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Coordination polymers as heterogeneous catalysts for oxidation reactions

By

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DECLARATION

I declare that the "**Coordination polymers as heterogeneous catalysts for oxidation reactions**" is a dissertation generated from my own work, that it has not been submitted for any degree or examination in any other University and that all sources I have used or quoted have been indicated and acknowledged by complete references.

Zohra Alarbi **May 2014**

Signed ………………

ABSTRACT

This study describes the synthesis and characterisation of coordination polymers complexes of Cu(II) and VO(IV) with two polymeric ligands N,N′ -1,2-phenylene bis(5-methylenesalicylidenamine)(L1) and N,N′ -1,4-butylene bis(5-methylenesalicylidenamine) (L2). Ligands L1 and L2 formed by condensation of 5,5′-methylene bis-(salicylaldehyde) with 1,2-phenylenediamine and 1,4-diaminobutane respectively. The ligands and the complexes were characterized by UV/Vis spectroscopy, proton and carbon nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C-NMR), Fourier transform infrared spectroscopy (FTIR), high resolution scanning electron microscopy (SEM) and thermogravimetric Analysis (TGA).

These coordination polymers complexes were screened as heterogeneous catalysts for liquid phase hydroxylation reactions such as phenol, benzene, styrene and cyclohexene using H_2O_2 as a green oxidant.

The results show a high activity and selectivity of both catalysts toward the formation of expected product from phenol, styrene, cyclohexene and a low activity in the oxidation of benzene. The reaction parameters viz., temperature, molar ratio, concentration of the oxidant, solvent type and volume has been optimised for the maximum oxidation of these substrates.

Furthermore, copper-based catalysts were more reactive than oxovanadium complexes in all oxidation reactions tested in this study.

ACKNOWLEDGMENTS

In the name of Allah, the Most Gracious and Most Merciful all Praises to Allah the Almighty, for thee (alone) we worship and thee (alone) we ask for help. Praises and Salutations upon Muhammad S.A.W. who guided and led us to the right path.

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To the colleagues of the catalysis group and all other colleagues in department of Chemistry, University of the Western Cape, South Africa, I say thank you for the good and the cordial working relationship I enjoyed during my studies.

Lastly, I would like to thank Libyan embassy for financial assistance.

DEDICATION

I dedicate this thesis to

My parents,

My husband,

My son and daughter

and

All my family in Libya

POSTER PRESENTATIONS AT CONFERENCE

1. Post graduate research open day, New Life Science Building, University of Western Cape, Bellville, Cape Town, South Africa, November 2013.Win the second prize.

GLOSSARY

Abbreviations

Bal	Benzaldehyde
CAT	Catechol
$CDCl_3$	Deuterated chloroform
CyO	Cyclohexene oxide
CyOl	Cyclohex-2-ene-1-ol
CyONE	Cyclohex-2-ene-1-one
CydiOl	Cyclohexane-1,2-diol
d	Doublet
DCM	Dichloromethane
EtOH	Ethanol
FT-IR spectroscopy	Fourier transform infrared
g	Gram
GC	Gas chromatography
h	Hours
HQ	Hydroquinone
M	Molar
m	Multiplet
MeCN	Acetonitrile
ml	Millilitres
nm	Nanometre
NMR	Nuclear magnetic resonance
PhOH	Phenol
mbsal	Methylene bis-(salicylaldehyde)

ppm	Parts per million
SEM	Scanning electron microscope
StO	Styrene oxide
s	Singlet
sh	Shoulder
st	Strong
t	Triplet
UV/Vis	Ultraviolet-visible spectroscopy
w	Weak
°C	Degrees celcius

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CHAPTER 1

1.1 Introduction

In the last few decades many researchers have devoted intensive attention to study various oxidation reactions using different catalytic systems, especially transition metal coordination polymers [1-3].

Coordination compounds are at present undergoing rapid development in many fields as technological and industrial applications such as metallic conductors [4-5], heterogeneous catalysis [6-7] and ion exchange [8].

Coordination polymer networks are made mainly from neutral or anionic ligands (linkers) with at least two anchoring sites like nitrogen, oxygen or sulphur (obtained by the polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound) which coordinate to metal ions or aggregates (nodes). Depending on the number of donor atoms and their orientation in the linker, and on the coordination number of the node, different one (1D), two (2D) and three (3D)-dimensional constructs are accessible such as $[Co(H_2O)_4(pyrazine)](NO_3)_2\cdot2H_2O]_n$, $[Mn(N_3)_2(bix)_2]_n$ and $[Cd(3,3'\text{-}azdb)_2](H_2NMe_2)(NH_4)]_n$ respectively [9,10].

The advantages of these materials as catalysts are due to the ease of separation, safety of handling, possible recovery and reusability. Moreover, coordination polymers have high thermal stability which makes them suitable for industrial application [11].

In this work, the coordination polymer complexes are Schiff-base ligands coordinated to metal ions. There have been many reports utilizing these materials as heterogeneous catalysts [12-14]. An advantage of Schiff-base complexes is that most of these complexes show high catalytic activity in various reactions such as epoxidation of olefins [15,16], oxidation of alcohols [17], oxidation of cyclohexene [18] and styrene [19,20].

Several industrially important reactions were studied such as phenol, benzene, cyclohexene and styrene oxidation. The products of these oxidation reactions are very important due to their potential use in commercial products viz. starting materials in pharmaceutical industries and in synthesizing fine chemicals.

Phenols are a large group of pollutants in industrial effluents and, due to their low degradability by conventional effluent treatment, even at low concentrations they present toxicity and bioaccumulation problems [21]. Phenol is commonly used as raw material in many chemical, coke production, food industries, petrochemical, pharmaceutical, textile and agricultural industries. As a sequence of their toxicity to the environment and stream water many technologies has been developed [22] to improve various catalysts for phenol degradation and conversion to less harm products.

Catalytic oxidation of phenol under mild conditions gives catechol and hydroquinone [23, 24] as well as para-benzoquinone in some cases. These products are widely used as flavouring agents, perfumes, antioxidants, photographic developers, and pharmaceutical industries [25, 26].

Hydroxylation of benzene is usually carried out in three steps to give a low phenol yield and other products such as acetone and α-methylstyrene by using cumene process [27]. This highly energy-consuming process is a three step reaction as well as producing by products. One-step oxidation of benzene to phenol through direct hydroxylation of an aromatic ring using green oxidants would be a good option for chemical industries as it is more energy safe and produce only one product i.e. phenol.

Two other industrially important reactions investigated were cyclohexene and styrene oxidation. The products of these respective reactions were studied in details due to their potential use in commercial products [28, 29].

The cyclohexene oxidation product such as cyclohexenol is widely used as a possible alternative route for the production of cyclohexadiene, which is a key intermediate in the manufacture of Nylon- 66 polymer [30]. Cyclohexene oxide is a highly reactive and selective organic intermediate widely used in the synthesis of enantioselective drugs, epoxy paints and rubber promoters [31]. Other products of cyclohexene oxidation such as cyclohexene-1-ol, 2-cyclohexene-1-one and 1,2-cyclohexanediol are very useful synthetic intermediates [32]. Oxidation of styrene draws interest from academics as well as the industry, mainly in the production of fine chemicals such as benzaldehyde [33]. Benzaldehyde is used in the manufacturing of perfumes, dyes, and flavourings [34]. It is also used to synthesize cinnamic acid and mandelic acid. Anther product is styrene oxide which is used as a chemical intermediate in the production of styrene glycol and its derivatives, cosmetics, surface coatings, and agricultural and biological chemicals [35].

The aim of this research study is to synthesize new catalysts that exhibit both high catalytic activity and selectivity for different industrial applications.

1.2 Objectives

The focus of this study is to synthesize and characterize new Schiff base ligands and different types of transition metal coordination polymers and investigate its applicability towards various oxidation reactions. To achieve this, the following must be met:

- Synthesis of two polymeric Schiff base ligands derived from the monomer unit of 5,5′-methylene bis-(salicylaldehyde) with o-phenylenediamine (1,2-diaminobenzene) and 1,4-butanediamine.
- Synthesis of two series of transition metal coordination polymers.
- Characterization of these synthesized catalysts using different physcio-chemical techniques such as FT-IR, UV-VIS, NMR, SEM and TGA.
- Catalytic activity and selectivity studies of these new catalysts for different oxidation reactions.

1.3 Thesis structure

This thesis is comprises of seven chapters and is structured as follows:

Chapter 1 - Introduction

In this chapter a brief introduction to the importance of coordinated polymers and homogeneous transition metal complexes and the aims and objectives for this research study.

Chapter 2 - Literature review

Present a review of the literature, which covers different reactions catalyzed by various types of catalysts i.e. homogenous and heterogeneous and particularly coordination polymers, and their applications for oxidation reactions.

Chapter 3 - Materials and method

Provides the reagents and materials used in the experiments and explaining in detail the protocols involved in the synthesis of the polymeric ligands and its coordinated complexes as well as gives an account on the specific instrumentation used in the analysis.

Chapter 4 – Characterization

Describes the details of the characterization of Schiff base ligands. Their coordination polymers were characterized by various physico-chemical techniques in the present study.

Chapter 5 – Result and disscusion of copper(II) and oxovanadium(IV) L1complexes

Describe the catalytic activity of copper(II) and oxovanadium(IV) complexes with 5,5′-methylene bis-(salicylaldehyde) towards phenol, benzene, cyclohexene and styrene oxidation and the optimization of reaction conditions for maximum conversion which used in this study.

Chapter 6 - Result and disscusion of copper(II) and oxovanadium(IV) of L2 complexes

Describe the catalytic activity of copper(II) and oxovanadium(IV) complexes with N,N′ -1,2-phenylene bis(5-methylenesalicylidenamine) as potential catalysts in the oxidation of phenol, benzene, styrene and cyclohexene.

Chapter 7- Conclusion and future work

Conclusion of this thesis by summarizing the main highlights points and recommendations as well as future work.

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CHAPTER 2

2.1 LITERATURE REVIEW

Inorganic polymers (co-ordination polymers) are non metallic derivatives; various organometallic and non metallic substances are often included in inorganic polymers [1]. Great interest has been produced to obtain inorganic polymers in which the molecular skeleton is formed by the coordination link of the atoms or metal ion. Bailer defined coordination polymer as one in which a metal ion is coordinated with organic ligand, so as to form a polymers in which there is a metallic atom or ion for each monomer unit [2]. Coordination polymers have provided and supported future research to meet the challenges of science, as they have high thermal and chemical stability, insolubility and porosity [3].

As compared to the organic polymers which are useful because of their long range of elasticity, high viscosity and plasticity, inorganic polymers are generally stronger, harder, more brittle and mostly insoluble material in many polar and non polar solvents [4].

These features as insolubility, high modulus and lack of ductility are typical characteristics of polymers with a highly cross linked network and many properties of inorganic polymers can be ascribed to their cross link structures [5].

In coordination polymers, metal is either a part of the main chain polymers or bound to the polymer chain as pendant group [6]. Nobue Hagihara *et al* have been studied formal types of linear polymers on the basis of metallocene containing polymer, linear “Werner” type coordination polymer and polymers containing sigma bonded metal in the main chain [7].

The formation of macromolecular (large polymers chain) may be expected for ligands with two chelating sides, which for steric reasons cannot interact with the same metal ion.

A large number of chelating ligands containing different functional groups have been reported in the literature[8-10]. The biologicall property in coordination polymers can possibly enhance using bioligand coordinated with metal ion. Metalloenzyme is a kind of polymer metal complex which is biologcally important, in which a metal ion is bounded by a giant protein molecule.

Many attempts have been made to modify the properties of coordination polymers by changing their degree of polymerization or adding some soluble component in the structure to form a linear coordination polymer which have high moleculer weight [11,12].

2.1.1 The importance of coordination polymers

1. The incorporation of metal ions in supramolecular networks allows controlled positioning of the metal atom in the final material, and adds properties to the material which are not only based on the metal ions alone, but also on the interplay between the main binding partners, ligands [13].

2. The variety of ‘‘nodes and linkers’’ offers to the chemist an infinite number of possibilities for building new species with intriguing architectures, topologies and properties [14].

2.1.2 The building blocks of coordination polymers

There are four different kinds of building blocks used for the construction of infinite metal-organic frame works, which are organic ligands, metal ions or clusters, counter anions and sometimes, solvent molecules [14,15].

1. The organic ligands: act as bridging organic groups between the metal ions. In support of possible infinite expansion, ligand molecules have to be multidentate with at least two donor atoms, mostly N, O or S donors. Ligand molecules are may differ from each other in their charges, the most used ligands are neutral or anionic. Another structure-determining factor is the body of the organic ligands, their shapes (rigid or not); their lengths (distance between the coordination functions); their functionalities (further presence of heteroatoms, aromatic rings, alkyl chains). finally, the ligand molecules can be symmetric, chiral [16].

2. The metal ions or clusters: which are involved in the structure are depending on their size, hardness/softness, ligand-field stabilization energy and coordination geometries.

3. Counter ions: are present in the structure when charge ligands are used. They can influence the metal ion environment (more or less coordinating counter ions), as well as the overall structure, substitute as guest molecules in void spaces in the solid state or involved in weak interactions.

2.1.3 Synthesis of coordination polymers

The characteristic metal ion and nature of ligands greatly influence the synthesis of coordination polymers. The synthesis of coordination polymers is achieved by one of the following procedures [17-18].

2.1.3.1 Formation through complexation of polymeric ligand with metal metal ion

The reaction of the polymeric ligand with metal ion or metal complex generally results in various coordination structures as follows:

(i) Pendant Complexes

Monodentate pendant complexes formes when a metal ion or metal complex has one labile ligand which can easily be substituted by a polymeric ligand and when other coordination sites are inactive. The complex formed will have a straightforward structure of monodentate type [scheme 2.1]

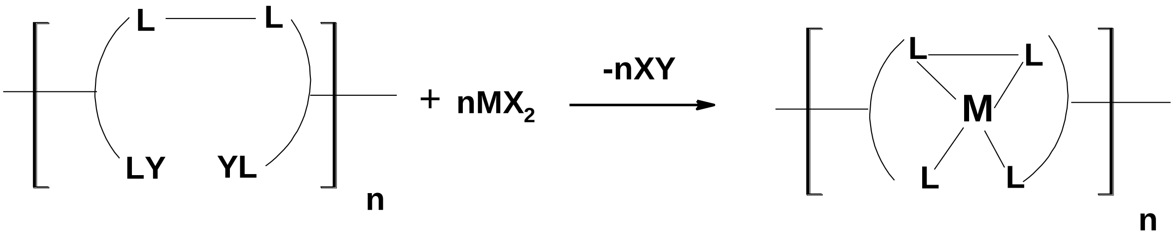
Scheme 2. 1 Schematic illustration of the formation of monodentate pendant complexes

Polydentate pendant complexes forms when a polymer pendant coordinating H group has a polydentate structure [Scheme 2.2]. This type of complex is considered to be accompanied by a bridge structure.

