

**SYNTHESIS AND CHARACTERISATION OF COBALT(II)-IMIDAZOLYL
COMPLEXES AS POTENTIAL CATALYSTS IN THE OXIDATION OF PHENOL
AND STYRENE**

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DECLARATION

I declare that the dissertation hereby submitted to the University of Limpopo (Turfloop campus) for the degree of Master of Science has not been previously submitted by me for a degree at this or any other university, that it is my own work both in design and execution, and that all material contained herein has been duly acknowledged.

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Date

DEDICATIONS

This work is dedicated to my lovely son, Leago, my parents Mampholodi and Mathibedi Sebati, my brothers, Machipi and Matumela and my sisters Matladi, Ngoanamoshadi and Mamphatlo. To my aunt Mahlalo Monyela, thank you for all the support you have given me during my years of study. Granny Ngoanamoshadi Molepo, you stood by me through all and gave me the reason to look into the future.

ABSTRACT

This study deals with the synthesis and characterisation of cobalt complexes of nitrogen-donor imidazolyl-salicylaldimine ligands and their potential catalytic activity in the oxidation reactions of phenol and styrene.

Five ligands were used in the study, four of which are new. Compound 2,4-di-tert-butyl-6[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-phenol (**L1**), was synthesised according to a literature procedure. The other imidazole-based salicylaldimine compounds 2-ethoxy-6[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-phenol (**L2**), 4-methoxy-6[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-phenol (**L3**), 1[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-benzene (**L4**) and 4-methyl-1[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-benzene (**L5**) were prepared by Schiff base condensation reaction of histamine dihydrochloride with 3-ethoxy-2-hydroxybenzaldehyde, 5-methoxy-2-hydroxybenzaldehyde, benzaldehyde, 4-methylbenzaldehyde respectively. **L1-L5** were characterised by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, IR and UV-vis spectroscopy and high resolution mass spectrometry (HRMS). Reactions of **L1-L5** with CoCl_2 yielded complexes **C1-C5**, while complexes **C6-C10** were synthesised by reactions of **L1-L5** with CoBr_2 all in a ratio of 1:1 of ligand to metal precursor. The cobalt(II) complexes were characterised by IR and UV-vis spectroscopy, elemental analysis and high resolution mass spectrometry due to their paramagnetic nature. All the characterisation data point to complexes **C1-C10** being formulated as $[\text{Co}(\kappa^3\text{-L})\text{X}]$ (where **L** = ligand and **X** = halide). However, single crystal X-ray diffraction showed that the prolonged stay of complex **C6** in a solution gave a new structure as complex **C11**.

The imidazole-based salicylaldimine cobalt(II) complexes (**C1-C10**) were tested as catalysts for the oxidation reactions of phenol and styrene with H_2O_2 , O_2 and 3-chloroperbenzoic acid as oxidants. The complexes were found not to be active for the oxidation of both substrates (phenol and styrene) with 0% conversion, even when the reactions were left for 1 week. Analysis of the oxidation reactions were performed with GC and ^1H NMR spectroscopy. Both analysis methods showed the presence of unreacted substrates at the end of the reaction period. Effects of concentration of pre-catalysts, substrates and oxidants, time and temperature of

reaction and nature of solvent on catalytic activity were also investigated, however the conversions remained at 0% conversion.

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LIST OF ABBREVIATIONS

NLO	nonlinear optics
EL	electroluminescence
DTBP	2,6-di-tert-butylphenol
TON	turnover number
DOPA	3,4-dihydroxyphenylalanine
CoSMDPT	[bis(salicylidene- γ -iminopropyl)methylamine]cobalt(II)
NMR	nuclear magnetic resonance
IR	infrared
UV	ultraviolet
vis	visible
HRMS	high resolution mass spectrometry
s	Singlet
d	Doublet
t	Triplet
J	coupling constant
ESI	electrospray ionisation
m/z	mass/charge
MS	mass spectrometry
DMSO	dimethylsulfoxide
THF	tetrahydrofuran
GC	gas chromatography

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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1. INTRODUCTION

This chapter gives a brief introduction of Schiff base compounds and their metal complexes. This includes the importance and uses of Schiff base compounds and their metal complexes. Lastly the objectives and outline of the current work are given.

1.2. BACKGROUND

Oxidation of organic substrates by oxidants such as dioxygen, hydrogen peroxide, alkylhydroperoxide, sodium hypochlorite or iodobenzene into various organic molecules, under mild conditions in both chemical and biological catalysis is a big challenge [1-2]. This has resulted in a number of researchers in the world looking for efficient catalysts to perform this reaction. Oxidation of organic substrates lead to by-products, some of which could be harmful; but the use of the above oxidants in most cases leads to less harmful products, concept that is “preached” by “green chemists”.

Research under the theme “green chemistry” strives to develop environmentally and economically sustainable processes for industrial applications [3]. “Green chemistry” is an approach to synthesis, processing and use of chemicals that reduces risks to humans and the environment [4]. Selective oxidation of organic compounds with simple oxidants such as cheap, abundant and non-toxic dioxygen is therefore an attractive approach for wide variety of ecologically sustainable chemical processes [3].

Some important natural enzymes for oxidation reactions include cytochrome P-450, peroxidases and catalases. All these enzymes have iron(III) porphyrin as a central unit. Hence, several investigations have been conducted on the reactions of synthetic metalloporphyrins to understand the mechanism of action of porphyrin containing enzymes in oxidation process. In spite of the progress made to understand metalloporphyrins catalysed oxidation reactions, yields are not good

enough to be commercially viable [5]. A variety of high-valent metalloporphyrins have been used as catalysts for the oxidation of organic substrates. The synthesis of metalloporphyrins is difficult and generally proceeds in very low yield. This has led to the search for other ligands to make novel complexes that can be used as catalysts in oxidation reactions [5-7]. Schiff base transition metal complexes have been found to be attractive oxidation catalysts because of their ease of synthesis and their chemical and thermal stability [5]. The metal in the catalyst is also important depending on how it binds with ligand. Several considerations go into choosing a metal, one of which has to be cost. Cobalt(II) complexes offer more effective and affordable approaches to oxidise phenols and styrene to useful substrates since cobalt is non-expensive and non-toxic [6, 7] .

1.2.1. Schiff base compounds

Schiff bases are compounds which were first prepared by Hugo Schiff in 1864 [8]. They have the general structure $RR_1C=NR_2$ ($R = R_1 = R_2 =$ alkyl, aryl or hydrogen). When R is alkyl or aryl and R_1 is a hydrogen, the compounds are referred to as aldimines ($R-CH=NR_2$) but when both R and R_1 are alkyl or aryl groups they are known as ketimines and R_2 can either be an alkyl or aryl group [9]. They are generally prepared *via* condensation of an aldehyde with an amine, in refluxing alcohol [10-11].

Ligands are classified according to the number of donor atoms they contain, as bidentate (1), tridentate (2), tetradentate (3) or polydentate (4) (**Figure 1.1**) [12] and are capable of forming very stable complexes with transition metals. When the Schiff base has a hydroxyl group sufficiently near the site of condensation, they can react in such a way that a five or six membered ring can be formed when reacting with a metal ion [12]. In this dissertation, Schiff base compounds derived from aromatic amines and aromatic aldehydes were targeted in order to prepare potentially bidentate or tridentate ligands similar to what has been reported in the literature for the applications in biological, inorganic and analytical chemistry [12-13].

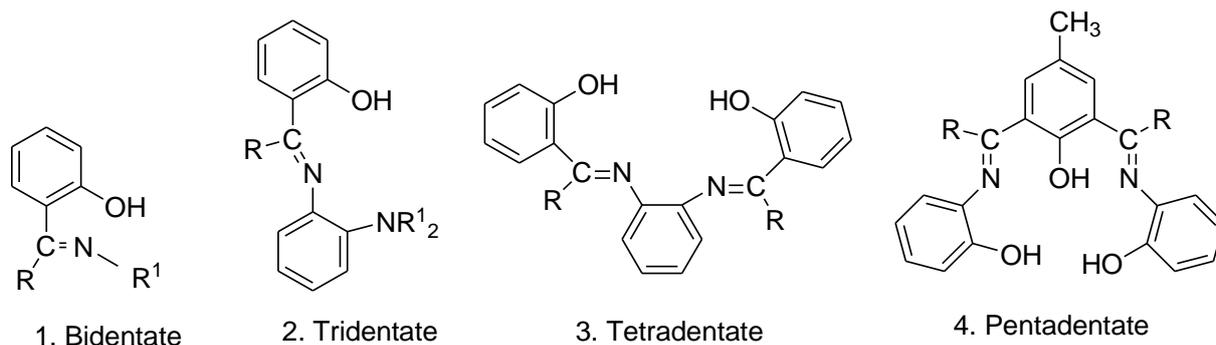


Figure 1.1: Some classes of Schiff base ligands [12]

1.2.2. Schiff base transition metal complexes

Metal complexes of Schiff bases continue to occupy a central role in the development of coordination chemistry after the work of Jorgenson and Werner several years ago. This has led to several studies of Schiff base metal complexes because they have a lot of applications. They serve as models for biologically important species and find applications in biomimetic and catalytic reactions [14]. One such example is cobalt tetradentate Schiff base complexes that have been extensively used to mimic cobalamin (B12) coenzymes, dioxygen carriers and oxygen activators [15]. These and many other Schiff base metal complexes are prepared by treating metal salts with Schiff base ligands under suitable conditions [16].

1.3. APPLICATIONS OF SCHIFF BASES AND THEIR METAL COMPLEXES

The versatility of Schiff base ligands can be seen in biological, analytical and industrial applications of their metal complexes which make investigations in this area of chemistry highly desirable. The applications of the Schiff bases and their metal complexes are therefore briefly discussed here.

1.3.1. In non-linear optical devices

Schiff base metal complexes are used in non-linear optics (NLO). NLO deals with the interactions of applied electromagnetic fields with various materials to generate new electromagnetic fields, altered in frequency, phase, or other physical properties. Such materials are able to manipulate photonic signals efficiently; and are of importance in optical communication, optical computing, and dynamic image processing [17-18]. It is in this connection that Schiff base ligands are important

because they, together with transition metals, are able to form complexes that have various excited states as well as ability to tailor metal-organic-ligand interactions that creates NLO [19-20].

1.3.2. As electroluminescent materials

Another application of Schiff base metal complexes is in electroluminescence (EL). EL is an optical and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field. Organic electroluminescent devices have been useful in novel-type flat-panel display since Tang *et al.*, [21] first reported on high-performance organic EL devices. Their discovery was based on employing a multilayer device structure containing an emitting layer and a carrier transport layer of suitable organic materials. Organic dyes, chelate metal complexes and polymers are three major categories of materials used in the fabrication of EL devices. This requires electron-rich functional group and it is this property of Schiff base compounds that allows their use in EL applications. Schiff base complexes, especially those of Zn(II), are now a days used as electroluminescent materials [22]. Zinc complex of the Schiff base, N,N'-bis(2-hydroxy-1-naphthylidene)-3,6-dioxo-1,8-diaminooctane, emits blue light with an emission peak at 455 nm having maximum brightness of 650 cd m², when it is used as the emitting layer in an electroluminescence device.

1.3.3. In electrochemical sensors

Schiff base compounds can be used to prepare supramolecules that are important in making sensing material in the construction of potentiometric ion-selective electrodes for lanthanide series. Here Schiff bases are used as carriers in the preparation of potentiometric sensors for the detection of cations and anions [23].

1.3.4. Biological and medicinal applications

Many ligands have been designed to mimic the function of natural carriers in recognising and transporting specific metal ions, anions in neutral molecules and in understanding and reproducing the catalytic activity of metallo-enzymes and proteins. Schiff bases are some of the best known ligands that form intermediates in many enzymatic reactions. Here interaction of an enzyme with an amine or carbonyl group of the substrate allows for the development of new drugs as well as understanding of biological process that explains the action of drugs [24].

1.3.5. Catalytic applications

All the above applications show how versatile Schiff base ligands are, but it is in catalysis that Schiff base ligands have found the most application. Schiff base complexes play a central role in various homogeneous catalytic reactions and the activity of these complexes varies with the type of ligands, coordination sites and metal ions [16]. Literature reports reveal that a large number of Schiff base metal complexes exhibit catalytic activities including oxidations, hydroxylation, aldol condensation and epoxidation. In Schiff base metal complexes, the environment at the coordination centre can be modified by attaching different substituents to the ligand [25]. As the aim of this study was on the oxidation reaction catalysed by Co(II) complexes, the discussion that follow will be limited to oxidation reactions.

1.3.5.1. Oxidation reactions

Oxidation of organic compounds is an extensively used reaction in academic laboratories and on a large scale in the chemical industry. Different reagents and methods are available for the oxidation of organic molecules. Even though these methods exist, most of them share common disadvantages from an industrial point of view [26-27]. Many industrial oxidation reactions are currently performed with oxidants such as high oxidation state metal oxides, peroxides and nitric acid. These oxidants are either expensive or generate organic and heavy metal wastes [27]. Therefore alternative and environmentally benign oxidants are desirable for greener industrial applications.

An ideal oxidant for oxidation reaction should be easily accessible, cheap and non-toxic. The best oxidant to fit this description is dioxygen or hydrogen peroxide. Oxygen is easily available since it is present in air and the only by-product from its reaction with organic substrates is water [27-28]. Certain aspects make the use of molecular oxygen and hydrogen peroxide as oxidants challenging. Although both have a high oxidation potential, they are not very reactive towards organic molecules. An appropriate catalyst is therefore needed for efficient use of these oxidants as it activates the oxidant molecule and mediates the oxidation potential to the right oxidation reaction [27]. If the oxidants (alkylhydroperoxide, sodium hypochlorite or iodobenzene) are to be replaced by dioxygen and hydrogen peroxide, catalysts which are able to activate these oxidants at mild reaction conditions and in solution phase are required. The most promising solution to this

challenge is homogeneous transition metal complexes which have been reported in literature to catalyse oxidation reactions under mild conditions by using dioxygen or hydrogen peroxide as oxidants. Cobalt complexes offer some of the best examples as catalysts in this regard [27].

The selective oxidation of phenol to catechol and hydroquinone and oxidation of styrene to a ketone and an alcohol are industrially useful processes and has been carried out using various transition metal complexes [29-30]. The oxidation of phenol and styrene in the presence of dioxygen or hydrogen peroxide, in particular, is normally an activation process that is accomplished in the presence of cobalt catalysts.

The propensity of cobalt(II) salen complexes to bind with molecular oxygen and the use of those dioxygen-cobalt complexes as catalysts in various oxidation reactions has been a subject of intensive research in recent years [31-32]. The dioxygen-cobalt complexes formed from cobalt(II) salen complexes in presence of oxygen are known to catalyse a variety of organic reactions like oxidation of thiols, phenols, aldehydes and hydrocarbons involving hydrogen abstraction or one electron transfer [31]. It was therefore the general ability of cobalt-dioxygen to perform oxidation of organic compounds that led us to prepare suitable metal complexes, which we hope would be active catalysts for the oxidation of phenols and styrene in this project.

1.4. OBJECTIVES

The objectives of this project, therefore, were formulated based on some of the above narrative. Firstly, we set out to synthesise and characterise some new imidazolyl-salicyldimine compounds and to studied their coordination chemistry with cobalt(II) precursors. The resulting complexes were then to be tested for their ability to catalyse the oxidation of phenol and styrene using various oxidants.

The effect of halogens (Cl or Br) and ligand structure (hydroxyl containing and non-containing) on the cobalt precursors in the presence of oxygen on Schiff base cobalt complexes, as well as variations of reaction temperature, concentrations of cobalt complexes, substrates and oxidants, and time on the activity of Schiff base cobalt complexes for oxidation reactions also formed part of the objectives.

1.5. OUTLINE

Chapter 1 provides an introduction of Schiff base compounds and their metal complexes. A brief summary of the importance and uses of these Schiff base compounds and their metal complexes is presented. In Chapter 2 a literature review on Schiff base ligands and their transition metal complexes as catalyst precursors for oxidation reactions is presented. Chapter 3 describes the synthesis and characterisation of Schiff base ligands and cobalt complexes investigated in this project. In Chapter 4 the catalysis evaluation of the synthesised cobalt complexes in the oxidation of phenol and styrene is discussed. Finally Chapter 5, provides a summary of the overall outcomes of this project and future directions.

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CHAPTER 2

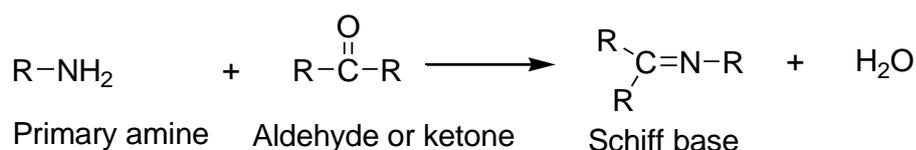
REVIEW ON SCHIFF BASE LIGANDS AND THEIR TRANSITION METAL COMPLEXES AS CATALYST PRECURSORS FOR OXIDATION REACTIONS

2.1. INTRODUCTION

Oxidation reactions are important as they provide a means of synthesising several materials that are used as intermediates in a wide range of applications. These reactions include phenols and styrene oxidation reactions. Phenol oxidation produces hydroquinone and catechol which are used as intermediates in the production of pharmaceuticals, pesticides, photographic film developer, flavors, fragrances and polymerisation inhibitors [1-3]. Epoxides, acetophenone and phenylalcohols obtained from styrene oxidation are important intermediates in pharmaceuticals and for the preparation of oxygen containing natural products, fine chemicals as well as for the production of epoxy resins [4]. For most industrial reactions, highly effective catalysts are required to accelerate processes such as oxidation reactions [5]. Therefore, developing organometallic complexes that can catalyse these phenol and styrene reactions is important and gaining more attention. One such group of complexes are those containing nitrogen donor ligands, particularly those of imine functional groups popularly known as Schiff bases.

2.2. SCHIFF BASE CONTAINING COMPOUNDS

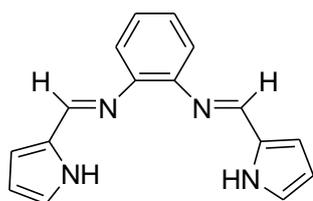
Schiff bases (named after Hugo Schiff), are formed when any primary amine reacts with an aldehyde or a ketone under appropriate conditions [6]. A Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine group (C=N) [7-10] as shown in **Scheme 2.1** [11-12].



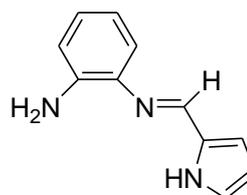
R = alkyl or aryl group

Scheme 2.1: **Preparation of Schiff base compounds** [11-12]

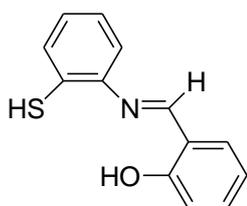
Schiff bases that contain alkyl substituents are substantially more stable and more readily synthesised while those that contain aryl substituents are relatively unstable [13-14]. This is due to the effective conjugated system by the aryl substituent and the imine, making them more stable while aliphatic analogues lack this feature and also easily polymerise [13-16]. The drawback of Schiff base compounds is the ease with which they undergo hydrolysis to the starting materials in the presence of water or on a silica column during purification [16]. The lone pair of electrons of the sp^2 hybridised nitrogen atom of the imine group is readily available, making the nitrogen atom a strong σ donor, which form stable bonds with metal centres [16]. Examples of Schiff base compounds are shown in **Figure 2.1**. The good donor ability of the nitrogen atom, the ease in synthesis and the flexibility in varying the chemical environment about the C=N group makes Schiff bases interesting ligands in coordination chemistry [16].



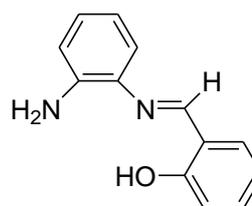
N,N'-bis(pyrrole-2-carboxalidene)-1,2-diaminobenzene



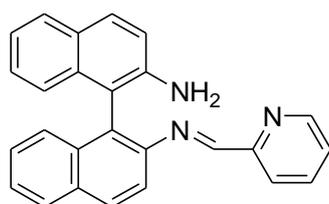
N-pyrrole-2-carboxalidene-1,2-diaminobenzene



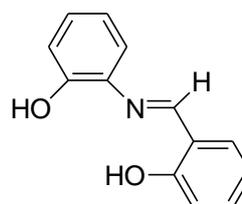
N-salicylidene-2-aminothiophenol



N-salicylidene-1,2-aminobenzene



N-pyridene-2-carboxalidene-1,1'-binaphthyl-2,2'-diamine

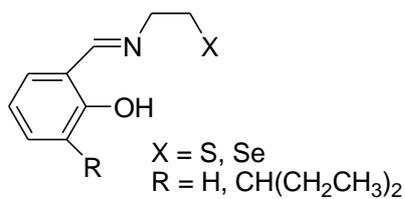


N-salicylidene-2-aminophenol

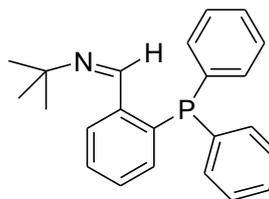
Figure 2.1: Some examples of Schiff base compounds [16]

The first preparation of imines was reported in the 19th century by Schiff (1864), when he performed a condensation reaction of a carbonyl compound with an amine under azeotropic distillation with molecular sieves serving as a drying agent [12]. Since then various methods for the synthesis of imines have been described. In the 1990s an *insitu* method which eliminates water was developed. In this reaction, dehydrating solvents such as tetramethyl orthosilicate or trimethyl orthoformate were used [12]. In 2004, Chakraborti *et al.*, [17] demonstrated that efficiency of these methods depend on the use of highly electrophilic carbonyl compounds and strongly nucleophilic amines. They also proposed an alternative route which makes use of Bronsted-Lowry or Lewis acids to activate the carbonyl group of aldehydes, catalyse the nucleophilic attack by amines, and dehydrate the system.

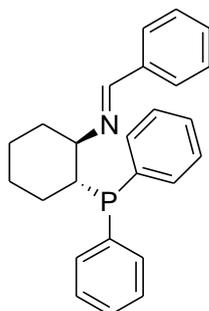
Different sources of amine have been used in the synthesis of Schiff base compounds depending on the target ligand design. The amine sources can be alkyl amines such as compounds **2.1** [18] and **2.2** [19], aryl amines as in **2.3** [20] and **2.4** [21] and five-membered ring heterocyclic compounds such as imidazolyl-amines found in imidazolium salt **2.5** [22]. Compound **2.5** is a tridentate ligand reported by Ulusoy *et al.*, [23] to stabilise the corresponding metal complex for homogeneous catalytic reactions. The synthesis of compounds **2.6** will be discussed in this dissertation. These compounds incorporate imidazolyl-amines (**2.6**) in the ligand design and they are potential tridentate ligands similar to compound **2.5**.



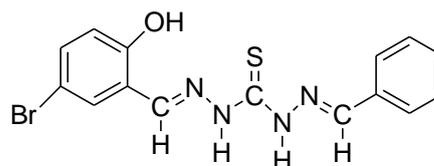
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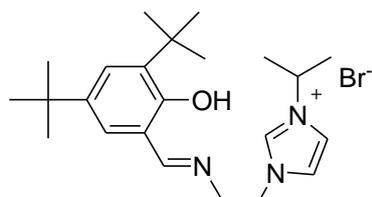
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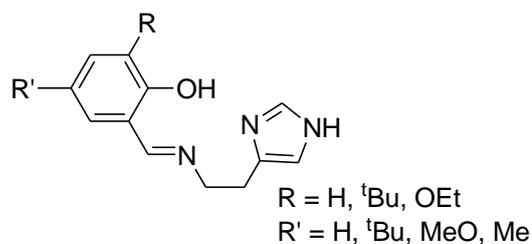
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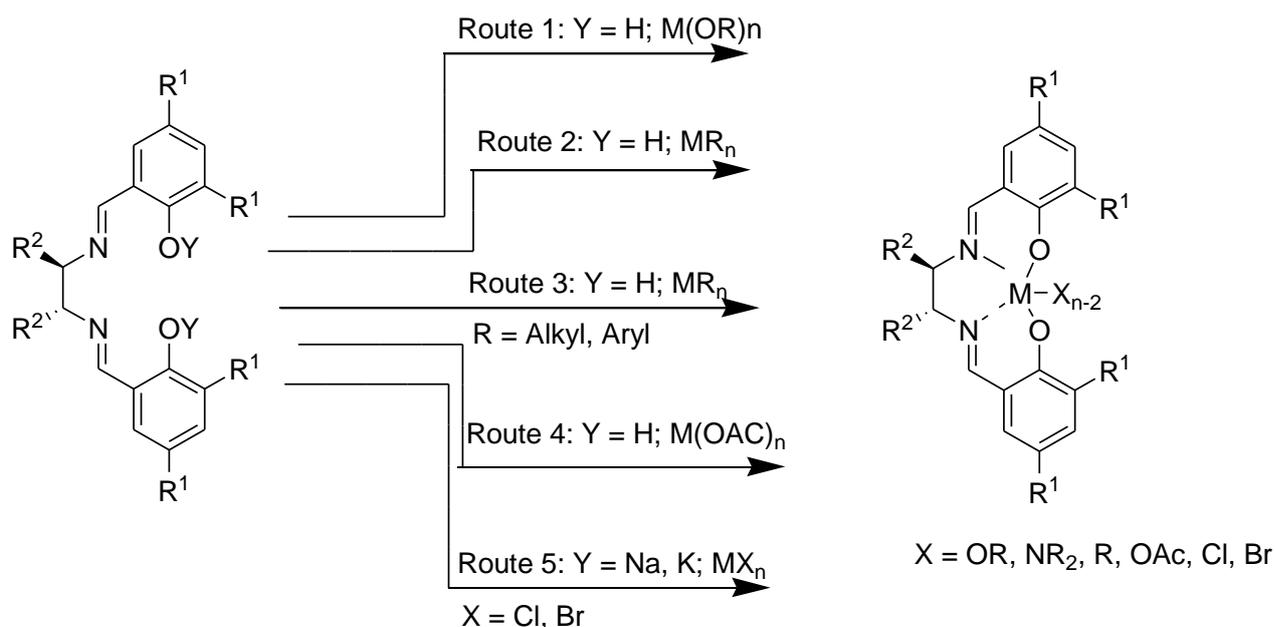
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2.6

2.3. SCHIFF BASE TRANSITION METAL COMPLEXES

The treatment of Schiff base ligands with metal salts under suitable experimental conditions give stable metal complexes. The common synthetic routes for the preparation of metal complexes with phenolic Schiff base ligands was reported by Cozzi [23-24], as shown in **Scheme 2.2**.



Scheme 2.2: Common routes for the synthesis of Schiff base metal complexes [23-24]

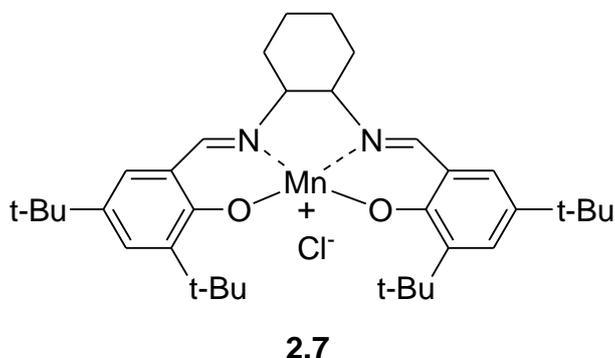
Route 1 employs metal alkoxides ($M(OR)_n$), which are mainly early transition metal ($M = \text{Ti, Zr}$). This route is not suitable for metal alkoxides such as lanthanide derivatives due to their high moisture sensitivity.

Route 2 makes use of metal amides of early transition metals of the form $M(NMe_2)_4$ ($M = \text{Ti, Zr}$). One significant observation of this route is the elimination of the acidic proton of the ligand by the amide to volatile $NHMe_2$.

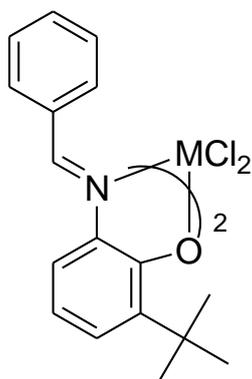
The reaction of Schiff bases with metal alkyl is another route for the preparation of Schiff base metal complexes (Route 3) [24]. In route 4 complexes are synthesised using the Schiff bases and metal acetate under reflux conditions.

The route 5 presents a schematic outline for effective preparation of salen-type metal complexes which involves a two-step reaction, based on deprotonation of the phenolic proton and subsequent complexation with metal halides. Excess sodium hydride (NaH) or potassium hydride (KH) are the common bases used in the deprotonation usually in coordinating solvents. The deprotonation step is normally rapid and the resulting species are stable under reflux conditions [24].

A well-known Schiff base complex, N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride **2.7** known as Jacobsen's catalyst has been synthesised by route 4 (**Scheme 2.2**) where the ligand was reacted with manganese (II) acetate followed by oxidation in air [23, 24].



Non-symmetric bidentate [N⁺O] salicyldiminato ligand family has been shown to form highly active catalysts for both early [25] and late [26, 27] transition metals to understand coordination chemistry of transition metal ions. Fujita and co-workers [28-33] have synthesised a family of group 4 metal complexes featuring salicyldiminato ligands also known as phenoxy-imine ligands. Reacting two equivalents of the phenoxy-imine ligand with metal complexes results in the formation of bis(phenoxy-imine) group 4 metal complexes (**2.8-2.9**). The coordination of phenoxy-imine to zirconium and titanium show distorted octahedral structures with two oxygen atoms situated in the *trans*-position, while two nitrogen and two chlorine atoms are situated in the *cis*-positions [29].



M = Zr, **2.8**
M = Ti, **2.9**

Recently late transition metals such as cobalt(II) with various modifications of salicyldiminato ligands have been synthesised for homogeneous catalytic reactions

[34]. As a result of this, a number of cobalt(II) catalysts have been reported to be active for oxidation reactions [35]. Other modifications include the introduction of a third donor atom into the ligand to make a tridentate Schiff base system with heteroatoms such as O, N, S and P to form complexes with late transition metals [21, 36]. One such complex is the tridentate [O^{^-}N^{^+}N^{^+}] naphthol-imine chromium(III) complex with bulky ortho-triphenylsilyl substituent which is an acetonitrile adduct [37].

It is quite clear from the review of the coordination chemistry of the Schiff base ligands that they have interesting coordination chemistry. Their metal complexes equally have interesting catalytic properties. Furthermore, the catalytic properties are determined by the properties of donor atoms in the ligand [36]. So by combining the salicyladimine motif with heterocycles like imidazolyl-groups we expect to develop other class of Schiff base compounds (**2.6**) which will form metal complexes that can be used as catalysts in oxidation reactions of phenol and styrene.

