest. This is important in understanding the chemistry of pyrocatechase enzymes and oxidases[219]. Martell and co-workers have reported kinetic studies on the autoxidation of 3,5-di-tert-butylcatechol in 50% methanol by manometric, ESR and spectrophotometric methods [220]. Also, studies of the metal chelate catalysed oxidation of pyrocatechol to o-benzoquinone in which bidentate chelating agents such as 4-nitrocatechol and tetrabromocatechol have been used as auxiliary ligands, have been reported[221].

Tsuruya and co-workers have reported the oxidation of 3,5-di-tert-butylcatechol in a nonaqueous solution catalysed by a variety of cobalt chelate complexes, in which 3,5-di-*tert*-butyl-o-benzoquinone alone is the oxidation product[222]. Catalytic activity of a series of cobalt complexes with tetra- and quinquedentate Schiff base ligands in the oxidation of 2,6-di-tert-butylphenol was studied by Sasakai *et al.*[223]

Many Fe(II) and Cu(II) complexes have been reported to effect the oxidative cleavage of catechol[224-227]. Malkin *et al.* reported that copper(II) ions have relatively high redox potential, being readily reduced to copper(I) by ascorbic acid, hydroquinones and catechols[228]. We have studied the catalytic activity of two series of our complexes *i.e.*, complexes of cobalt(II) and copper(II), in the oxidation of 3,5-di-*tert*-butylcatechol (DTBC) to 3,5-di-*tert*-butylquinone (DTBQ) by atmospheric oxygen and the results of our studies are presented in this chapter.

9.2 EXPERIMENTAL

9.2.1 Materials

Details about the syntheses of cobalt(II) and copper(II) complexes used in the study are given in Chapter V and Chapter VII respectively. CoSalen was synthesised according to the reported procedure in literature[229]. DMSO was selected as solvent in order to avoid vaporisation during the experiment. The solvent was made 0.1 molar with respect to triethylamine (15 mL / L of DMSO) to increase the basicity of the solvent. The DTBC solution (0.022 g in 90 mL solvent) was prepared afresh before each experiment in order to avoid slow aerial oxidation. The same solvent was used to prepare the catalyst solution (100 mL). A catalyst substrate ratio 1:10 was selected for the present study. The weight of the catalyst taken to prepare 100 mL solution is given in Table IX.1.

Table IX.1

Catalyst	Weight of catalyst taken (g)	Catalyst	Weight of catalyst taken (g)
$[Co(QED)]_2$	0.0085	$[Cu(QED)]_2$	0.0087
[Co(QPD)]	0.0095	[Cu(QPD)]	0.0096
$[Co(QHD)]_2$	0.0080	$[Cu(QHD)]_2$	0.0081
[Co(QDT)]	0.0094	[Cu(QDT)]	0.0095
CoSalen	0.0065	Blank	0.0000

9.2.2 Catalytic experiments

All the kinetic runs were carried out in a 250 mL beaker using atmospheric oxygen as oxidant. The intimate contact with air was maintained by magnetically stirring the solution. The reaction vessel was thermostated to keep the temperature constant at 28 ± 1^{o}C. The reaction was initiated by mixing the catalyst solution (10 mL) and the DTBC solution. The course of the reaction (Fig. 9.1) was

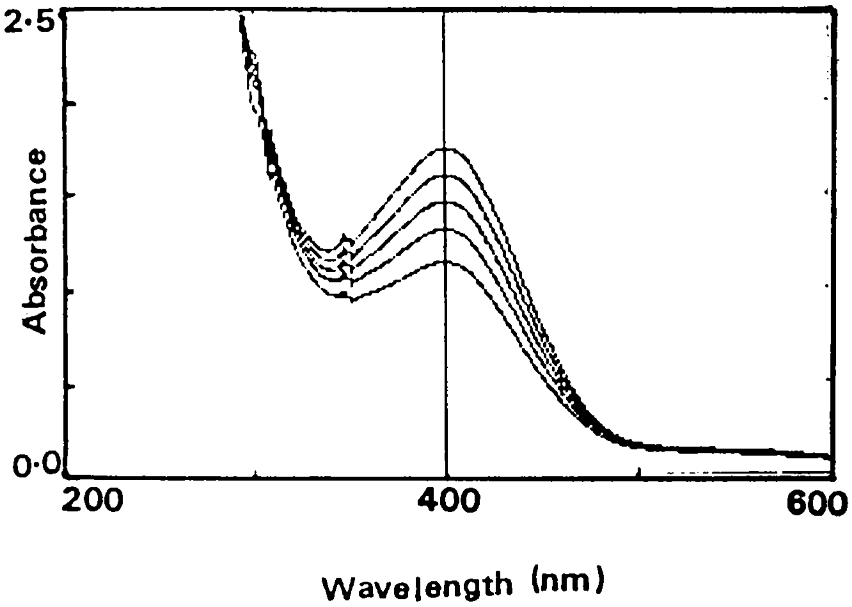


Fig. 9.1 Oxidation of DTBC to DTBQ
Spectra recorded at 5 minutes intervals in the presence of CoSalen

monitored by measuring the change in absorbance of the product at 400 nm. A solution of the catalyst with the same concentration as that of the reaction mixture was used as the reference. The rate of the conversion was obtained from the concentration *versus* time data by a computerised technique[218]. The concentration of DTBC undergoing oxidation in moles being derived from the molar extinction coefficient (ε) value of DTBQ.