Scheme 2. 2 Schematic illustration of the formation of polydentate pendant complexes.

(ii) Introduction of transition metal ion into polymer ligand

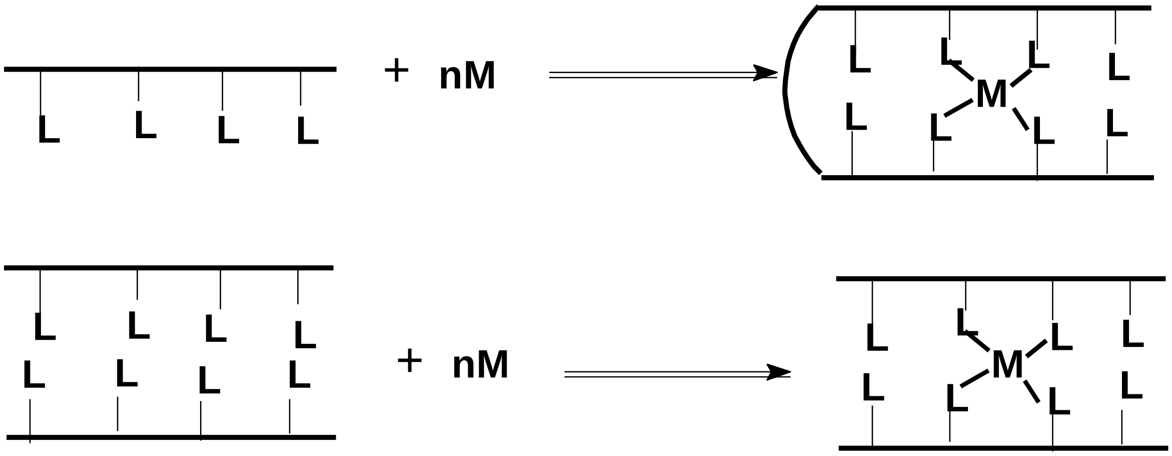
This type formed when metal ion inserted into synthesised polymeric ligand, which contains hetro atom (mainly nitrogen, oxygen, sulphur) or coordinating group [Scheme 2.3]



Scheme 2. 3 Illustration of the introduction of transition metal ion into polymer ligand.

(iii) Inter and /or intramolecular bridging

The reaction of polymer ligand with metal ions very often results in inter and / or intramolecular bridging polymers [Scheme 2.4].

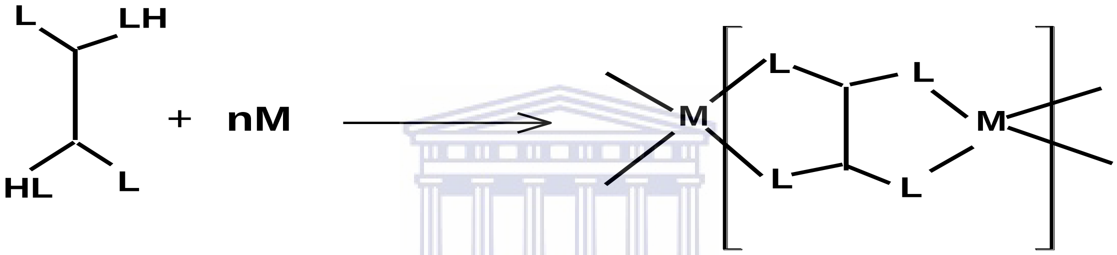


Scheme 2. 4 Schematic illustration of inter and /or intra molecular bridging.

2.1.3.2 The chain linked through complexation of bifunctional ligand with metal ion

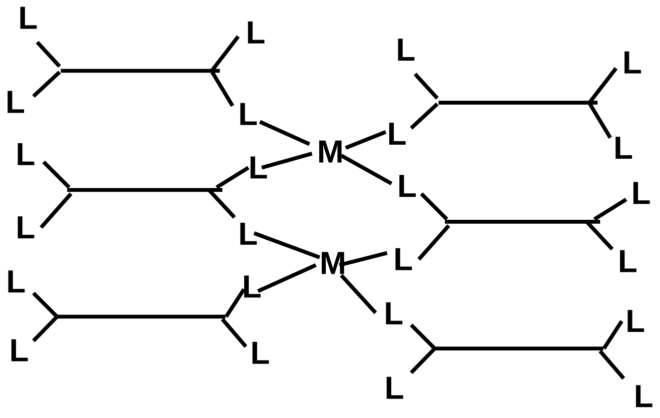
A metal complex may yield polymer material during its formation due to favourable donor groups. Bis chelating ligands coordinate with metal ions in a number of ways, as follows

I. One dimensional or linear coordination polymer when bifunctional ligands form a complex with metal ions having more than two labile ligands which are easy to be substituted, a polymer complex is formed through metal ion bridging [Scheme 2.5]



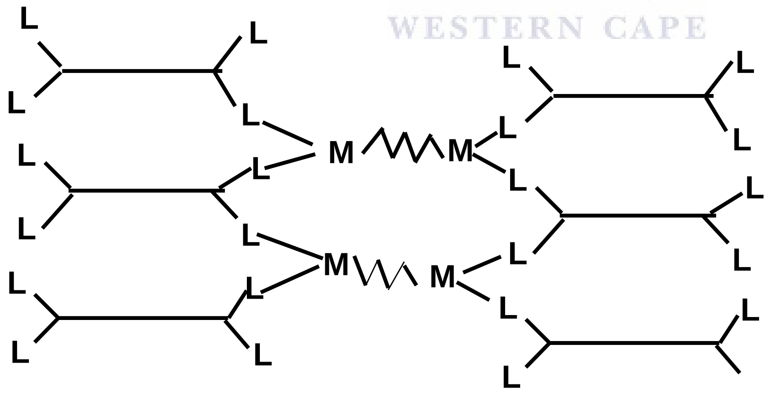
Scheme 2. 5 The complexation of bifunctional ligand with metal ion

II. Two dimensional or film of coordination polymer: when the metal ion coordinated with three different ligands, a two dimensional lattice structure will be obtained [Scheme 2.6] .



Scheme 2. 6 Two-dimentional coordination polymer

III. Three dimentional coordination polymers these form when each metal ion coordinates with three different ligand molecules [Scheme 2.7].[〰 denotes ligand molecules is prependiculer to the page]

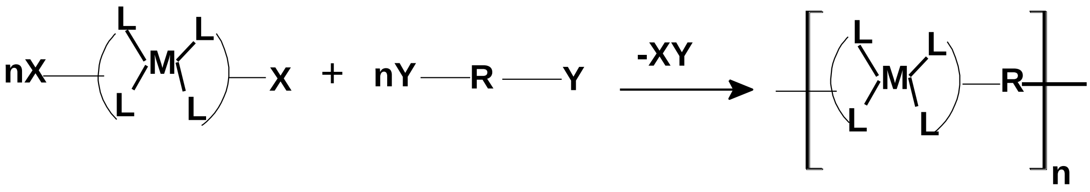


Scheme 2. 7 Three-dimentional coordination polymer

2.1.3.3 Formation through polymerization of metal complexes

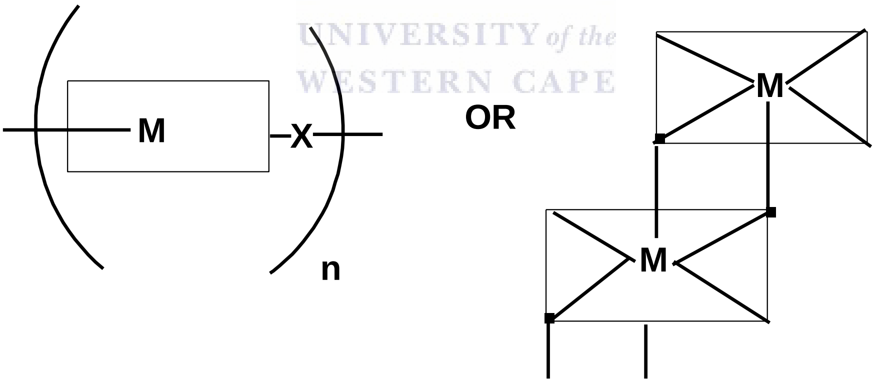
This can be achieved by one of the following:

(i) Polymerization of monomeric chelates the polymer synthesis involving polycondensation of monomeric chelate containing groups with other organic molecules [Scheme 2.8]



Scheme 2. 8 Polymerization of monomeric chelate

(ii) Ligand acting as a bridge a metal complex as a bridge ligand giving a polymeric structure [Scheme 2.9].



Scheme 2. 9 The metal complex as a bridge ligand

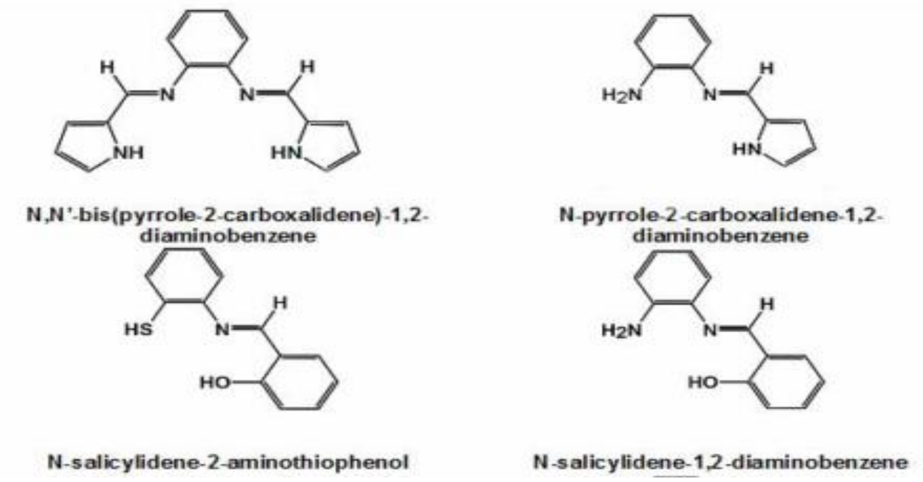
2.2 Schiff bases overview

Schiff bases have been playing an important part in the development of coordination chemistry. Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas [19].

Schiff bases, which usually are known as azomethine derivatives, are compounds that have carbon-nitrogen double bonds with the nitrogen being linked to an aryl or alkyl group. It is capable of forming coordinate bonds with many metal ions through both azomethine and phenolic groups. These compounds have found a wide range of applications in chemistry, and they are also important intermediates for the synthesis of various bioactive compounds. Furthermore, they are reported to show a variety of biological activities, including antibacterial, antifungal, anticancer, and catalytic activity [20].

Schiff base ligands are typically formed by the condensation of primary amines and aldehydes. The formed imine can bind metal ions via the lone pair electrons on the nitrogen. Ketones can also form Schiff-base ligands but aldehydes are more reactive than ketones [21]. Schiff base condensation allows for the design of new ligand systems which are selective to specific metal ions. This makes them suitable to be applied as metal extracting agents in liquid-liquid or solid phase extraction techniques [21, 22].

When the aldehyde is a salicylaldehyde derivative and the amine is a diamine derivative, condensation produces interesting N_2O_2 Schiff base compounds, which are called salens as they are tetradentate bis-Schiff ligands [23, 24].



Scheme 2. 10 Examples of different types of Schiff base ligands

2.3 The application of coordination polymers

In recent years more research interest was focus on coordination polymers complexes due to the use of these compounds in many fields as technological and industrial applications such a following

2.3.1 Luminescence

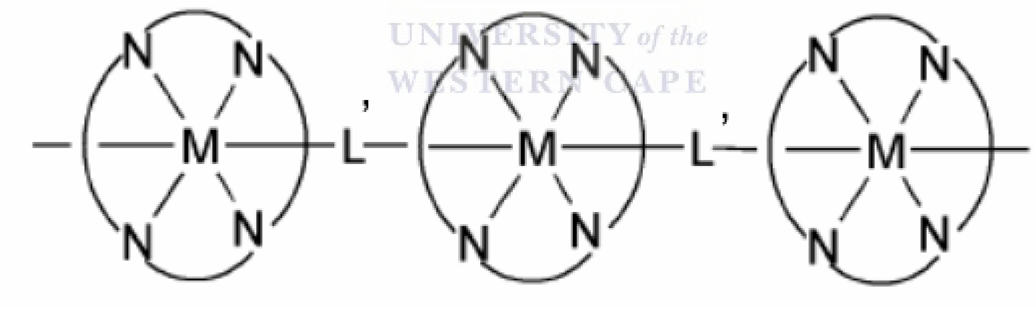
Luminescence occur when an electronic transition from an excited state to the ground state, caused by photo excitation, resulting in the emission of light [25, 26]. Luminescence can be divided into two categories: fluorescence and phosphorescence, depending on the nature of the excited state.

Although organic polymers can display luminescence behaviour, coordination polymers are potentially the most versatile material as their emission properties being coupled with guest exchange. Coordination polymers are usually more thermally stable than organic species.

Coordination polymer complexes, especially those of Zn(II), were recently used as electroluminescent materials [27, 28]. Zinc complex of N,N’-bis(2-hydroxy-1-naphthylidene)-3,6-dioxa-1,8-diaminooctane, emits blue light with an emission peak at 455 nm having maximum brightness of 650 cd m^{-2} when it is used as the emitting layer in an electroluminescence device.

2.3.2 Conductivity

Coordination polymers can have short inorganic and conjugated organic bridges in their structures, which provide pathways for electrical conduction. Some of one-dimensional coordination polymers [ML (-L)] $_n$ as shown in below, exhibit conductivity in a range of 1.10-6 S.cm^{-1} to 2×10^{-1} S.cm^{-1} [29]. The conductivity is due to the interaction between the metal d-orbital and the π * orbital of the bridging ligand L.