2.3.1. Transition metal complexes of imidazolyl Schiff base

Imidazole (**Figure 2.2**) is a cyclic, planar molecule that consists of a five-membered ring containing three carbons and two nitrogen atoms, with the nitrogen atom at positions 1 and 3. The nitrogen in position 1 is “pyrrole” type nitrogen and the nitrogen in position 3 is “pyridine” type nitrogen [38-39].

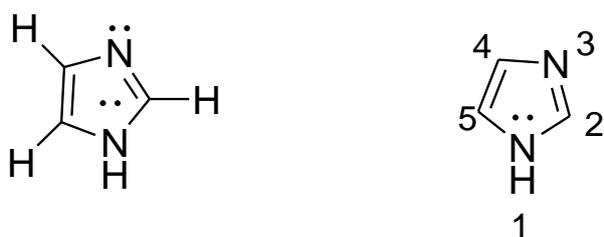


Figure 2.2: Imidazole [38-39]

The imidazole compound (**Figure 2.3**) is aromatic with a six π -electron system. Each carbon atom in the ring has a p orbital perpendicular to the ring and the π cloud contains three pairs of π electrons. The lone-pair of electrons on N on position 1 are part of the cloud as they are in a p orbital, while the lone-pair on N on position 3 are not part of the cloud as they are in sp^2 orbital, perpendicular to the p orbitals and

thus providing a point of attack for protons and other electrophiles [38]. The presence of two nitrogen atoms in the ring results in a lowering of the energy levels of the π -orbital compared to that of benzene or pyridine, which makes electrophilic attack on the carbons more difficult than the corresponding pyrrole or furan. On the other hand, the inductive and electron-withdrawing effects of nitrogen atom has a stabilising effect on negatively charged reaction intermediates, such as those occurring during nucleophilic addition elimination reaction [38].

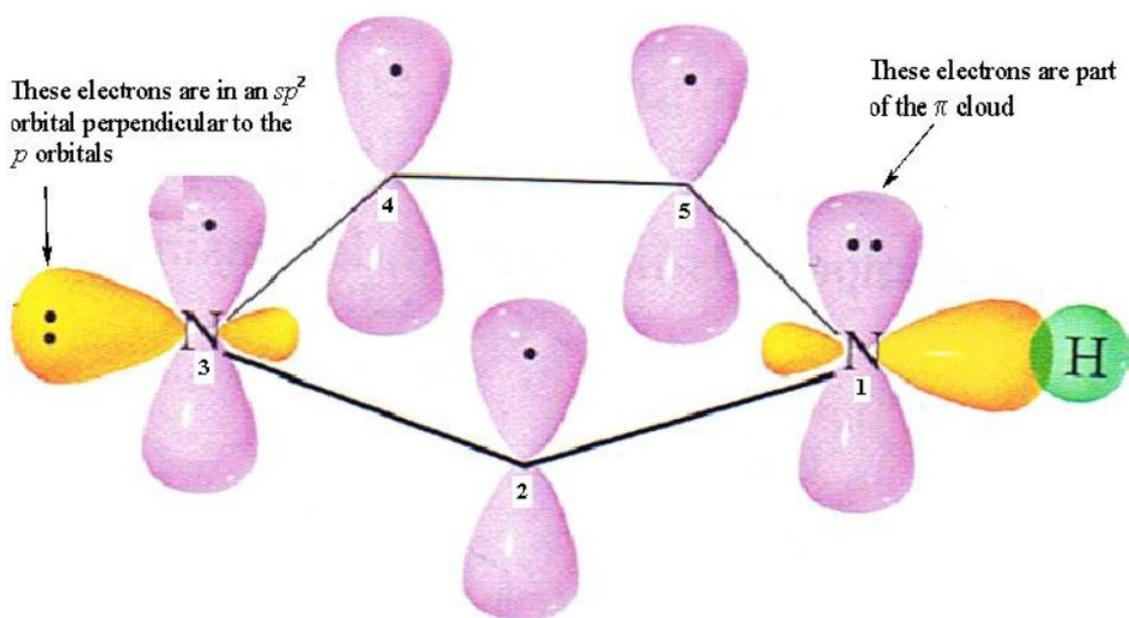


Figure 2.3: Orbital structure of imidazole [38]

The five membered aromatic heterocycles such as imidazole can be reacted with Schiff bases compounds to form imidazolyl- compounds that form metal complexes in which the metal coordinate to the sp^2 nitrogen atom. This report considers the imidazolyl-salicylaldehyde derived compounds where imidazoles (histamine), condenses with salicylaldehydes.

2.4. APPLICATIONS OF SCHIFF BASE TRANSITION METAL COMPLEXES

Major applications of Schiff base complexes are in catalysis. However, some are used for non-linear optical devices [40-42], as electroluminescent materials [43-45], materials for electrochemical sensors [46-48] and in medicinal chemistry [49-51] as stated in Chapter 1.

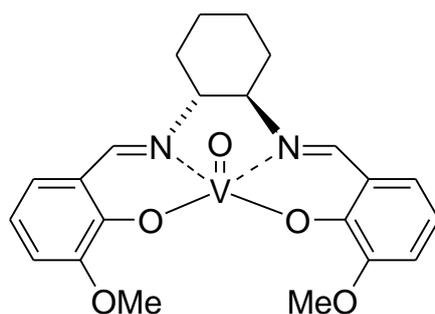
2.4.1. Schiff base metal complexes in catalysis

Schiff base transition metal complexes are efficient catalysts both in homogeneous and heterogeneous reactions. The activity of these complexes varies with the type of ligands and metal [52, 57]. Metal complexes with accessible coordination sites can be effective catalysts for two reasons. Firstly, they can have several oxidation states and can take part in electron transfer reactions. Secondly, they can provide sites at which reactions can take place [53].

Schiff bases ligands form metal complexes with p-block and d-block metals and these complexes have been known to act as highly efficient catalysts in various reactions [54-58]. Many Schiff base complexes of ruthenium and palladium are used as catalysts in the synthesis of polymers. Unique asymmetric catalysis of metal complexes of salen and related Schiff base ligands has been reviewed by Katsuki [59]. The review summarises the generation of *cis* metallo-salen and its related complexes, structural features and their application in asymmetric synthesis. Wang *et al.*, [60] in 1999 reported the effective oxidation of olefins using Mn(III) amino acid Schiff base complexes. Gupta and Sutar [52] reviewed the catalytic activities of transition metal complexes both simple and polymer anchored. They have highlighted the potency of Schiff base complexes as catalysts towards oxidation, hydrogenation, polymerisation, various coupling reactions and ring closures [52, 61].

2.4.1.1. Schiff base complexes for oxidation reactions

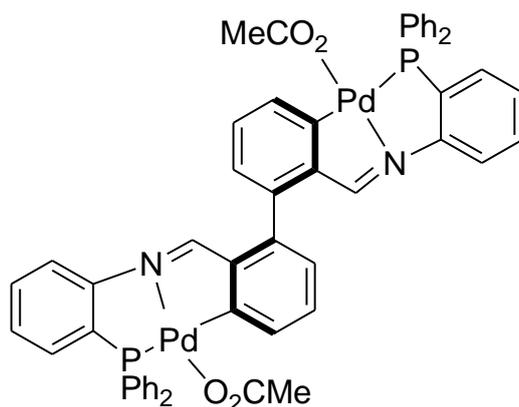
In 1986 Nakajima *et al.*, [52] studied the oxidations of enantioselective sulfide using tetradentate Schiff base-oxovanadium(IV) complex **2.10** as a catalyst. In their work, enantioselectivity of 42% was achieved for the oxidation of methylphenyl sulfide to the corresponding sulfoxide. Various vanadium Schiff base complexes have been reported to catalyse enantioselective sulfoxidations [63-66].



2.10

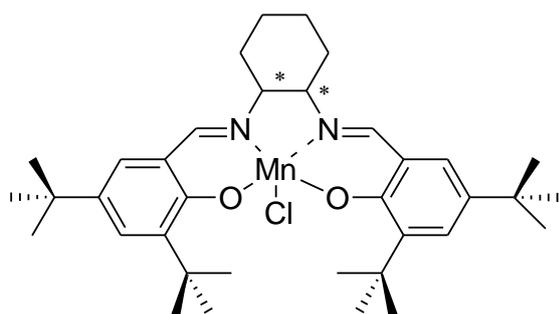
Other transition metals such as titanium(IV), palladium(II), copper(II) and zinc(II) used as metal precursors to complex Schiff base ligands of $O^{\wedge}N^{\wedge}O^{\wedge}$ type have been used in various asymmetric chemical transformations [67, 68].

The binuclear palladium (**2.11**) and copper(II) Schiff base complex were found to be effective catalysts in direct oxygenation of unfunctionalised hydrocarbons and phenols [12, 69, 70].

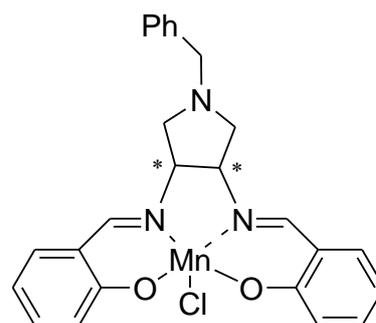


2.11

The activity of [Zr(salen)] complexes in Baeyer-Villiger oxidation of cyclobutanone with H_2O_2 or urea hydrogen peroxide adduct has been reported [71-73]. The oxidation of a range of ketone silyl enol ethers and silyl ketene acetals by using complexes **2.12-2.13** as catalysts in acetonitrile at room temperature lead to the formation of α -hydroxyketones when iodosylbenzene was used as an oxidant [64].

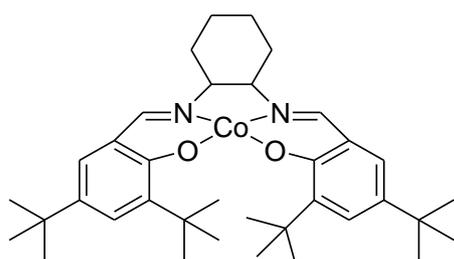


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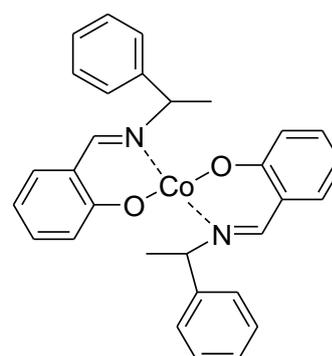


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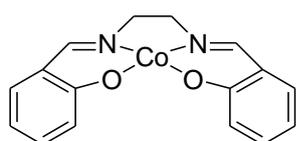
Cobalt(salen) and its analogues **2.14-2.18**, have been used as catalysts for the oxidation of phenols and with dioxygen as oxidant [73]. Reports on oxidation of alkenes to a ketone, oxide and alcohol [74-77] also exist. In order to efficiently bind dioxygen to the catalytically active Co(salen) site need an axial ligand (**Figure 2.4**). The dioxygen is coordinated orthogonally to the square planar coordination sphere of Co(salen). The axial ligand is needed to fill the sixth coordination site, opposite to dioxygen to activate the cobalt complex. Pyridine is the most common axial ligand used in the Co(salen) catalysed oxidation reactions [73]. Other bases, for example, imidazole and pyrimidine have also been used [24]. An alternative way to provide an axial ligand is to use modified salen structure, which has extra nitrogen, for intramolecular axial coordination in the ligand system (**Figure 2.4**).



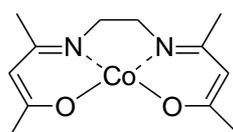
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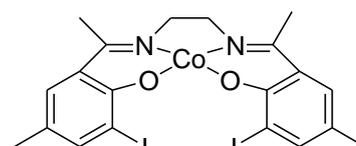
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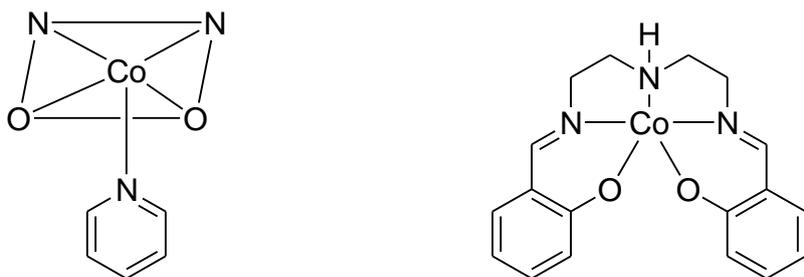


Figure 2.4: Axial ligands in cobalt Schiff base complexes [73]

2.5. SCHIFF BASE COBALT COMPLEXES AS CATALYSTS FOR STYRENE AND PHENOL OXIDATION REACTIONS

There is a large number of important organic transformation reactions such as, hydrogenation, hydroformylation, carboxylation, polymerisation, coupling reactions and oxidation. Due to their importance, there is still continuous interest in studying their catalytic transformation reactions by transition metal complexes. Information regarding their complex structure, environment of the metal atom and the number of ligands attached are useful in determining the catalytic behaviour of the complex [2]. Thus, design of catalysts which lead to better selectivity is possible. Many Schiff base complexes show excellent catalytic activity at reasonable temperatures *i.e* below 100 °C. Similarly the activities of the complexes are varied by changing the nature of the ligand. The oxidation of organic compounds has been considered as a reaction of academic and industrial interest. The common oxidants for this reaction are dioxygen and H₂O₂ which makes them industrially applicable [1-2].

2.5.1. Oxidation of phenol

The oxidation of phenol by hydrogen peroxide (H₂O₂) is a widely applied process in the chemical industry for the preparation of the dihydroxylated derivatives. This oxidation process occurs through the decomposition of H₂O₂ to an unstable electrophilic intermediate, which then attacks the phenol nucleus to give a phenoxy ion. This ion is the precursor to the various products (hydroquinone, catechol and benzoquinone) usually formed in this process [1-3]. Phenol and its derivatives are found in waste-waters from oil refining, petrochemical, coke and coal gasification industries. Removal of phenol from such waste waters is a challenge for chemists. Diphenols, *i.e.*, catechol and hydroquinone are considered as important chemicals in industrial chemistry. Manufacture of diphenols through phenol oxidation with H₂O₂ as

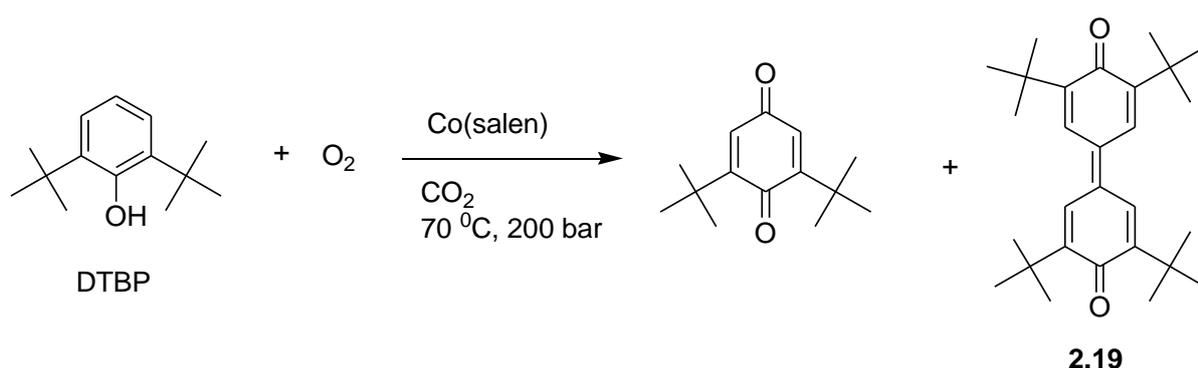
the oxidant has become one of the promising approaches in the 21st century, as the process produces little environmental pollution [3].

First factor in the oxidation of phenol is the introduction of a second hydroxyl substituent onto the aromatic nucleus which tends to activate the molecule towards further reaction and this leads to the formation of a mixture of unwanted tarry by-products or a mixture of hydroquinone and catechol. Hydroquinone and catechol are generally used for different purposes. For example, hydroquinone is a photographic development agent and catechol is an intermediate in the production of industrial anti-oxidants, pharmaceuticals, agrochemicals, flavors and polymerisation inhibitors [1-3]. One has to obtain hydroquinone or catechol selectively. A commercial catalytic process has been developed for oxidising phenol using hydrogen peroxides which tends to produce mixtures containing a major fraction of catechol. A significant fraction of hydroquinone was also formed. The proportion of tarry by-products has been controlled by limiting the use of very low mole ratios of hydrogen peroxide to phenol but, inevitably this restricts the extent of conversion of the phenol [3].

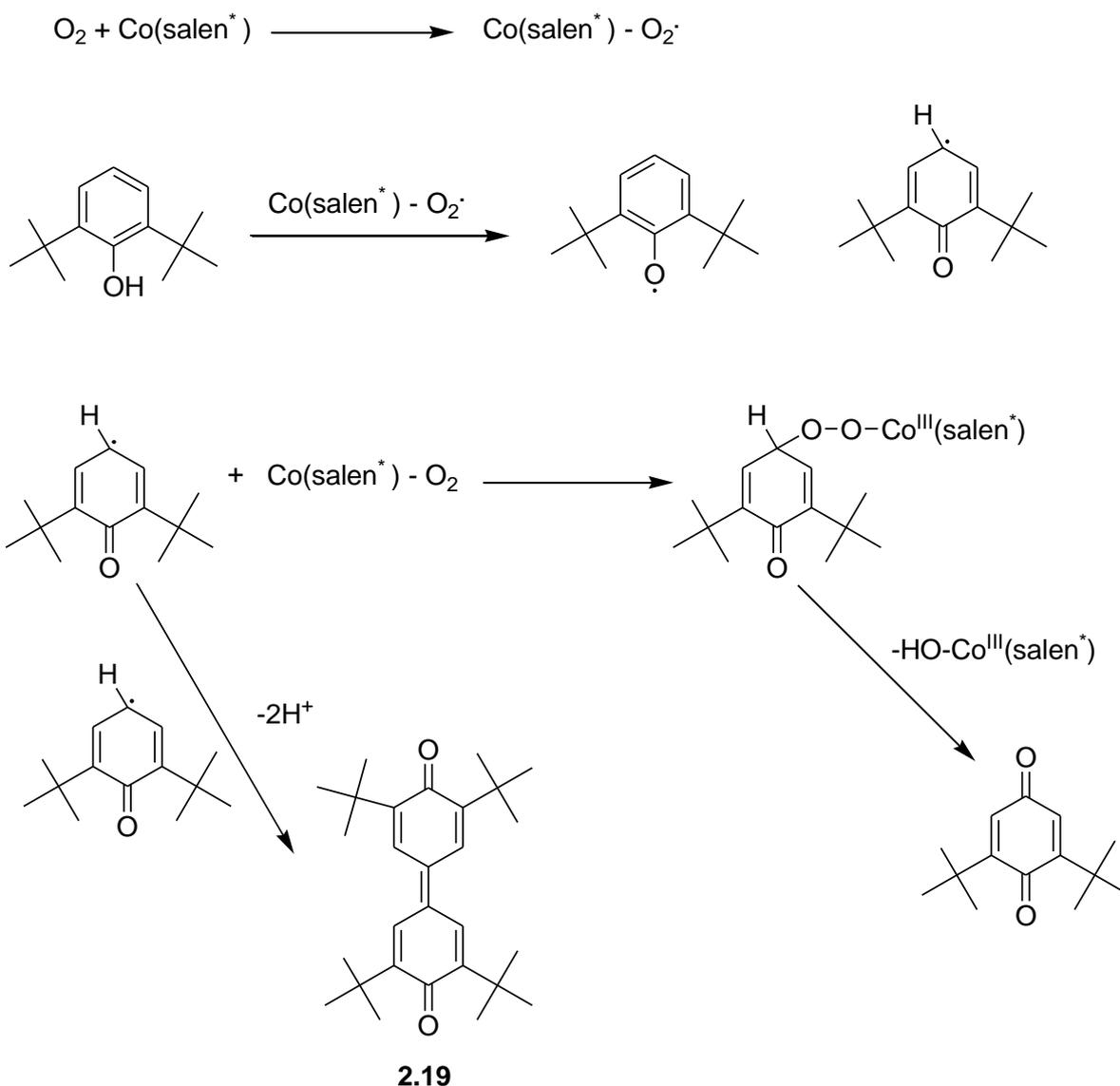
The catalysts reported to be used in phenol oxidation to date are molecular sieves, copper-aluminium hydrotalcite-like compounds and metal complexes. These catalysts have some catalytic activity for phenol oxidation, but the reaction lacks industrial value because of their relatively low yield. Therefore catalysts with high activity and high selectivity have become an important target in this field [74].

Many Schiff base complexes are used for catalytic phenol oxidation reaction. The cobalt(II) complexes were effective in the oxidation of aldehydes and phenols. The phenoxy radicals were assumed to be responsible for the oxidation of phenols in the presence of cobalt(II) complexes [74]. These complexes showed high catalytic activity in the oxidation of phenols, hydrocarbons and lignins in super critical CO₂ (ScCO₂) which suggested that this high activity of cobalt(II) salen complex in ScCO₂ would expand the range of substrates for oxidation. The oxidation resistant substrates such as hydrocarbons and lignins could be oxidised using these catalysts in ScCO₂ [74-76]. Transition metal complexes such as iron and chromium of meso tetrakis (2,6-dichloro-3-sulfophenyl)-porphyrin chloride Schiff base were used as catalyst in the presence of hypochlorite as terminal oxidant [76].

Cobalt(II) salen complexes were also used as catalyst in oxidation of 2,6-di-tert-butylphenol (DTBP) in ScCO_2 [80]. Selectivity in favour of oxygen-transfer, the reaction produced di-tert-butylbenzoquinone **2.19** over self-coupling phenoxy radicals (**Scheme 2.3**) was observed on varying the concentration of oxygen and total pressure. The cobalt(salen) dioxygen complex as effective oxidant in both initial radical formation step and in oxygenation of phenoxy radical was studied but no direct reaction was found between phenoxy radicals and O_2 . The observed behaviour of radicals has provided support for the mechanism proposed for these reactions (**Scheme 2.4**) [81]. Although ScCO_2 is useful over conventional solvents in homogeneous catalysis, it requires high pressures to ensure adequate solubility of salen complexes in CO_2 [74]. However, the addition of fluorocarbon has enhanced the solubility of metal complexes in ScCO_2 at moderate pressures but is expensive. Recently poly-ether-carbonate copolymers were used as suitable substituents to enhance the solubility of complexes in ScCO_2 at low pressure [82].



Scheme 2.3: Cobalt(II) salen catalysed aerobic oxidation of DTBP [82]



Scheme 2.4: Proposed reaction mechanism for the oxidation of DTBP by cobalt(II) salen [82]

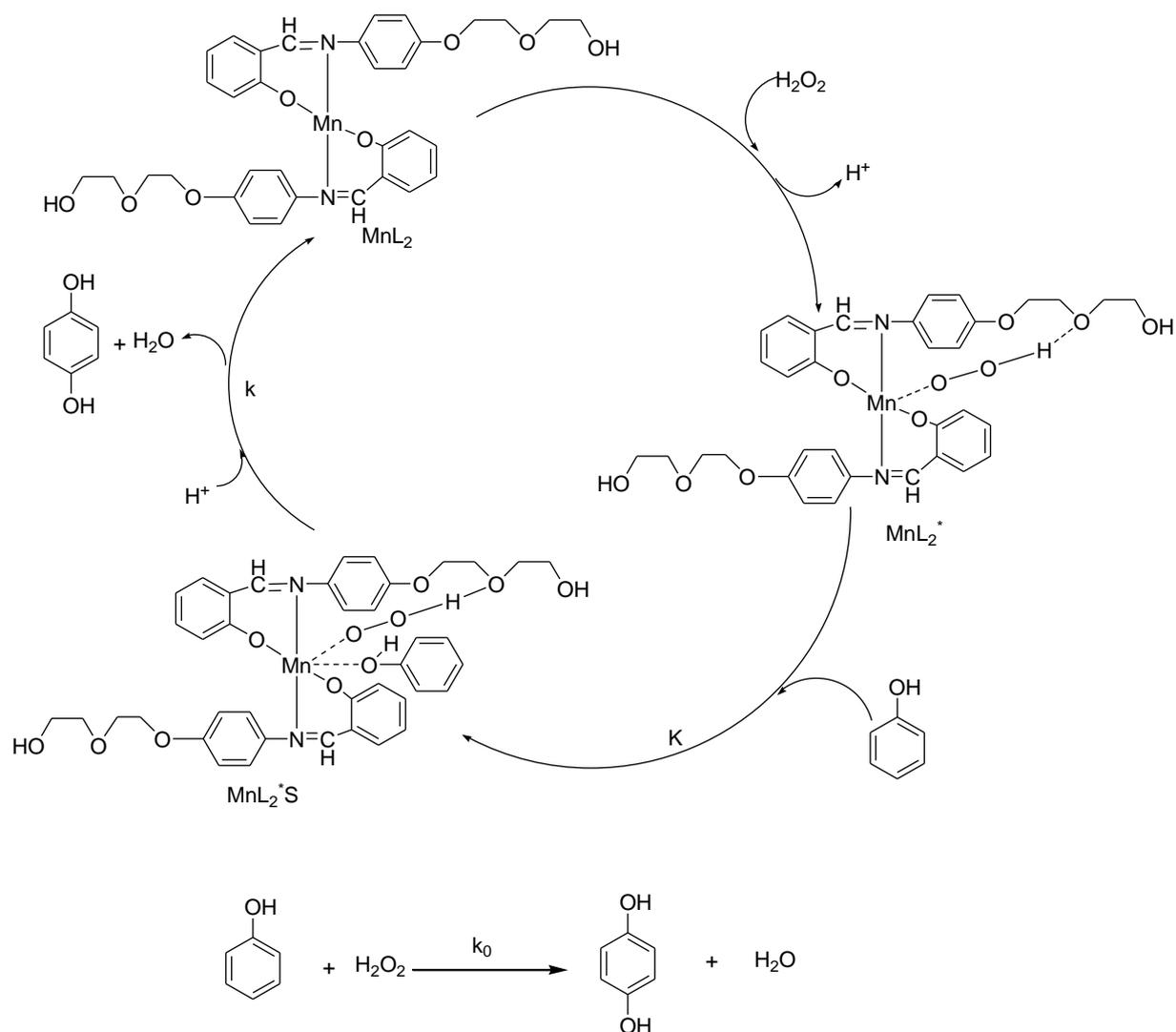
The polymer anchored transition metal complexes, iron(III), cobalt(II) and nickel(II) of N,N'-bis(o-hydroxy acetophenone)ethylene diamine were prepared and the catalytic activity of free and polymer anchored Schiff base complexes was evaluated by studying the oxidation of phenol at 70 °C. The percentage conversion of phenol and turnover number (TON) was found to be optimum at 1:1:1 molar ratio of phenol, H₂O₂ and metal ions in both free and polymer supported metal complexes [83]. Catalytic oxidation of phenol in aqueous phase over a copper catalyst supplied by Engelhard (Cu-0203T) produce benzoquinone and maleic acid, this reaction takes place both on solid surface and in liquid phase [84].

The chitosan supported cobalt(II) complexes of bis(salicylidine ethylene diamine) catalysed the oxidation of 3,4-dihydroxyphenylalanine (DOPA) in the presence of oxygen and the catalyst was compared with unsupported monomeric complexes. The catalytic activity of cobalt(II) salen complex in ScCO_2 was evaluated for oxidation of phenols in the presence of organic peroxides as oxidant [85].

Cobalt supported on tetrabutylammonium salts called lacunary Keggin were used as catalysts for phenol oxidation in acetonitrile solution with iodosobenzene diacetate as single oxygen donor. Deposition of cobalt ions in the lacunary Keggin anions strongly increases the catalytic activity. The conversion of phenol is proportional to concentrations of catalyst and single oxygen donor [86].

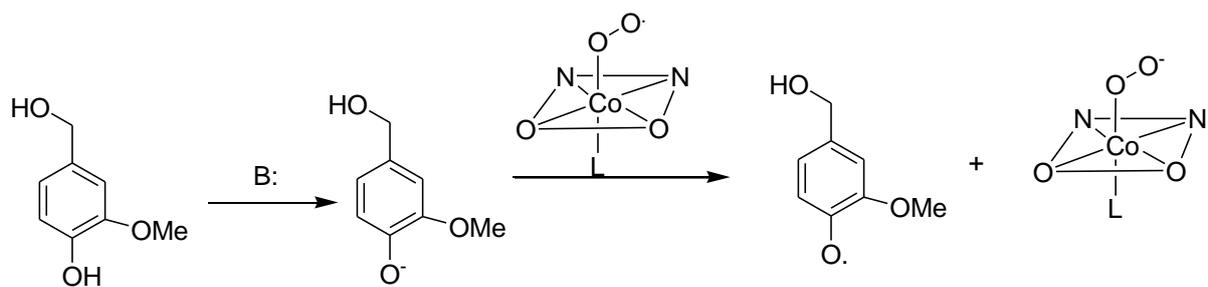
Many Schiff base complexes are used for catalytic phenol oxidation reaction. Copper(II) salicylaldimine complexes have been successfully employed in oxidation of phenol [86]. Van wyk *et al.*, [87] reported the catalytic oxidation of phenol in aqueous media using cobalt(II) N-(aryl) salicylaldimine Schiff base complexes. They reported catechol and hydroquinone as the products and at higher pH, benzoquinone was also obtained.

The proposed mechanism by Zhang *et al.*, [88] for oxidation reaction of phenol is shown in **Scheme 2.5**. The reaction proceeds through the formation of the active species from hydrogen peroxide, OOH^- which initially forms as an intermediate with the metal ion. In the next step a new intermediate, phenol-metal-OOH is formed. This intermediate facilitates the attack of OOH^- at the *ortho* and *para* position of the phenol to form catechol and hydroquinone.



Scheme 2.5: The mechanism of the oxidation of phenol catalysed by Schiff base complexes [88]

The oxidation of guaiacyl and syringyl-like phenols readily occurred with 5-coordinate cobalt catalysts on which one of the ligands is a monodentate pyridine or imidazole base that coordinates axially to the metal. Formation of p -quinones with this system depends on the coordination of the axial base to the metal as influenced by its pK_a and its size. The yield of p -quinones from guaiacyl models was markedly improved by the addition of a sterically hindered aliphatic nitrogen base that does not coordinate to the catalyst [89]. A mechanism involving deprotonation of the phenol substrate by the bulky base is proposed in **Scheme 2.6**.