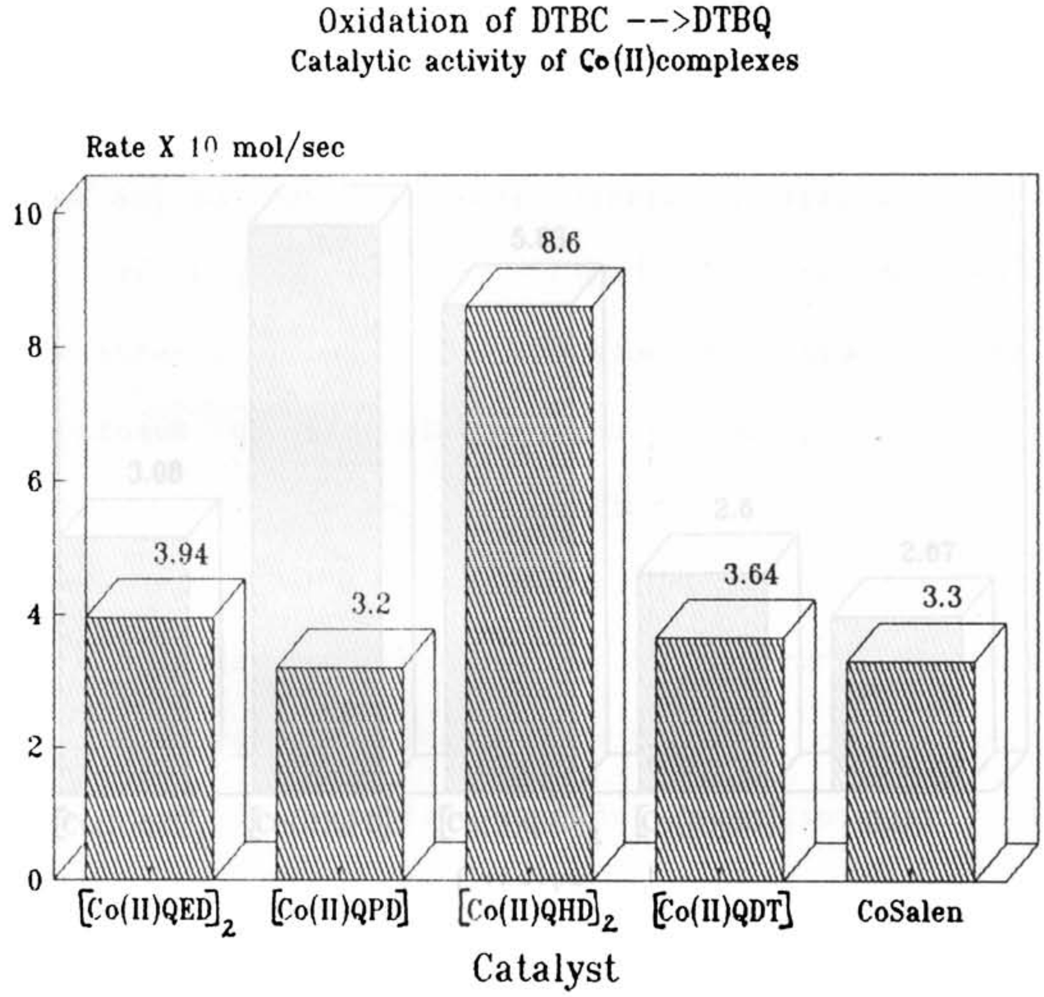
9.3 RESULTS AND DISCUSSION

Since the autoxidation of catechol is negligible in the absence of the catalyst, we have added triethylamine to increase the basicity of the solvent, DMSO. The reaction mechanism assumed here include the associative oxygen species adsorbed on metal ions. In the catalytic reaction, the first step may be the interaction between DTBC and chelate catalyst. Prior to this step, DTBC may be partially dissociated in the presence of amine, so that it can easily interact with the metal ion. The intramolecular electron transfer within the ternary complex (DTBC-CoL-O_2) generates corresponding quinone.