Scheme 2. 11 [ML (-L)] $_n$ coordination polymers with M = Fe, Ru, Os; L’ octaethylporphyrinato, phthalocyaninato, N belongs to pyrazine 4,4’-bipyridine.

Sheets of silver (Three-dimensional structures) containing polymers show semi-conductivity behaviour when the metal centres are aligned, and conduction decreases as the silver atoms go from parallel to perpendicularly aligned to the sheet [30].

2.3.3 Coating and thermally stable material

One of the most important properties of coordination polymers is thermal stability, which has been studied by many workers [31]. Atta et al prepared epoxy resins which were cured with diamine based on pentaethylene hexamine (PEHA) and p-phenylene diamine (PDA). Thermal stability data indicates that the cured epoxy resins with aromatic amine possesses higher thermal stability than if cured with aliphatic amine. The cured epoxy–amine systems were evaluated in coating applications [32].

2.3.4 Catalysis

The majority interest in reactive coordination polymers falls in their application as heterogeneous catalyst. The advantages of these materials include improved catalyst recovery, enhanced stability and size or shape selectivity [33].

Maksimchuk and co-workers described the synthesis of titanium and cobalt-monosubstituted Keggin heteropolyanions which were electrostatically bound to the chromium terephthalate polymer matrix MIL-101. Both transition metal Co-POM/MIL-101 and Ti-POM/MIL-101 composites were assessed in the oxidation of three alkenes α-pinene, caryophyllene, and cyclohexene using molecular oxygen and aqueous hydrogen peroxide as oxidants. The composite POM/MIL-101 materials showed fairly good catalytic activity and selectivity in α-pinene allylic oxidation (81–84% verbenol/verbenone selectivity at 15–25% substrate conversion) and caryophyllene epoxidation (100% selectivity at 88% conversion) with molecular oxygen (Co-POM) and hydrogen peroxide (Ti-POM). However, the MIL-101 matrix is destroyed at higher H_2O_2 concentrations and higher temperatures, the MIL-101 matrix is destroyed, and the POM/MIL-101 catalyst undergoes deactivation as it shows with cyclohexene oxidation [34].

The synthesis structure of new transition metal coordination polymers with the general formula [M (II) X_2(4,4’bipyridine)] (Fig 2.1), where (M(II) = Co, Ni, Cu; X = Cl−, CH_3OCO−, and acetylacetonate) towards the epoxidation of cyclohexene with O_2 in the presence of isobutyraldehyde as reductant was reported by Angelescu *et al* [35]. The catalytic activity of these complexes towards cyclohexene epoxidation shows over 88% conversions. The complex containing Co(II) cations and acetate as ligand X, [Co(II)(CH_3OCO)$_2$(4,4‘bipyridine)] presents the highest catalytic activity. This fact could possibly be linked to the lower strength of the bonds between acetate ligand and the transition metal cation which may result in coordination defects in the structure leading to an increase in the number of potential active sites. However, this research can conclude that, cyclohexene conversion depends on the nature of both the transition metal cation and the ligand X.

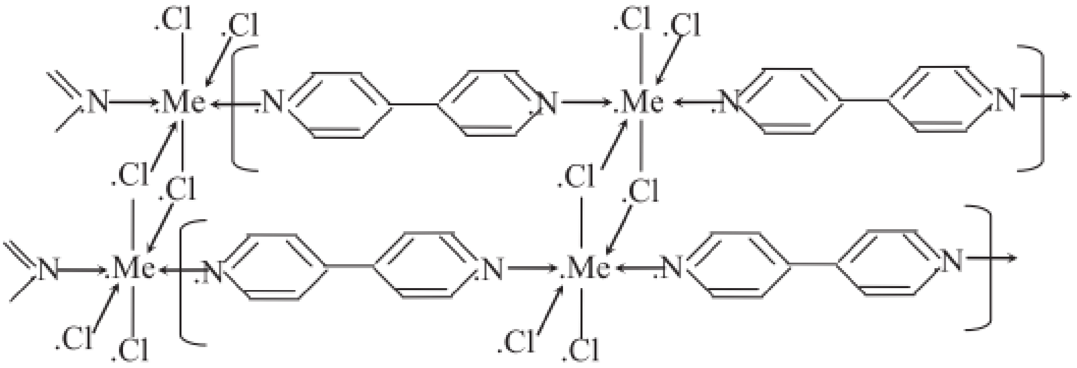


Figure 2. 1 One dimensional covalently linked chain [Me(II)Cl_2(4,4’bpy)], [M= Co, Cu, Ni]

The catalysis of Knoevenagel condensation reactions of benzaldehyde with each of the active methylene compounds (malononitrile, ethyl cyanoacetate, and cyanoacetic acid tert-butyl ester) by a cadmium coordination polymer $\{[Cd(4\text{-}btapa)_2(NO_3)_2],6H_2O,2DMF\}_n$, which formed from the reaction of $Cd(NO_3)_2$, $4H_2O$ and 1,3,5-benzene tricarboxylic acid tris[N-(4-pyridyl)amide]) ligand was reported by Kitagawa *et al* [36] . The cadmium ions are fully saturated (they are surrounded by six pyridyl donors) and the reaction is base catalysed by the amide groups of the ligands and is size selective. The result of the reaction of benzaldehyde with malononitrile gave 98% conversion, whereas the equivalent reaction with ethyl cyanoacetate gave only 7% conversion and no reaction was observed for cyanoacetic acid tert-butyl ester.

Other coordination polymer transition metal complexes [Cu(2- hydroxypyrimidinolate)$_2$] and [Co(phenylimidazolate)$_2$] where prepared by Xamena *et al*. The combination of Cu^{2+} and Co^{2+} complexes were utilized as catalyst for the aerobic oxidation of tetralin, yielding α-tetralone (T=O) as the main product [37]. The results show the combination of catalysts (90 Co/10 Cu mixture) gives 30% conversion with good selectivity towards T=O formation (high T=O/T–OH ratio) and low reduction time, comparing the use of each individual catalyst.

New coordination polymers, lanthanum polychelates, were synthesised from the 4f block elements (La (III), Pr (III), Nd (III), Sm (III), Gd (III), Tb (III)), by reacting the polymeric ligand 2-hydroxy-4-ethoxybenzophenone-1,4butylene with metal acetate as described (Fig 2.2) by Joshi *et al*.

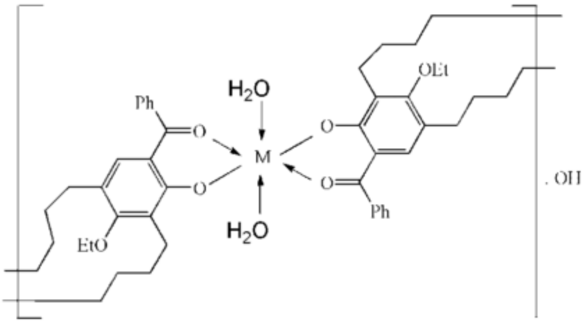


Figure 2. 2 Polychelate where M= La (III), Pr (III), Nd (III), Sm (III), Gd (III), Tb (III) and Dy (III); X= H_2O

The synthesis of Nd (III)and Sm(III) polymer–metal complexes were used for the Biginelli three-component, one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones, and the results of the synthesis obtained ≥90% yield [38].

Lin and co-worker reported preparation of a bi-functional MOF containing tetranuclear Zn clusters as Lewis acid centers and a chiral Mn−salen ligand. The authors studied the formation of a chiral epoxide directly from achiral substrates catalyzed by the Mn−salen complex, followed by the acid-catalyzed ring-opening with trimethylsilyl azide (fig 2.3). Yields of the final ring open product of up to 60% with enantio selectivities of up to 81% were obtained. In addition, the ring-opening step was highly regioselective, with only one pair of enantiomers of the four possible pairs being formed [39].

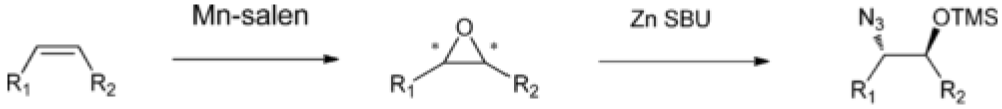


Figure 2. 3 The direct formation of a chiral epoxide from achiral substrates

Maurya *et al.* prepared polymeric oxovanadium(IV) complexes (Fig 2.4) with the polymeric Schiff bases derived from 5,5-methylenebis(salicylaldehyde)(1) or 5,5-dithiobis(salicylaldehyde)(2) and 1,2-diaminocyclohexane. Both complexes exhibit good catalytic activity towards the oxidation of styrene (76%), cyclohexene (98%) and trans-stilbene (33%) using tert-butyl hydroperoxide as an oxidant [40].

Figure 2. 4 The polymeric oxovanadium complexes

Other metal complexes (copper, nickel and cobalt) derived from polymeric coordinating ligands $[–CH_2H_2$ (salen)$–]_n$ and$[–CH_2H_2$(salpn)$–]_n$ (Fig 2.5) were utilized as hetrogenous catalyst for liquid phase hydroxylation of phenol using H_2O_2 as an oxidant. The catalytic activities of these coordination polymers exhibit 36–53% conversion of phenol to the product [41].

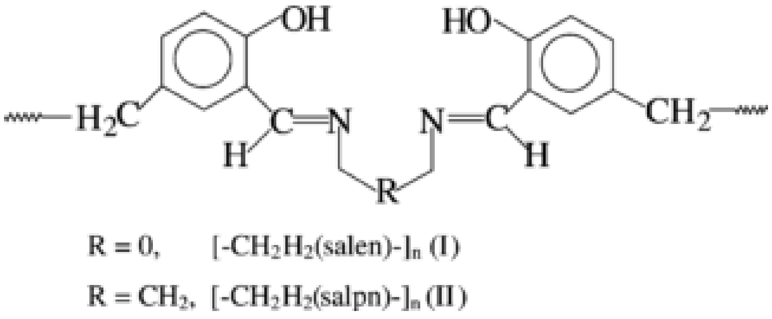
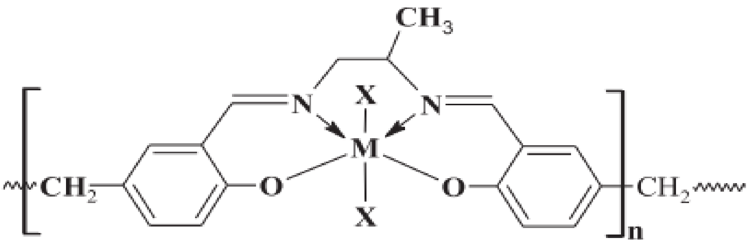


Figure 2. 5 The polymeric ligand [–CH_2H_2 (salen)–]$_n$(I) and [–CH_2H_2(salpn)–]$_n$ (II)

The same group as above also prepared polymeric oxovandium(IV) complexes with polymeric tetradentate coordination ligand. These complexes were tested for hydroxylation of phenol and oxidative bromination of salicylaldehyde. The resulting 38-40% conversion of phenol and 86-92% conversion of salicylaldehyde was observed, using these complexes [42].

Abbo *et al.* prepared coordination polymers of Ni(II) and Cu(II) complexes (Fig 2.6) derived from polymeric Schiff base N,N'-1,2-propylenebis-(5-methylenesalicylidenamine). These coordinated polymers were assessed as catalysts for liquid phase hydroxylation of phenol and benzene using H_2O_2 as oxidant. The results demonstrated a high activity and selectivity of both catalysts towards the formation of product for phenol, and a low activity in the case of benzene oxidation [43].



X = 0; M = Cu; 1

X = DMF; M = Ni; 2

Figure 2. 6 Copper and nickel coordination polymers

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CHAPTER 3

3. Materials and Method

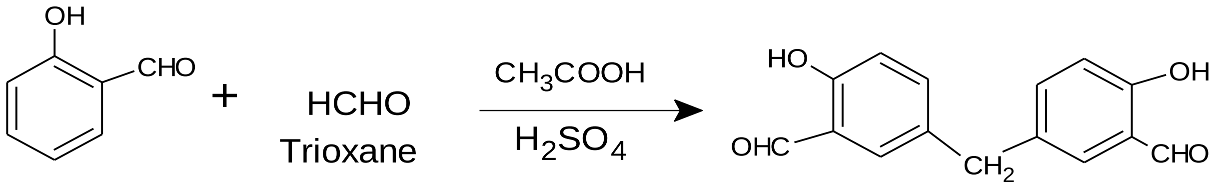
3.1 Chemicals and Reagents

All chemicals and reagents were used without further purification: trioxane, salicylaldehyde, styrene, cyclohexene (redistilled), benzene, methanol (99%), absolute ethanol (99%), acetonitrile (99%), petroleum ether, hydrogen peroxide (29-32%), sulfuric acid (98%), vanadyl acetylacetonate, 1,4-diaminobutane, 1,2-phenylenediamine dihydrochloride (99%), and potassium carbonate were purchased from Sigma Aldrich. Cupric acetate basic was purchased from Kanto chemicals, and glacial acetic acid and phenol purchased from Sarchem.