Scheme 2.6: Proposed mechanism for the oxidation of guaiacyl models in the presence of a hindered base [89]

Uliana *et al.*, [90] presented results on the oxidation of different mono-phenols as substrates with Co^{II} (salen) as a catalyst. The oxidants tested are cobalt, nickel and copper metals with a selection of different salen type ligands. Investigation of the use of hydrogen peroxide, oxone, dimethyl dioxirane and iodoxybenzoic acid was also performed. It was found that above mentioned oxidants easily and cheaply available, can oxidise mono-phenols in reasonable to excellent yields and in a highly regioselective manner in the formation of the isomeric *ortho*-benzoquinone products.

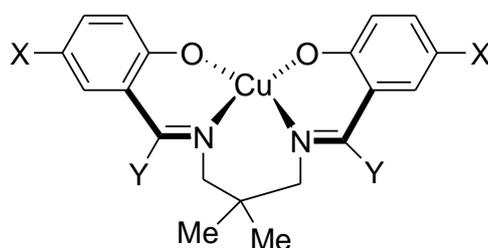
2.5.2. Oxidation of styrene

Epoxidation is an important industrial process for both economic and environmental reasons because they form intermediates for the preparation of oxygen containing natural products, fine chemicals as well as for the production of epoxy resins. The direct epoxidation of alkenes generally uses expensive per-acids and produces large amount of effluents [4]. Much effort has been directed to the development of processes for the direct and selective epoxidation of olefins by use of molecular oxygen. Therefore, it is desirable to replace conventional processes that use stoichiometric oxidants with environmentally benign ones or processes that could selectively oxidise hydrocarbons using either dioxygen or air under mild conditions.

Transition metal catalysed transfer of oxygen atoms to organic substrates is of interest in the study of bioinorganic mechanisms. In particular, the catalysis of alkene oxidation by soluble transition metal complexes is of interest in both biomimetic and synthetic chemistry [91-93]. The catalytic activity of Schiff base complexes depends on the nature of the substituents as well as the metal centre [94]. Oxidants such as iodosylbenzene [95], molecular oxygen [96], H_2O_2 [97], Bu_4NIO_4 [98],

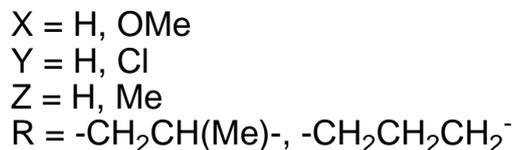
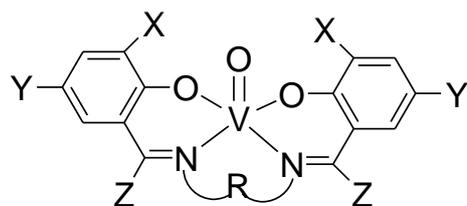
dimethyldioxirane [99] and *m*-chloroperbenzoic acid [100] with these complexes were also considered.

A few reports showed that some copper(II) and oxovanadium(IV) based catalytic systems were efficient for the oxidation of styrene when using H₂O₂ as oxidant [101-105]. A report by Komia *et al.*, [106] has shown the role of different aldehydes in the oxidation of various alkenes and alkanes using copper salts, copper-crown ether complex and a mixture of copper salt and crown ether. Heshmatpou *et al.*, [91] evaluated the catalytic performance of the copper(II) Schiff base complexes **2.20** derived from 2,2'-dimethyl-propandiamine for the oxidation of styrene to benzaldehyde with tert-butyl hydroperoxide. The styrene conversion was found to be strongly dependent on the solvent nature.



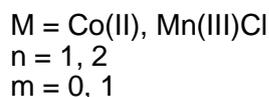
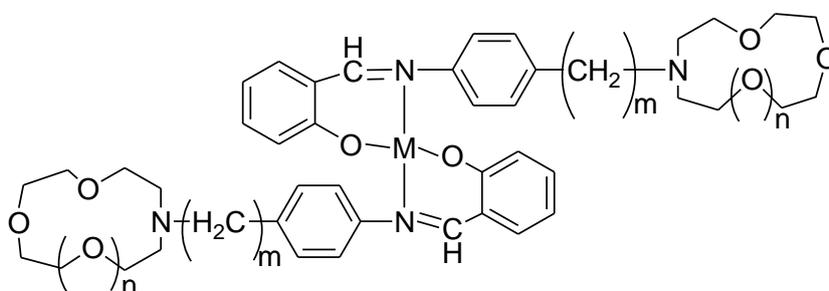
2.20

A practical catalytic method for efficient oxidation of olefins using tert-butyl hydroperoxide catalysed by N₂O₂ tetradentate Schiff base-VO(IV) complexes **2.21** has been developed. Using these catalytic systems for the oxidation of styrene gives styrene oxide and benzaldehyde as major products in excellent yields (100%). The efficiency of the catalysts is strongly influenced by the nature of solvent, reaction time, temperature, tert-butyl hydroperoxide concentration and also catalyst concentration [107].



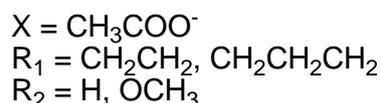
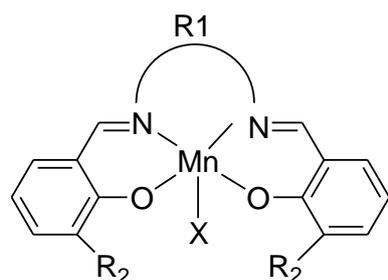
2.21

Very limited studies on the oxidation catalysed by aza crown substituted Schiff base complexes **2.22** were reported. A crown ring with special conformation will endow functional molecular with novel performance and character for its hydrophobicity of outer ethylene group and orderly arrangement of inner oxa atom [108]. Moreover, crown ether-containing Schiff bases are known to bind cations in the crown ether cavity in addition to the coordination of transition metal centre through the N_2O_2 donor atoms. Co-complexation of a hard cation close to the transition-metal centre is believed to play an important role in perturbing its oxygen-binding properties [109].

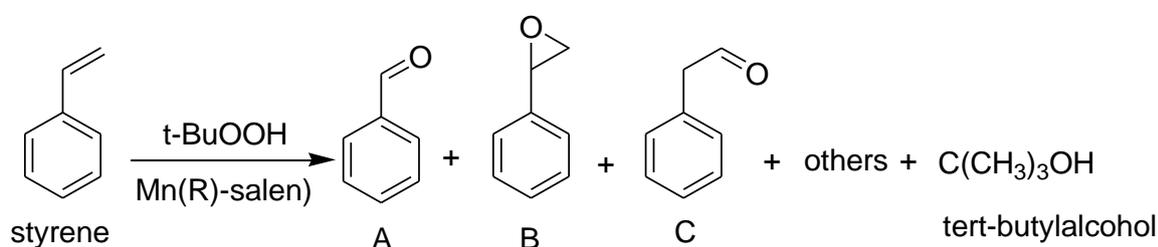


2.22

Styrene oxidation was investigated using manganese(III) salen complexes **2.23** as catalysts in homogeneous media using tert-butylhydroperoxide as the oxygen source. The oxidation of styrene led to formation of benzaldehyde, styrene oxide and phenylacetaldehyde with minor amounts of phenyl-1,2-ethane-diol (**Scheme 2.7**). Complexes with ligands functionalised with methoxy groups showed similar styrene conversions and chemoselectivities in styrene epoxide and benzaldehyde [110].



2.23

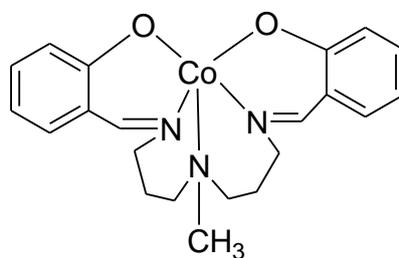


Scheme 2.7: Products of the catalytic oxidation of styrene in the presence of the Schiff base complexes: (A) benzaldehyde (B) styrene oxide (C) phenylacetaldehyde [110]

Cobalt phthalocyanines/salens are an important class of catalysts for the oxidation of alkenes as well as alkanes in the liquid phase. By suitable substitution on the aromatic ring a variety of phthalocyanine/salen derivatives have been prepared in an attempt to improve their catalytic performance. Cobalt phthalocyanines are comparatively cheap and effective selective oxidation catalysts [111].

In the oxidation of styrene catalysed with Schiff-base cobalt complexes, O_2 is applied as an oxidant and isobutyl aldehyde as a reductant. During the process, styrene epoxide was produced and isobutyl aldehyde was also transformed to carboxylic acid [112]. As the aldehyde and cyclic ketone as reductant influenced the formation and selectivity of products, only molecular oxygen was intended to be used as oxidant [113]. The cobalt complex [bis(salicylidene- γ -iminopropyl)methylamine]

cobalt(II), CoSMDPT **2.24** has been shown to catalytically oxidise olefins in the presence of dioxygen or hydrogen peroxide. When terminal olefins are oxidised, the methyl ketone and corresponding secondary alcohol are produced selectively. Internal as well as terminal olefins can also be oxidised [114].



2.24

Cobalt(II) Schiff base complexes catalyse the oxidation of styrene in the presence of dioxygen and excess pyridine. The effect of the reaction conditions on the styrene oxidation was studied by varying solvent, nature and amount of the catalyst and substrate. The catalytic behaviour of the studied complexes was shown to be dependent on the conditions applied. In all reactions, acetophenone and 1-phenylethanol were the only observed products [4].

2.6. REFERENCES

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CHAPTER 3

SYNTHESIS AND CHARACTERISATION OF COBALT(II)-IMIDAZOLYL COMPLEXES

3.1. INTRODUCTION

Cobalt(II) complexes are important in biology mainly because of coenzyme B₁₂ [1]. Electronic properties of cobalt(II) compounds have received substantial attention [2] in part due to the fact that many of these complexes bind oxygen reversibly [3] and are model systems for vitamin B12. Cobalt is a necessary trace element in mammals and has many uses in medicine, magnetic resonance imaging, and drug delivery [4]. Cobalt ethylenediamine complexes are potent antimicrobial agents [5]. Low-spin cobalt porphyrins [6] are also of interest since cobalt-substituted hemoglobin, “coboglobin,” binds oxygen in a cooperative fashion [7].

The growth of cobalt chemistry has necessitated the development of models to account for and predict the spectroscopic properties of cobalt(II) complexes. Cobalt(II) compounds have interesting magnetochemistry, as shown in a recent review on magnetic metal-organic frameworks [8]. Strong magnetic anisotropy of high-spin cobalt(II) is at the origin of the increasing interest in polynuclear compounds containing this metal ion [9]. Several examples of high nuclear complexes with six-coordinate cobalt(II) behaving as single molecular magnets and single chain magnets have been reported [10].

In this project, the focus was on cobalt(II) complexes with 2,4-di-tert-butyl-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol (**L1**), 2-ethoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol (**L2**), 4-methoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol (**L3**), 1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene (**L4**) and 4-methyl-1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene (**L5**) as ligands. The complexes were synthesised by reacting Schiff base ligands with cobalt halides and characterised by FTIR and UV-vis spectroscopy, elemental analysis and HRMS.

3.2. EXPERIMENTAL

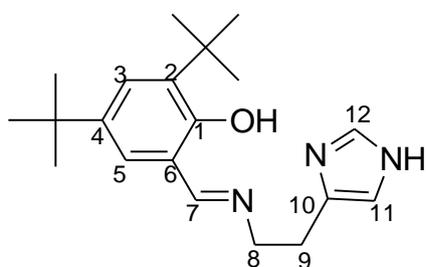
GENERAL

Synthesis of ligands was performed under reflux and synthesis of cobalt complexes was performed under pure nitrogen. All solvents were of analytical grade and were dried and distilled prior to use; dichloromethane was dried and distilled over phosphorus pentoxide (P_2O_5) and hexane was dried from sodium metal lumps and stored over molecular sieves. The starting materials 3,5-di-tert-butyl-2-hydroxybenzaldehyde, 3-ethoxy-2-hydroxybenzaldehyde, 5-methoxy-2-hydroxybenzaldehyde, benzaldehyde, 4-methylbenzaldehyde and histamine dihydrochloride were obtained from Sigma-Aldrich and were used as received.

1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer (at University of Venda) using deuterated $CDCl_3$ with reference signals for the 1H and ^{13}C spectra at 7.25 ppm and 77.0 ppm respectively. Deuterated CD_3OD was used to run the 1H NMR spectra of Schiff base compounds prepared from 5-methoxy-2-hydroxybenzaldehyde, benzaldehyde and 4-methylbenzaldehyde, with reference signals for the 1H and ^{13}C spectra at 3.31 ppm and 48.80 ppm respectively. Coupling constants (J) are given in hertz (Hz) while chemical shifts are expressed in parts per million (ppm). Infrared (IR) spectra were obtained using Bruker Tensor 27 spectrometer equipped with diamond ATR at University of Johannesburg. Elemental analyses were performed on a Vario III microtube CHNS analyser at Rhodes University. High resolution mass spectra were recorded at Stellenbosch University on a Waters API Quattro micro spectrophotometer.

3.2.1. Synthesis of ligands

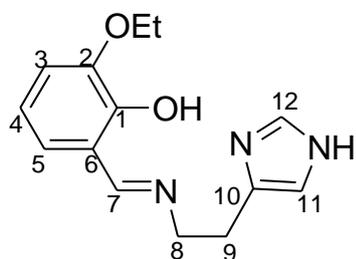
3.2.1.1. 2,4-di-tert-butyl-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol (L1)



L1

3,5-di-tert-butylhydroxybenzaldehyde (4.68 g, 0.02 mol) and histamine dihydrochloride (4.00 g, 0.02 mol) were mixed in methanol (50.00 mL). NaHCO₃ (3.36 g, 0.04 mol) was added to the reaction mixture while stirring. Six drops of formic acid was added to the reaction mixture which was then stirred under reflux for 24 h. The reaction mixture was then filtered and the filtrate was placed under a rotary evaporator to remove the solvent resulting in the formation of an oily product. Dichloromethane (15.00 mL) was then added to the oily product to form a solid which was then filtered to give a bright yellow solid as a product (4.98 g, 76%), δ_{H} (400 MHz; CDCl₃) 1.28 (9H, s, C₆H₂-4-C(CH₃)), 1.44 (9H, s, C₆H₂-2-C(CH₃)), 3.02 (2H, t, J = 6.8 Hz, CH₂-C-C-N), 3.86 (2H, t, J = 6.8, N-CH₂), 6.83 (1H, s, N-CH=C), 7.04 (1H, d, J = 2.4 Hz, 3-C₆H₂-OH), 7.37 (1H, d, J = 2.4 Hz, 5-C₆H₂-OH), 7.56 (s, 1H, N-CH-N), 8.28 (1H, s, CH=N); δ_{C} (100 MHz; CDCl₃) 28.8 (C₆H₂-2-C(CH₃)), 29.4 (C₆H₂-4-C(CH₃)), 31.4 (C₆H₂-4-C(CH₃)), 34.1 (C₆H₂-2-C(CH₃)), 35.0 (im-N-C-CH₂), 59.1 (N-CH₂), 117.8 (HN-CH), 125.8, 126.9, 134.6 (CH-C₆H₂), 136.7 (im-N-C), 140.0 (-N-CH-N), 158.1 (ipso-C₆H₂-OH), 166.4 (-CH=N); ν_{max} (ATR)/cm⁻¹ 1630.77 ν (C=N) imine. HRMS (ESI) found: m/z = [M+H]⁺ = 328.2383 (100%); calc.: 328.2388.

3.2.1.2. 2-ethoxy-6[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-phenol (**L2**)

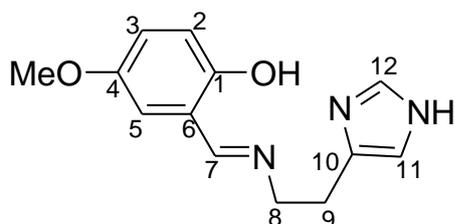


L2

The experimental procedure described for the synthesis of compound **L1** was employed to prepare **L2**, using 3-ethoxy-2-hydroxybenzaldehyde (3.32 g, 0.02 mol) and histamine dihydrochloride (4.00 g, 0.02 mol) to give compound **L2** (5.00 g, 96%); δ_{H} (400 MHz; CDCl₃) 1.44 (3H, t, J = 7.2 Hz, C₆H₃-2-O(CH₂CH₃)), 3.00 (2H, t, J = 6.4 Hz, CH₂-C-C-N), 3.88 (2H, t, J = 6.4 Hz, N-CH₂), 4.09 (2H, q, J = 6.8 Hz, C₆H₃-2-O(CH₂CH₃)), 6.72 (1H, s, 4-C₆H₃-OH), 6.76 (1H, dd 5-C₆H₃-OH), 6.82 (1H, dd, 3-C₆H₃-OH), 6.90 (1H, s, N-CH=C), 7.55 (1H, s, N-CH-N), 8.23 (1H, s, CH=N); δ_{C} (100 MHz; CDCl₃) 14.8 (C₆H₃-2-O(CH₂CH₃)), 28.6 (im-N-C-CH₂), 57.3 (C=N-CH₂), 64.3

(C₆H₃-2-O(CH₂CH₃)), 115.3 (HN-CH), 116.0, 117.1, 117.9, 123.1 (CH-C₆H₃), 134.9 (im-N-C), 148.1 (-N-CH-N), 154.7 (ipso-C₆H₃-OH), 165.3 (-CH=N); ν_{\max} (ATR)/cm⁻¹: 1634.08 ν (C=N) imine. HRMS (ESI) found: $m/z = [M+H]^+ = 260.1398$ (100%); calc.: 260.1399.

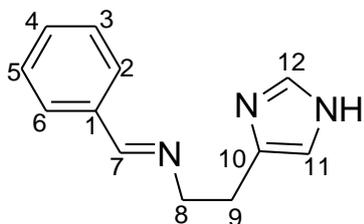
3.2.1.3. 4-methoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol (**L3**)



L3

The experimental procedure described for the synthesis of compound **L1** was employed to prepare **L3**, using 5-methoxy-2-hydroxybenzaldehyde (1.66 g, 0.01 mol) and histamine dihydrochloride (2.00 g, 0.01 mol) to give compound **L3** (1.91 g, 78%); δ_{H} (400 MHz; CD₃OD) 3.02 (2H, t, $J = 5.6$ Hz, CH₂-C-C-N), 3.76 (3H, s, C₆H₃-4-O(CH₃)), 3.90 (2H, t, $J = 6.0$ Hz, N-CH₂), 6.78 (1H, d, $J = 2.8$ Hz, 2-C₆H₃-OH), 6.88 (1H, d, $J = 3.2$ Hz, 3-C₆H₃-OH), 6.93 (1H, s, N-CH=C), 6.96 (1H, s, 5-C₆H₃-OH), 7.84 (1H, s, N-CH-N), 8.34 (1H, s, CH=N). δ_{C} (100 MHz; CD₃OD) 29.3 (im-N-C-CH₂), 56.3 (C₆H₃-4-O-CH₃), 59.3 (C=N-CH₂), 115.7 (HN-CH), 117.8, 118.7, 119.6, 121.0 (CH-C₆H₃), 135.7 (im-N-C), 135.8 (-N-CH-N), 153.4 (ipso C₆H₃-OH), 157.3 (-CH=N); ν_{\max} (ATR)/cm⁻¹ 1633.91 ν (C=N) imine, HRMS (ESI) found: $m/z = [M+H]^+ = 246.1254$ (100%); calc.: 246.1243.

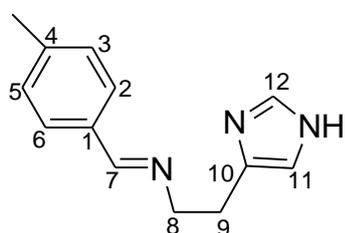
3.2.1.4. 1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene (**L4**)



L4

The experimental procedure described for the synthesis of compound **L1** was employed to prepare **L4**, using benzaldehyde (2.30 g, 0.02 mol) and histamine dihydrochloride (4.00 g, 0.02 mol) to give compound **L4** (2.36 g, 60%); δ_{H} (400 MHz; CDCl_3) 3.02 (2H, t, $J = 6.4$ Hz, $\text{CH}_2\text{-C-C-N}$), 3.64 (2H, t, $J = 6.4$ Hz, N-CH_2), 7.27 (1H, s, C=CH-N), 7.29, 7.35, 7.36 (3H, m, 3,4,5- C_6H_5), 7.37 (1H, s, N-CH-N), 7.53 (2H, 2,6- C_6H_5), 8.58 (1H, s, CH=N); δ_{C} (100 MHz; CDCl_3) 44.8 (im-N-C- CH_2), 61.0 (C=N-CH_2), 131.8, 132.0, 132.3 (C_6H_5) 134.7 ($\text{CH}_2\text{-C-N}$), 137.8 (N-C-N), 145.3 (1- C_6H_5), 167.3 (-CH=N); ν_{max} (ATR)/ cm^{-1} : 1618.09 $\nu(\text{C=N})$ imine. HRMS (ESI) found: $m/z = [\text{M+H}]^+ = 200.1187$ (100%); calc.: 200.1188.

3.2.1.5. 4-methyl-1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene (**L5**)

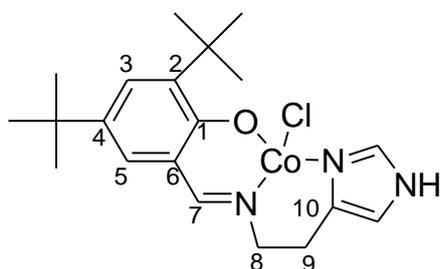


L5

The experimental procedure described for the synthesis of compound **L1** was employed to prepare **L5**, using 4-methyl-benzaldehyde (2.40 g, 0.02 mol) and histamine dihydrochloride (4.00 g, 0.02 mol) to give compound **L5** (2.85 g, 67%). δ_{H} (400 MHz; CDCl_3) 2.33 (3H, s, 4- $\text{C}_6\text{H}_5\text{-CH}_3$), 3.18 (2H, t, $J = 6.4$ Hz, $\text{CH}_2\text{-C-C-N}$), 3.34 (2H, t, $J = 5.6$ Hz, N-CH_2), 6.99 (1H, s, C=CH-N), 7.18 (3 and 5- C_6H_4), 7.57 (1H, s, N-CH-N), 7.67 (2 and 6- C_6H_4), 8.58 (1H, s, CH=N); δ_{C} (100 MHz; CDCl_3) 26.9 ($\text{C}_6\text{H}_4\text{-4-CH}_3$) 40.8 (im-N-C- CH_2), 49.6 (C=N-CH_2), 117.0 (C=CH-N) 129.4, 129.8 (C_6H_4), 130.2 ($\text{CH}_2\text{-C-N}$), 135.5 (N-CH-N), 136.7 (1- C_6H_4), 170.4 (-CH=N); ν_{max} (ATR)/ cm^{-1} 1626.97 $\nu(\text{C=N})$ imine. HRMS (ESI) found: $m/z = [\text{M+H}]^+ = 214.1346$ (100%); calc.: 214.1344.

3.2.2 Synthesis of cobalt complexes with CoCl₂

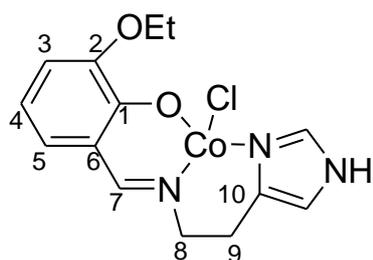
3.2.2.1. 2,4-di-tert-butyl-6[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-phenol Co(II) complex **C1**



C1

Cobalt dichloride, CoCl₂ (0.48 g, 3.67 mmol) was added to a solution of 2,4-di-tert-butyl-6[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-phenol **L1** (1.20 g, 3.67 mmol) in dichloromethane (30.00 mL). The solution turned dark green and was stirred for 24 h under nitrogen. Hexane (20.00 mL) was added to precipitate compound **C1** (1.47 g, 77%) as a dark green solid. (Found: C, 49.69; H, 6.82; N, 8.21. Calc. for C₂₀H₂₈N₃OCiCo.CH₂Cl₂: C, 49.86; H, 5.97; N, 8.35); ν_{\max} (ATR)/cm⁻¹ 1620.01 ν (C=N) imine. HRMS (ESI) m/z = [M-Cl]⁺ = 385.1563 (23%), [M-Cl-CH₃+1]⁺ = 369.1251 (10%).

3.2.2.2. 2-ethoxy-6[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-phenol Co(II) complex **C2**

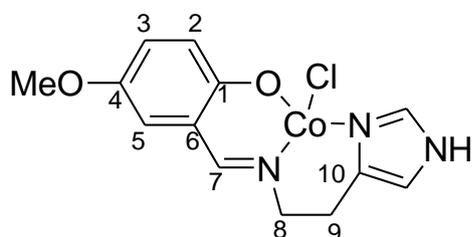


C2

Cobalt dichloride, CoCl₂ (0.60 g, 4.63 mmol) was added to a solution of 2-ethoxy-6[[2-(1H-imidazol-4-yl)-ethylimino]-methyl]-phenol **L2** (1.20 g, 4.63 mmol) in dichloromethane (30.00 mL). The solution turned dark green and was stirred for 24 h under nitrogen. Hexane (20.00 mL) was added to the mixture to give compound **C2** (1.52 g, 95%) as a dark green solid. (Found: C, 44.59; H, 4.78; N, 11.04. Calc. for

$C_{14}H_{16}N_3O_2ClCo \cdot 0.5 CH_2Cl_2$: C, 44.14; H, 4.30; N, 10.60); ν_{max} (ATR)/ cm^{-1} 1620.24 $\nu(C=N)$ imine. HRMS (ESI) $m/z = [M+H]^+ = 353.0325$ (5%), $[M-Cl]^+ = 316.0541$ (3%).

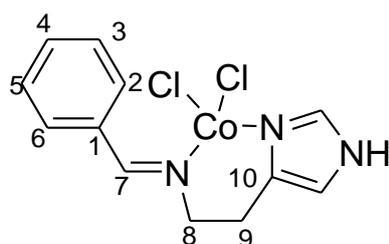
3.2.2.3. 4-methoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol Co(II) complex **C3**



C3

Cobalt dichloride, $CoCl_2$ (0.27 g, 2.12 mmol) was added to a solution of 4-methoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol **L3** (0.52 g, 2.12 mmol) in dichloromethane (30.00 mL). The solution turned dark green and was stirred for 24 h under nitrogen. Hexane (20.00 mL) was added to the mixture to give compound **C3** (0.67 g, 77%) as a dark green solid. (Found: C, 42.02; H, 4.46; N, 10.37. Calc. for $C_{13}H_{14}N_3O_2ClCo \cdot 0.5 CH_2Cl_2$: C, 42.50; H, 3.96; N, 11.02); ν_{max} (ATR)/ cm^{-1} 1625.95 $\nu(C=N)$ imine. HRMS (ESI) $m/z = [M-Cl+1]^+ = 303.0417$ (5%), $[L3]^+ = 245.1167$ (3%).

3.2.2.4. 1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene Co(II) complex **C4**

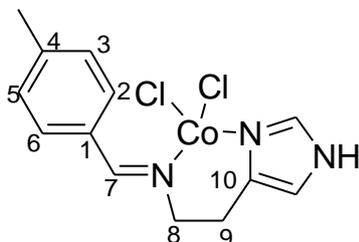


C4

Cobalt dichloride, $CoCl_2$ (0.98 g, 7.53 mmol) was added to a solution of 1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene **L4** (1.50 g, 7.53 mmol) in dichloromethane (30.00 mL). The solution turned dark blue and was stirred for 24 h under nitrogen. Hexane (20.00 mL) was added to the mixture to give compound **C4** (2.30 g, 63%) as a dark blue solid. (Found: C, 37.09; H, 4.75; N, 17.05. Calc. for $C_{12}H_{13}N_3Cl_2Co \cdot CH_2Cl_2$: C, 37.70; H, 3.65; N, 10.15); ν_{max} (ATR)/ cm^{-1} 1671.40

$\nu(\text{C}=\text{N})$ imine. HRMS (ESI) $m/z = [\text{M}]^+ = 327.9436$ (10%), $[\text{M}+\text{Na}+\text{H}]^+ = 351.0262$ (4%).

3.2.2.5. 4-methyl-1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene Co(II) complex **C5**

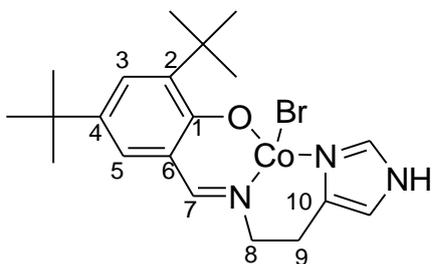


C5

Cobalt dichloride, CoCl_2 (0.59 g, 4.53 mmol) was added to a solution of 4-methyl-1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene **L5** (0.97 g, 4.53 mmol) in dichloromethane (30.00 mL). The solution turned dark blue and was stirred for 24 h under nitrogen. Hexane (20.00 mL) was added to the mixture to give compound **C5** (0.12 g, 75%) as a dark blue solid. (Found: C, 38.05; H, 5.25; N, 8.37. Calc. for $\text{C}_{13}\text{H}_{15}\text{N}_3\text{Cl}_2\text{Co}\cdot\text{CH}_2\text{Cl}_2$: C, 39.2; H, 4.00; N, 9.81); ν_{max} (ATR)/ cm^{-1} 1669.65 $\nu(\text{C}=\text{N})$ imine. HRMS (ESI) $m/z = [\text{M}-\text{Cl}+1]^+ = 307.0308$ (38%), $[\text{M}-\text{CH}_3]^+ = 327.9440$ (38%).

3.2.3. Synthesis of cobalt complexes with CoBr_2

3.2.3.1. 2,4-di-tert-butyl-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol Co(II) complex **C6**

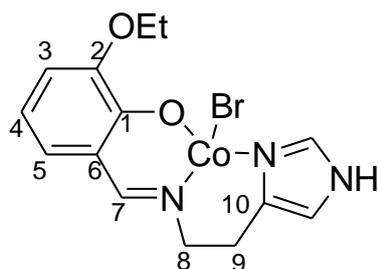


C6

To a solution of 2,4-di-tert-butyl-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol **L1** (1.2 g, 3.67 mmol) in dichloromethane (30.00 mL) was added CoBr_2 (0.80 g, 3.67 mmol). The solution turned brown and was stirred for 24 h under nitrogen. Hexane

(20.00 mL) was added to the mixture to give compound **C6** (1.63 g, 96%) as a brown solid. (Found: C, 51.03; H, 6.99; N, 9.02. Calc. for $C_{20}H_{28}N_3OBrCo$: C, 51.60; H, 6.06; N, 9.03); ν_{max} (ATR)/ cm^{-1} 1619.70 $\nu(C=N)$ imine. HRMS (ESI) $m/z = [M-Br+H]^+ = 385.1569$ (49%), $[L1]^+ = 327.2314$ (55%).