The results of the studies are given in Table IX.2. The rate of conversion data clearly reveals that all of these complexes are catalytically active in the oxidation of DTBC—>DTBQ. All the cobalt complexes show nearly ten times greater activity than copper complexes. In order to understand the influence of the ligand on the catalytic activity, the reaction was also studied in the presence of CoSalen, which is a known catalyst for this reaction. The rate of oxidation of our cobalt complex was compared with that of CoSalen. It is found that CoQHD shows a much greater activity than CoSalen. The other three cobalt complexes are

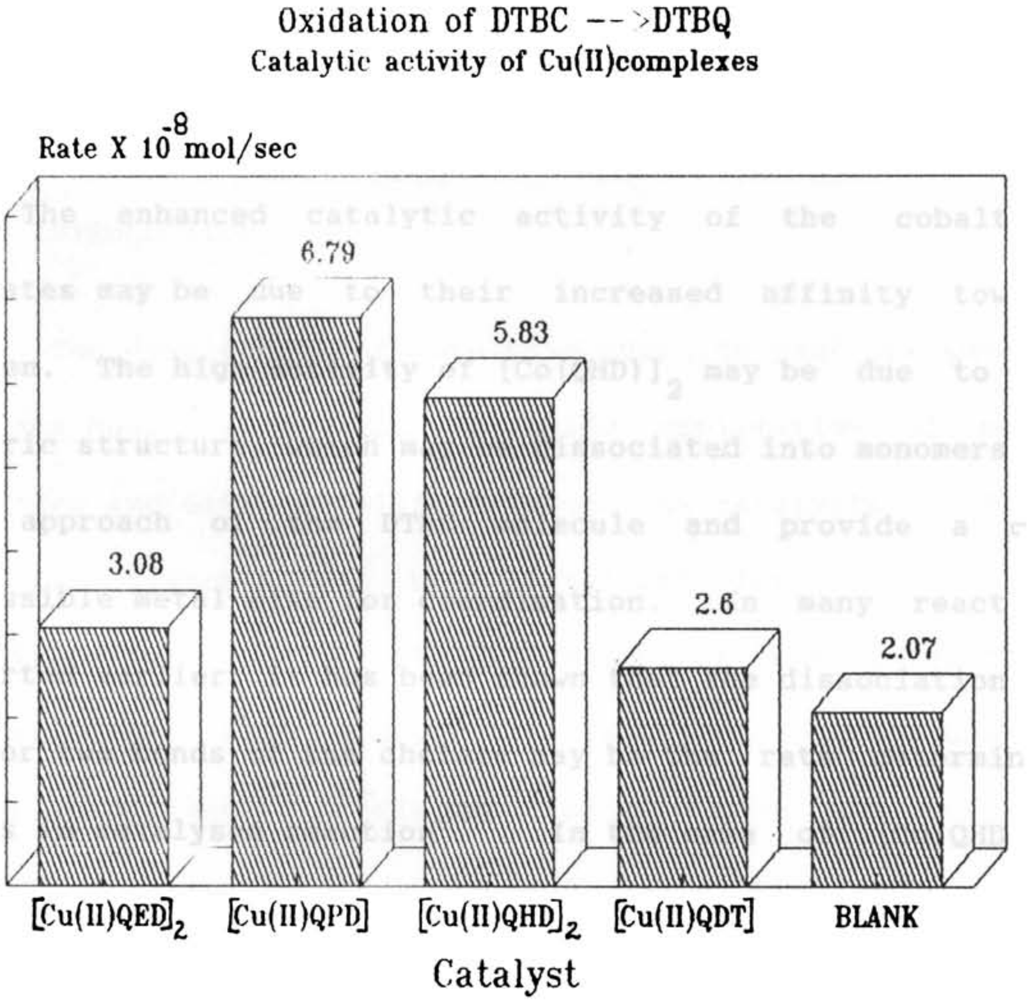
Table IX.2

Catalyst	Rate of conversion (mol dm^{-3} s^{-1})	Catalyst	Rate of conversion (mol $dm^{-3}s^{-1}$)
$[Co(QED)]_2$	3.94×10^{-7}	$[Cu(QED)]_2$	3.01×10^{-8}
[Co(QPD)]	3.20×10^{-7}	[Cu(QPD)]	6.79×10^{-8}
$[Co(QHD)]_2$	8.60×10^{-7}	$[Cu(QHD)]_2$	5.83×10^{-8}
[Co(QDT)]	3.64×10^{-7}	[Cu(QDT)]	2.60×10^{-8}
CoSalen	3.30×10^{-7}	Blank	2.07×10^{-8}



Oxidation of DTBC -->DTBQ

Catalytic activity of Co(II)complexes


Oxidation of DTBC -->DTBQ
Catalytic activity of Cu(II)complexes
Rate X 10^-8 mol/sec
0
1
2
3
4
5
6
7
8
3.08
6.79
5.83
2.6
2.07
[Cu(II)QED]2
[Cu(II)QPD]
[Cu(II)QHD]2
[Cu(II)QDT]
BLANK
Catalyst

comparable in catalytic activity to CoSalen. All the copper complexes are found to be catalytically active, but only to a much lesser extent.