3.2 Synthesis of Schiff-base ligand L1 and its complexes

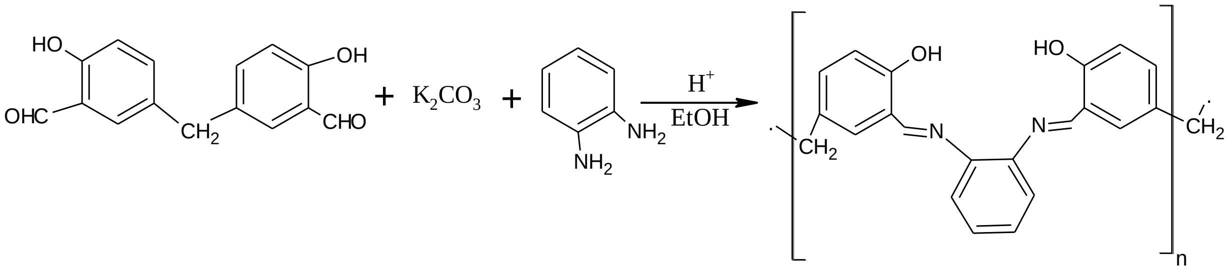
3.2.1 Preparation of 5,5′-methylene bis-(salicylaldehyde) (5,5′-mbsal)

5,5′-mbsal was prepared using the Marvel and Tarkoy method, with slight modifications [1]. Trioxane (1.4 g, 0.206 mol) was dissolved in 3 ml glacial acetic acid and salicylaldehyde (16 g, 0.655 mol) was added stepwise [salicylaldehyde: formaldehyde ratio 1.6:1]. A mixture of glacial acetic acid (0.5 ml) and conc. H_2SO_4 (0.1 ml) was added slowly to the stirred solution under nitrogen and then heated on oil bath to 90 ^{o}C for 22h. An excess of trioxane (0.6 g) was added after the 12h reaction time. The reaction mixture was then poured into 1 litre of iced water and allowed to stand overnight in the refrigerator. The deposited solid was decanted from water and triturated with petroleum ether, three times. Recrystallization of the crude product was done using acetone and the solution was cooled overnight in the refrigerator to a produce pale brown pure solid. Yield (2.8 g, 70.56%); m.p (140-142 ^{o}C). (Lit (141-142) [1].



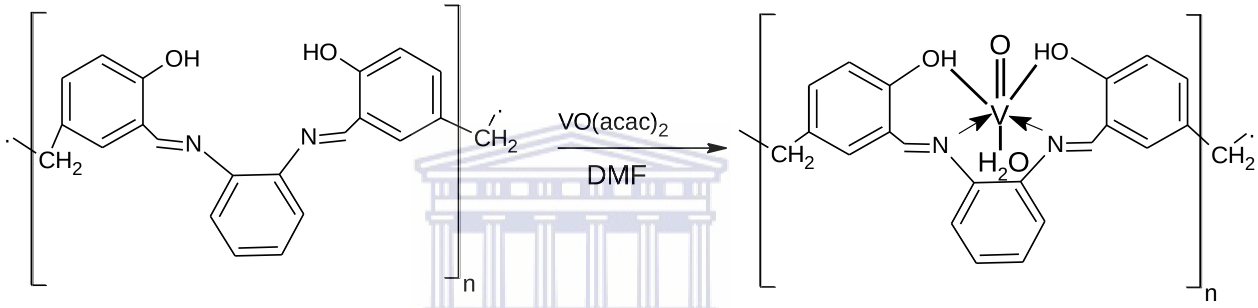
3.2.2 Synthesis of (N,N′ -1,2-phenylene bis(5-methylenesalicylidenamine) polymeric Schiff base ligand

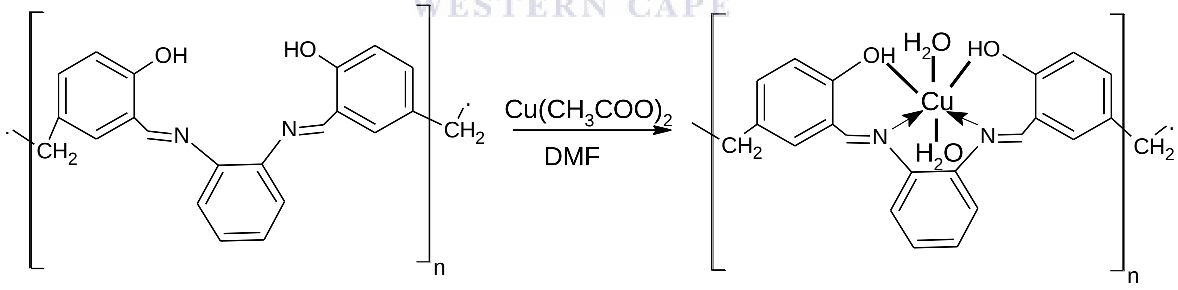
A two-neck flask (0.5 L) equipped with a condenser, magnetic stirrer, and thermometer was charged with 5,5′-mbsal (0.266 g), absolute ethanol (2 ml) and glacial acetic acid (8ml). 1,2-Phenylenediamine dihydrochloride (0.334 g) and potassium carbonate (0.51 g) were mixed in a 25 ml beaker with 0.5 ml of water and 2 ml of glacial acetic acid until dissolved completely. This solution was added slowly to the former mixture (a bright yellow precipitate formed immediately) and methanol (2 ml) was added and stirred for 2h. The solid precipitate was filtered, washed with DMF, followed by methanol and dried under vacuum to give the product, as a fine yellow powder (yield 0.291 g, and 68.52%).



3.2.3 Synthesis of coordinated metal complexes

The coordinated metal complexes were prepared by dissolving the polymeric Schiff base ligand (0.219 g, 0.002 mol) in 3 ml (DMF) at 90 ºC. To this solution, the respective Cu(II) acetate and $VO(acac)_2$ (0.246 g and 0.219 g respectively, 0.002 mol) dissolved in 3 ml of DMF were added. In the case of copper, dark green precipitate was formed, and olive green precipitate with oxovanadyl(IV) ion. The solid was filtrated, washed with methanol and dried in an oven. Yield 53.1% and 44.2% for Cu and VO-based catalysts respectively.

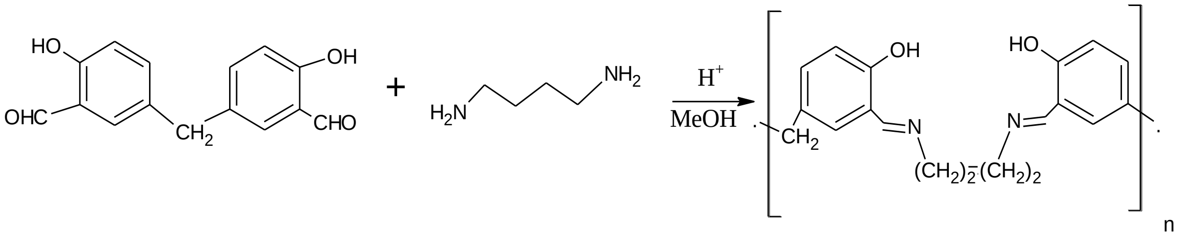




3.3 Synthesis of Schiff-base ligand L2 and its complexes

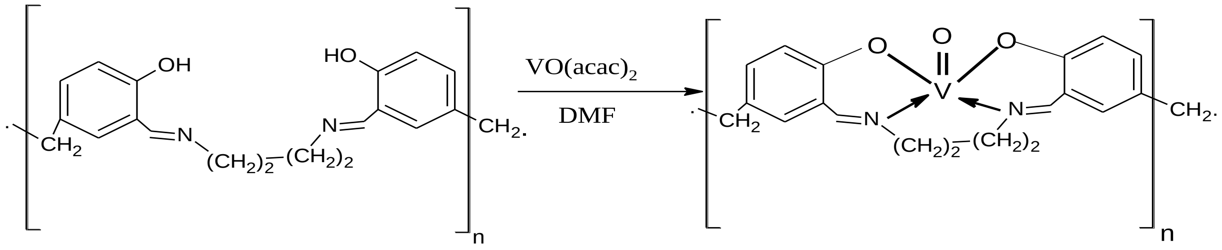
3.3.1 N,N′ -1,4-butylene bis(5-methylenesalicylidenamine) polymeric ligand

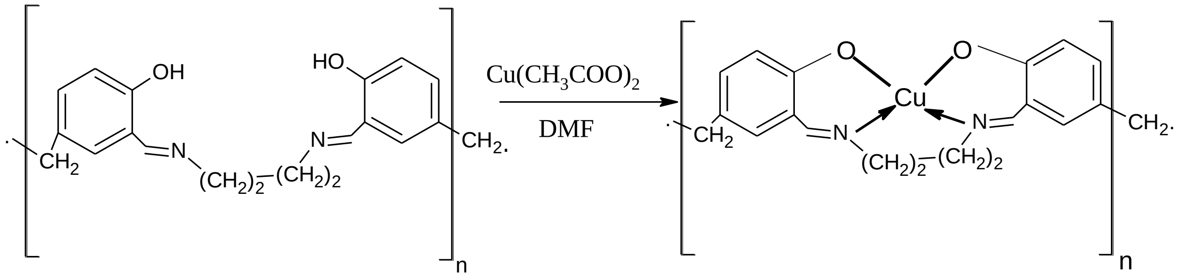
0.853 g of 5,5′-mbsal was dissolved in 2 ml glacial acetic acid and 3ml of methanol and the resulting mixture was heated until completely dissolvtion. To this solution 1,4-diaminobutane (0.293 g) in methanol 3 ml was added and stirred overnight. The separated solid was filtered and purified by refluxing with methanol for 2 h. The hard yellowish solid obtained was dried in anoven, Yield 47.8%.



3.3.2 Synthesis of coordinated metal complexes

The coordinated metal complexes were prepared by dissolving the polymeric Schiff base ligand (0.308 g, 0.002 mol) in DMF and methanol heated at 90ºC with stirring for 4 h until completely dissolvation. To this solution, the respective metal acetate [M = Cu(II) and V (IV)] (0.002 mol) dissolved in DMF was added untill dissolved completely. In case of copper a dark green precipitate was formed and green olive precipitate with oxovanadyl ion. The solid was filtrated, washed with methanol and dried in the oven. Yield (0.265 g, 33.7%) for oxovanadium and (0.354 g, 45.4%) for copper complexes.





3.4 Characterization techniques

3.4.1 Nuclear Magnetic Resonance (NMR) spectroscopy

Nuclear Magnetic Resonance Spectroscopy (^{1}H and ^{13}C NMR) was used to resolve the molecular structures of the ligands. The samples were prepared by dissolving 5 mg of dried ligands in deuterated chloroform or dimethylesulfoxide (depending on the solubility of the ligand). ^{1}H and ^{13}C NMR spectra were recorded using a Varian Gemini 2000 spectrometer (^{1}H at 200 MHz, ^{13}C at 50.3 MHz) and chemical shifts are indicated in ppm. Sample signals are relative to the resonance of residual protons on carbons in the solvent.

3.4.2 Fourier Transform Infrared (FT-IR) Spectroscopy

Fourier Transform Infrared (FT-IR) spectra were recorded using a (Perkin Elmer Spectrum 100 FTIR spectrometer) coupled to an Attenuated Total Reflectance (ATR) sample holder. This technology provided specific information about chemical bonding and molecular structures of the sample. Chemical bonds vibrate at characteristic frequencies, when exposed to infrared radiation; they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces a spectrum that can be used to identify the compounds. FT-IR was used to obtain information and confirmation of the functional groups of both ligands and complexes.

3.4.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) imaging and analysis techniques were used to determine the particle size and morphologies of the polymeric ligands and its complexes. SEM of the samples recorded on field-emission scanning electron microscopy (Auriga Zeiss SEM) with accelerating voltage: 5 keV. The samples were coated with Au-Pd for 30s using a Quorum Q150TES sputter coater to prevent surface changes and to protect the surface material from thermal damage by the electron beam.

3.4.4 Gas Chromatography (GC)

GC-FID is a destructive technique for resolving a complex mixture into its individual fractions or compounds which based upon the rate flow of the mobile phase and a stationary phase to separate the components in a mixture. The retention time of all peaks was compared with authentic samples. Agilent 7890 gas chromatograph fitted with flame ionization detector fitted with HP-5 (phenylmethylsilicon) capillary column (30 m x 330 pm x 0.25 μm film thickness, Agilent technologies) was used to monitor the reaction progress and determine percentage conversion and selectivity of the products.

3.4.5 Ultraviolet-Visible spectroscopy (UV-Vis)

UV-Vis spectrometer is an instrument used to measure the amount of ultraviolet and visible light absorbed by a solution. The light used in UV-Vis spectroscopy, is a very narrow portion of electromagnetic spectrum. The sample is placed between a light source and detector depending on the sample, light absorbed causing electrons to be promoted from one energy level to another. Since different metal ions, have different absorption patterns, UV-Vis spectroscopy was used to identify metal ions in complexes as well as the electronic transitions of the ligand and the complexes. The samples were recorded on a GBC UV/VIS 920 UV–Visible spectrophotometer using a 1 cm quartz cell and DMSO as solvents, with concentration of 10^{-4} M in the UV region, and at a concentration of 10^{-3} M in the visible region.

3.4.6 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 600°C (Maximium temperature). The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. Thermal analysis was measured using a Perkin Elmer TGA Q500 Thermobalance.

3.4.7 Magnetic susceptibility measurements

Magnetic susceptibility is the degree of magnetization of a material in response to an applied magnetic field. If magnetic susceptibility is positive then the material can be paramagnetic, or antiferromagnetic. In this case the magnetic field is strengthened by the presence of the material. On the other hand, if magnetic susceptibility is negative the material is diamagnetic. As a result, the magnetic field is weakened in the presence of the material. The samples were measured using a Sherwood Scientific MK1 magnetic susceptibility balance.

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CHAPTER 4

4. Characterizations

The monomeric ligand, 5,5’-methylene-bis(salicylaldehyde) was obtained in 70.6% yield by reacting salicylaldehyde with trioxane in the presence of sulphuric acid in acetic acid solution. The yield of 5,5’-methylene-bis(salicylaldehyde) is related to the amount of sulphuric acid as catalyst used and this relationship can be rationalized on the assumption that the salicylaldehyde to formaldehyde ratio must be very high in order that dialdehyde be formed rather than a polymeric product [1]. This low acid concentration helps keep the ratio of salicyaldehyde to formaldehyde favourable for the preparation of the monomeric dialdehyde.

The polymeric Schiff base ligand was synthesized by the condensation of equimolar of 5,5’-methylene-bis(salicyaldehyde) with o-phenylenediamine and 1,4-diaminobutane as shown in chapter 3.

4.1 Characterization of N,N′ -1,2-phenylene bis (methylenesalicylidenamine)(L1) and its coordinated complexes

4.1.1 FT-IR spectroscopic studies

4.1.1.1 5,5′-methylene bis-(salicylaldehyde) (5,5’-bmsal)

The IR spectrum of 5,5’-bmsal exhibits two broad bands in the region 3100-3300 cm^{-1} attributed to the stretching vibration of phenolic OH groups and C-H groups of the aromatic rings [2]. A medium intensity peak at 2842 cm^{-1} is assigned for -CH$_2$ methylene group. A sharp band at 1648 cm^{-1} is assigned for *v*(C=O) stretching vibration which confirmed the presence of the aldehyde group [3]. The appearance of two peaks in the regions of 1605-1480 cm^{-1} are attributed to the *v*(C=C) bond of the aromatic ring Fig 4.1. [3].