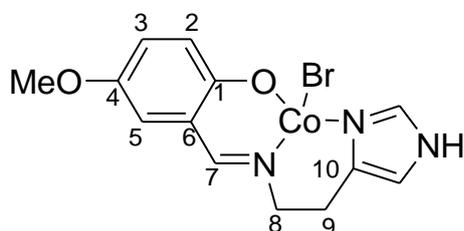
3.2.3.2. 2-ethoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol Co(II) complex **C7**



C7

To a solution of 2-ethoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol **L2** (1.20 g, 4.63 mmol) in dichloromethane (30.00 mL) was added $CoBr_2$ (1.01 g, 4.63 mmol). The solution turned dark green and was stirred for 24 h under nitrogen. Hexane (20.00 mL) was added to the mixture to give compound **C7** (1.71 g, 93%) as a dark green solid. (Found: C, 40.30; H, 3.93; N, 10.19. Calc. for $C_{14}H_{16}N_3O_2BrCo \cdot 0.5 CH_2Cl_2$: C, 39.60; H, 3.89; N, 9.56); ν_{max} (ATR)/ cm^{-1} 1618.67 $\nu(C=N)$ imine. HRMS (ESI) $m/z = [M]^+ = 395.9751$ (10%), $[M-CH_3+H]^+ = 381.9610$ (20%).

3.2.3.3. 4-methoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol Co(II) complex **C8**



C8

To a solution of 4-methoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol **L3** (0.9 g, 3.67 mmol) in dichloromethane (30.00 mL) was added $CoBr_2$ (0.80 g, 3.67 mmol).

To a solution of 4-methyl-1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene **L5** (0.25 g, 1.17 mmol) in dichloromethane (30.00 mL) was added CoBr₂ (0.26 g, 1.17 mmol). The solution turned blue and was stirred for 24 h under nitrogen. Hexane (20.00 mL) was added to the mixture to give compound **C10** (0.50 g, 98%) as a dark blue solid. (Found: C, 32.60; H, 4.11; N, 12.07. Calc. for C₁₃H₁₅N₃Br₂Co.CH₂Cl₂: C, 32.50; H, 3.31; N, 8.13); ν_{max} (ATR)/cm⁻¹ 1630.34 ν (C=N) imine. HRMS (ESI) m/z = [M-Br]⁺ = 350.9772 (30%).

3.2.4. Molecular structure determination by single crystal X-ray diffractometry

Single crystals complex **C11**, suitable for X-ray analysis were grown and used to determine the molecular structure of this compound.

Crystal quality evaluation and data collection were performed on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K_{α} radiation (50kV, 30mA) using the APEX 2 [11] data collection software. The initial cell constants were obtained from ω -scans of width 0.5° and 512 x 512 bit data frames. Data reduction was successfully carried out using the program *SAINT+* [12] and face indexed absorption corrections were made using the program *XPREP* [12].

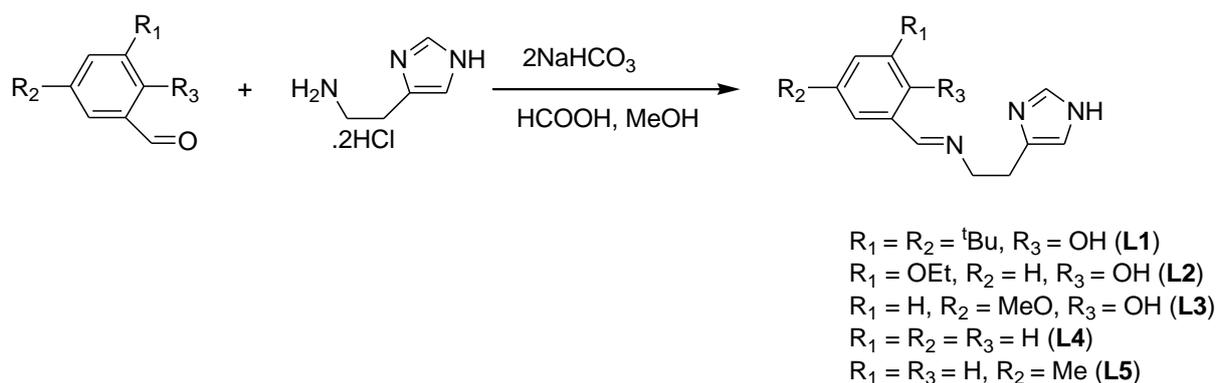
The structure was solved by direct methods and refined by least squares techniques using *SHELXTL* [13]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using *SHELXTL*. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication quality material were generated using *SHELXTL*, *PLATON* [14] and *ORTEP-3* [15], and structural refinement of this data. X-ray structure was determined by Mr. Collins Obuah at the University of Johannesburg.

3.3. RESULTS AND DISCUSSION

3.3.1. Synthesis and properties of ligands

Compounds **L1**, 2,4-di-tert-butyl-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol, **L2**, 2-ethoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol, **L3**, 4-methoxy-6{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-phenol, **L4**, 1{[2-(1H-imidazol-4-yl)-ethylimino]-methyl}-benzene and **L5** 4-methyl-1{[2-(1H-imidazol-4-yl)-ethylimino]-

methyl}-benzene, were synthesised by Schiff base condensation reaction of the corresponding aldehyde with histamine dihydrochloride salt in refluxing methanol (**Scheme 3.1**). Two equivalents of NaHCO₃ were added to neutralise the dihydrochloride salt of the amine. The condensation reaction proceeded in the presence of a catalytic amount of formic acid. Other acids such as *p*-toluenesulfonic acid can be used but were not used in this project [16].



Scheme 3.1: Synthetic Scheme for ligands **L1-L5**

The condensation reaction can be performed in the absence of a catalyst; however a mixture of product and starting material was obtained whenever attempts were made to prepare the ligands without a catalyst. The aldehyde can be removed by column chromatography using a mixture of diethyl ether and ethyl acetate as eluant. This, however, resulted in lower yields (41%) of products isolated. Water is a by-product of all Schiff base condensation reactions, which has the propensity to hydrolyse the imine back to an aldehyde. In all our reactions, the amount of water produced during the condensation did not cause hydrolysis of the resulting imine. Ligands **L1-L5** are soluble in common organic solvents such as chlorinated solvents, Et₂O, THF, DMSO, toluene, acetonitrile. Ligands **L1-L5** are air stable and can be stored without the usual precaution of keeping compounds in dry and air free environment.

NMR and IR spectroscopies and HRMS were used to characterise these compounds. The spectroscopic data used to identify the compounds **L1-L5** are discussed in the next section.

3.3.2. Characterisation of ligands L1-L5

3.3.2.1. NMR studies of L1-L5

The spectra assignment of **L1** will be used to illustrate how NMR spectroscopy was used to characterise the ligands. The ^1H NMR spectrum of **L1** (**Figure 3.1.a**) shows two singlets associated with protons of tert-butyl substituents in positions 4 (1.29 ppm) and 2 (1.44 ppm) of the phenolic ring, two triplets corresponding to the $-\text{CH}_2-\text{CH}_2-$ linker appear in positions 9 (3.02 ppm) and 8 (3.86 ppm), imidazole protons in positions 11 and 12 as two singlets at 6.83 ppm and 7.56 ppm respectively, two doublets for the phenolic protons in positions 3 (7.04 ppm) and 5 (7.376 ppm) and the imine proton at 8.28 ppm. Downfield shifts of the phenolic $-\text{OH}$ protons (13.82 ppm) have been reported for the same ligand [17]. In **L1** this peak was not found. This is due to the intramolecular hydrogen bonding interaction between the phenolic $-\text{OH}$ proton and the imine N, (phenolic $-\text{HO}\dots\text{N}=\text{C}$ (imine N)). ^1H NMR spectrum for **L2** shows similar results except for the doublet of a doublet for the phenolic protons in positions 5 (6.76 ppm) and 3 (6.82 ppm) (**Figure 2.1.b**). ^{13}C NMR spectrum of **L1** (**Figure 2.1.c**) showed the imine carbon (166.4 ppm), the carbon bearing the phenolic $-\text{OH}$ (158.1 ppm), the phenolic carbons and the carbons on the imidazole (117.8-140.0 ppm) downfield of the spectrum while the $-\text{CH}_2-\text{CH}_2-$ carbons (35.0-59.4 ppm) and the tert-butyl carbons (28.8-34.1 ppm) appear upfield. ^{13}C NMR spectrum of **L2** (**Figure 2.1.d**) shows similar results except for ethyl carbons at 14.8 ppm and 64.3 ppm.

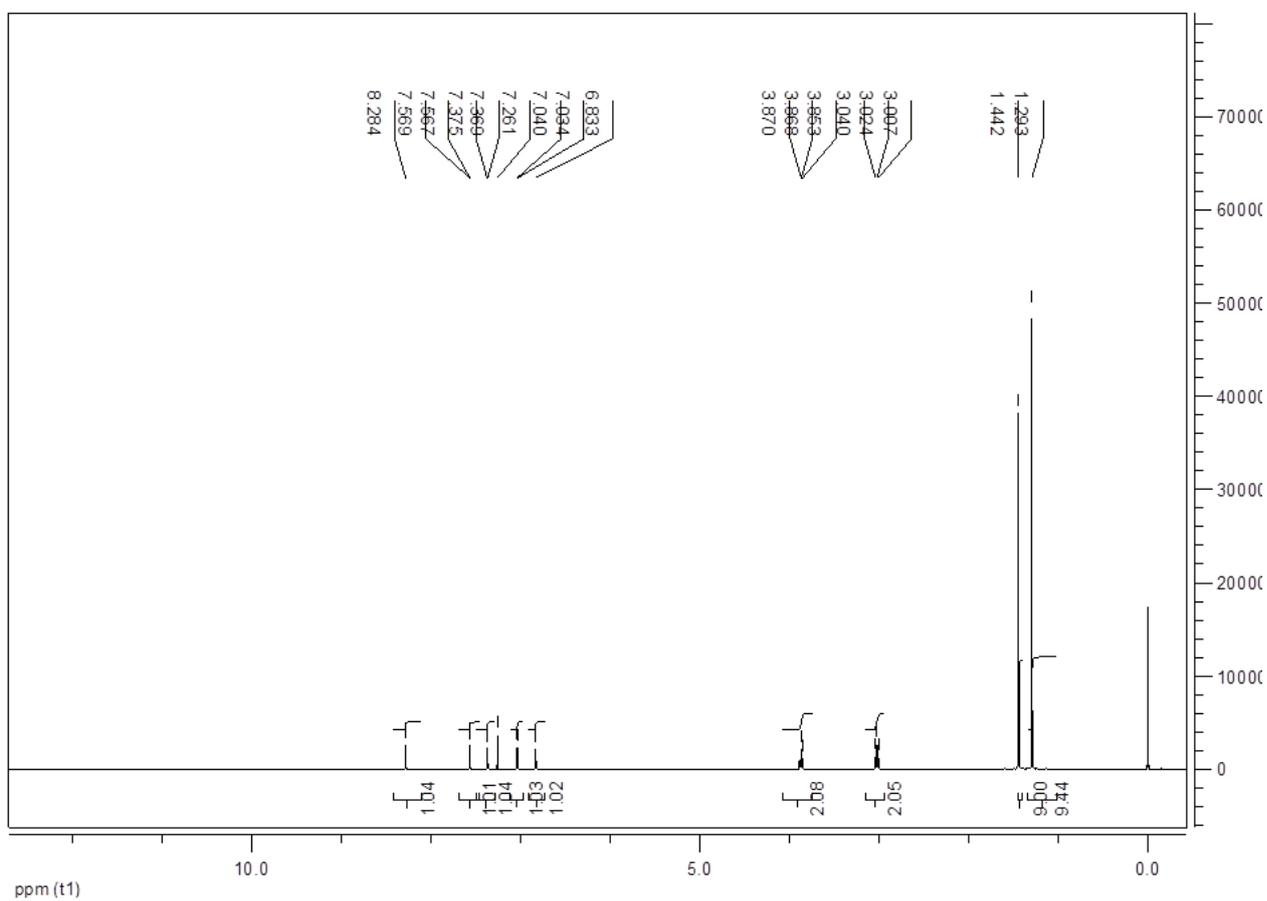


Figure 3.1a: ^1H NMR spectrum of ligand **L1**

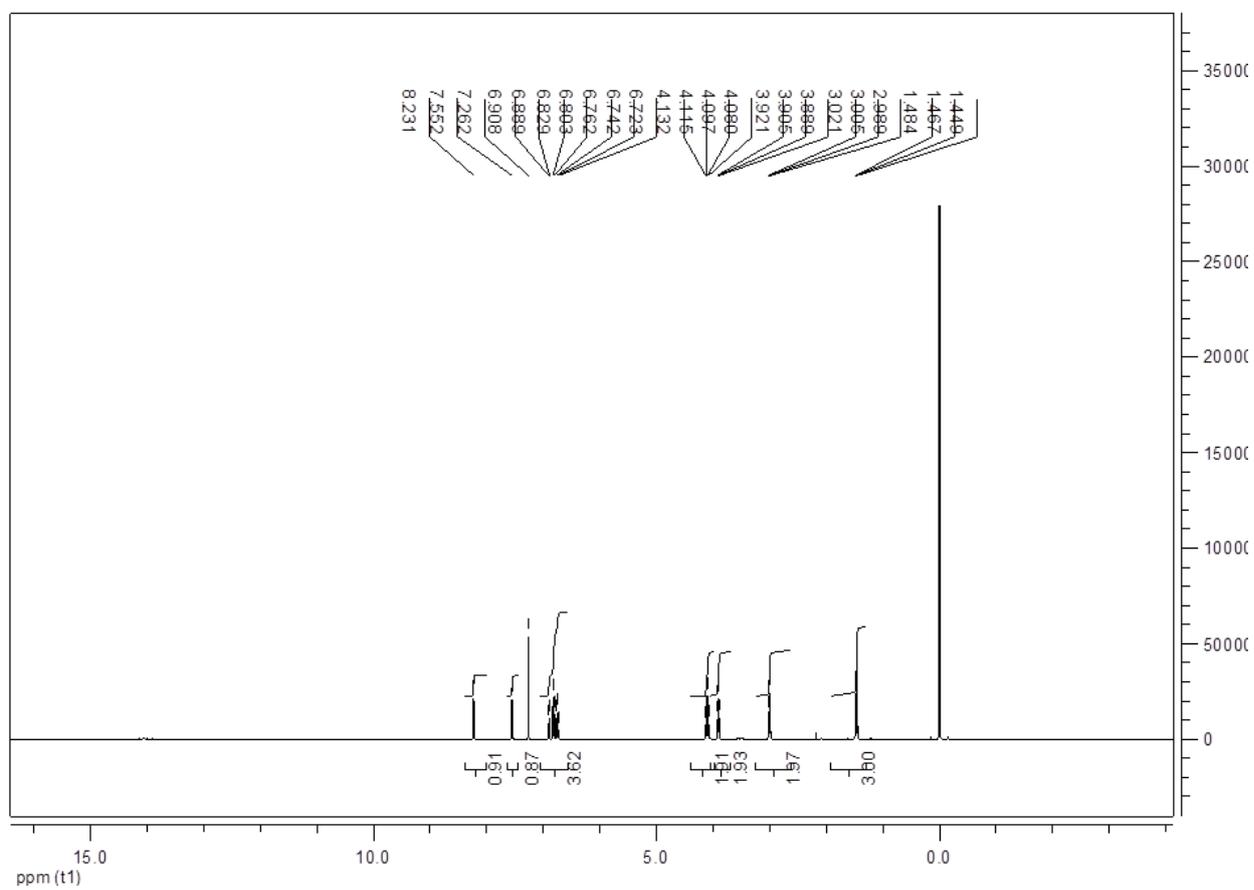


Figure 3.1b: ^1H NMR spectrum of ligand L2

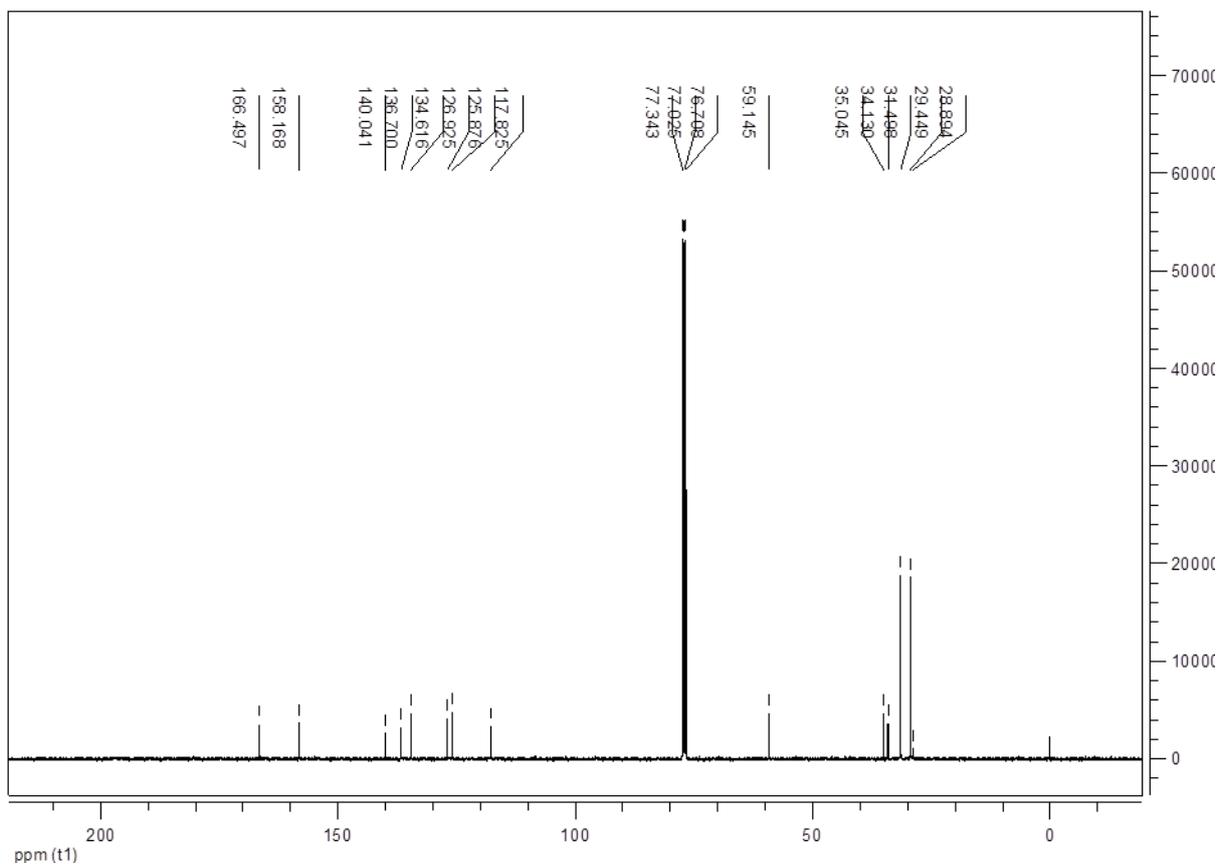


Figure 3.1c: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of ligand L1

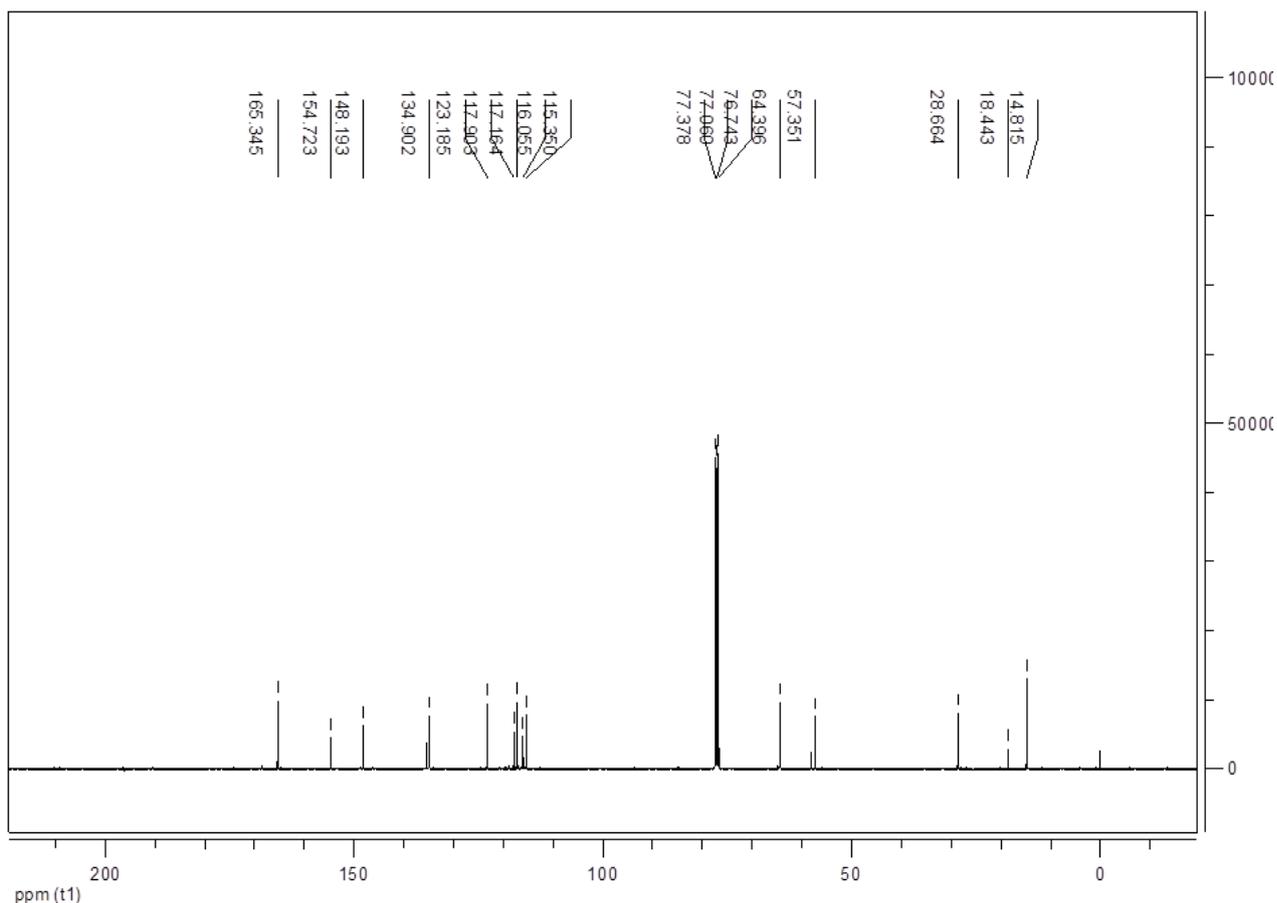


Figure 3.1d: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of ligand **L2**

3.3.2.2. IR studies

Infrared spectroscopy was used mainly to determine the imine functionality in the ligands. The imine moieties (C=N) of the ligands appeared at **L1** (1630.77), **L2** (1634.08), **L3** (1633.91), **L4** (1618.48), **L5** (1656.97) cm^{-1} . A typical IR spectrum for these compounds is depicted by the spectrum of **L2** (**Figure 3.2**). These bands indicate the formation of desired ligands as the condensation product should contain imine functional groups that the C=N peaks in the infrared spectra show. The position of the bands varies with the molecular structure [18]. The spectra also exhibit medium to strong bands at 1595-1560 cm^{-1} corresponding to ν (C=N) of the imidazole ring.

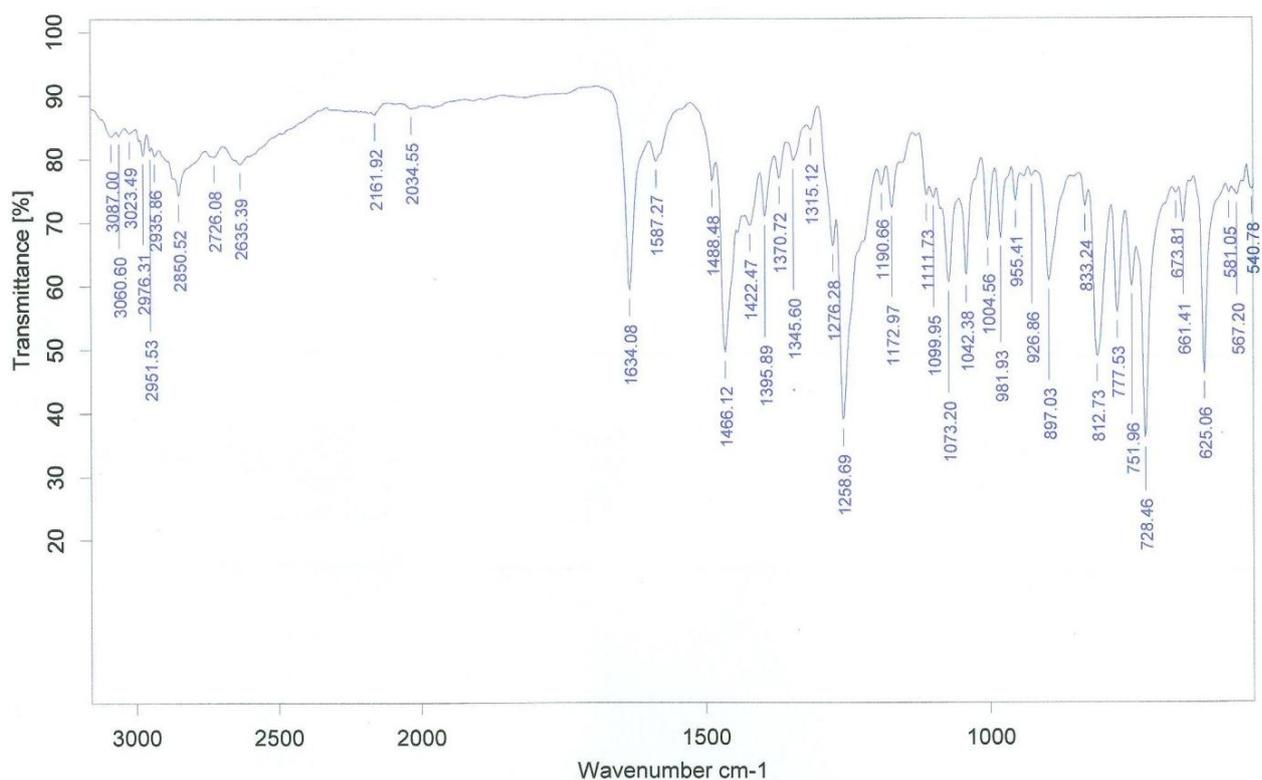


Figure 3.2: IR spectrum of ligand **L2**

3.3.2.3. Mass spectral analysis of ligands **L1-L5**

Ligands **L1-L5** were characterized by electrospray ionisation (ESI) mass spectrometry. The positive ion spectra (ESI (+)) of **L1-L5** does not show molecular ion peaks of the ligands but show peaks with m/z values of 328.2383 (100%), 260.1398 (100%), 246.1246 (100%), 200.1187 (100%), 214.1346 (100%) corresponding to the $[M+H]^+$. The spectrum of **L3** (**Figure 3.3**) is used as an illustration; but since these are HRMS they can also be used to establish the purity of all five ligands and as such we did not report CHN analysis of **L1-L5**.

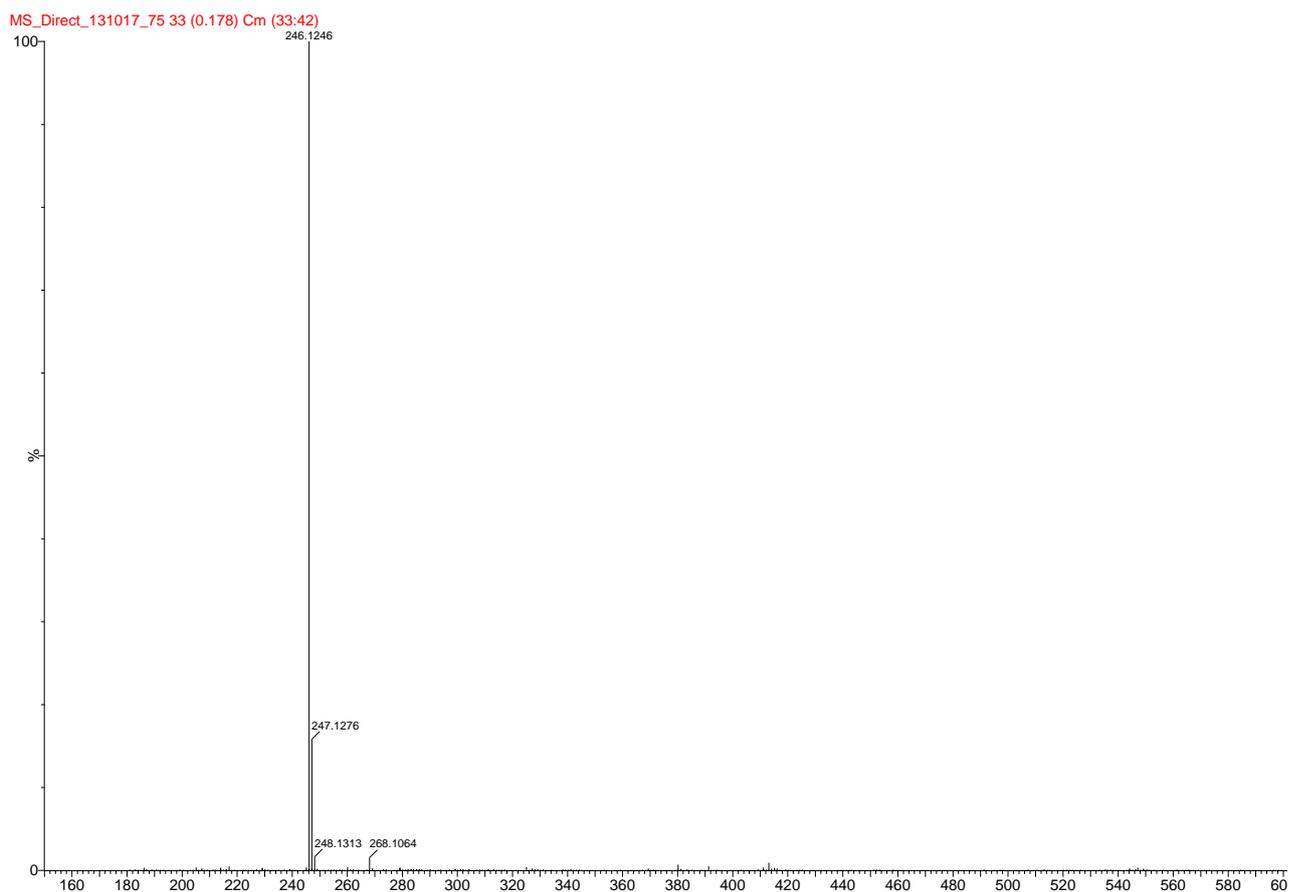


Figure 3.3: ESI mass spectrum of ligand **L3**

3.3.2.4. Electronic spectra

Electronic spectra of the ligands were run in methanol in the range 800-200 nm. The absorption maxima are listed in **Table 3.1.**, and the spectra are shown in **Figure 3.4.** The UV-vis spectra exhibit mainly three bands. The band on the higher energy side at 220 nm is due to the excitation of the π electrons (π - π^* transitions) of the imidazole ring. The second band at 260 nm is due to n - π^* of N=C lone pairs and the third band at 300 nm is due to π - π^* transitions of a benzene ring. Hamil *et. al.*, [19] observed bands due to phenyl rings and C=N group on Schiff base ligands.