The enhanced catalytic activity of the cobalt(II) chelates may be due to their increased affinity towards oxygen. The high activity of $[Co(QHD)]_2$ may be due to its dimeric structure, which may be dissociated into monomers on the approach of the DTBC molecule and provide a more accessible metal site for coordination. In many reactions reported earlier, it has been shown that the dissociation of one or two bonds of the chelate may be the rate determining steps in catalysed reaction[230]. In the case of $[Cu(QHD)]_2$, the dimer unit may be strongly bonded resulting in least activity towards this oxidation.

CHAPTER X

OXIDATION OF ASCORBIC ACID USING IRON(III) COMPLEXES SUPPORTED ON SERALITE SRC 120 RESIN AS CATALYSTS

10.1 INTRODUCTION

The development of catalysis over the past few decades has been characterised by the wide application of metal complexes and organometallic compounds as catalysts. Novel catalytic systems have been developed for the use in industrial processes for the production of substances like polypropylene, high density polyethylene, acetaldehyde, acetic acid, and alcohols in large scale, and for the synthesis of expensive compounds in relatively small quantities, e.g. asymmetric amino acids[231-233]. The application of heterogeneous catalysts is more convenient for technological developments. Such catalysts could be derived from supporting complex catalysts on insoluble supports[234-235].

Ascorbic acid, an important reducing agent in biochemical systems, is easily oxidised by many transition metal centers to dehydroascorbic acid[236-238]. A number of papers have been published on the hexacyanoferrate(III) oxidation of ascorbic acid in acidic or strongly acidic media[239-243]. In this chapter, we present the results of our study on the oxidation of ascorbic acid using Fe(III) complexes supported on Seralite SRC 120 resin as catalysts.

10.2 EXPERIMENTAL

The complexes were supported using the following procedure:

Seralite SRC 120 resin (1 g. SRL) was refluxed with Fe(III) complexes (50 mg) in alcohol for 2 h. It is approximated that in this process the labile Fe-Cl bond ruptures and the complex gets supported on the resin. The resin changes its colour from pale yellow to brown after the incorporation of the complex. The resin was collected by filtration and the filtrate was analysed for the presence of chloride ions. The oxidised product, dehydroascorbic acid, was estimated by Roe's method[244] at the end of each experiment.

10.2.1 Analysis of the iron content in the resin

The resin (200 mg) was treated with 10 mL of 0.5 M HNO_3. The mixture was warmed for 1 h and filtered after cooling. The process was repeated three times and the total iron content of the filtrate was determined spectrophotometrically. The iron content of the complexes is given in Table X.1.

Table X.1 Analytical data of the resin

Compound supported on the resin	Iron content/ g of resin(g)
$[Fe(QED)Cl]_2$	1.20×10^{-4}
$[Fe(QPD)Cl]$	1.30×10^{-4}
$[Fe(QHD)Cl]_2$	1.18×10^{-4}
$[Fe(QDT)]_2Cl_2$	1.25×10^{-4}

10.2.2 Catalytic experiments

The following general procedure was used to study the oxidation:

To the freshly prepared ascorbic acid solution (2.5×10^{-4} M, 50 mL), 500 mg resin was added and stirred. The absorbance at 250 nm was noted at an interval of 10 minutes. The absorbance obtained was converted into concentration from the ε value of ascorbic acid at 250 nm. The rates of the reaction were computed from the concentration *versus* time data by a computerised technique[218].