4.1.1.2 N,N′ -1,2-phenylene bis(5-methylenesalicylidenamine)(L1)

Figure 4.2 represents the IR spectrum of the ligand (L1). A broad band in the range 3200-3100 cm^{-1} is assigned to Ph-O stretching vibrations. The stretching vibration in the region of 2841cm^{-1} is due to *v*(C-H) aliphatic bond which confirms the presence of methylene groups. A new strong sharp peak at 1618 cm^{-1} is assigned to the *v*(C=N) stretch of azomethine. The two bands at 822 and 780 cm^{-1} may be attributed to out of plan bending of the aromatic rings and indicates the formation of a 1,2,4-trisubstituted ring [4]. The weak peak at 1653 cm^{-1} is attributed to the presence of the aldehyde end group.

4.1.1.3 Coordinated metal complexes

The IR spectra of the Cu(II), and VO(IV) complexes of L1 are show in (Fig 4.3). L1 spectra exhibit a sharp peak at 1618 cm^{-1} due to the azomethine *v*(C=N) stretching vibration. This band is shifted to lower frequency by 3-8 cm^{-1} in the spectra of the Cu and VO complexes indicating the coordination of azomethine nitrogen to the central metal [5]. The presence of the sharp band in the region of 2923-2840 cm^{-1} in the polymeric ligand and their complexes confirm the presence of the bridging methelene group. Thus, each repeating unit of the polymeric ligand behaves as a dibasic tetradentate ONNO donor [6]. The metal complexes exhibit weak-medium peaks in the far IR region (400 - 600 cm^{-1}) which are assigned to *v* (M-O) and *v* (M-N) modes, indicating coordination of metal to nitrogen and oxygen atom of the respective ligands [7]. The VO(IV) complex exhibits an additional sharp peak at 977 cm^{-1}, assigned to the *v* (V=O) stretch [5].

Table 4. 1 FT-IR vibrations of the ligands, and the Cu(II) and VO(IV) complexes

Compound	**ν (cm^{-1})**		
	***v*(C=N)**	***v*(M-O)/(M-N)**	***v*(C-H)**
5,5'-bmsal	-	-	2843(s)
L1	1618(s)	-	2841(s)
Cu(L1)	1615(s)	540(s),482(s)	2912(s)
VO(L1)	1613(s)	529(s),465(s)	2923(s)

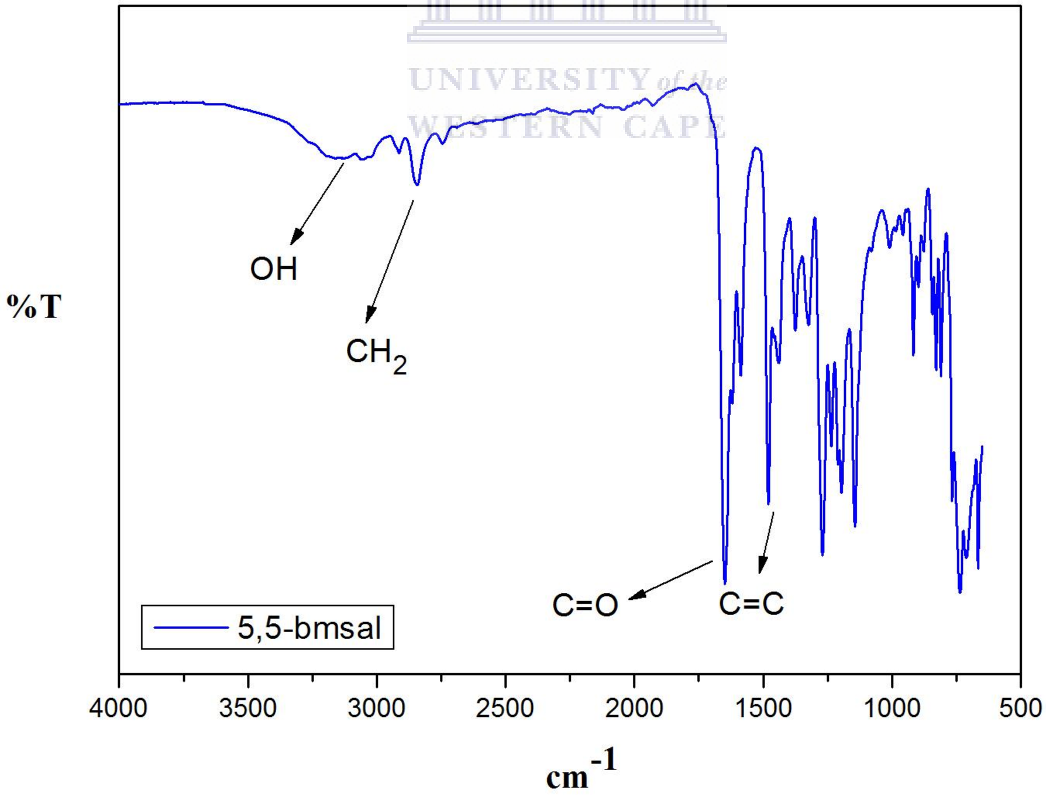


Figure 4. 1 IR spectra of 5,5′-methylene bis-(salicylaldehyde)

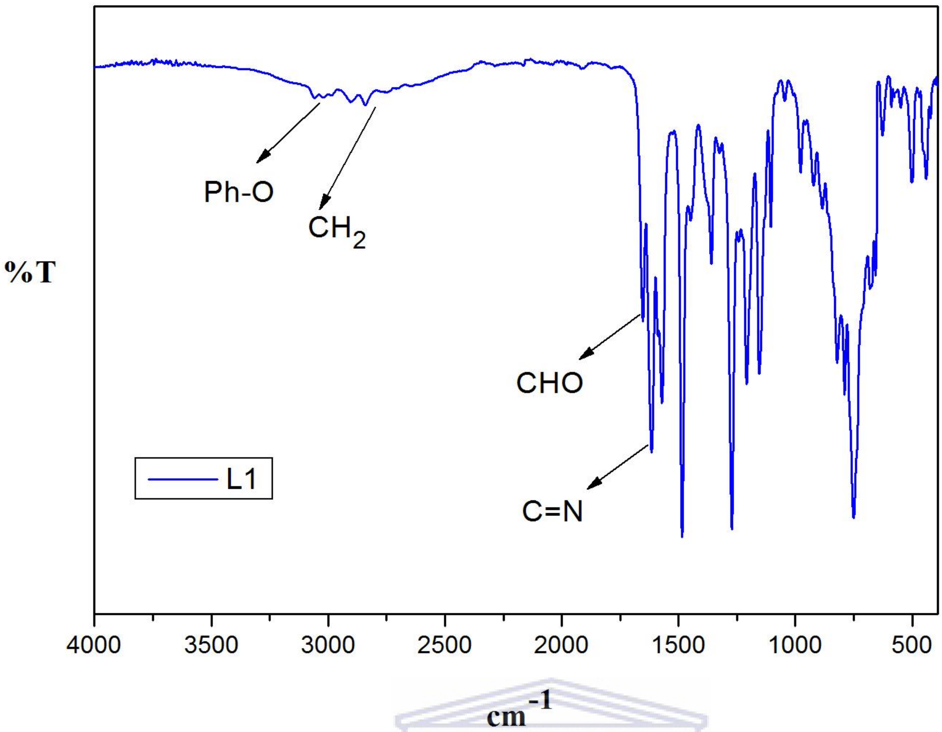


Figure 4. 2 IR spectra of N,N′ -1,2-phenylene bis(5-methylenesalicylidenamine)(L1)

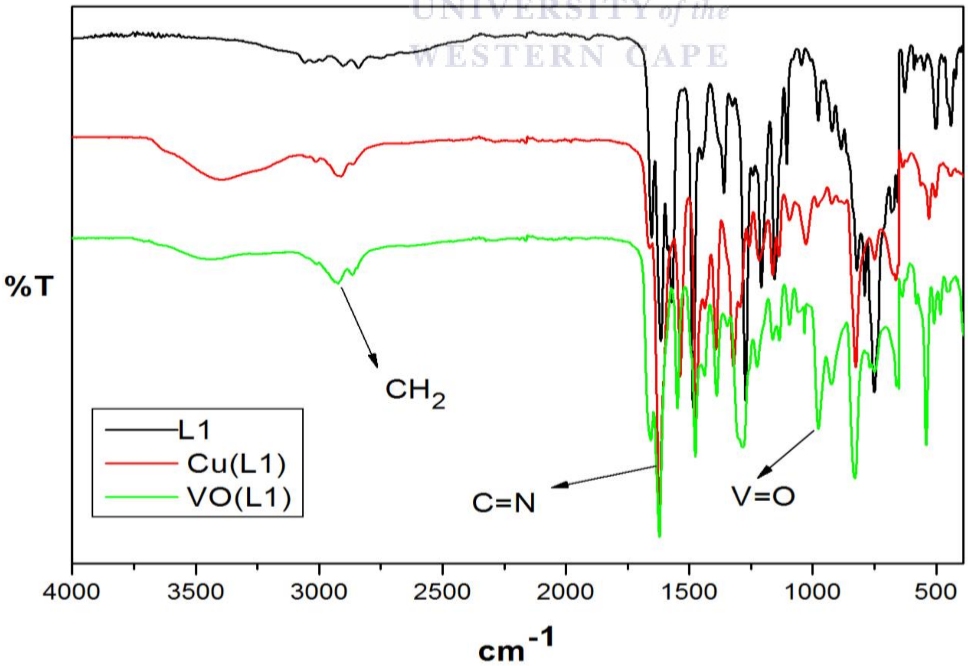


Figure 4. 3 IR spectra of ligand (L1), copper catalyst (Cu(II)), and oxovanadium catalyst VO(IV).

4.1.2 ^{1}H and ^{13}C NMR spectroscopic studies of Schiff-base ligands

The ^{1}H NMR spectrum of 5,5′-methylene bis-(salicylaldehyde) is shown in Fig 4.4 and Table 4.2. The spectrum shows a sharp peak at 10.89 ppm assigned for two phenolic protons of the salicylaldehyde repeating unit. The protons of the aldehyde groups in the structure of the ligand are confirmed by the existence of strong peak at 9.79 ppm [8]. The multiplet peak at 7.3-7.1 ppm and a sharp peak at 3.92 ppm are assigned to the aromatic protons and protons of the methylene group, respectively [8].

The ^{13}C NMR spectrum of 5,5′-mbsal exhibited seven peaks as shown Fig 4.5 at 196.4, 160.1, 133.2, 137.5, 120.4, 131.9, 117.9, 39.28 ppm. The signals observed at 196.4 and 39.38 ppm are assigned to the aldehyde carbon and methylene groups [2].

The ^{1}H NMR spectrum of L1 in Fig 4.6 and Table 4.3 shows a strong sharp peak at 10.91 ppm assigned to the proton of the phenolic OH group. Sharp doublet peaks at 9.83 ppm are assigned to the CH=N group. The multiplet peak at 7.3-7.1 ppm and a sharp peak at 3.95 ppm are assigned to the aromatic proton and proton of the methylene group, respectively.

The ^{13}C NMR spectrum of L1 exhibiteds twenty one peaks as shown in Fig 4.7 which confirmed the proposed structure.

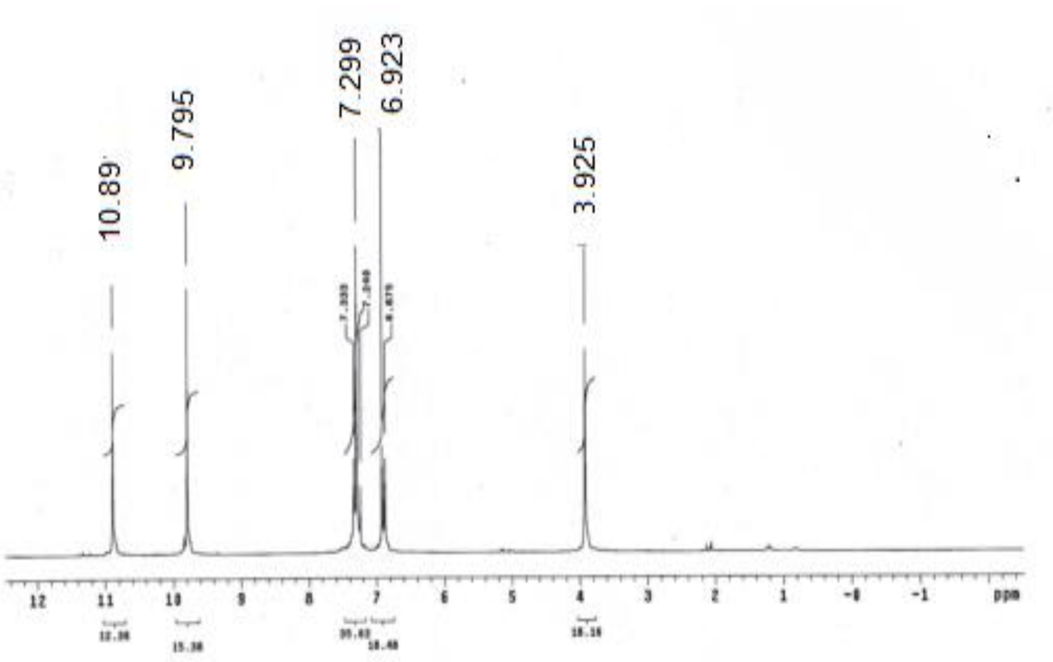


Figure 4. 4 ^{1}H NMR of 5,5′-methylene bis-(salicylaldehyde)