Table 3.1: UV-vis spectral data of ligands **L1-L5** in methanol

Compound	Absorption maxima (nm)	Assignments
L1	220 260 370	π - π^* imidazole ring n - π^* -C=N π - π^* benzene ring
L2	220 300	π - π^* imidazole ring π - π^* benzene ring
L3	220 300	π - π^* imidazole ring π - π^* benzene ring
L4	220 260	π - π^* imidazole ring π - π^* benzene ring
L5	220	π - π^* imidazole ring

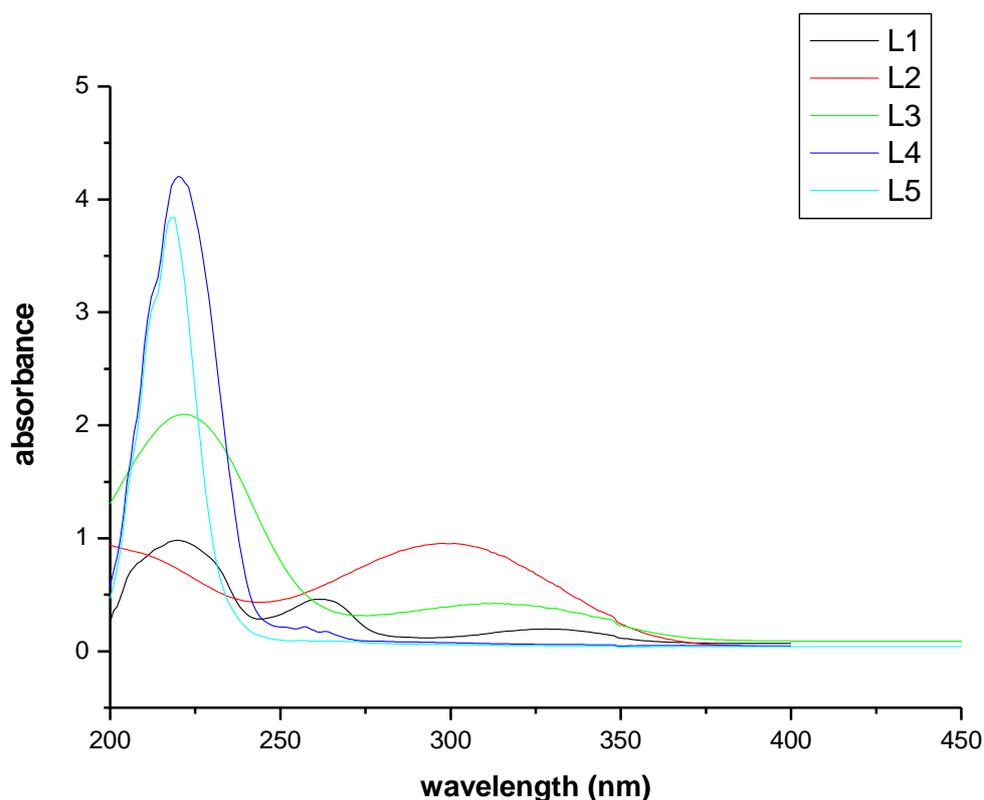
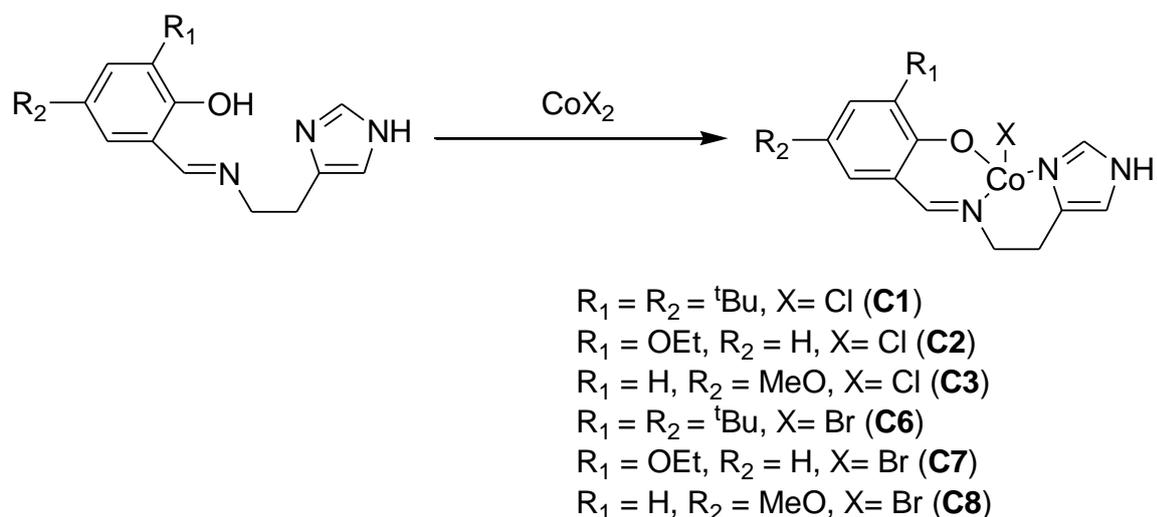


Figure 3.4: Electronic absorption spectra of ligands **L1-L5**

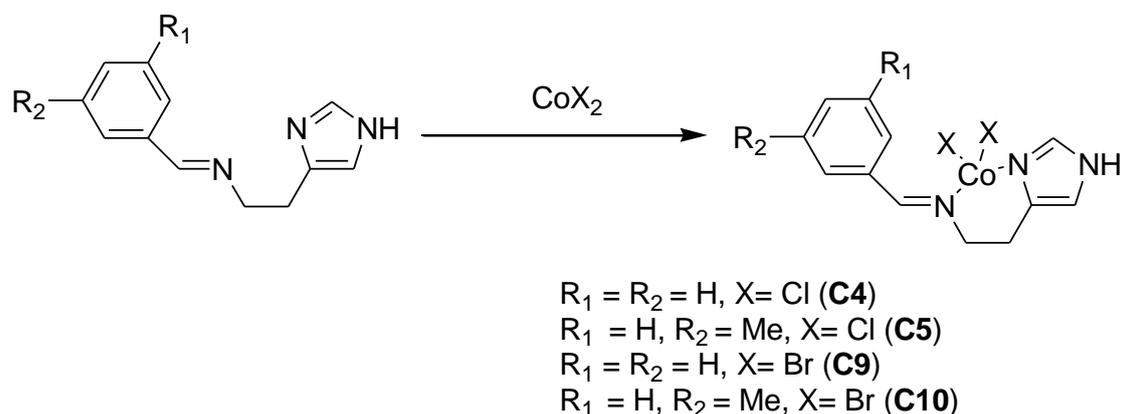
3.3.3. Synthesis of cobalt(II) complexes with L1-L5

Complexes **C1-C10** were prepared by the reaction of ligands **L1-L5** with either CoCl_2 or CoBr_2 in a 1:1 ratio. The products obtained with **L1** were soluble in CH_2Cl_2 but the other complexes were insoluble in this solvent. The insolubility of the other complexes was due to few or lack of substituents on the ligand backbone, rendering them insoluble in CH_2Cl_2 . Workup afforded dark green (**C1-C3**, **C7-C8**), dark brown (**C6**) and dark blue solids (**C4-C5**, **C9-C10**) respectively in moderate to excellent yields. The hydrogen of the phenolic $-\text{OH}$ is acidic enough and is deprotonated without use of a base to form pincer type complexes with cobalt dihalides in which the oxygen, the imine nitrogen and the imidazole nitrogen of the ligands are bound to the cobalt metal centre (**Scheme 3.2**). Usually deprotonation of acidic phenolic hydrogen is realised using bases such as lithium alkyls (MeLi , BuLi), sodium or potassium hydrides and Et_3N [16]. With **L4-L5** the cobalt metal centre is only bound to imine nitrogen and imidazole nitrogen since they lack phenolic $-\text{OH}$ group.

Complexes **C1** and **C6** show good solubility in other chlorinated solvents like CHCl_3 , toluene, acetonitrile, DMSO and THF while complexes **C2-C3**, **C7-C8** were soluble only in acetonitrile and DMSO, and complexes **C4-C5**, **C9-C10** were only soluble in organic solvents after heating. Elemental analysis showed that complex **C6** is pure while elemental analysis of complexes **C1-C5**, **C7-C10** showed that they are pure but contain 0.50 and 1.00 mol of CH_2Cl_2 .



Scheme 3.2a: Synthetic scheme for formation of complexes **C1-C3** and **C6-C8**



Scheme 3.2b: Synthetic scheme for formation of complexes **C4-C5** and **C9-C10**

3.3.4. Characterisation of cobalt(II) complexes C1-C10

3.3.4.1. NMR studies of complexes C1-C10

All the complexes are paramagnetic in nature, therefore NMR spectroscopy could not be used to characterise them. **Figure 3.5** is an example of the ^1H NMR spectrum of complex **C1** that clearly demonstrate that this and the other complexes are paramagnetic. The peaks in the figure are broad; typical of NMR signals for paramagnetic compounds, that is an indicative of fast relaxation of the sample because of unpaired electron spin [20].

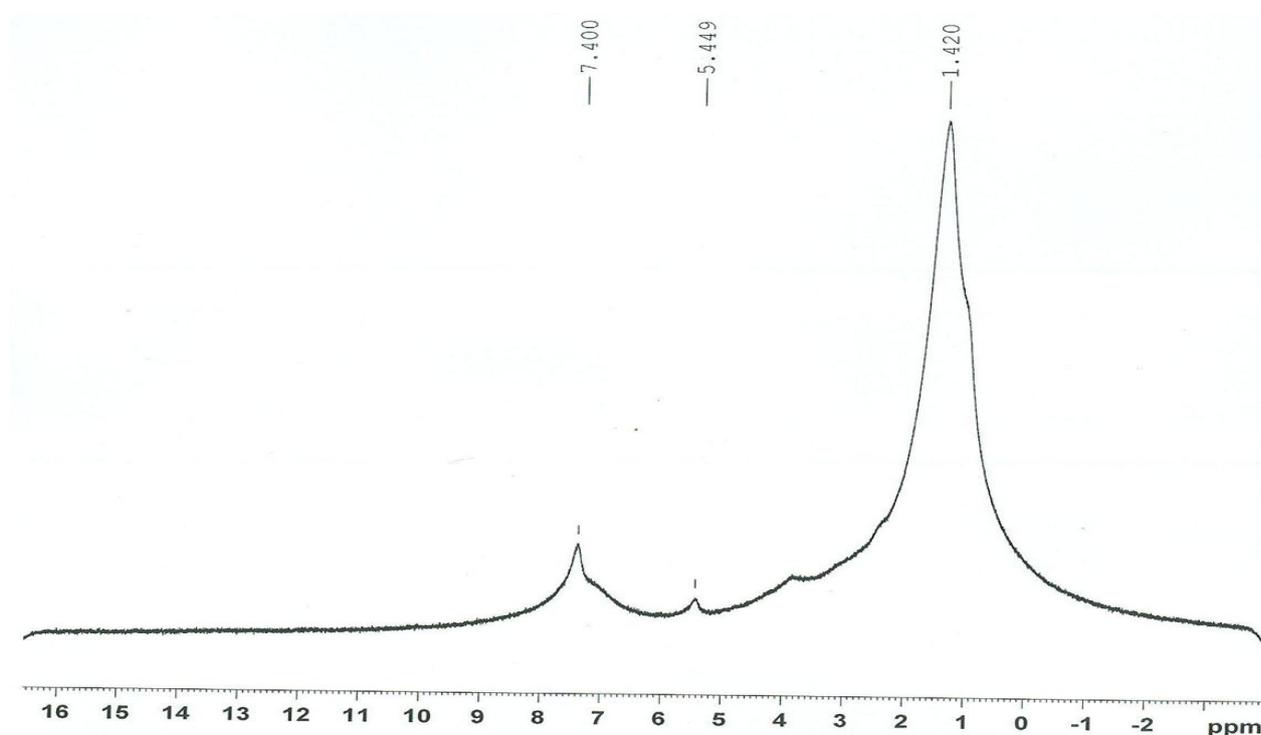


Figure 3.5: ^1H NMR spectrum of complex **C1**

3.3.4.2. IR studies

The IR spectra of complexes **C1-C10** showed imine peaks between 1618 cm^{-1} and 1671 cm^{-1} (**Table 3.2**). On complexation the $\nu(\text{C}=\text{N})$ bands of the ligands shift to lower or higher frequencies in the spectra of all the complexes, indicating coordination of the azomethine nitrogen [9]. The $\text{C}=\text{N}$ - stretching of the imidazole

ring undergoes a small shift on complexation due to coordination of metal centre to imidazolyl nitrogen such small shifts have been reported when ring nitrogen are involved in coordination involving ligands that have IR active functional groups [21].

Table 3.2: IR data of complexes and their respective ligands

Complex	$\nu(\text{C}=\text{N}) \text{ cm}^{-1}$	Ligand	$\nu(\text{C}=\text{N}) \text{ cm}^{-1}$
C1	1620.01	L1	1630.77
C2	1620.24	L3	1634.08
C3	1625.95	L3	1633.91
C4	1671.40	L4	1618.09
C5	1669.65	L5	1626.97
C6	1619.70	L1	1630.77
C7	1618.67	L2	1634.08
C8	1618.91	L3	1633.91
C9	1632.06	L4	1618.09
C10	1630.34	L5	1626.97

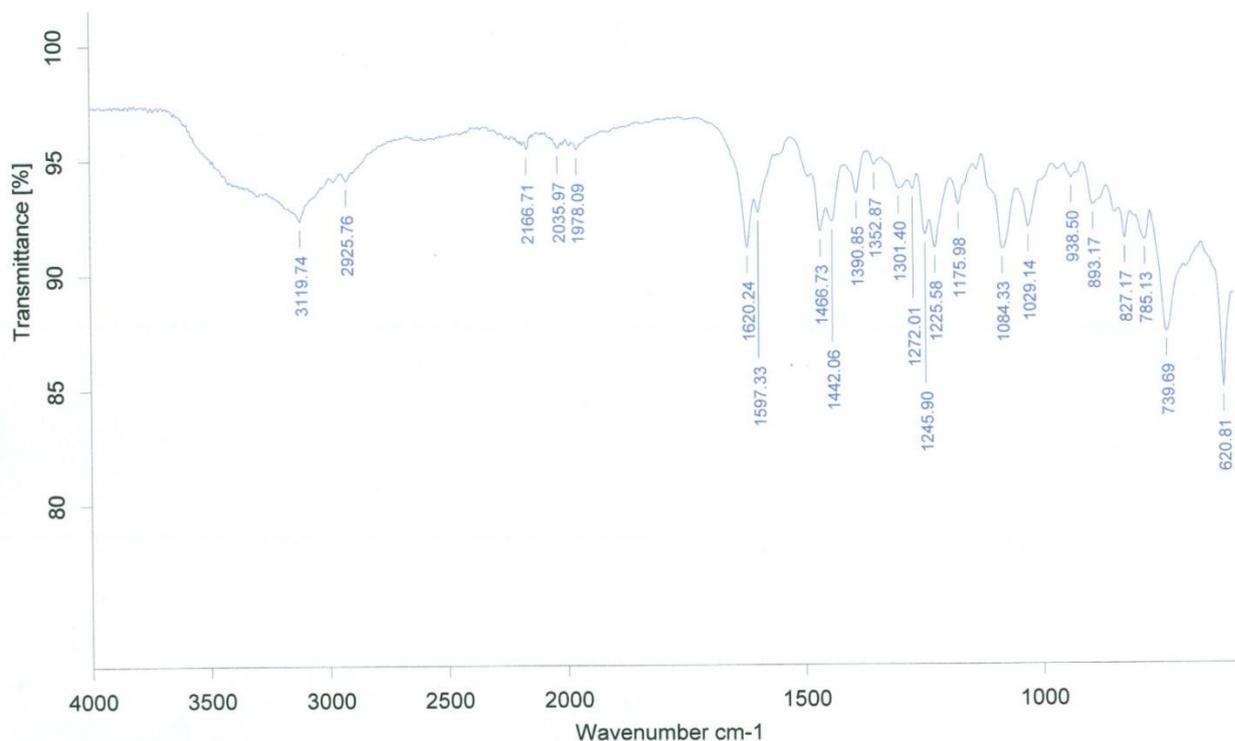


Figure 3.6: IR spectrum of complex **C2**

3.3.4.3. UV-vis study of complexes

The electronic spectra of ligands and their respective cobalt(II) complexes were run. They generally have similar features as such the spectra on only **L1**, **C1** and **C6** are reported here in **Figures 3.7** and **3.8**. The spectra display four bands each. The first higher energy band is due to $\pi\text{-}\pi^*$ of imidazole ring, the second band is due to $n\text{-}\pi^*$ of (C=N) and the third band is due to $\pi\text{-}\pi^*$ of benzene ring. These bands are also observed in free ligands indicated as **L1** in the figure. A new band is observed at 400 cm^{-1} of the complex due to charge transfer transition [22]. This confirms coordination of a metal to free ligand. The electronic absorption spectra of complexes **C2** and **C6** were measured in four different organic solvents of different polarities such as ethanol, methanol, dimethylsulfoxide (DMSO), tetrahydrofuran (THF) (**Table 3.3**). The spectra indicated that the bands due to localised electron transitions are slightly influenced by the nature of the solvent used.

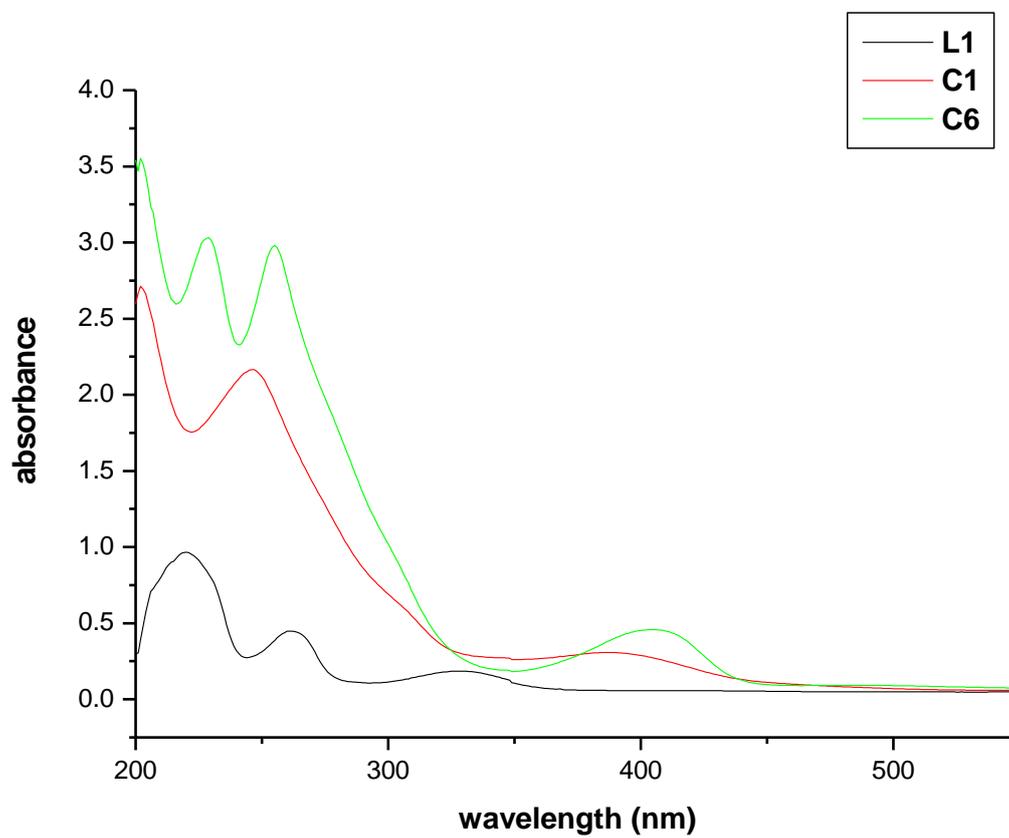


Figure 3.7: Electronic spectra of ligand **L1**, complexes **C1** and **C6** in methanol

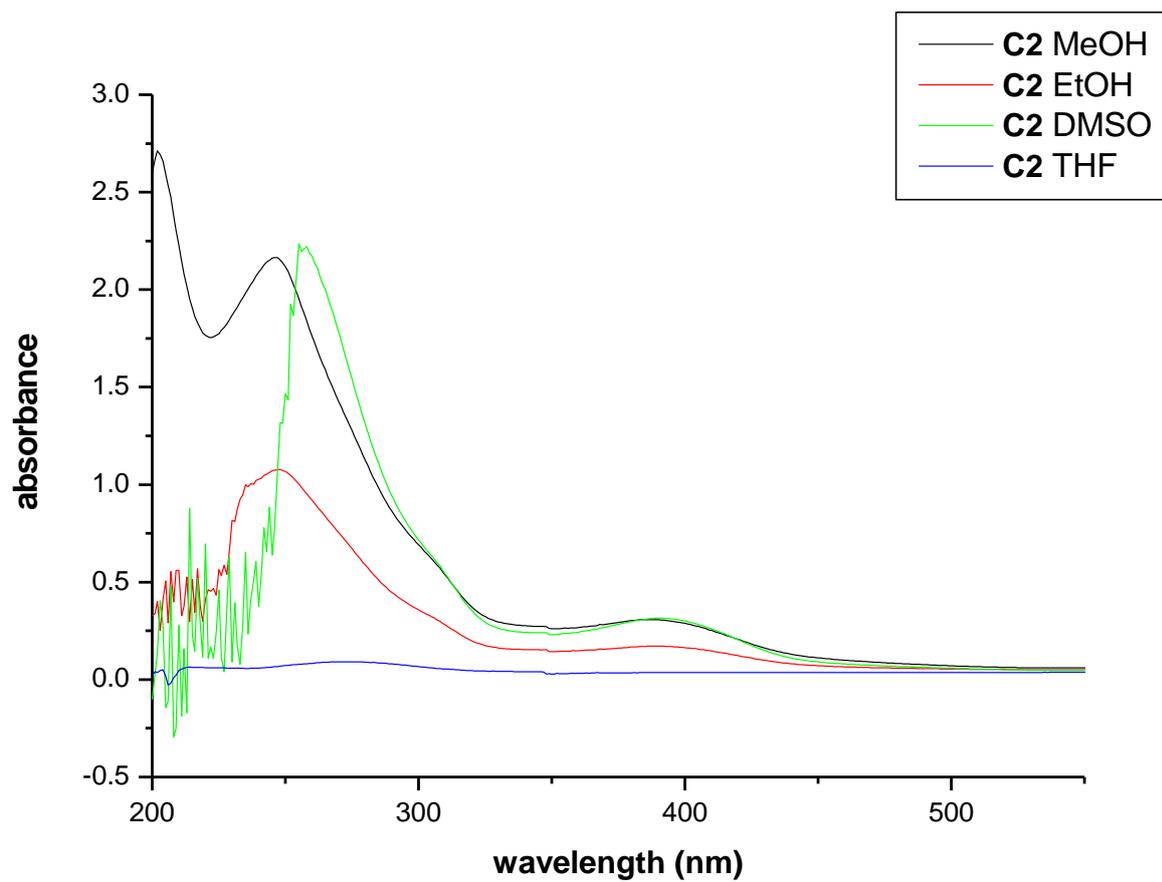


Figure 3.8.a: Electronic spectra of complex C2 in different solvents

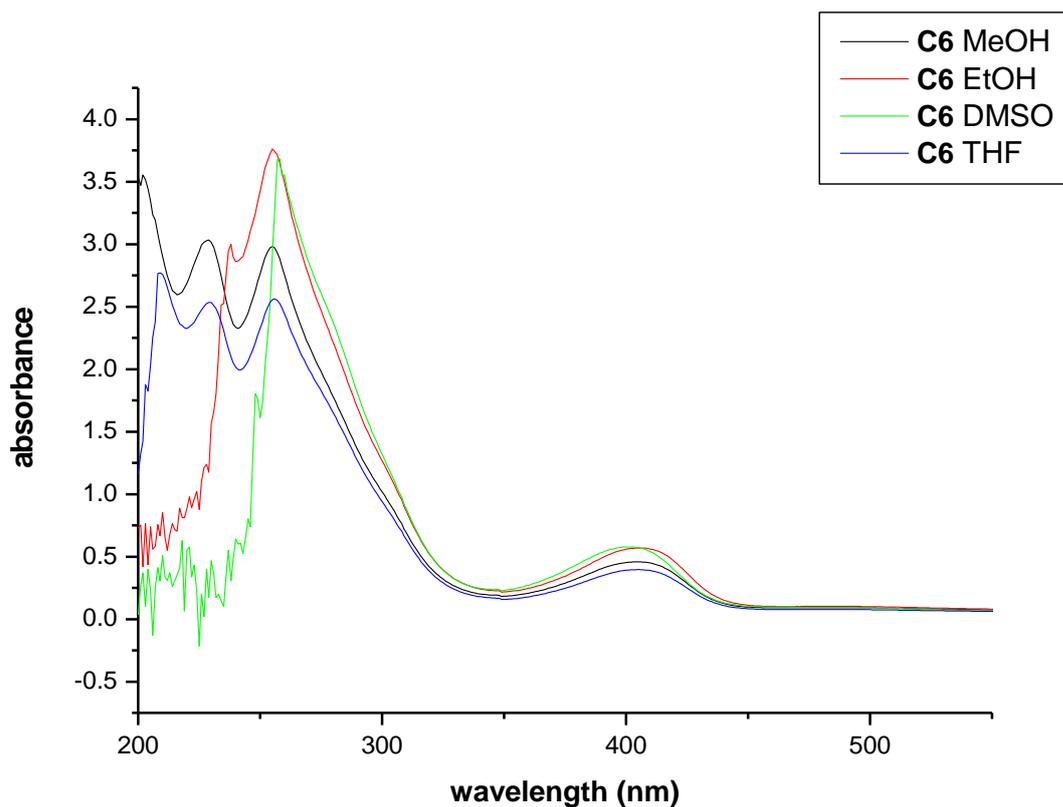


Figure 3.8b: Electronic spectra of complex **C6** in different solvents

Table 3.3: UV-vis spectral data of cobalt complexes in organic solvents of varying polarities

Complex	Solvent	Band A $\lambda(\text{nm})$	Band B $\lambda(\text{nm})$	Band C $\lambda(\text{nm})$	Band D $\lambda(\text{nm})$ (absorbance)
C2	Methanol	205	240	300	400 (0.3)
	Ethanol	-	242	300	400 (0.3)
	DMSO	-	255	300	400 (0.2)
	THF*				
C6	Methanol	202	230	250	400 (0.4)
	Ethanol	-	240	250	400 (0.6)
	DMSO	-	248	253	400 (0.6)
	THF	205	231	250	400 (0.3)

THF*=insoluble in THF

3.3.4.4. Mass spectral analysis of metal complexes

Positive ion electrospray (ESI) mass spectrometry data were collected on complexes **C1-C10**. The spectra of **C4** and **C7** gave peaks with m/z values of 327 (10%) and 395 (8%) corresponding to the molecular ions of the complexes respectively. Other complexes showed various ions associated with fragments as shown in **Table 3.4**. **Figure 3.9** is an ESI mass spectrum of complex **C2** and is representative of most of the mass spectral data of the complexes. The mass spectrum of **C2** is one of the complexes that did not show the molecular ion, instead it showed fragmentation ion with $m/z = 317.05$ (100%). All the other complexes followed this fragmentation pattern and would explain why only **C4** and **C7** gave the expected molecular ions in their mass spectra. The loss of either Cl or Br in the fragmentation inadvertently also confirmed the presence of either Cl or Br in the cobalt complexes; an observation that helped in proposing structures of the cobalt complexes as described earlier in the reaction Schemes.