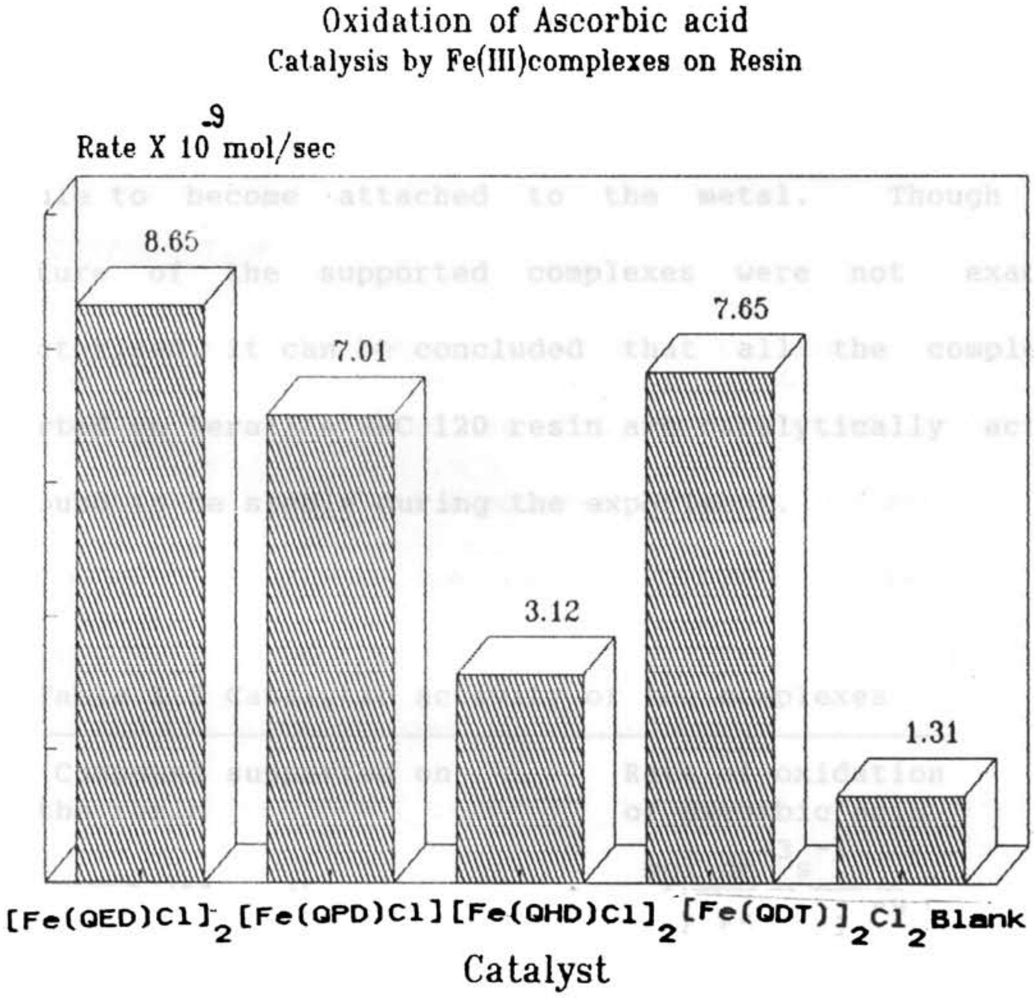
10.3 RESULTS AND DISCUSSION

The IR spectra of the resin supported complex show a peak at about 1670 cm^{-1} due to the $C{=}N$ stretching showing the presence of the complex in the resin. Furthermore, the solution collected after the filtration of the resin-supported complex showed the presence of chloride ions which indicate that anchoring of the complex has occured through the displacement of the chlorine atom.

Ascorbic acid is a two electron reducing agent, which can be readily oxidised in one-electron steps by metal ions and metal complexes in their high valent state. The rate of the reaction is known to depend on molecular oxygen concentration. It has been shown that a dissociative mechanism is the probable pathway for the oxidation. The rate may therefore be expected to depend on the stability of the complex. As our system contains metal chelates supported on an ion exchange resin, the exact nature of the supported chelate is unknown to us and it would be difficult to put forward any crucial facts regarding the catalytic behavior of these complexes. However, for an inner sphere oxidation, the formation of the transition state requires the displacement of one or more groups of the coordinated ligand. It is expected that a considerable steric factor would be associated with such displacement and that these effects would vary from one complex to the other depending upon the nature of the ligand.

No leaching out of the metal chelate from the resin was observed during the experiment. The rate of oxidation of ascorbic acid obtained for each complex supported on the resin are given in Table X. 2. The $[Fe(QED)Cl]_2$ and $[(FeQDT)_2]Cl_2$ shows more activity towards the oxidation.

It is interesting to note that the complexes with more flexible ligands, say $[Fe(QED)Cl]_2$ and $[Fe(QDT)]_2Cl_2$ show


Oxidation of Ascorbic acid
Catalysis by Fe(III)complexes on Resin
Rate X 10^{-9} mol/sec
8.65
7.01
3.12
7.65
1.31
[Fe(QED)Cl]$_2$
[Fe(QPD)Cl]
[Fe(QHD)Cl]$_2$
[Fe(QDT)]$_2$Cl$_2$
Blank
Catalyst

greater activity than the complexes of the rigid ligands. The rigid nature of the ligand, QPD, may be the reason for the lesser activity in its complex. In $[Fe(QHD)Cl]_2$ dimer, the ligand can provide steric inhibition to the ascorbic acid molecule to become attached to the metal. Though the structure of the supported complexes were not exactly characterised, it can be concluded that all the complexes supported on Seralite SRC 120 resin are catalytically active and found to be stable during the experiment.