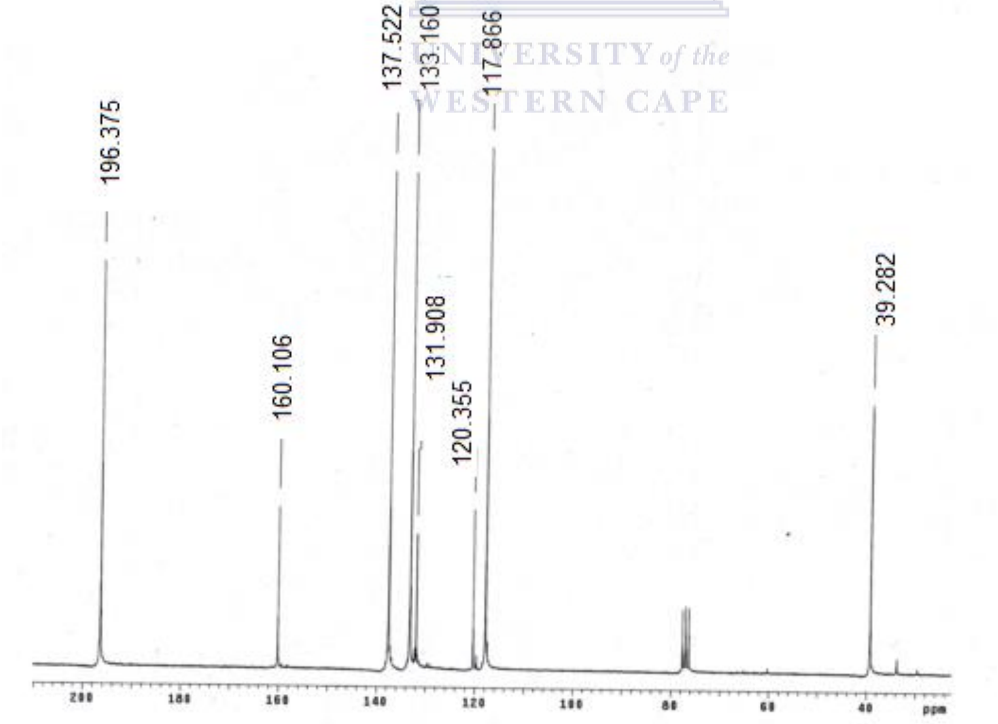
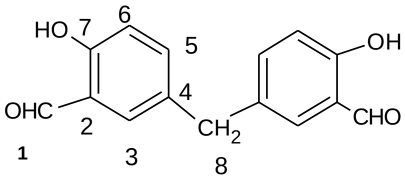


Figure 4. 5 ^{13}C NMR of 5,5′-methylene bis-(salicylaldehyde)

Table 4. 2 ^{1}H NMR data of 5,5-methylene-bis-salicylaldehyde

Ligand structure	**Proton position**	**Chemical Shift (ppm)**	**No. of protons**	**Multiplicity**	**Assignment**
 **5,5-mbsal**	1	9.79	2	s	CHO
	7	10.89	2	s	OH
	3,5,6	7.3-7.1	3	m	Ar
	8	3.92	2	s	CH_2

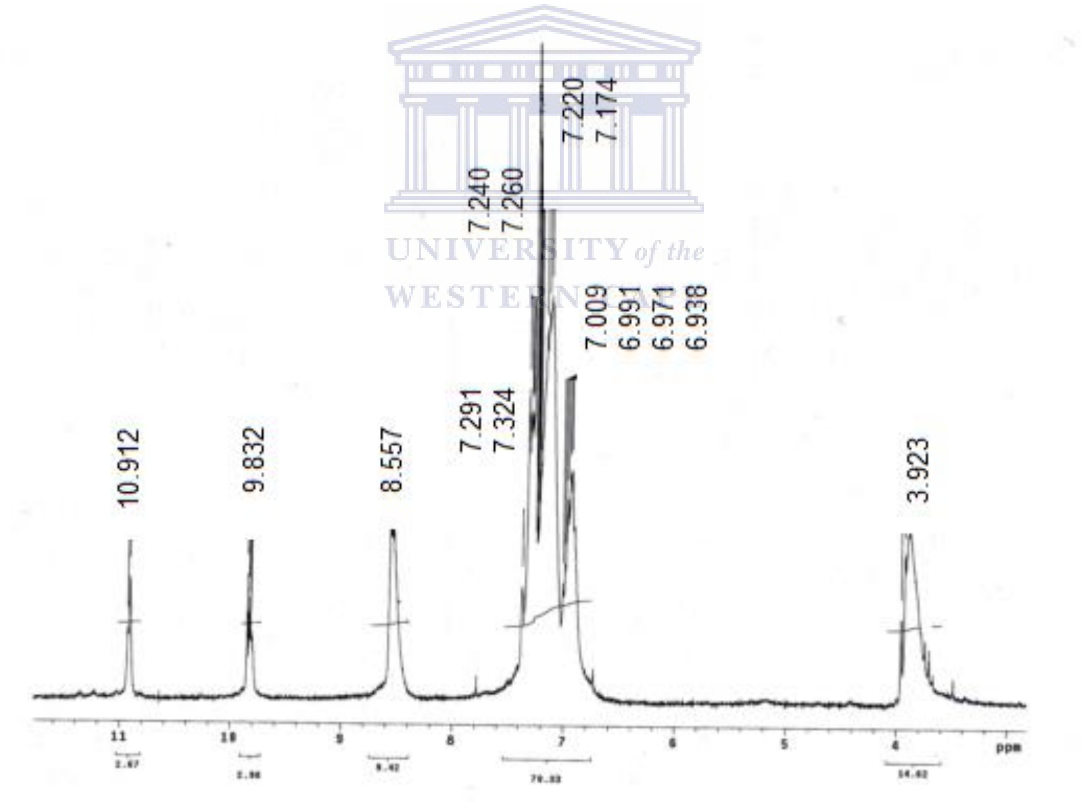


Figure 4. 6 ^{1}H NMR of N,N′ -1,2-phenylene bis(5-methylenesalicylidenamine)(L1)

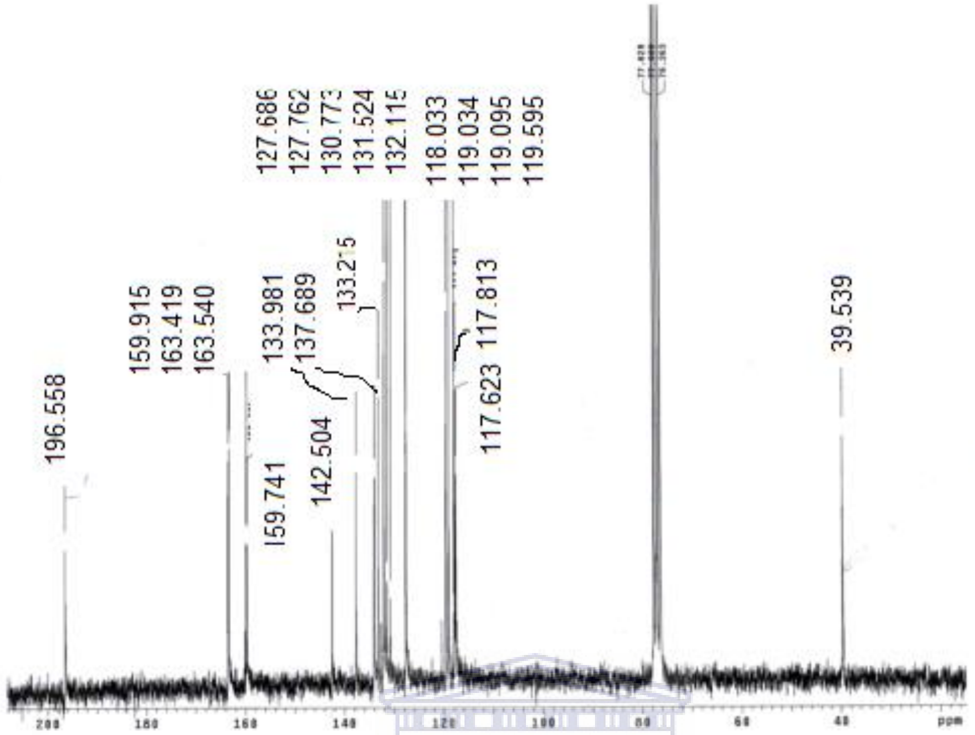
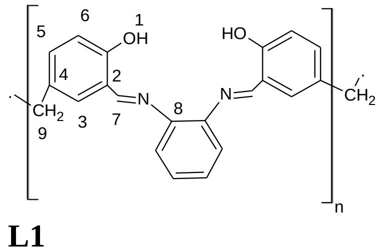


Figure 4. 7 ^{13}C NMR of N,N′ -1,2-phenylene bis(5-methylenesalicylidenamine)(L1)

Table 4. 3 ^{1}H NMR data of L1

Ligand structure	**Proton position**	**Chemical Shift (ppm)**	**No. of protons**	**Multipliciy**	**Assignmnet**
 **L1**	1	10.92	2	d	OH
	7	8.56	1	s	CH=N
	3,5,6	7.3-7.1	6	m	Ar
	9	3.95	2	s	CH_2

4.1.3 UV/Vis electronic spectral studies

The electronic spectral data of the Schiff base ligands and complexes were recorded in methanol and DMSO over the range 200-900 nm.

4.1.3.1 Schiff-base ligands

The UV-visible spectrum of 5,5′-mbsal ligand is shown in Fig 4.8, Three bands at 225, 255, 336 nm, are assigned for to $\varphi \rightarrow \varphi^*$(benzene ring) and $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ (aldehyde group) transitions, respectively [9, 10]. Electronic spectral data of L1 shows (Fig 4.9) three bands at 225 with (weak shoulder at 208), 260 and 330 nm. These bands are assigned to $\varphi \rightarrow \varphi^*$and $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (assigned to benzene ring and non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base complexes) respectively [11, 12].

4.1.3.2 Coordinated metal complexes

The spectral profiles of the metal complexes below 400 nm are similar to the ligand transitions ($\pi\rightarrow\pi$ * and $n\rightarrow\pi$ *), wher the shift to lower energy values indicates the coordination of the ligand to the metal ions. These are further supported by the appearance of a low intensity sharp band in the 436 nm region in the Cu(II) complex (Fig 4.10) and a sharp band at 414 nm in the case of vanadium complex (Fig 4.11), assigned to Metal-Ligand Charge Transfer (MLCT) transitions [10, 13]. The VO(IV) complexes exhibit a new weak broad band at 619 nm due to the d-d transition. The Cu(II) complex shows a band at 701 nm attributed to d-d transition [14].

Table 4. 4 Electronic spectral data of the ligands (L1) and Cu(II), VO(IV) complexes.

Complex	**λ_m/nm (ε/M^{-1} cm^{-1})**
5,5-bmsal	225, 255, 336
L1	208, 225, 260, 330
Cu(L1)	250, 304, 436, 701
VO(L1)	253, 326, 414, 619

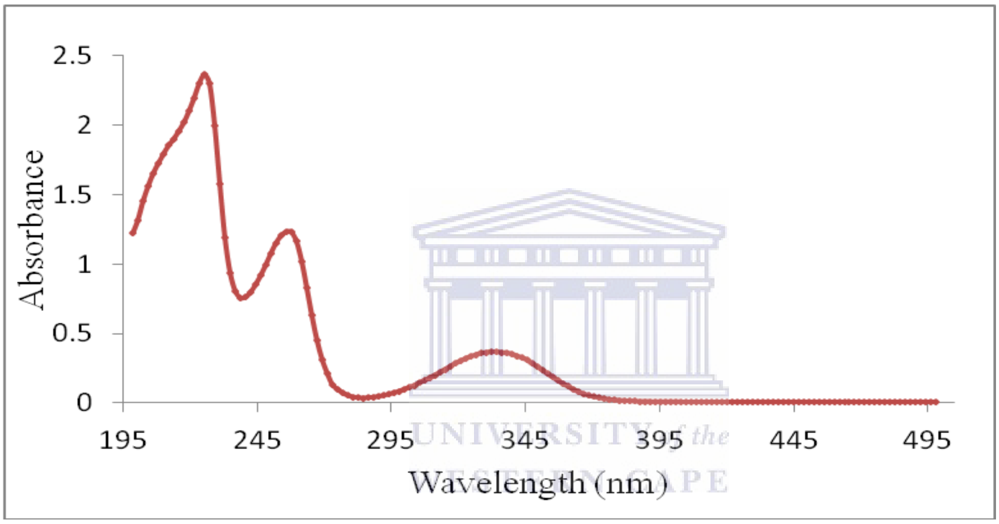


Figure 4. 8 Electronic spectra of 5,5′-methylene bis-(salicylaldehyde)

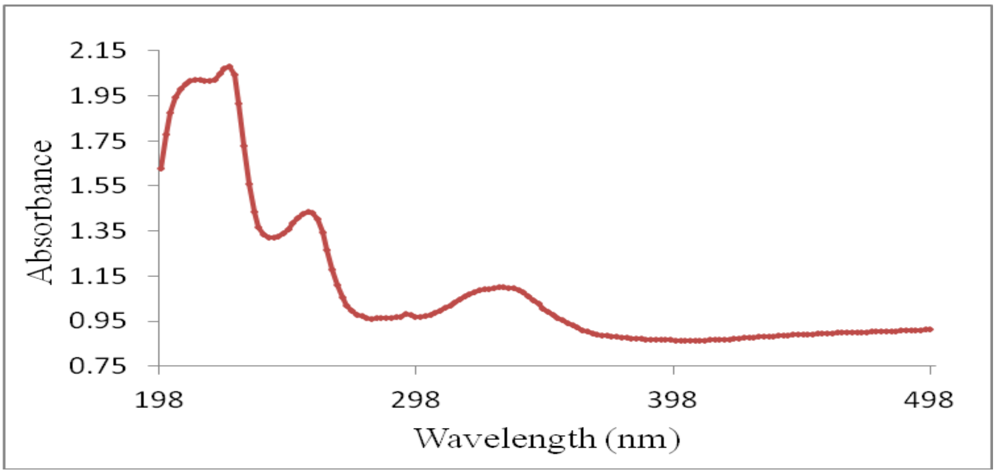


Figure 4. 9 Electronic spectra of N,N′ -1,2-phenylene bis(5-methylenesalicylidenamine) (L1)

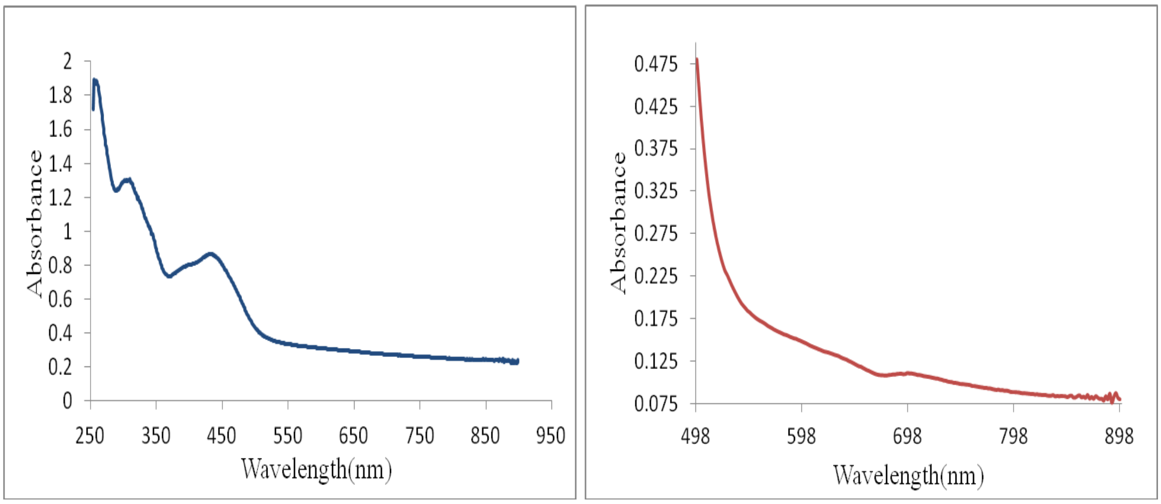


Figure 4. 10 Electronic spectra of copper catalyst (Cu(II)) in the UV (left) and Vis. (right) region.