Table 3.4: Positive ion mass spectroscopy data of complexes

Complex	Expected Molecular mass	Observed ion	m/z (%) of observed ion
C1	420.13	$[M-Cl]^+$	385.16 (23%)
C2	352.64	$[M-Cl]^+$	317.05 (3%)
C3	338.64	$[M-Cl]^+$	303.04 (5%)
C4	327.98	$[M]^+$	327.94 (10%)
C5	342.00	$[M-CH_3]^+$	327.94 (35%)
C6	465.26	$[M-Br]^+$	385.12 (49%)
C7	395.98	$[M]^+$	395.98 (8%)
C8	383.09	$[M-Br]^+$	303.04 (60%)
C9	415.88	$[M-Br]^+$	334.91 (100%)
C10	429.90	$[M-Br]^+$	350.98 (30%)

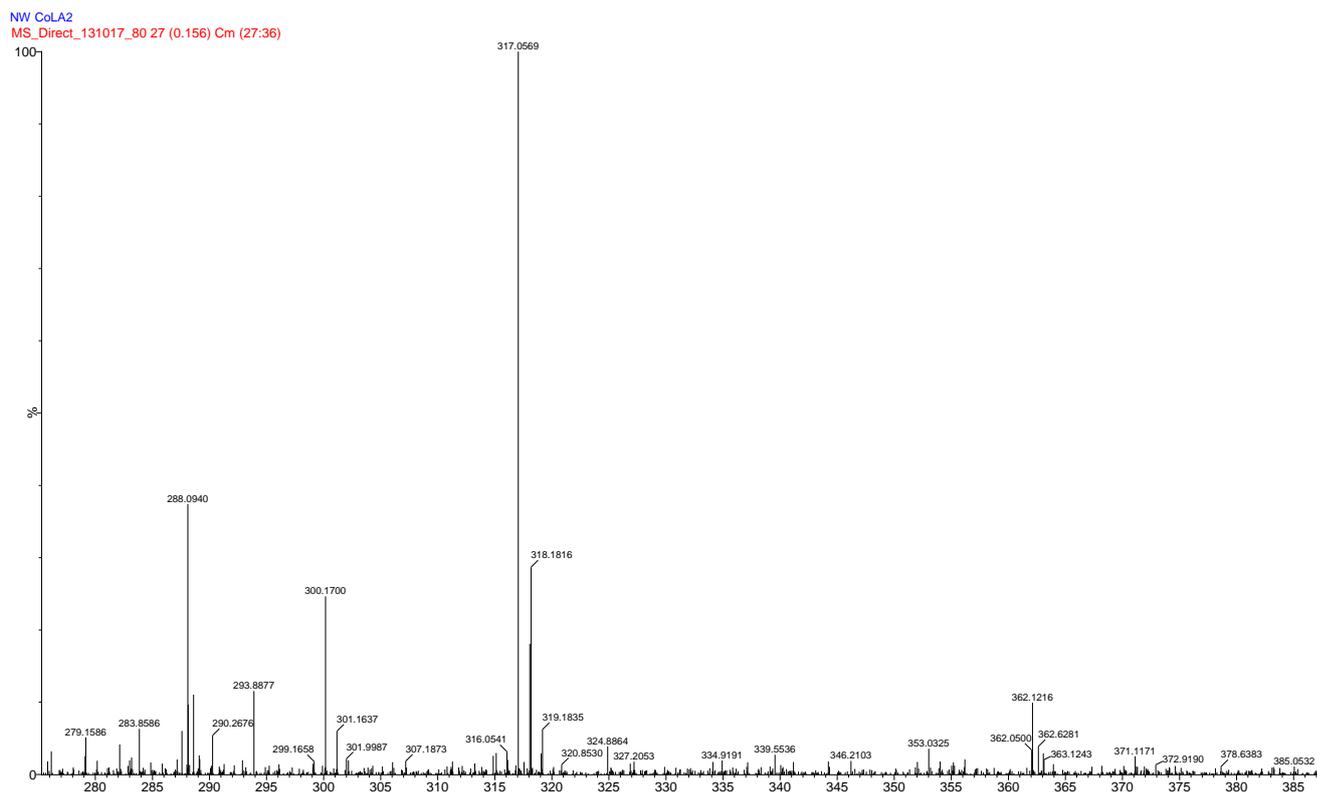


Figure 3.9: Positive mass spectrum of complex **C2**

3.3.5. Molecular structure of complex **C11**

In an attempt to obtain single crystals of **C6** for crystal structural determination, a brown powder of **C6** was dissolved in CH_2Cl_2 and layered with methanol after which the solution was kept at $-4\text{ }^\circ\text{C}$ for several days. Brown crystals suitable for structural analysis were eventually harvested and used for single crystal X-ray diffraction studies. The crystal data, together with data collection and structural refinement parameters are presented in **Table 3.5** while selected bond lengths and bond angles are given in **Tables 3.6** and **3.7** respectively. **Figure 3.10** shows two molecules of the structure of what appears to be a different compound from **C6**, labelled **C11**, which consists of two cationic species and two bromides as counter ions. These molecules appear with six H_2O and one MeOH solvates in the unit cell of the crystal, and are held together by hydrogen bonding interactions of the water molecules, the bromide ions and the imidazolyl NH . **Table 3.8** shows all the hydrogen bonding interactions in **C11**.

The structure of **C11**, with atoms labelled, is shown in **Figure 3.11**. In this figure the cobalt(II) atom is hexa-coordinate and at the centre of an octahedron, with four nitrogen and two oxygen donor atoms from two identical N[^]N[^]O tridentate ligands bound to the cobalt. The coordination geometry around the cobalt is best described as a distorted octahedron with a CoN₄O₂ core (**Figure 3.11**) because the bond angles all deviate from the ideal octahedral angles of 180° and 90°. The angles that deviate from 180° are: N(3)-Co(1)-N(6) (177.02(14)°), O(1)-Co(1)-N(2) (173.40(12)°) and O(1)-Co(1)-N(5) (172.28(12)°) (**Table 3.7**). There are eight other angles in **Table 3.7** that should have ideal angles of 90°, but of all which are either smaller or larger than 90°, confirming the distortion from an ideal octahedral geometry. The imine N atoms bonded to the cobalt have Co-N(3) and Co-N(6) bond lengths of 1.939(3) Å and 1.944(3) Å respectively; while the cobalt bonds with the imidazole nitrogen are: Co-N(2) (1.964(3) Å) and Co-N(5) (1.952(3) Å). To the best of our knowledge only similar (O[^]N[^]N_{pz})Co complexes have been reported [23] in the literature that can be used to compare the bond lengths in **C11**. The Co-N_{imine} bond distances in (O[^]N[^]N_{pz})Co are: 1.970(2) Å (for 3,5-diMepz) and 1.9743(19) Å (for 3,5-diPhpz), which are only slightly longer than the Co-N_{imine} distances observed for **C11**. The Co(1)-O(1) and Co(1)-O(2) bond lengths in **C11** are 1.883(3) Å and 1.882(3) Å respectively. These bond lengths also do not differ by much from those observed for (O[^]N[^]N_{pz})Co: 1.8876(17) Å (for 3,5-diMepz) and 1.8899(16) Å (for 3,5-diPhpz).

Table 3.5: Crystal data and structure refinement for complex **C11**

Empirical formula	C _{80.6714} H _{123.7791} Br ₂ Co ₂ N ₁₂ O ₁₁
Formula weight	1715.52
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	P2 ₁ /c
a/Å	38.955(5)
b/Å	12.516(5)
c/Å	18.508(5)
α/°	90.000(5)
β/°	98.229(5)

$\gamma/^\circ$	90.000(5)
Volume/ \AA^3	8931(4)
Z	4
$\rho_{\text{calc}}/\text{mg}/\text{mm}^3$	1.276
m/mm^{-1}	1.327
F(000)	3615.0
Radiation	MoK α ($\lambda = 0.71069$)
2 Θ range for data collection	5.67 to 56.716 $^\circ$
Index ranges	$-51 \leq h \leq 51$, $-16 \leq k \leq 16$, $-24 \leq l \leq 24$
Reflections collected	125732
Independent reflections	21982 [$R_{\text{int}} = 0.1273$, $R_{\text{sigma}} = 0.1158$]
Data/restraints/parameters	21982/0/1028
Goodness-of-fit on F^2	1.044
Final R indexes [$ I \geq 2\sigma(I)$]	$R_1 = 0.0596$, $wR_2 = 0.1321$
Final R indexes [all data]	$R_1 = 0.1406$, $wR_2 = 0.1777$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.07/-0.58

Table 3.6: Bond lengths [\AA] for complex **C11**

Co(1)-O1	1.883(3)
Co(1)-(O2)	1.882(3)
Co(1)-(N2)	1.964(3)
Co(1)-(N3)	1.939(3)
Co(1)-(N5)	1.952(3)
Co(1)-(N6)	1.944(3)
N(6)-C(35)	1.286(5)
O(1)-C(8)	1.304(4)

Table 3.7: Bond angles [°] for complex **C11**

O(1)-Co(1)-N(2)	173.40(12)
O(1)-Co(1)-N(3)	94.40(12)
O(1)-Co(1)-N(5)	88.80(13)
O(1)-Co(1)-N(6)	84.36(12)
O(2)-Co(1)-N(2)	89.33(12)
O(2)-Co(1)-N(3)	92.42(13)
O(2)-Co(1)-N(5)	172.28(12)
O(2)-Co(1)-N(6)	94.34(12)
N(3)-Co(1)-N(2)	92.13(13)
N(3)-Co(1)-N(5)	89.75(13)
N(3)-Co(1)-N(6)	177.02(14)
N(5)-Co(1)-N(2)	90.29(13)
N(6)-Co(1)-N(2)	89.16(13)
N(6)-Co(1)-N(5)	92.93(13)
C(8)-O(1)-Co(1)	127.5(2)
C(35)-N(6)-Co(1)	122.4(3)

Table 3.8: Hydrogen bonding data for complex **C11**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N10	H10	O5 ¹	0.86	1.98	2.842(4)	173.9
C51	H51C	O4	0.96	2.36	3.000(4)	123.8
C52	H52A	O4	0.96	2.35	2.980(4)	122.7
C60	H60	O7 ¹	0.93	2.47	3.179(4)	133.2
C72	H72C	O3	0.96	2.35	2.964(4)	121.5
C73	H73A	O3	0.96	2.35	2.990(4)	123.8
N4	H4	O9 ²	0.86	1.87	2.729(4)	172.9
C11	H11A	O1	0.96	2.36	2.988(4)	122.6

C13	H13C	O1	0.96	2.28	2.941(4)	125.5
C21	H21C	O2	0.96	2.31	2.943(4)	123.0
C22	H22A	O2	0.96	2.37	3.007(4)	123.5
O11	H11	O10 ¹	0.82	2.10	2.906(6)	168.3
O9	H9A	O10	0.85	1.94	2.758(5)	162.7
O8	H8A	O7	0.85	1.99	2.836(5)	171.4
O10	H10C	O8	0.85	1.86	2.699(5)	169.9
O6	H6A	O5	0.85	2.00	2.824(4)	162.6
O7	H7A	O6	0.85	1.97	2.804(4)	166.8

¹+X,1+Y,+Z; ²+X,-1/2-Y,-1/2+Z

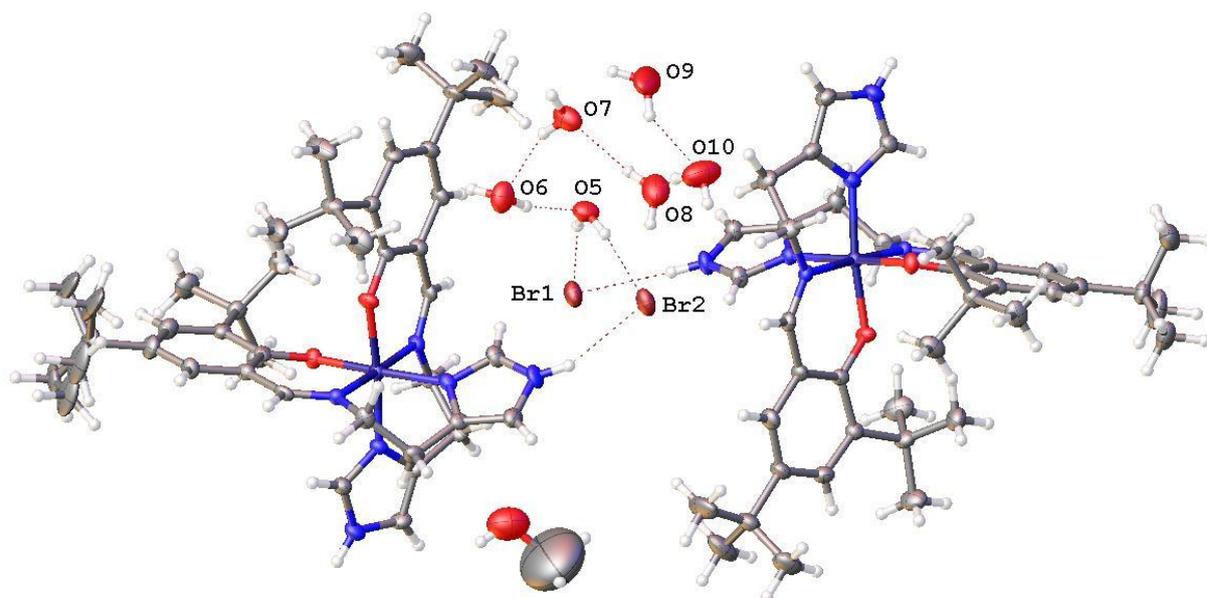


Figure 3.10: Molecular structure of complex **C11**. Ellipsoids are drawn at 50% probability level

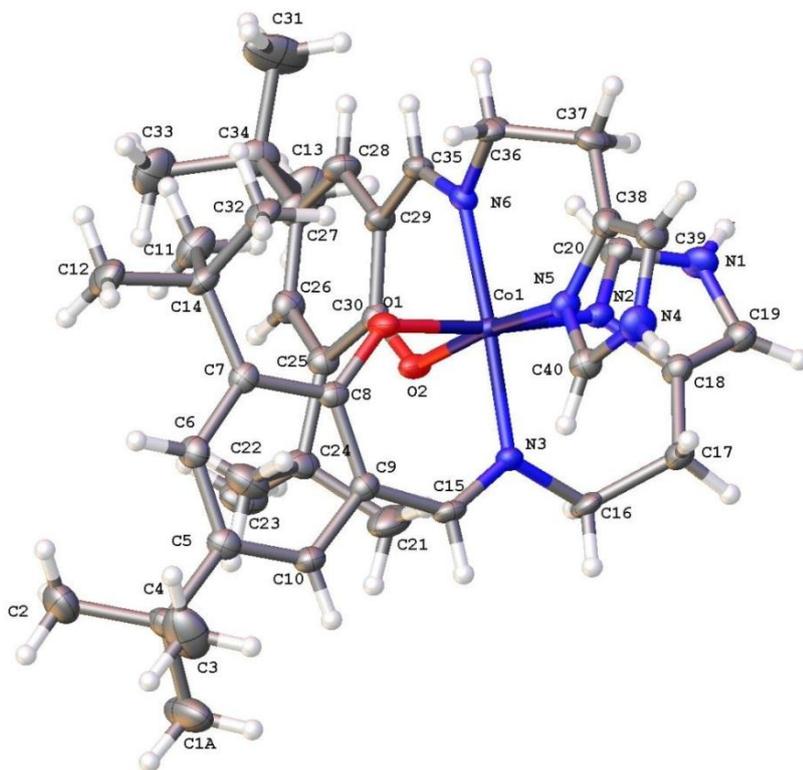
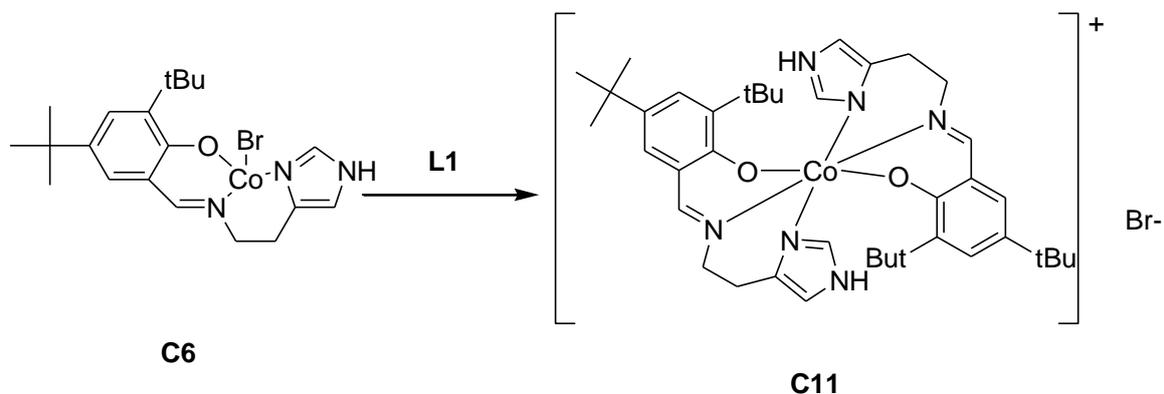


Figure 3.11: Labelled molecular structure of complex **C11** showing only one molecule leged: counterion omitted. Ellipsoids are drawn at 50% probability level

The structure of complex **C11** suggests that all the cobalt complexes with the five ligands **L1-L5** maybe unstable for prolonged period in solution and that a possible transformation route from **C6** to **C11** could be by **Scheme3.3**



Scheme 3.3: Possible route of conversion from **C6** to **C11**

3.4. CONCLUSION

The reactions of ligands **L1-L3** with cobalt halides lead to the formation of tridentate (O⁻N⁻N) cobalt(II) monohalide complexes in which the phenolic proton in these ligands are deprotonated; thereby enabling the phenoxide oxygen to bind to the cobalt. Proposed structures of these tridentate cobalt complexes were mainly based on CHN and mass spectral data as all attempts to obtain single crystals for X-ray crystallography were unsuccessful. However, upon prolonged stay in solution **C6** was able to produce crystals that enabled us to determine the structure of **C11**. However, the structure of **C11** is not what the proposed structure of **C6** is. This therefore suggests that **C6** was transformed from a mono-ligand cobalt complex to a bis(ligand)cobalt salt. The structure of **C11**, nonetheless, helped us to confirm the tridentate nature of **L1-L3** via the phenoxide coordination mentioned above. Ligands **L4** and **L5**, on the other hand produced bidentate [Co(L)X₂] complexes (where **L** = **L4** or **L5** and X = Cl or Br) whose structures were proposed from CHN and mass spectral data.

3.5. REFERENCES

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CHAPTER 4

EVALUATION OF THE CATALYTIC ACTIVITIES OF IMIDAZOLYL-SALICYLALDIMINE COBALT(II) COMPLEXES FOR PHENOL AND STYRENE OXIDATION REACTIONS

4.1. INTRODUCTION

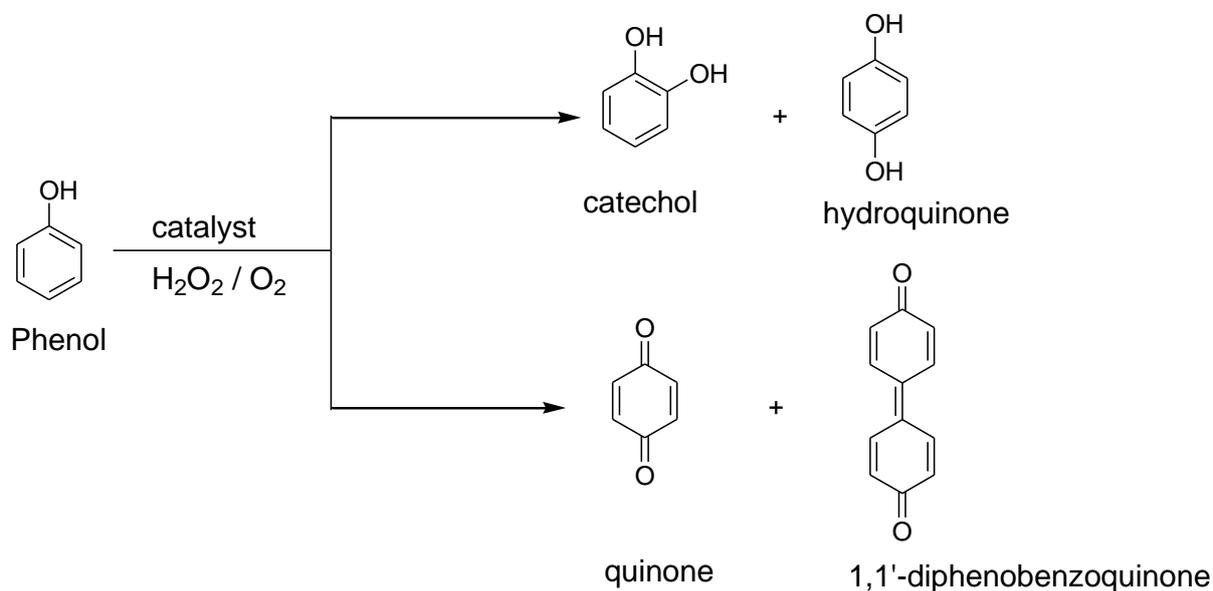
The oxidation of organic compounds is an important and widely used reaction in both industrial and academia. There are different reagents and methods available for the oxidation of organic compounds. The selection of solvent, oxidant, reaction conditions such as temperature, pressure and reaction steps is crucial in affecting the rate of reaction, and quantity of products produced. Schiff base transition metal complexes are a family of attractive oxidation catalysts for a variety of organic substrates because of their cheap, easy synthesis, as well as their chemical and thermal stability [1].

This chapter deals with investigating the Schiff base cobalt complexes prepared in Chapter 3 as catalysts for the oxidation of phenol and styrene. Section 4.2 describes the attempts made with the study of the catalytic activity of the Schiff base cobalt(II) complexes in the oxidation of phenol while section 4.3 describes similar attempts employing the same cobalt complexes in the oxidation of styrene.

4.2. SCHIFF BASE METAL COMPLEXES AS CATALYST TOWARDS CATALYTIC OXIDATION OF PHENOL

The oxidation of organic substrates with aqueous hydrogen peroxide and dioxygen is very attractive from the viewpoint of industrial and synthetic organic chemistry since aqueous hydrogen peroxide is cheap, environmentally clean and easy to handle [2]. Transition metal complexes containing nitrogen and phenolic oxygen donor atoms are of considerable interest in inorganic and biomimetic chemistry due to their potential application in catalysis, their biological relevance and potentially interesting magnetic properties. Schiff base transition metal complexes have been used to oxidise phenol to quinone, hydroquinone, catechol and 1,1'-diphenobenzoquinone (**Scheme 4.1**) [3, 4]. The oxidation products are widely used as intermediates in the production of fine chemicals, pesticides, photographic film development [5],

fragrances and polymerisation inhibitors [6]. In the present study attempts to oxidise phenol was carried out using the cobalt(II) complexes prepared in Chapter 3 of this dissertation.



Scheme 4.1: Oxidation of phenol to different products

4.2.1. Experimental

All the reactions were carried out under nitrogen. Reagents were purchased from Sigma Aldrich and were used as received without any other purification unless otherwise stated. Samples from the oxidation reactions were analysed by ¹H NMR spectra on a Bruker AVANCE III 400 MHz NMR using CDCl₃ as a solvent and Varian 3900 gas chromatography.

4.2.2. General procedure for phenol oxidation reaction

The catalytic activity study was carried out in a parallel reactor that runs 12 reactions simultaneously. In a typical reaction, (0.05 mmol) of a cobalt complex was dissolved in 5 mL of acetonitrile and (1.00 mmol) phenol was added. An aqueous solution of 30% H₂O₂ (2.00 mmol) was added to the reaction mixture with continuous stirring and the reaction was considered to be started at this time. Small aliquots of the mixture were drawn periodically and were analysed by NMR spectroscopy and gas chromatography to confirm the identity of the products.

4.2.3. Results and discussion

Oxidation of phenol by cobalt complexes **C1-C10** using H₂O₂ as an oxidant was studied in CH₃CN and the results are given in **Table 4.1**. Product analysis indicated that very little conversion of substrate to products occurred; hence these reactions were largely seen as having 0% conversions. In order to further explore if changing reaction conditions would affect activity we studied changing temperature, reaction time, pre-catalysts loading and solvents on the oxidation. The observations made are described below; but the outcome of it is that conversions remained very low and thus were all seen as 0%.

Table 4.1: Catalytic activity of cobalt complexes towards phenol oxidation

Catalyst	% Conversion
C1	0
C2	0
C3	0
C4	0
C5	0
C6	0
C7	0
C8	0
C9	0
C10	0

Reaction conditions: substrate (1.00 mmol), catalyst (0.05 mmol), oxidant (2.00 mmol) and total reaction volume of 5.00 mL. The reaction time was 24 h at 25 °C

From **Table 4.1**, it was observed that these catalysts were not efficient enough in the phenol oxidation at 25 °C and a reaction time of 24 h since phenol was observed in the NMR spectrum (**Figure 4.1**), the phenolic protons are observed at 6.38, 6.69, 7.08 ppm. This was also confirmed by GC results (**Figure 4.2**), where solvent and phenol peaks are observed at 3 and 13 min retention times. Different parameters such as reaction temperature, time, catalyst loading, oxidant effect and solvent effect were also investigated and are discussed in detail in the next section.

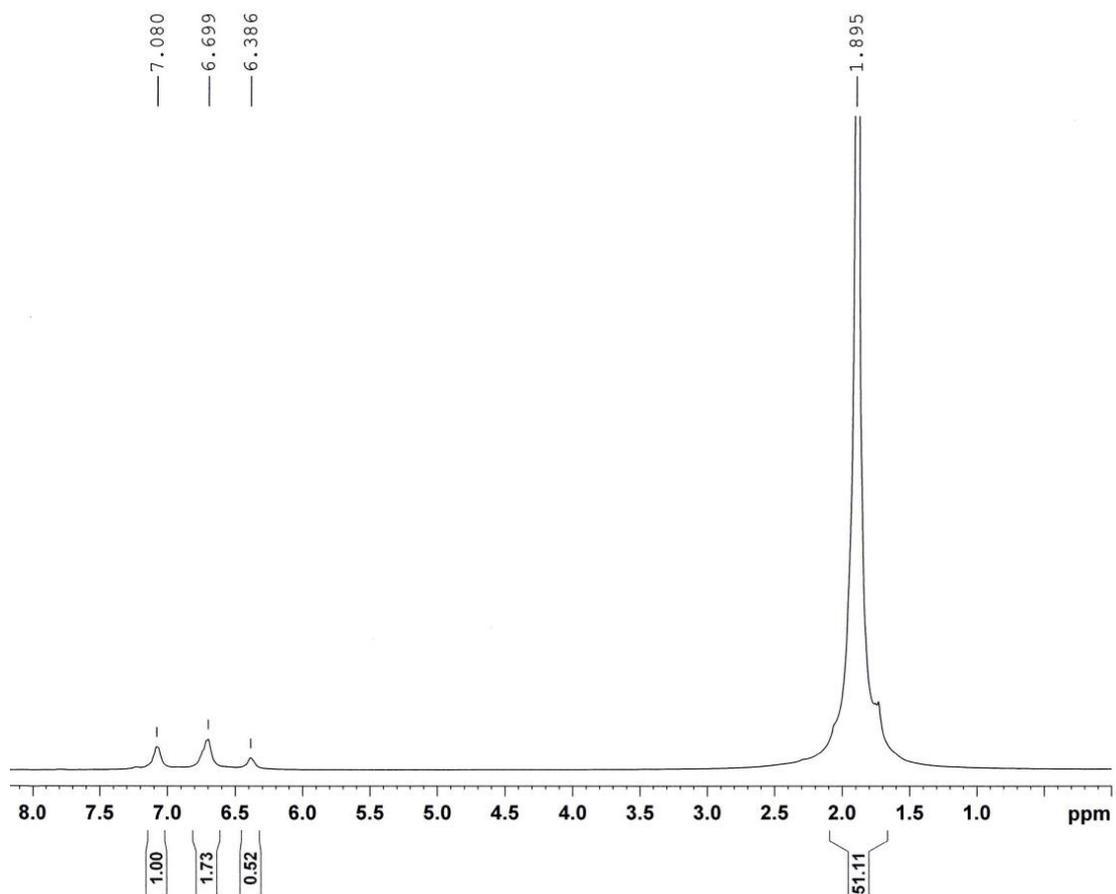


Figure 4.1: ^1H NMR spectrum of phenol oxidation using **C2** catalyst at 25 °C and 24 h

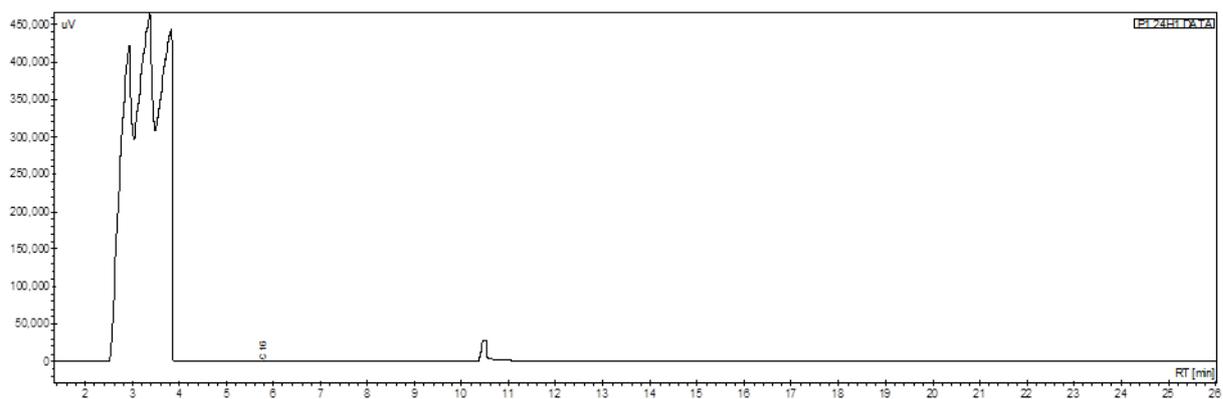


Figure 4.2: GC spectrum of phenol oxidation using **C2** catalyst

4.2.3.1. The effect of temperature

In order to investigate the effect of temperature on the oxidation reactions of phenol, cobalt(II) complexes were used as catalysts at 25 °C, 30 °C, 60 °C and 70 °C with catalyst loading of 0.05 mmol. Samples of the reaction mixture were taken after 1 h in each reaction and analysed by ¹H NMR spectroscopy and GC, while the reaction was allowed to run for 24 h. **Figure 4.3** shows the NMR results at 70 °C and 24 h. The spectrum also shows chemical shifts due to phenol protons meaning no new peaks corresponding to the product were formed which are expected to be at 5.0, 6.56 and 6.65 ppm for catechol and hydroquinone. Product peaks were also expected at 6.68 ppm for quinone, 6.62 and 7.06 ppm for 1,1'-diphenobenzoquinone. M Sebastian [9] observed that below 70 °C the conversion of phenol was very poor and above 70 °C, decomposition of H₂O₂ gets accelerated which is not beneficial to phenol oxidation. Low catalytic activity of cobalt(II) complexes was also observed. Therefore 70 °C was found to be minimum required temperature to supply sufficient energy to reach the energy barrier of phenol transformation. Hu *et al.* [10] observed that cobalt(II) complexes as mimic peroxidases have an optimum temperature which is 45 °C in phenol catalytic oxidation. Lower temperatures could not be used because phenol freezes at room temperature meaning that it would be inactive at low temperatures.