Table X.2 Catalytic activity of the complexes

Compound supported on the resin	Rate of oxidation of ascorbic acid mol $dm^{-3}s^{-1}$
$[Fe(QED)Cl]_2$	8.654×10^{-9}
$[Fe(QPD)Cl]$	2.014×10^{-9}
$[Fe(QHD)Cl]_2$	3.125×10^{-9}
$[Fe(QDT)]_2Cl_2$	7.653×10^{-9}
Blank	1.315×10^{-9}

CHAPTER XI

OXIDATION OF THIOCRESOL BY THE COBALT(II) COMPLEXES SUPPORTED ON CHARCOAL

11.1 INTRODUCTION

Autoxidation reactions of many inorganic and organic compounds are accelerated in the presence of first row transition metal ions and complexes in which the metal center has access to more than one stable oxidation state[245,246]. The catalytic properties of divalent and trivalent metal complexes with phthalocyanine, porphyrin, and Schiff base derivatives have been compared to those of catalyse, peroxidase, oxidase and oxygenase enzymes[247-248]. In this chapter, we report our studies on the oxidation of *p*-thiocresol by some new cobalt(II) complexes supported on charcoal, The oxidation of thiols by supported metal complexes are important from an industrial point of view.

11.2 EXPERIMENTAL

11.2.1 Materials

Analytical grade p-thiocresol (Fluka AG) were used without further purification. The synthesis of the Co(II) complexes used are already described in Chapter V.

Preparation of charcoal supported complexes

Cobalt(II) complexes (2.5 X 10^{-5} mol) were refluxed with activated granular charcoal pieces (10 g) in ethanol (200 mL) for 2 h.. After the complete adsorption, the solution would be colourless and the catalyst sample was filtered and dried *in vacuo* for further use.

11.2.2 Catalytic experiments

The experimental set up is as shown in the Fig. 11.1. An aqueous-alcoholic-alkaline solution was used to study the reaction. The typical procedure for catalytic activity studies for a sample is as follows. The column was filled with 5 g of charcoal sample and some glass beads were added above it. Thiocresol solution in alcohol (10 mL; 5X10^{-5} M) was pipetted to a 50 mL standard flask and further 15 mL of ethanol was added to it. The solution was made up with NaOH (1M) and shaken well. This solution was poured into the column and the reaction was started by passing air through it at a constant flow rate while eluting through the column. The absorbance of p-tolylsulfide ion at 270 nm was noted after each elution. This process was repeated until the absorbance remained steady. A duplicate run was also carried out.

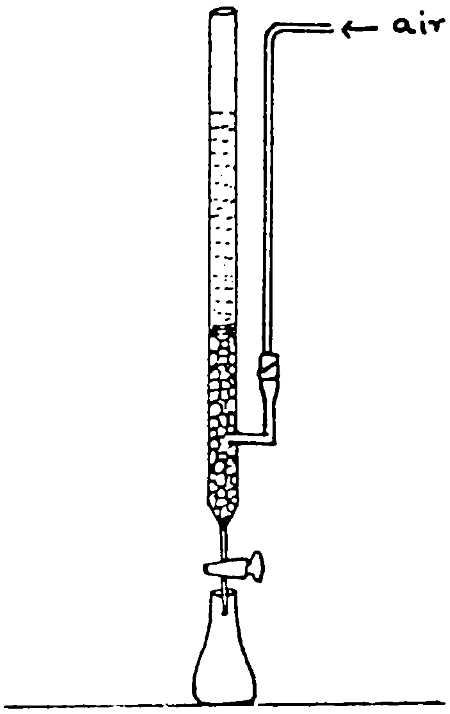
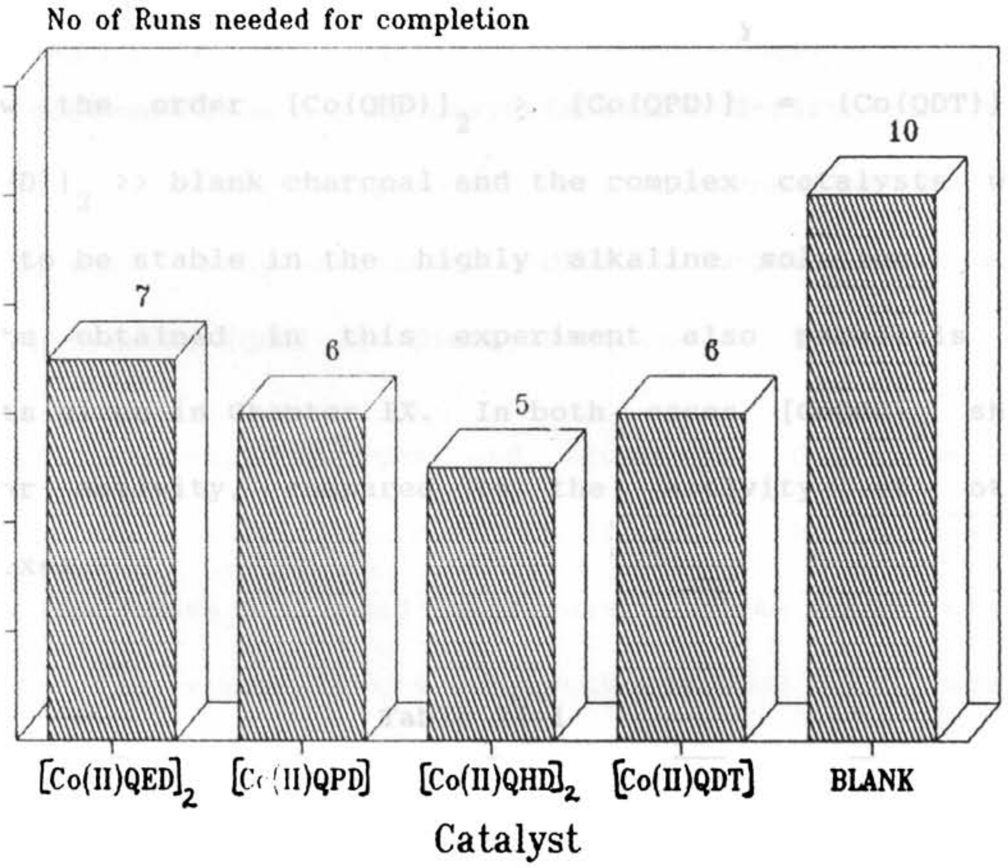