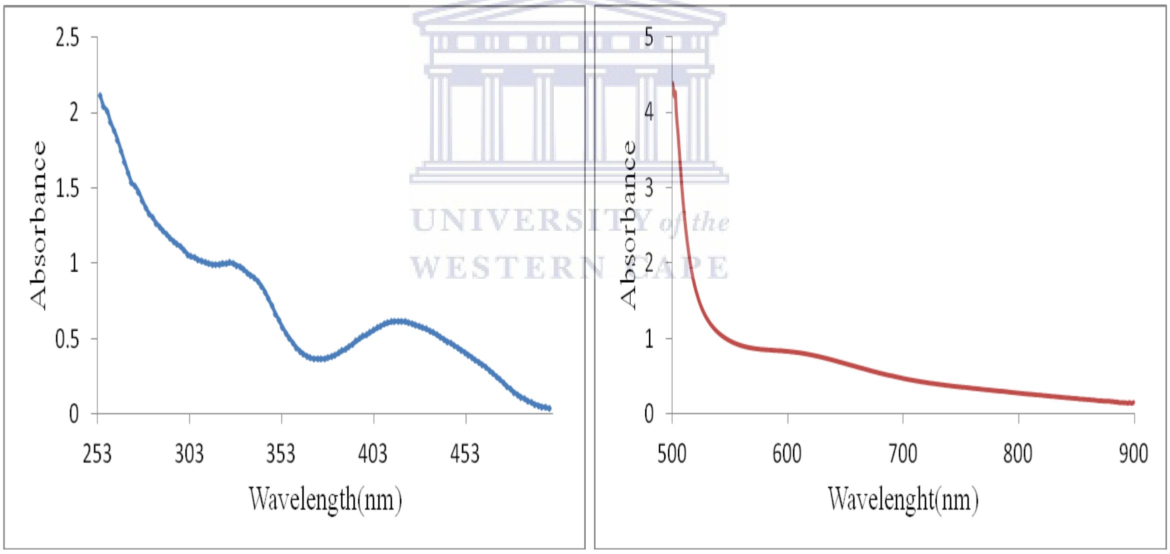
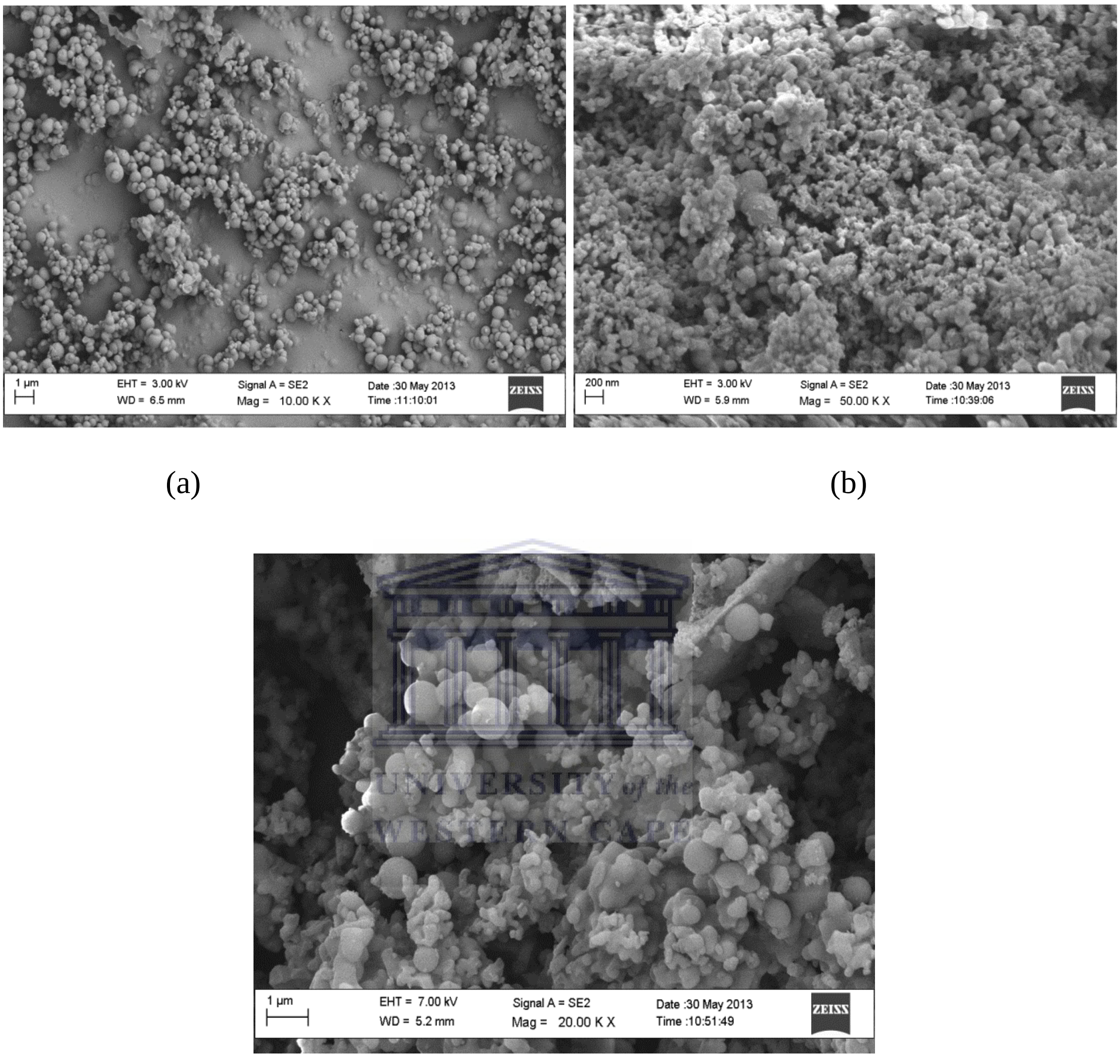


Figure 4. 11 Electronic spectra of vanadium catalyst VO(IV) in the UV (left) and Vis. (right) region.

4.1.4 Scanning electron microscopy of L1, Cu(II) and VO(VI) complexes

The SEM micrograph of the polymeric ligand (Fig 4.12) shows arough surfaces with irregulanties at are spherical in shape. On complexation with the metal ions the morphology of the ligand became accumulated, due to coordination with metal ions which indicates formation of the coordinated polymers [15].



(a) (b)

(c)

Figure 4. 12 Scanning electron micrographs of (a) L1, (b) Cu (L1) and (c) VO (L1).

4.1.5 Magnetic susceptibility measurements for L1 Complexes

The solid sample is tightly packed into a weighed sample tube of suitable length (l) and the sample weight (m) noted. Then the packed sample tube was placed into the tube guide of the balance and the reading (R) was noted. The mass susceptibility, χg, is calculated using:

$$\chi_g = \frac{C_{bal}\, l\,(R - R_o)}{10^9\, m}$$

Where: l = the sample length (cm)

m = the sample mass (g)

R = the reading for the tube plus sample

R_0 = the empty tube reading

C_{bal} = the balance calibration constant

The molar susceptibility, $\chi_m = \chi_g \times$ molecular formula, of the complex. The effective magnetic moment, μ_{eff}, is then calculated using the following expression:

$\mu_{eff} = 2.83\sqrt{T * \chi m}$ Where T= temperature (K)

The room temperature magnetic moments (μ_{eff}) value of the copper (II) complex one is 1.23 BM. This value is below the calculated spin (1.8-2.0 BM) [16]. The monomeric nature of Cu complex was confirmed by a magnetic moment value of 1.23 B.M and this value permits the assignment of a distorted octahedral structure around the copper (II) ion for the complex [17,18].

The magnetic moment (μ_{eff}) value of the oxovanadium (IV) complexe is 0.95 B.M. This value is much smaller than the spin-only moment for a d^1 system. The subnormal magnetic moments can be considered as due to an exchange interaction between vanadium(IV) ions [19, 20]. There are several reports on such binuclear structures proposed for a number of oxovanadium (IV) complexes with subnormal magnetic moments [21, 22].

4.1.6 Thermal analyses of L1and it is complexes

Thermal analyses of the ligand and complexes were carried out under nitrogen atmosphere at a heating rate of 10 °C min^{-1} from ambient temperature up to 600 °C. The % weight loss via temperature curves are shown in Figure 4.13

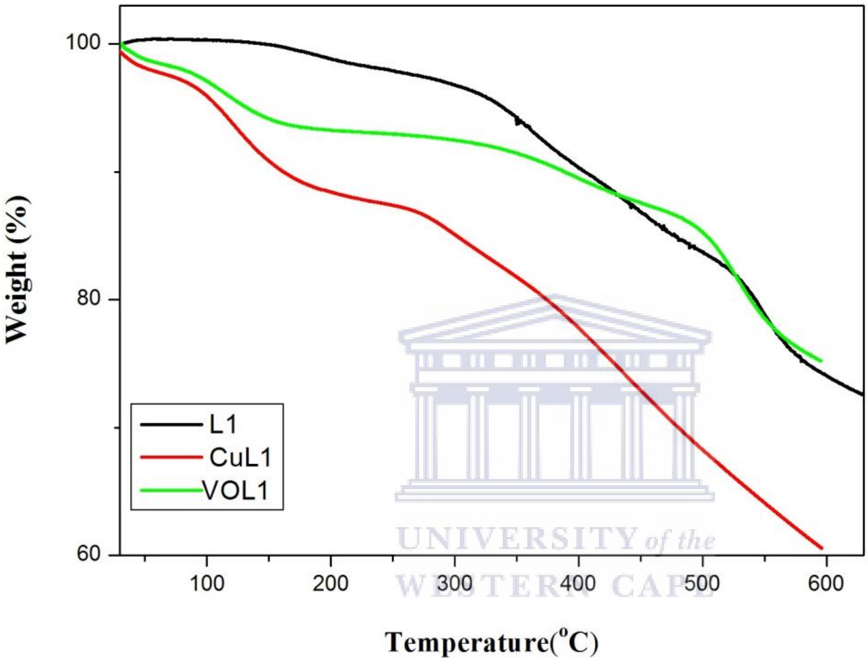


Figure 4. 13 The TGA thermograms of L1 and its complexes

The TGA are of L1 (Fig 4.13) shows two step continues weight loss. The first one shows 1.3 weight loss which may be due to the presence of water at 180 ^{o}C. The second step shows the major weight loss of 24.5(ca. 23.1) at (300-598 ^{o}C) due to the loss of Ph ring from the ligand.

The thermo-gravimetric analysis of copper complexes shows three steps continues weight loss as the temperature increases from room temperature to 600 ^{o}C. The first step shows

1% loss at 90 °C which due to presence of water moisture. Whereas, the second step shows weight loss of ~8% (ca.8.5) at (120-190 °C) which indicates the loss of coordinated water molecules. The last step shows continuous weight loss of about ~28% (ca. 27.5) from 250-550 °C due to the decomposition of Ph-N=C ofthe ligand and loss of the CH_2 group [15].

The VO-complex (Fig 4.13) exhibits three stage continues decomposition patterns, as is evident from the TGA cuarve. In the first two steps 2.5% and 4.2% (ca. 4.06) weight loss at ~92 °C and 112-190 °C due the water moisture present in the complex and CH_2 group respectively. The last step shows continus weight loss 17.8% (19.3) from (300-590 °C), which may be assigned to loss of the Ph –ring [14].

4.2 Characterization of L2 and it is complexes

4.2.1 FT-IR spectroscopic studies

4.2.1.1 N,N′ -1,4-butylene bis(5-methylenesalicylidenamine) (L2)

The IR spectrum of the L2 Schiff base in Fig 4.14 shows a broad band in the region of 2868 cm^{-1} which is assigned to the stretch vibration of intramolecularly hydrogen bonded OH group in the molecule. The high intensity band in the region of 1271 cm^{-1} is due to the phenolic C-O stretching frequency. The new absorption band which appeared at 1631 cm^{-1} was assigned to the azomethine ν (-N=C) stretch. The appearance of the methylene group was confirmed by the strong stretching at 2844 cm^{-1} [23].

4.2.1.2 Coordinated metal complexes

The IR spectra of the complexes are compared with that of the free ligand (Fig 4.15). The band at 1631 cm^{-1} is characteristic of the azomethine nitrogen present in the free ligand.

The lowering in this frequency region (1620-1618 cm^{-1}), observed in all the complexes, indicates the involvement of the azomethine nitrogen atom in coordination [24]. Appearance of multiple bands due to CH_2 groups in all complexes at nearly the same positions (~2922 cm^{-1}) suggests stability and presence of coordinated polymers after complexition. In addition to other bands, the vanadyl complex shows the characteristic V=O asymmetric stretching frequency at 975 cm^{-1} [25].