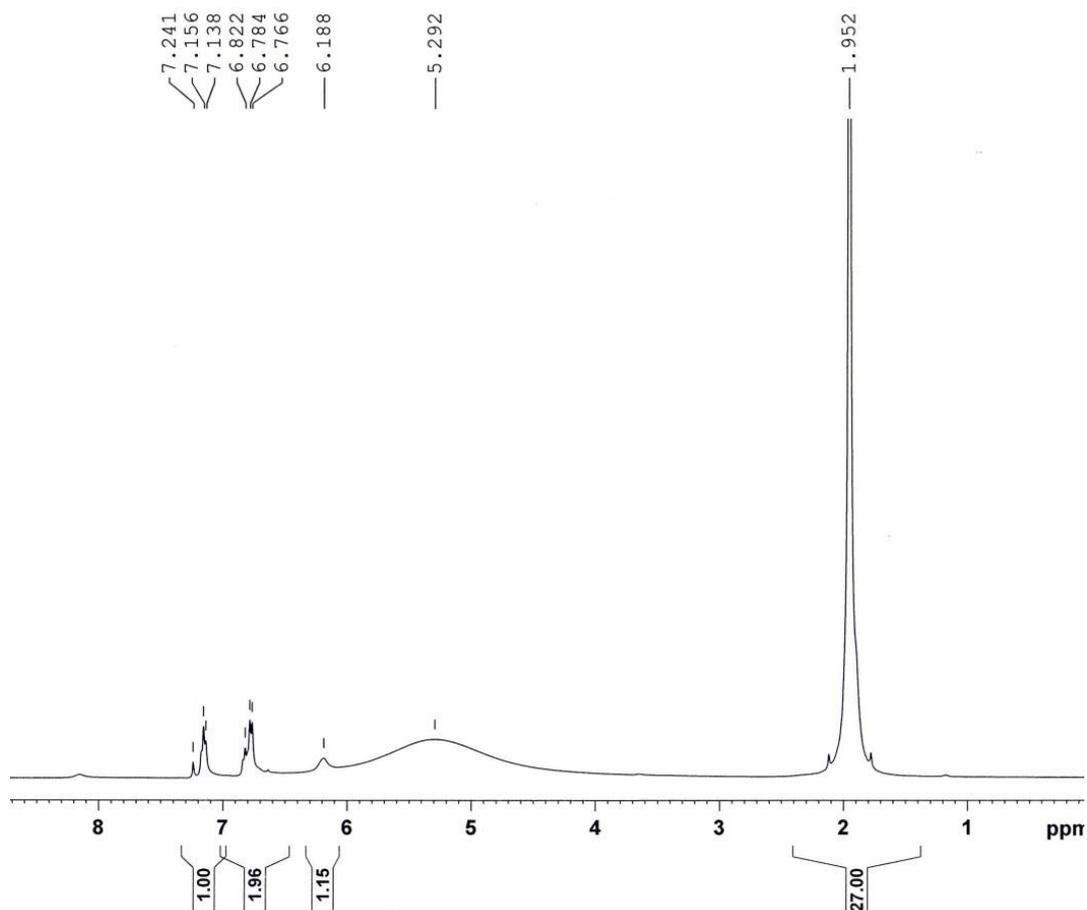


Figure 4.3: ^1H NMR spectrum of phenol oxidation using **C5** catalyst at 70 °C and 24 h

4.2.3.2. Effect of catalyst loading

The effect of catalyst loading on the activity was investigated on **C6** and **C8** at 70 °C. Catalyst loadings were 0.00 mol, 0.01 mmol, 0.05 mmol, 1.5 mmol at constant phenol: H_2O_2 ratio (1:2 mol) in 5 mL CH_3CN for 24 h. The results also show only phenol peaks, meaning that the catalysts could not transform phenol to expected products. Lowering the amount of catalyst resulted in the poor conversion thus, 1.5 mmol of catalyst was considered to be sufficient enough to give good performance in previous study [9]. A 2.5 mmol of a catalyst was used in the presence of pyridine as an axial base [11].

4.2.3.3. Effect of time

The effect of time on oxidation activity was investigated on complexes with 0.01 mmol catalyst and phenol: H₂O₂ mol ratio of 1:2 for 72 h being sampled every hour. The results are given in **Table 4.2** and they show that from 1 h to 72 h the phenol was not transformed. Two hours was found to be the fit reaction time because there was no significant change in the conversion and selective formation of catechol beyond 3 h [9].

Table 4.2: Effect of time on phenol oxidation

Catalyst	Time (h)	% Conversion
C3	24	0
	48	0
	72	0
C4	24	0
	48	0
	72	0

Reaction conditions: substrate (1.00 mmol), catalyst (0.05 mmol), oxidant (2.00 mmol) and total reaction volume of 5.00 mL. The reaction time was 72 h at 25 °C

4.2.3.4. Solvent effect

The effect of solvent on catalytic activity was done with complex **C1**. The reactions were prepared in acetonitrile, acetic acid, dichloromethane, toluene and solvent-free reaction. The samples were analysed with NMR spectroscopy and GC. Again no peaks which can be attributed to the product were observed. Acetonitrile [9] and acetic acid [12] were used in oxidation reactions of phenol.

Although it is difficult to explain the effect of solvent and to identify solvent parameters that are responsible for controlling the reaction rate, solvent plays a very significant role in controlling the overall % conversion. Abbo *et al.* [7] proposed that for phenol oxidation reaction, the solvent has a moderate influence on the ratio of catechol to hydroquinone. As the hydroxyl group present on phenol is *ortho* and *para*

directing, the oxidation of phenol is expected to give two products *viz.* catechol and hydroquinone using H₂O₂ [4, 8] or quinone and 1,1'-diphenbenzoquinone using O₂ [3].

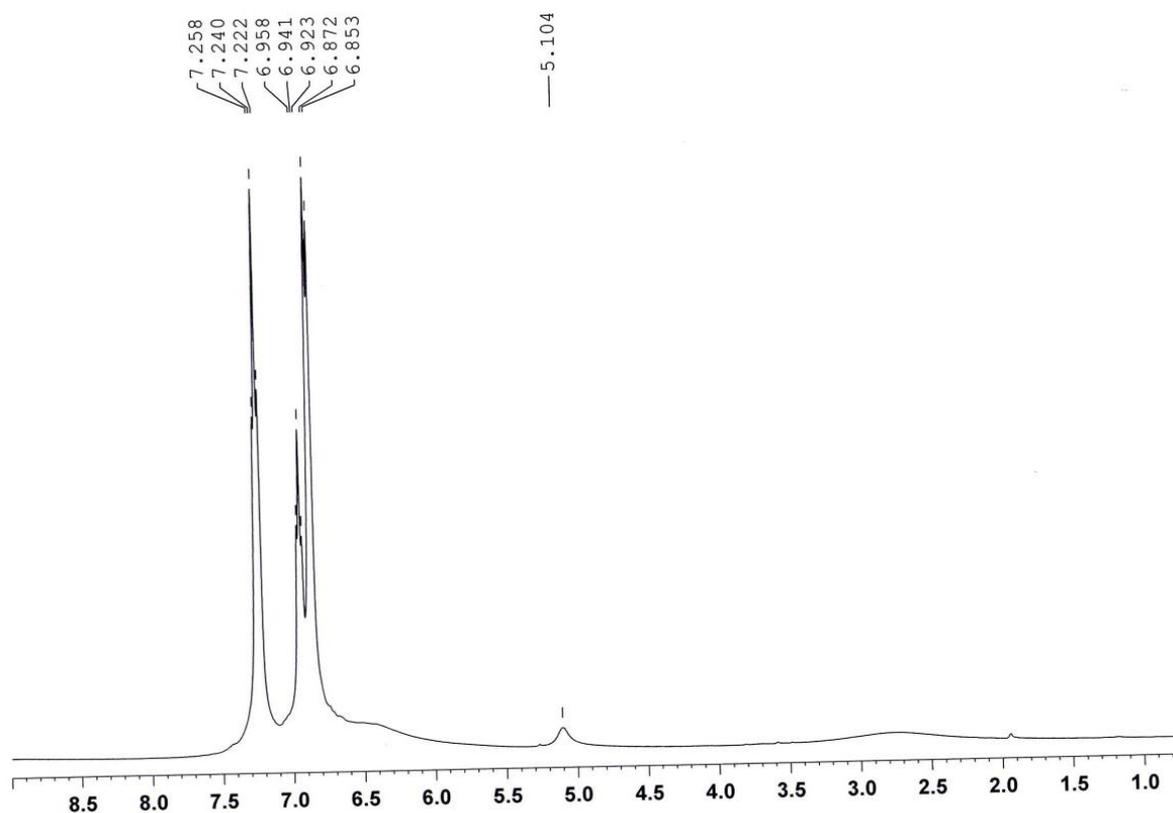


Figure 4.4: ¹H NMR spectrum of phenol oxidation without solvent at 30 °C and 72 h

4.2.3.5. Oxidant effect

The reactions were prepared with 0.05 mmol catalyst (**C1**, **C6**, **C8**), 1 mmol phenol and 2 mmol H₂O₂, 3-chloroperbenzoic acid and O₂ in acetonitrile for 24 h. The ¹H NMR (**Figure 4.5**) and GC spectra (**Figure 4.6**) of this reaction did not show any peaks that might be assigned to formation of product, therefore the catalyst did not oxidize phenol to expected products.

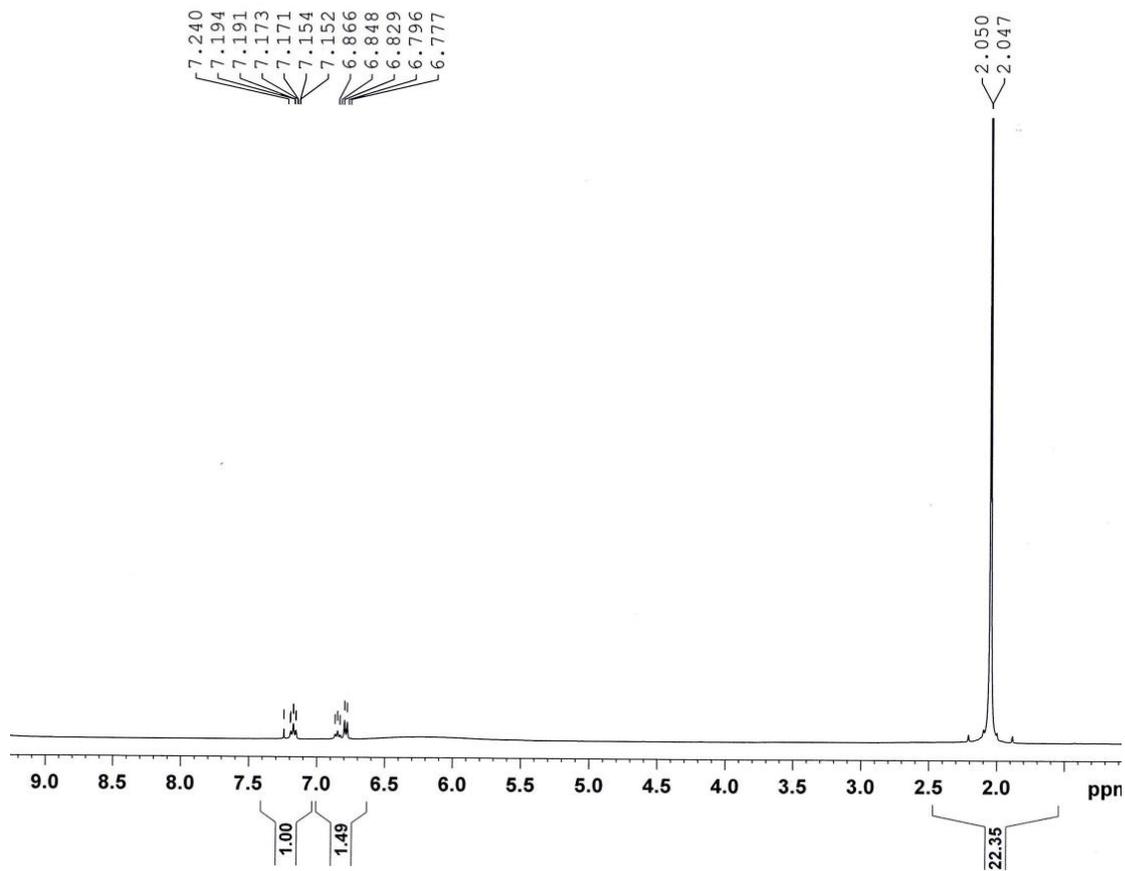


Figure 4.5: ^1H NMR spectrum of phenol oxidation using O_2 with **C6** at 60 °C and 24 h

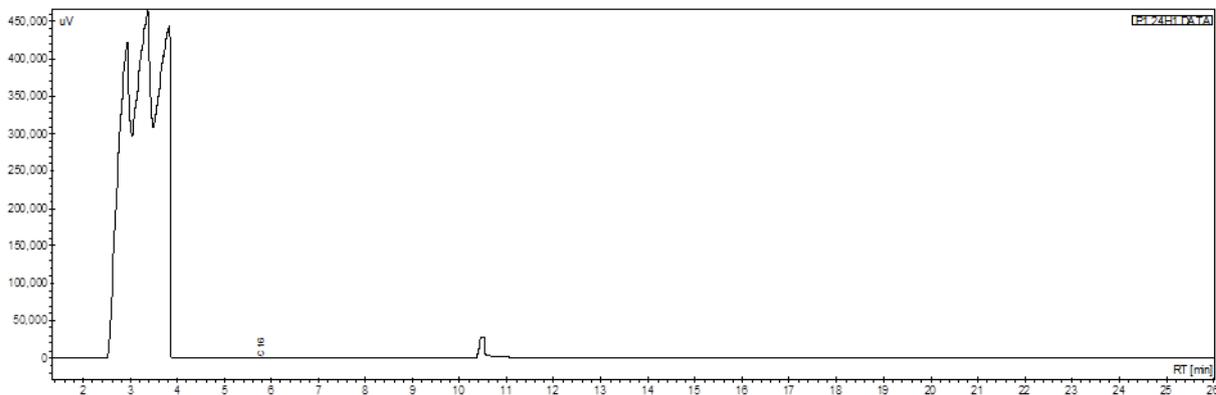


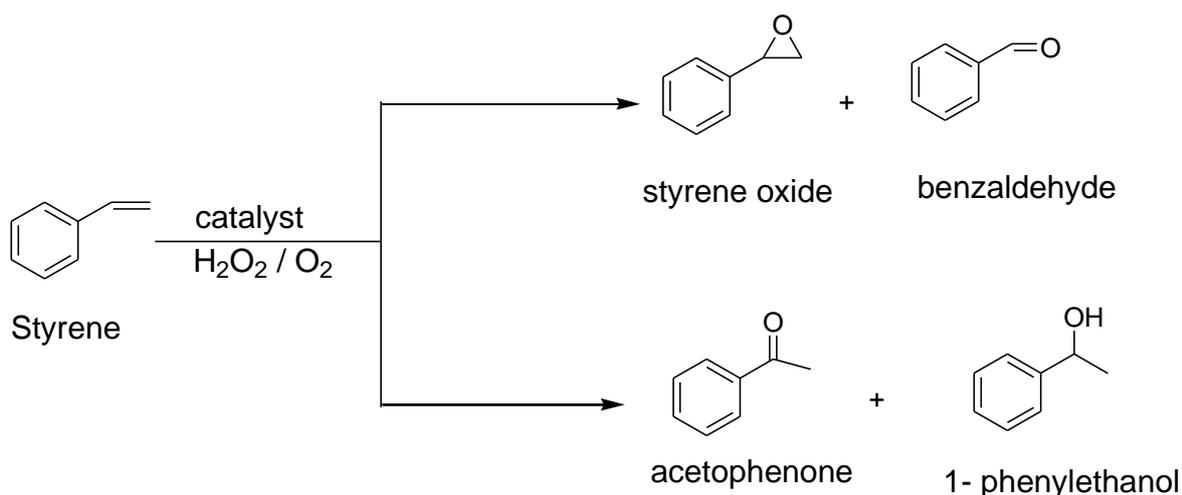
Figure 4.6: GC spectrum of phenol oxidation using O_2 with **C6** at 70 °C and 24 h

The reactive mechanism on phenol oxidation with H_2O_2 [13] and O_2 [3] catalysed by the Schiff base complexes have been proposed in literature. From the mechanisms, the first intermediate is generated when an oxidant attaches to the metal centre. The next intermediate forms when phenol joins to the first intermediate through the metal centre. In this process, the intermolecular oxidation–reduction reaction between phenol and H_2O_2 was transformed and the rate of phenol oxidation was largely enhanced. With oxygen as an oxidant the metal-O radical is used to form phenol radicals. All these mechanisms lead to the formation of phenol oxidation products mentioned above (**Scheme 4.1**).

Although the metal ions are the same in all the complexes, the structure of the ligands matters in controlling the spacial hindering effect of the central metal to form the complex-oxidant-substrate intermediate in the phenolic catalytic oxidation. The smaller the spacial hindering effect of the complex is, the easier the formation of the intermediate [3, 13]. From the ligand system used in preparing the cobalt(II) complexes, the spacial hindering effect is higher therefore, the complex-oxidant-phenol may not form leading to failure of product formation. Hence the cobalt(II) catalysts in above experiments failed to transform phenol to the respective products.

4.3. CATALYTIC ACTIVITY OF COBALT(II) SCHIFF BASE COMPLEXES IN THE OXIDATION OF STYRENE

Transition metal complexes as catalysts for epoxidation of olefin have attracted a great deal of attention in recent years [14]. In general, selected ligands include porphyrin derivatives, macrocyclic polyamines, and Schiff bases [15]. During the process of catalytic reaction, catalysts need a mono-oxygen source such as H_2O_2 , O_2 , *etc.*, to carry out oxygen transferring to the olefin. Various transition metal compounds (Co) have been reported as active catalysts for the oxidation of olefins [16] to a variety of products such as epoxides, carbonyl compounds and alcohol [17]. Various Schiff base complexes have been used to catalyse olefin oxidation to epoxide, aldehyde [18], acetophenone and 1-phenylethanol (**Scheme 4.2**) [16]. Styrene oxide is a very important intermediate in the field of pharmacy, spicery, plasticiser, epoxy resin thinner, flavoring agent, *etc.* [19]. Benzaldehyde and its derivatives are an important intermediate for chemical synthesis, and applied in many areas, such as medicine, dyestuff, food and cosmetics [20].



Scheme 4.2: Oxidation of styrene to different products

4.3.1. Experimental

All the reactions were carried out under nitrogen. Reagents were purchased from Sigma Aldrich and were used as received without any other purification. Samples from the oxidation reaction were analysed by ¹HNMR on a Bruker AVANCE III 400 MHz NMR using CDCl₃ as a solvent and Varian 3900 gas chromatograph.

4.3.2. General procedure for styrene oxidation reaction

The catalytic activity study was carried out in a parallel reactor. In a typical reaction, (0.01 mmol) of the complex was dissolved in 5 mL of ethanol and (1.00 mmol) styrene was added. An aqueous solution of 30% H₂O₂ (2.00 mmol) was added to the reaction mixture with continuous stirring and the reaction was considered to be started. Aliquots of the mixture were drawn periodically and were analysed by NMR and GC to confirm the identity of the products.

4.3.3. Results and discussion

Oxidation of styrene by cobalt complexes **C1-C10** using H₂O₂ as an oxidant was studied in ethanol and the results are given in **Table 4.3**. Ethanol was found to be a good solvent in styrene oxidation [16]. It was observed that these catalysts were not efficient enough in the styrene oxidation at 25 °C and a reaction time of 24 h since styrene protons were observed in the NMR spectrum (**Figure 4.7**) at 5.22, 6.70, 7.25, 7.31, 7.39 ppm. Styrene oxidation products were expected to be at 2.70, 2.95,

3.82, 7.19 ppm (styrene oxide), 7.45, 7.54, 7.81, 9.87 ppm (benzaldehyde), 2.55, 7.37, 7.45, 7.86 ppm (acetophenone), 1.49, 2.0, 4.68, 7.19 ppm (1-phenylethanol).

Table 4.3: Catalytic activity of cobalt complexes towards oxidation of styrene

Catalyst	% Conversion
C1	0
C2	0
C3	0
C4	0
C5	0
C6	0
C7	0
C8	0
C9	0
C10	0

Reaction conditions: substrate (1.00 mmol), catalyst (0.05 mmol), oxidant (2.00 mmol) and total reaction volume of 5.00 mL. The reaction time was 24 h at 25 °C

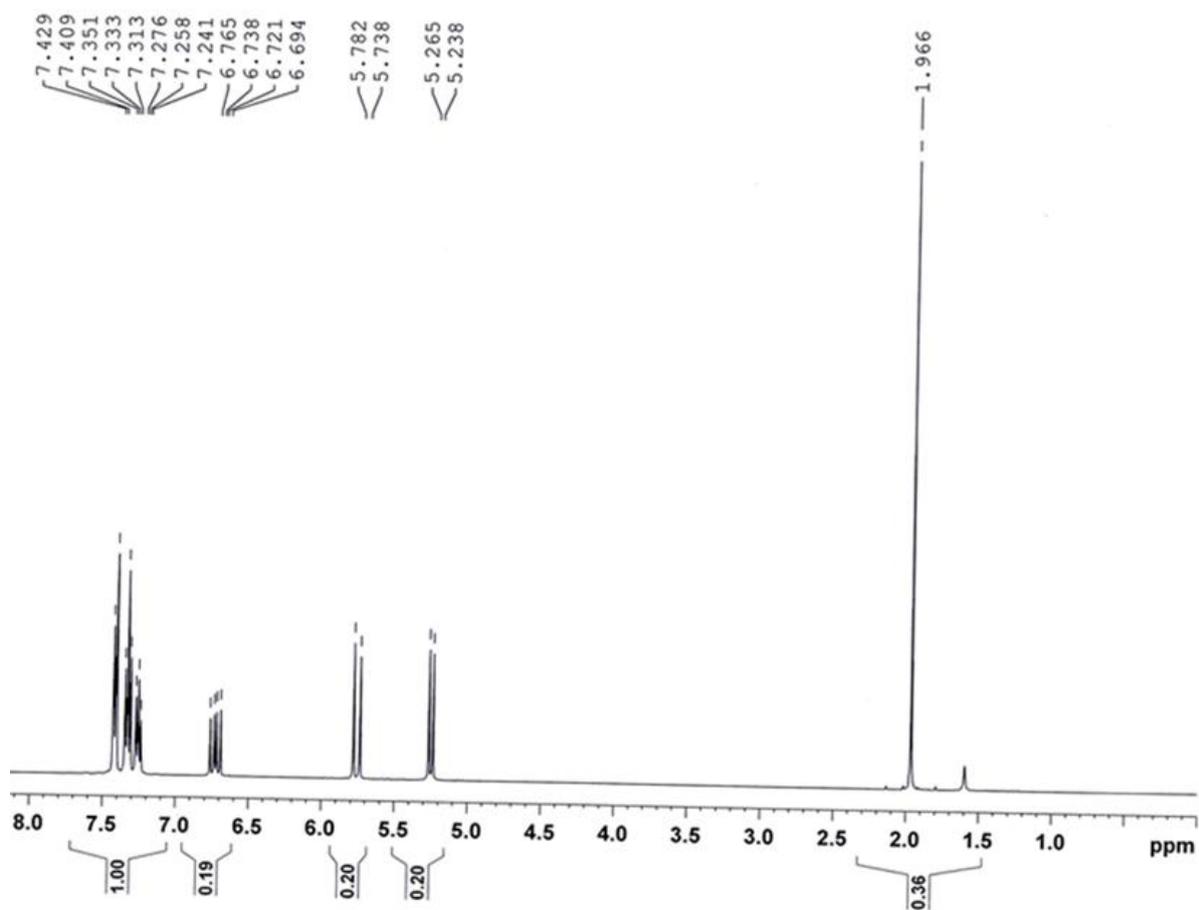


Figure 4.7: ^1H NMR spectrum of styrene oxidation using **C3** at 25 °C and 24 h

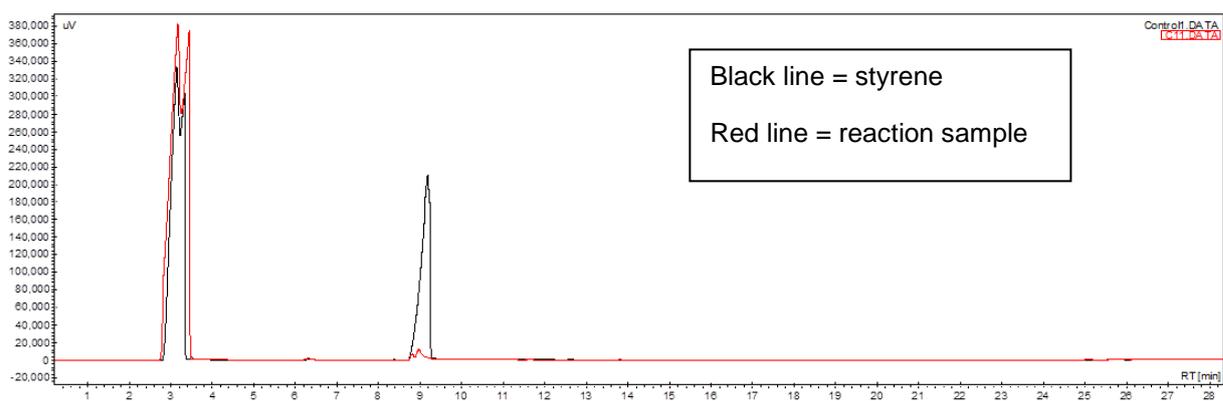


Figure 4.8: GC spectrum of styrene oxidation using **C3** at 25 °C and 24 h

4.3.4. Effect of reaction conditions on styrene

The catalytic activity was investigated using various reaction conditions of temperature, amount of catalyst, time, oxidant and solvent effect.

4.3.4.1. Effect of variation of time

The dependence of activity of cobalt(II) complexes in styrene oxidation on the reaction time is shown in **Table 4.5**. It is observed that styrene oxidation was not affected by reaction time as it does not show any improvement up to 72 h on styrene oxidation. Khandar *et. al.* [21] reported on obtaining more products in styrene oxidation the first 4 h.

Table 4.4: Effect of time on styrene oxidation

Catalyst	Time (h)	% Conversion
C1	24	0
	48	0
	72	0
C2	24	0
	48	0
	72	0
C3	24	0
	48	0
	72	0

Reaction conditions: substrate (1.00 mmol), catalyst (0.05 mmol), oxidant (2.00 mmol) and total reaction volume of 5.00 mL. The reaction time was 72 h at 25 °C

4.3.4.2. Effect of temperature

Four different temperatures (25, 30, 60, 70 °C) were considered, while keeping other parameters constant. The catalysts employed are found not to be active as there was no effect in increasing temperature. Drago *et. al.* and Khandar *et. al.* (using complexes of cobalt(II) with tetracoordinate Schiff base ligands) reported suitable temperature for styrene oxidation as 60 and 70 °C [16, 21]. The results of these

experiments (**Table 4.5**) show that the catalyst used were not able to transform styrene to the expected products since substrate peaks are observed in ^1H NMR spectra and GC.

Table 4.5: Effect of temperature on styrene oxidation

Temperature ($^{\circ}\text{C}$)	% conversion
25	0
30	0
60	0
70	0

Reaction conditions: substrate (1.00 mmol), catalyst (0.05 mmol), oxidant (2.00 mmol) and total reaction volume of 5.00 mL. The reaction time was 24 h

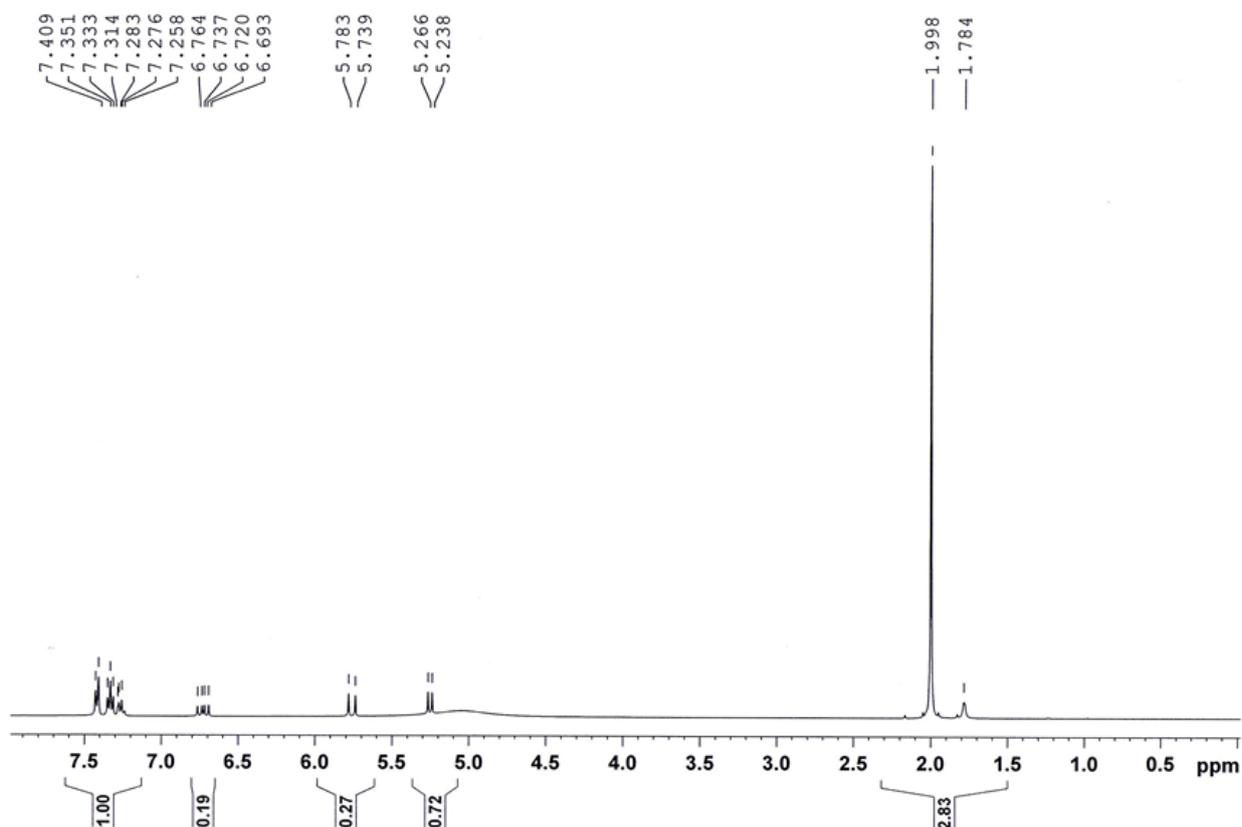


Figure 4.9: ^1H NMR spectrum of styrene oxidation using **C7** at $70\ ^{\circ}\text{C}$ and 24 h

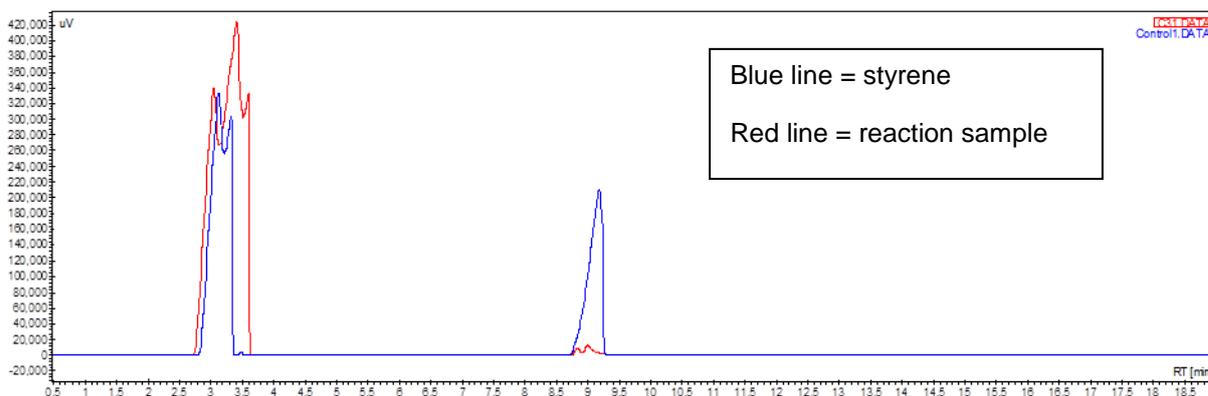


Figure 4.10: GC spectrum of styrene oxidation using **C7** at 70 °C and 24 h

4.3.4.3. Effect of the amount of catalyst

The experiments were carried out in absence of catalyst and in five different amounts of the catalyst (0.01, 0.034, 0.05, 1.47 mmol). The results are given in **Table 4.6**. On increasing the catalyst amount, the degree of conversion is not affected since 0% conversion is observed at 1.47 mmol. A 0.731 mmol and 0.939 mmol of catalyst was considered to be sufficient enough to give good performance [16, 21].