Fig. 11.1 Experimental set up for thiocresol oxidation

Oxidation of Thiocresol

Catalysis by Co(II)complexes on charcoal



11.3 RESULTS AND DISCUSSION

The catalytic activity of the samples was compared by the number of runs needed for completion of the reaction. The values are given in Table XI 1. The activity was found to follow the order $[Co(QHD)]_2$ > $[Co(QPD)]$ = $[Co(QDT)]$ > $[Co(QED)]_2$ >> blank charcoal and the complex catalysts were found to be stable in the highly alkaline solution. The results obtained in this experiment also parallels the results given in Chapter IX. In both cases $[CoQHD]_2$ shows greater activity, compared to the activity of other complexes.

Table XI.1

Compound supported on charcoal	No. of runs needed to complete the reaction
$[Co(QED)]_2$	7
$[Co(QPD)]$	6
$[Co(QHD)]_2$	5
$[Co(QDT)]$	6
Blank	10

SUMMARY

The thesis deals with the synthesis, characterisation and catalytic activity studies on manganese(II), iron(III), cobalt(II),nickel(II) and copper(II) complexes of the Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde. The Schiff bases were prepared by the condensation of the aldehyde with ethylenediamine (QED), *o*-phenylenediamine (QPD), hydrazine (QHD) and diethylenetriamine (QDT).

As the phenolic oxygen and azomethine nitrogens are linked to the electron deficient positions of the quinoxaline ring in the above mentioned Schiff bases, these atoms cannot be regarded as strong donors as in other common Schiff bases. Also, the electron deficient quinoxaline ring does not favour a π interaction with the metal ions. Due to the comparatively weaker ligand field, the d level splitting may be lesser in the complexes synthesised from the above Schiff bases. These complexes, therefore, show interesting magnetic properties. Furthermore, the nature of the ligands impose a particular geometry on the complexes. For example, the ligand QED is dibasic and tetradentate, and is expected to give square planar complexes, but all the complexes of QED reported herein are of dimeric in nature. This happens only

because the flexible ligands permits some distortion from a strictly planar structure. In the dimer the metal atom may probably be out of the plane of the donor atoms. As QPD does not favour such a distortion, it yields only monomeric complexes. The stereochemistry of QHD is not suitable for the coordination of all the four donor atoms (two phenolic oxygens, one azomethine nitrogen and a secondary nitrogen) to a single metal ion. Hence this ligand is found to form dimeric complexes with interesting structures. The QDT can act as a pentadentate ligand and is able to form square pyramidal complexes. However, QDT forms dimeric complexes in the cases of manganese(II) and iron(III).

The thesis is divided into eleven chapters. Chapter I presents a general discussion on the Schiff base ligands and their complexes with emphasis given to tetradentate Schiff bases and their complexes. The scope of the present investigation is also outlined in this chapter. Chapter II gives the procedures for the synthesis of the Schiff base ligands and the experimental procedures involved in the study.

Chapters III. IV, V, VI and VII deals with the studies on the synthesis and characterisation of thc complexes of the

Schiff base ligands QED, QPD, QHD and QDT. Chapter III presents the results of our studies on the manganese(II) complexes. The empirical formula of the complexes is found to be [ML], where L = QED, QPD, QHD or QDT. The non-electrolytic nature of these complexes was revealed by conductance measurements. The IR spectral data indicate the coordination of the azomethine nitrogens and the phenolic oxygens to the metal. In the case of QDT complex, the amino nitrogen of QDT is also found to participate in bonding. The magnetic moment values indicate that only QPD forms monomeric square planar complex with manganese. EPR spectra of the complexes yield a single g value = 2. The hyperfine splittings due to the manganese atom were also observed in the spectrum. The complexes can therefore be represented as $[Mn(QED)]_2$, $[Mn(QPD)]$, $[Mn(QHD)]_2$ and $[Mn(QDT)]_2$.

Chapter IV emphasises the effect of spin cross over equilibria observed in the iron complex of QDT. The empirical formula of the complex was found to be [MLCl]. All the complexes except the QDT were found to be non-electrolytes in pyridine. Also magnetic moment studies indicate antiferromagnetic interactions in the QED, QHD and QDT complexes. The complexes can be represented as $[Fe(QED)Cl]_2$, $[Fe(QPD)Cl]$, $[Fe(QHD)Cl]_2$ and $[Fe(QDT)]_2Cl_2$.

The magnetic, EPR and Mossbauer studies indicate that the dimeric $[Fe(QDT)]_2Cl_2$ is in spin equilibrium between the high spin and low spin states. The Mossbauer splitting pattern observed at 77 K suggest that the system have $S = 0$ ground state at lower temperatures due to antiferromagnetic coupling.

All the cobalt complexes prepared are non-electrolytes, and are formulated as [ML] type of complexes. The magnetic and EPR studies of cobalt(II) complexes indicate that these complexes are in a state of spin equilibrium at room temperature. The EPR spectra recorded at LNT exhibit metal hyperfine splittings and reveals the low spin nature of the cobalt(II) centre at this temperature. The QED and QHD complexes have been suggested to have dimeric structures. [Co(QPD)] is of monomeric nature with square planar structure. The geometry around cobalt in [Co(QED)] and [Co(QDT)] is suggested to be square pyramidal. These results are presented in Chapter V.

Chapter VI deals with studies on nickel(II) complexes. All the complexes are found to be non-electrolytes in pyridine. A dimeric structure has been proposed for the QED complex. [Ni(QPD)] is monomeric with a square planar geometry around Ni. The QHD complex is a dimeric molecule with a planar arrangement of donor atoms around each metal. [Ni(QDT)] is square pyramidal in geometry. The anomalous magnetic behavior obtained for these complexes have been explained on the basis of singlet - triplet transitions in the solid state *i.e.* the complexes are in spin equilibrium.

In Chapter VII, studies on copper(II) complexes have been described. All the complexes are found to be non-electrolytes. The magnetic moment studies show antiferromagnetic interaction in QED and QHD complexes of copper which may be dimeric in nature. [Cu(QPD)] and [Cu(QDT)] have been suggested to have square planar and square pyramidal structures respectively. The EPR studies also correlate with the above assumption. The very low magnetic moment value observed for [Cu(QHD)] may be due to the strong antiferromagnetism existing in this system.

Chapters VIII, IX, X and XI deal with the catalytic activity studies of the complexes reported herein. Chapter VIII presents the results of studies on the catalytic decomposition of hydrogen peroxide using the manganese(II) complexes . The activity has been studied by measuring the volume of oxygen evolved and found to be increasing in the following order $[Mn(QHD)]_2$ < $[Mn(QED)]_2$ < [Mn(QPD)] < $[Mn(QDT)]_2$.

Cobalt and copper complexes were screened for their catalytic activity in the autoxidation of 3,5-di-*tert*-butylcatechol to its quinone, and the results of this study are presented in Chapter IX. It is found that the cobalt complexes have ten times greater activity than the copper complexes. It was found that the catalytic activity increases in the order: [Cu(QDT)] < $[Cu(QED)]_2$ < $[Cu(QHD)]_2$ < [Cu(QPD)] for the copper(II) complexes, and in the order: [Co(QPD)] < [Co(QDT)] < $[Co(QED)]_2$ < $[Co(QHD)]_2$ for the cobalt(II) complexes.

In Chapter X, the method adopted for supporting the iron complexes, $[Fe(QED)Cl]_2$, [Fe(QPD)Cl], $[Fe(QHD)Cl]_2$ and $[Fe(QDT)]_2Cl_2$, on Seralite SRC 120 resin and their catalytic activity studies in the oxidation of ascorbic acid are described. The complexes are attached to the resin through the displacement of the chlorine atom in the complexes. Though the exact geometry of the supported complexes could not be resolved, the supported complexes are found to be catalytically active. The activity was found to be higher for complexes having the flexible ligands, QED and QDT and is smaller for the complexes having rigid ligands, QPD and QHD.

Activated charcoal was used to support cobalt complexes in the study of oxidation of thiocresol in aqueous-alcoholic-alkaline medium. All the samples are found to be catalytically active and the activity increases in the following order: [Co(QHD)] > [Co(QPD)] = [Co(QDT)] > [Co(QED)].

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