Table 4.6: Effect of catalyst loading on styrene oxidation

Catalyst	Concentration (mmol)	% Conversion
C8	0.01	0
	0.034	0
	0.05	0
	1.47	0
C9	0.01	0
	0.034	0
	0.05	0
	1.47	0
C10	0.01	0
	0.034	0
	0.05	0

	1.47	0
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Reaction conditions: substrate (1.00 mmol), oxidant (2.00 mmol) and total reaction volume of 5.00 mL. The reaction time was 24 h at 25 °C

4.3.4.4. Oxidant effect

Three different oxidants such as hydrogen peroxide, O₂, and 3-chloroperbenzoic acid with complexes **C3-C5** were used to investigate oxidant effect on styrene oxidation. The ¹H NMR spectrum (**Figure 4.11**) and GC results (**Figure 4.12**) on 3 oxidants do not differ as they show the presence of substrates after the experiment, meaning that the substrate could not be transformed to expected products. Oxidants, such as molecular oxygen [16, 22] and H₂O₂ [23] with transition metal Schiff base complexes were used in previously reported oxidation reactions of styrene. These oxidants were able to oxidise styrene to expected products.

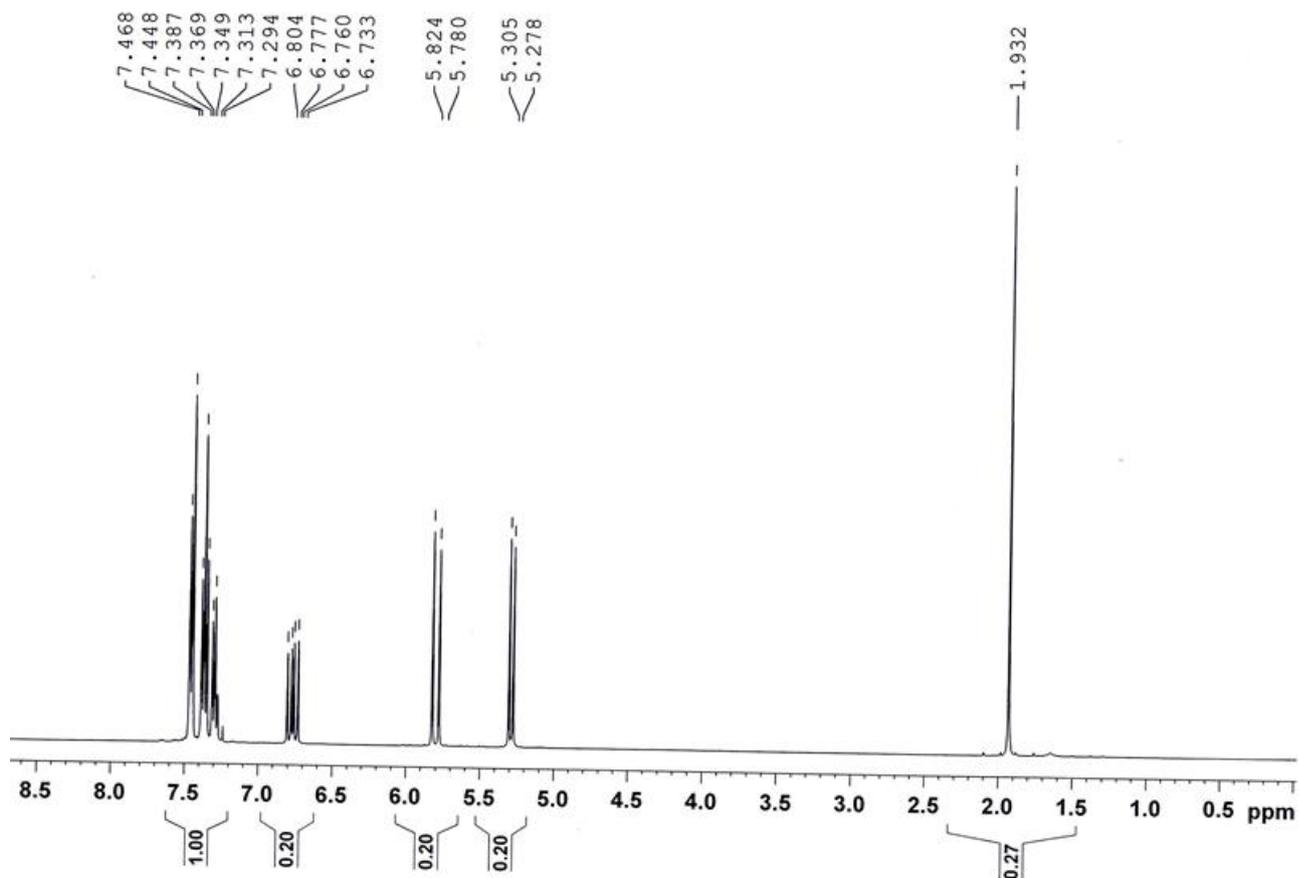


Figure 4.11: ^1H NMR spectrum of styrene oxidation using **C5** with O_2 at 60 °C and 24 h

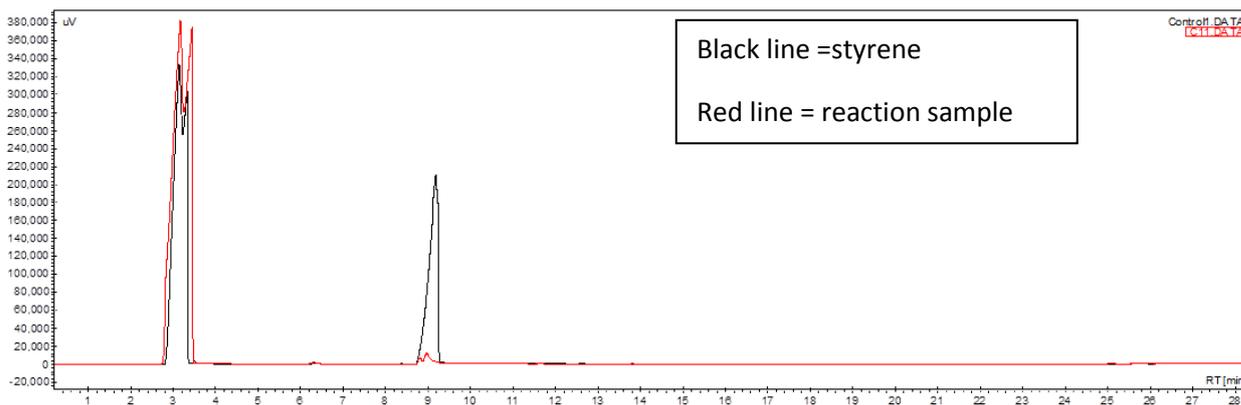


Figure 4.12: GC spectrum of styrene oxidation using **C5** with O_2 at 60 °C and 24 h

4.3.4.5. Solvent effect

Investigation of solvent effect on oxidation of styrene was conducted in different solvents such as ethanol, acetonitrile and chloroform using complexes **C1-C5**. Results are given in **Table 4.7** and **Figure 4.13**. The complexes could not convert styrene to any products. Solvents such as CH₃CN/CH₂Cl₂ [22] and ethanol [16] have been reported to be good solvents in styrene oxidation reactions.

Table 4.7: Solvent effect on styrene oxidation

Catalyst	Solvent	% Conversion
C1	Ethanol	0
	Acetonitrile	0
	Chloroform	0
C2	Ethanol	0
	Acetonitrile	0
	Chloroform	0
C3	Ethanol	0
	Acetonitrile	0
	Chloroform	0
C4	Ethanol	0
	Acetonitrile	0
	Chloroform	0
C5	Ethanol	0
	Acetonitrile	0
	Chloroform	0

Reaction conditions: substrate (1.00 mmol), catalyst (0.05 mmol), oxidant (2.00 mmol) and total reaction volume of 5.00 mL. The reaction time was 24 h at 25 °C

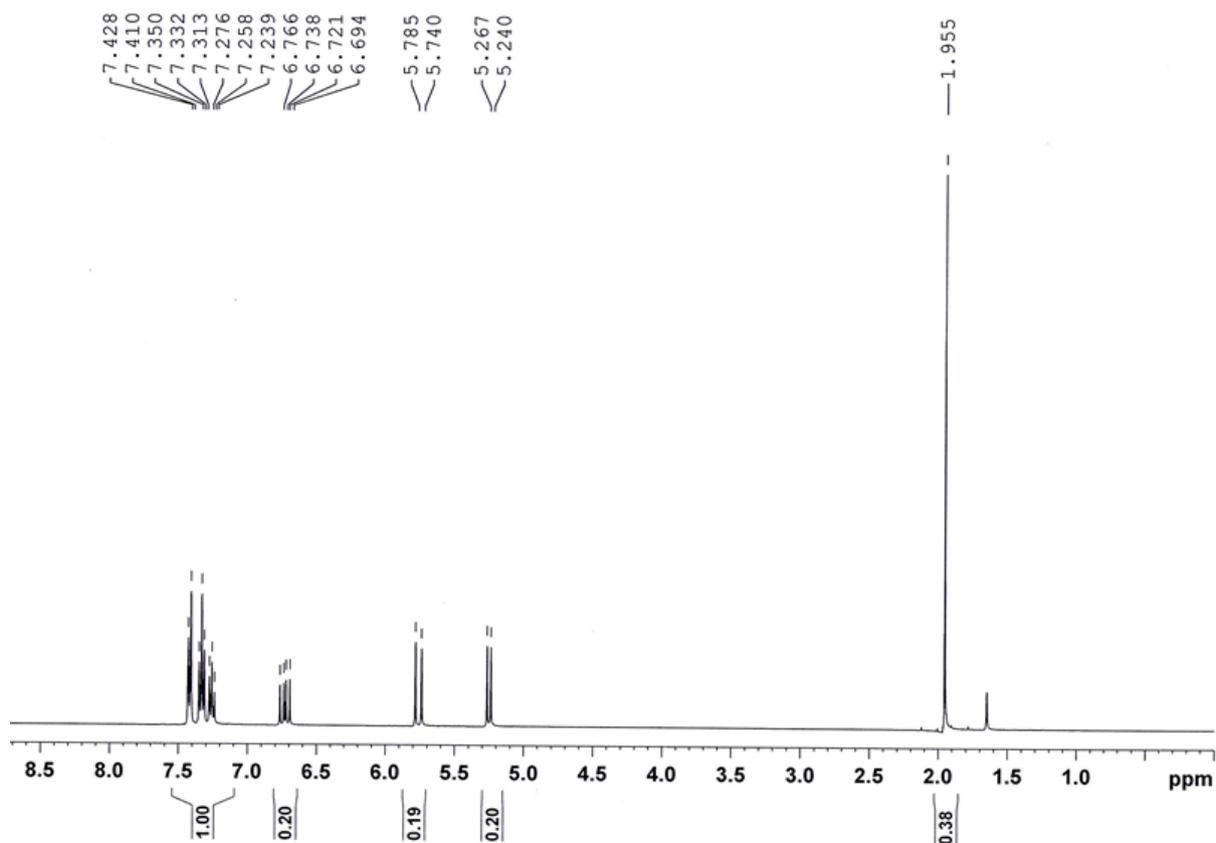


Figure 4.13: ^1H NMR spectrum of styrene oxidation with ethanol at 30 °C and 24 h

Since first-row transition-metal complexes commonly catalyse oxidation reactions, this mechanism is first considered for the Co(II)-catalysed oxidation of olefins. Abstraction of the allylic proton of an olefin generally takes place in oxidation since this leads to the most stable free-radical intermediate. Radical pairing with oxygen then takes place at this site, and the products observed are those that result from subsequent reaction of the resulting alkyl hydroperoxide intermediate [21]. Reaction of hydrogen peroxide with Co(II) occurs to form a cobalt hydroperoxide, which can be viewed as a stabilised hydroperoxy radical which has spin paired with the d_z^2 electron of Co(II). The cobalt hydroperoxide then adds to the olefin double bond, leading to formation of an alkyl hydroperoxide. Haber-Weiss decomposition of this alkyl hydroperoxide by Co(II) produces the observed ketone and alcohol products [21]. The alkyl hydroperoxide might not have formed in the oxidation of styrene since no products were observed in all experiments.

4.4. CONCLUSION

It is clear from our results that the cobalt(II) complexes with imidazole-based salicylaldimine prepared in Chapter 3 are not efficient catalysts for phenol and styrene oxidation since ¹HNMR spectra and GC showed only substrate peaks; at least not under the conditions and oxidants we used in this project.

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CHAPTER 5

SUMMARY AND CONCLUSIONS

Synthesis of new ligands and their reactions with an array of transition metals are being explored by researchers in both academia and industries. Ligands based on donor atoms such as oxygen and nitrogen or the combination of the two are being synthesised and used to replace the traditional use of phosphorus based ligands. In view of these developments, the aim of this study was to explore the coordination of nitrogen donor ligands in the form of imidazolyl compounds with cobalt(II) transition metal and to test these metal complexes as catalysts in homogeneous reactions such as oxidation reactions of phenol and styrene.

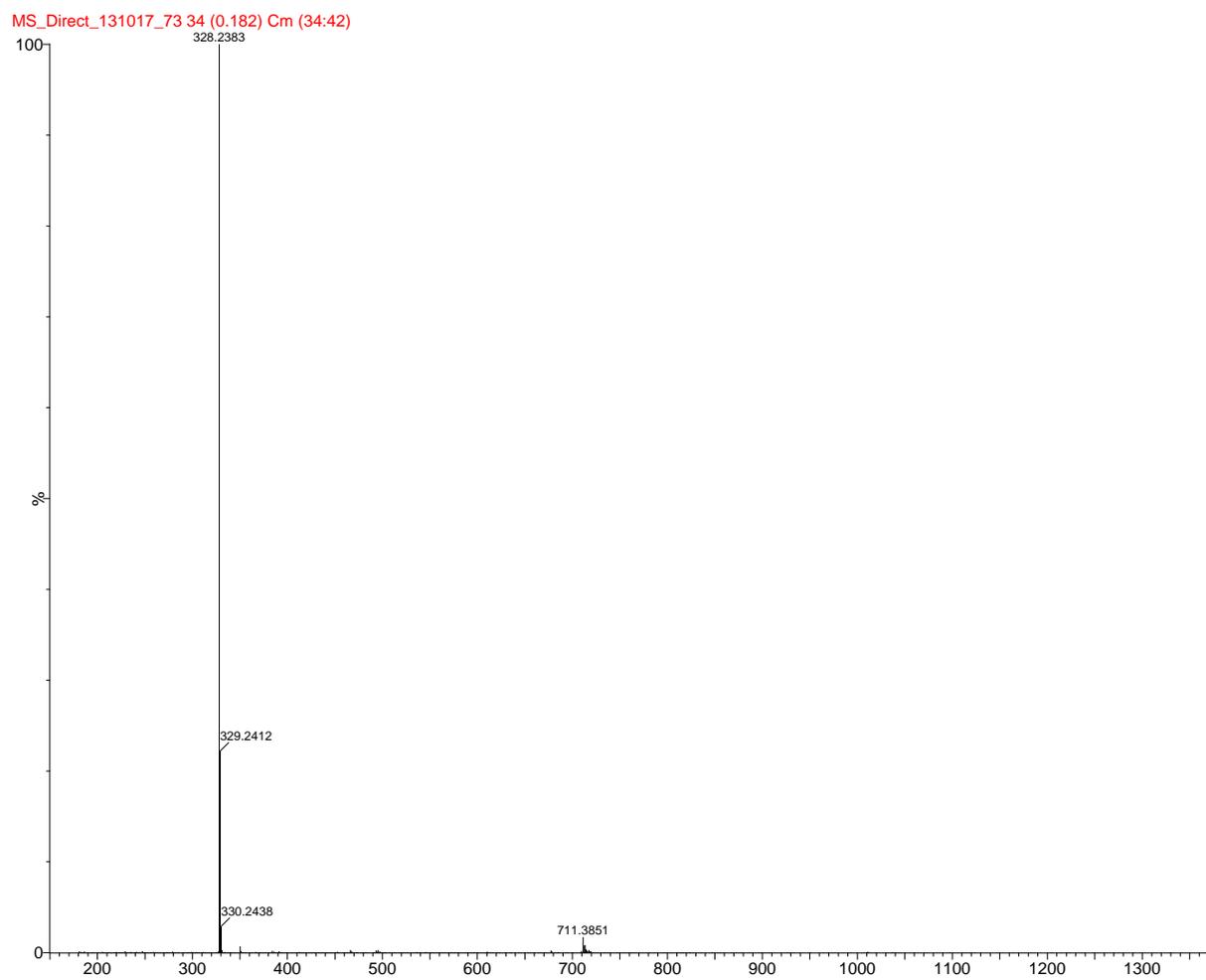
Imidazole-based types of ligands (**L1-L5**) were used to prepare catalyst precursors. The metal complexes (**C1-C10**) were made from ligands **L1-L5** and cobalt halides characterised by IR and UV-vis spectroscopy, elemental analysis and mass spectrometry. We inadvertently formed complex **C11** in process of growing crystals of complex **C6**. The crystal structure of **C11** was used to confirm O^NN tridentate coordination proposed for complexes **C1-C3** and **C6-C8**.

Catalytic activity of the prepared complexes in oxidation of phenol and styrene was studied using H₂O₂, O₂ and 3-chloroperbenzoic acid as oxidants. The oxidation products of the reactions were not isolated since substrate was present at the end of reactions. All the cobalt(II) complexes were found to be inactive, which may be due to the coordinative saturation around the metal centre. Detailed study of the catalytic activity studies was carried out by changing the different parameters like the concentration of catalyst and oxidant, reaction time, reaction temperature and nature of solvent. It was found that the parameters did not have effect on the reactions since the results remained the same.

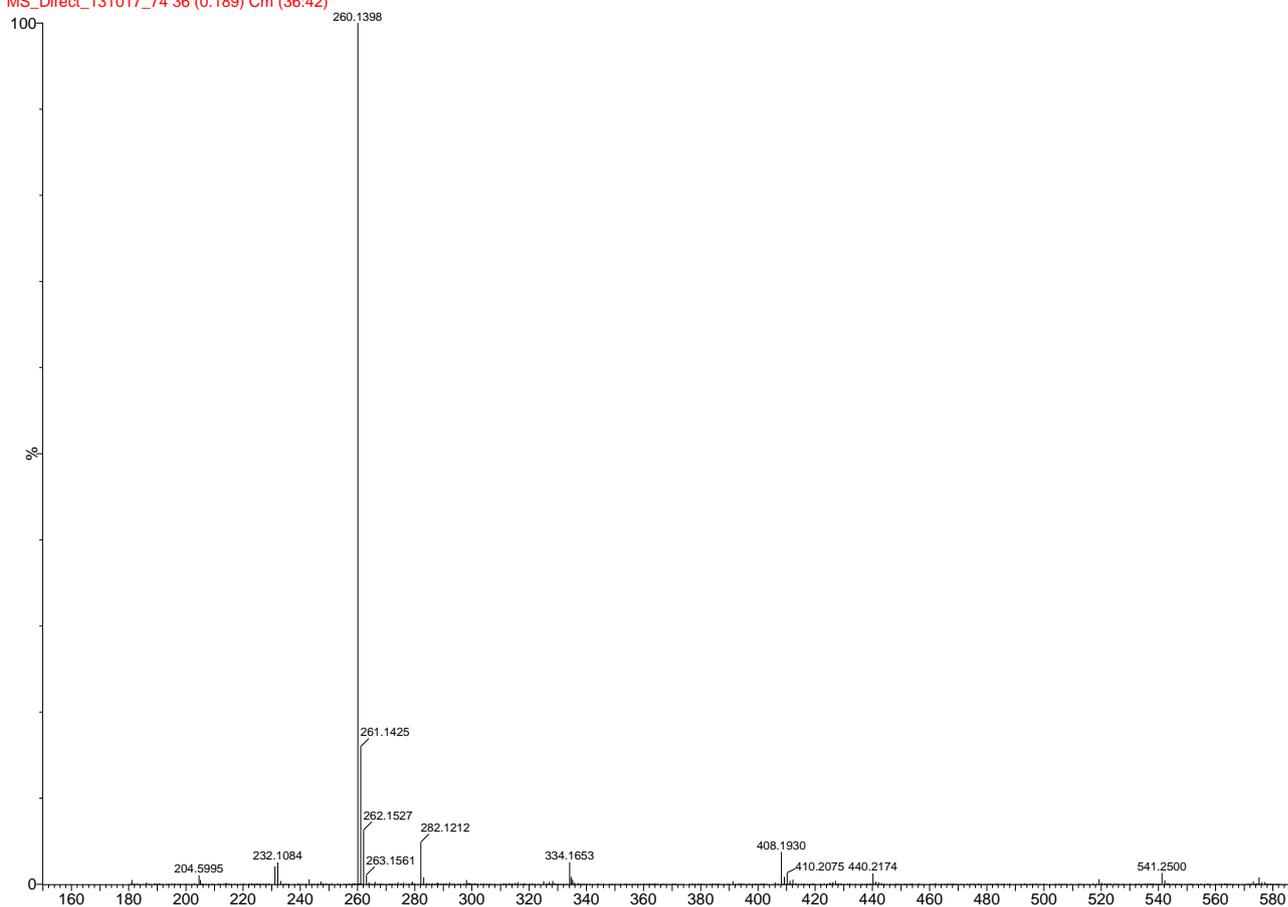
Transition metal complexes derived from salicylaldimine Schiff bases and their catalytic activity studies are the central topic of research described in this dissertation. In future, a broader range of substrates should be studied to investigate and correlate the selectivity and activity correctly to the structures of the catalysts. Lastly using systematically varied structures of the ligands, certainly more powerful catalysts are likely to be developed.

Appendix 1

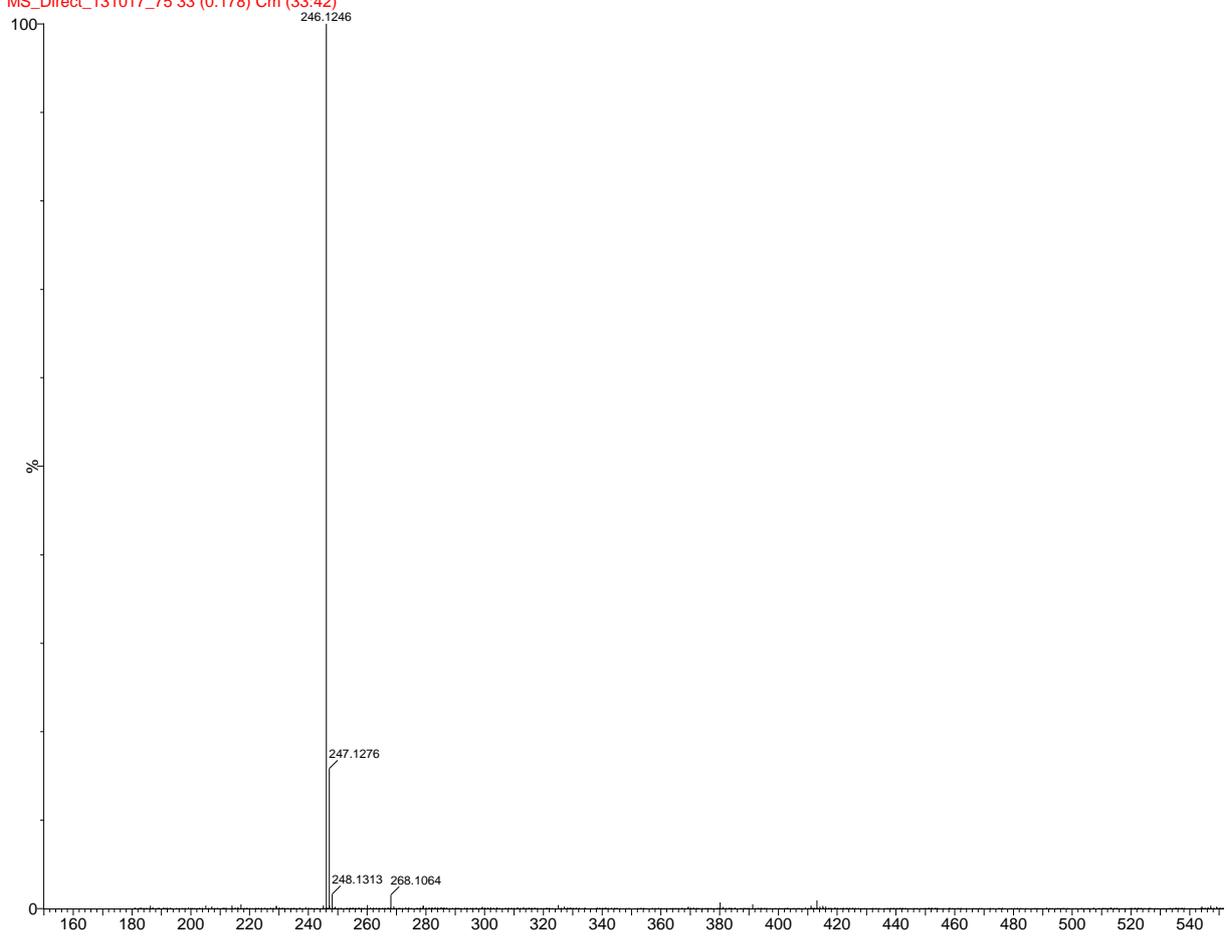
HRMS of ligands L1-L5



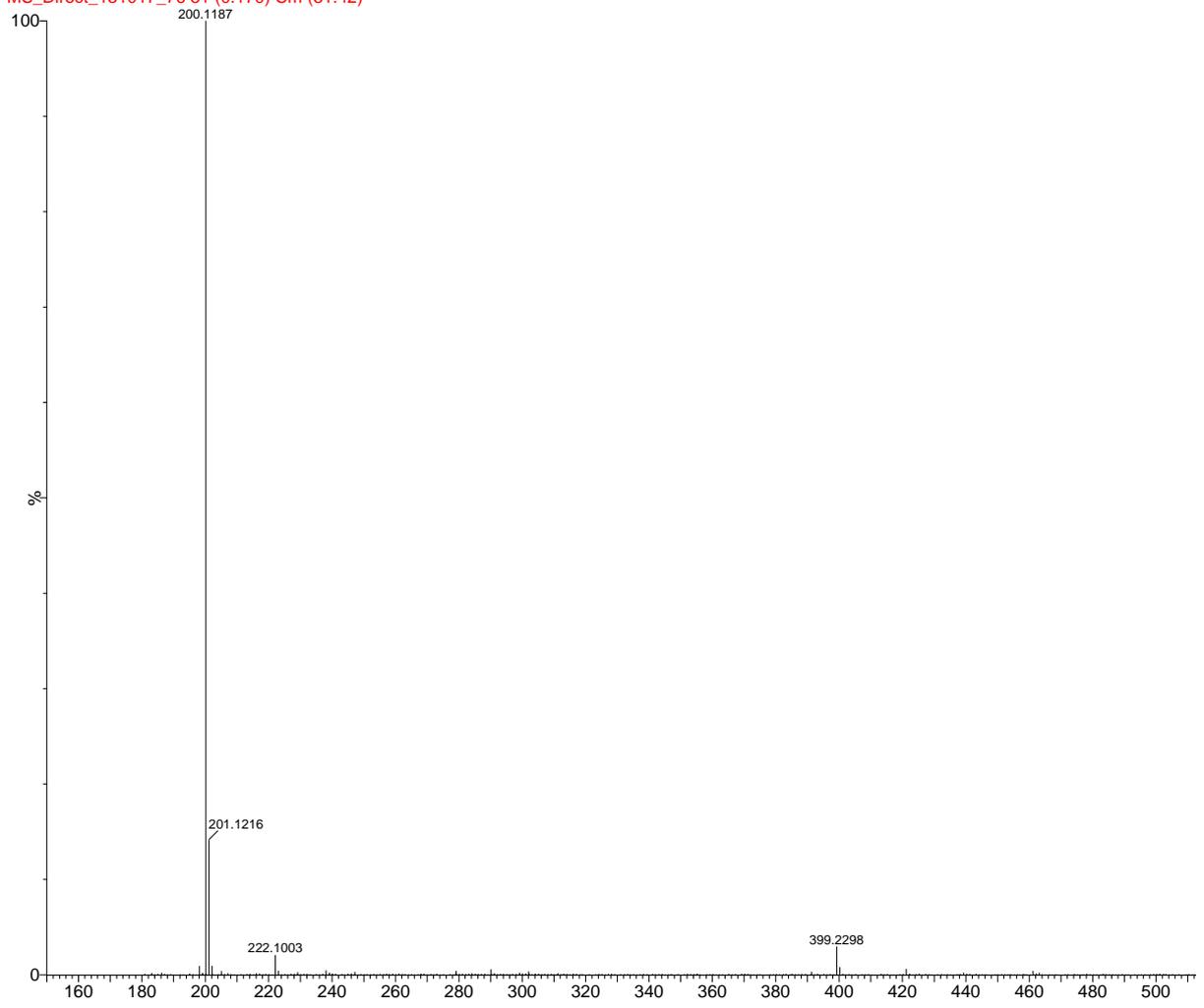
MS_Direct_131017_74 36 (0.189) Cm (36:42)



MS_Direct_131017_75 33 (0.178) Cm (33:42)



MS_Direct_131017_76 31 (0.170) Cm (31:42)



MS_Direct_131017_77 30 (0.167) Cm (30:38)