Table 4. 5 FT-IR vibrations of the ligand(L2), Cu(II) and VO(IV) complexes

Compound	**ν (cm^{-1})**		
	***ν*(C=N)**	**ν(M-O)/(M-N)**	***ν*(C-H)**
L2	1631(s)	-	2844(s)
Cu(L2)	1620(s)	542(s),474(s)	1922(s)
VO(L2)	1620(s)	535(s),472(s)	2923(s)

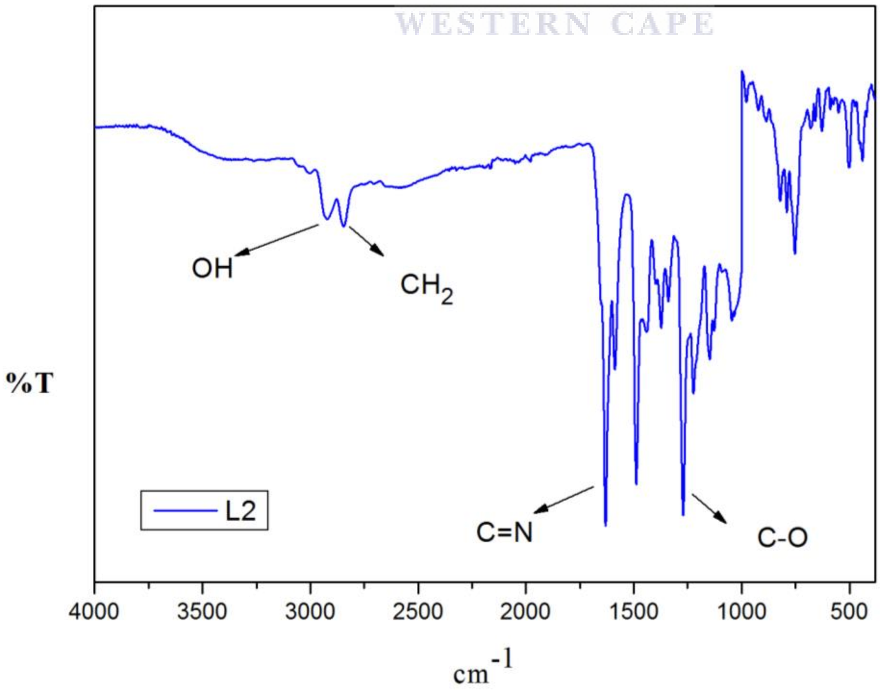


Figure 4. 14 IR spectra of N,N′ -1,4-butylene bis(5-methylenesalicylidenamine)(L2)

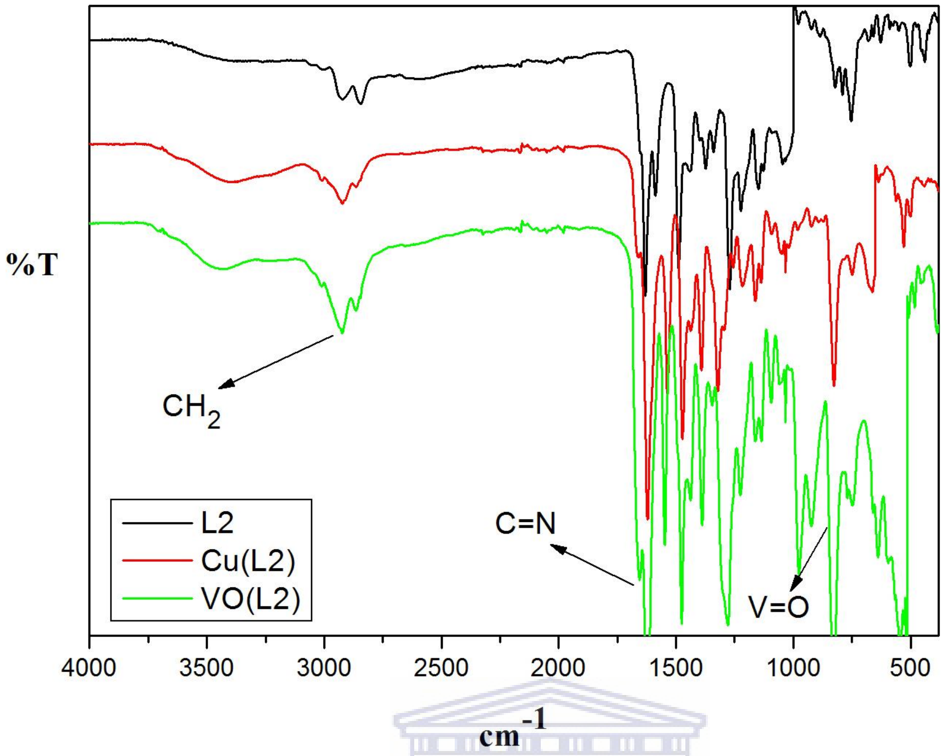


Figure 4. 15 IR spectra of ligand (L2), copper catalyst Cu(II), and vanadium catalyst (VO(IV)).

4.2.2 ^{1}H and ^{13}C NMR spectroscopic studies of Schiff-base ligand L2

The ^{1}H NMR spectrum of N,N′ -1,4-butylene bis(5-methylenesalicylidenamine) (L2) is shown in Fig 4.16, Table 4.6 shows a sharp doublet peak at 10.21 ppm assigned to the proton in the OH group. The signal at 8.44 ppm is assigned to the appearance of C=N groups. The multiplet peaks at 7.42-6.78 ppm are assigned to aromatic protons. Multiplet peaks appear in the region 3.78-2.53 ppm, which are assigned to 6 protons of the methylene groups and α-CH_2 and CH_2-$(CH_2)_2$-CH_2. The signal at 1.62 ppm is due to the β-$(CH_2)_2$ of CH_2-$(CH_2)_2$-CH_2 [26].

The ^{13}C NMR spectrum of N,N′ -1,4-butylene bis(5-methylenesalicylidenamine) shows nineteen peaks as shown in Fig 4.17 which supported the proposad structure.

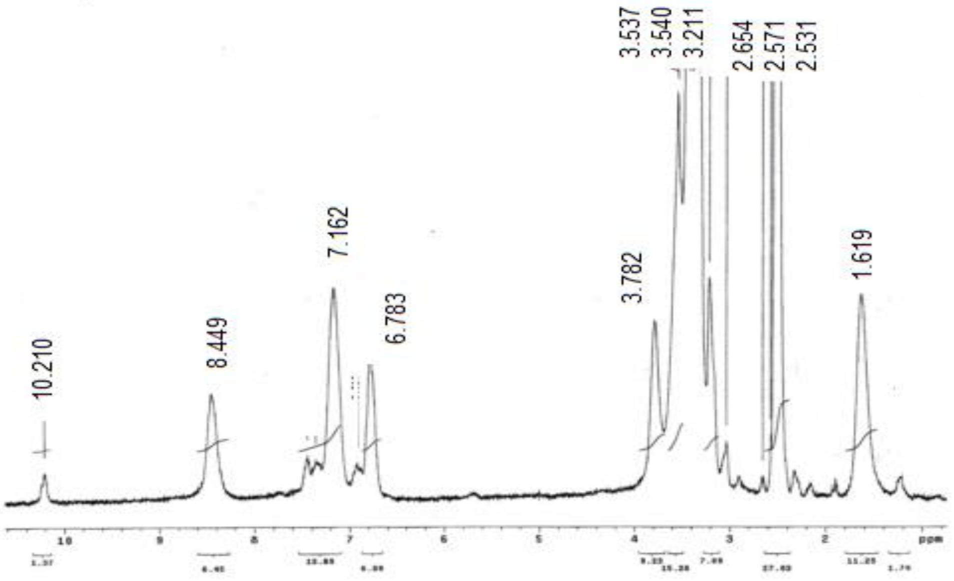


Figure 4. 16 ^{1}H NMR data of N,N′ -1,4-butylene bis(5-methylenesalicylidenamine) (L2)

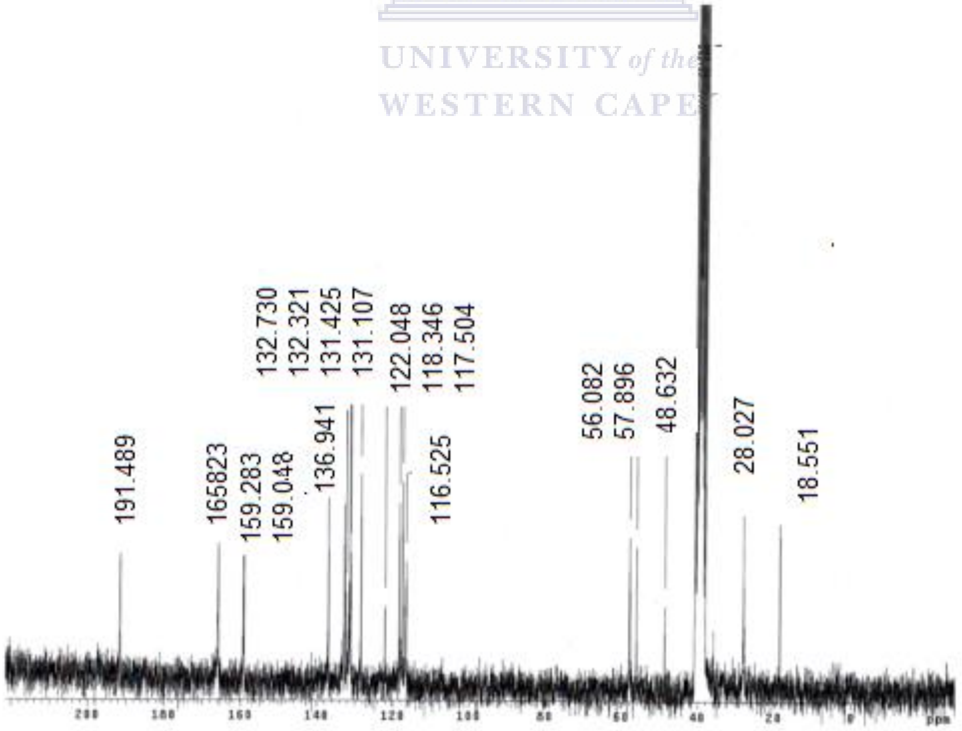
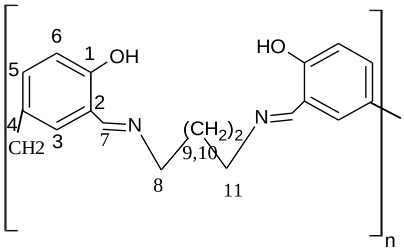


Figure 4. 17 ^{13}C NMR data of N,N′ -1,4-butylene bis(5-methylenesalicylidenamine) (L2)

Table 4. 6 ^{1}H NMR data of L2

Ligand structure	**Proton position**	**Chemical Shift (ppm)**	**No. of protons**	**Multiplicity**	**Assignment**
	1	10.21	2	d	OH
	7	8.45	2	d	CH=N
	3,5,6	7.4-6.4	6	M	Ar
	4	3.78	2	s	CH_2
	8,11	3.54	4	m	N-CH_2-C
L2	9,10	1.62	2	d	C-CH_2-C

4.2.3 UV/Vis electronic spectral studies

The electronic spectra of the ligand and its coordinated complexes were recorded in 10^{-3}M DMSO solution at room temperature.

4.2.3.1 Schiff base ligand (L2)

The polymeric ligand (Fig 4.18) exhibits two absorption bands in the regions of 260 and 330 nm. These bands are attributed to $\pi \rightarrow \pi^*$ transitions. The first band is due to transitions in the benzene ring and the second in the imino group [23].

4.2.3.1 Coordinated metal complexes

The electronic spectral data of the complexes also shows two bands due to the $\pi \rightarrow \pi^*$ transitions. The imino group $\pi \rightarrow \pi^*$ transition band is shifted to longer wavelength as a consequence of coordination to the metal, confirming the formation of Schiff base metal complexes[27]. VO and Cu(II) complexes exhibit new weak broad bands at 721 nm and 641 nm (Fig 4.19 and 4.20) attributed to d-d transition.

Table 4. 7 Electronic spectral data of the ligand (L2) and Cu(II), VO(IV) complexes.

Complex	**λ_m/nm (ε/M^{-1} cm^{-1})**
L2	260, 330
Cu(L2)	255, 308, 382, 641
VO(L2)	256, 328, 721, 721

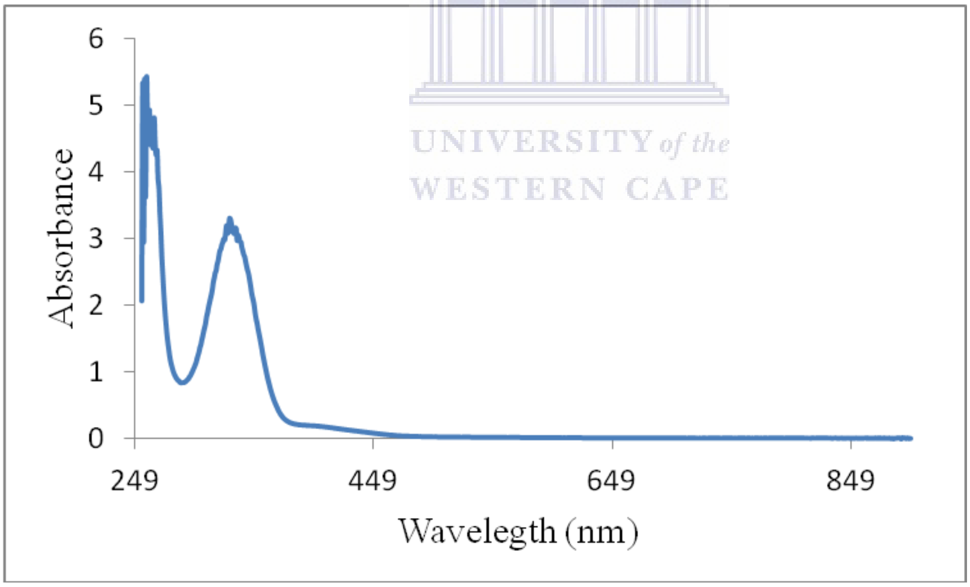


Figure 4. 18 Electronic spectra of N,N′ -1,4-butylene bis(5-methylenesalicylidenamine) (L2)

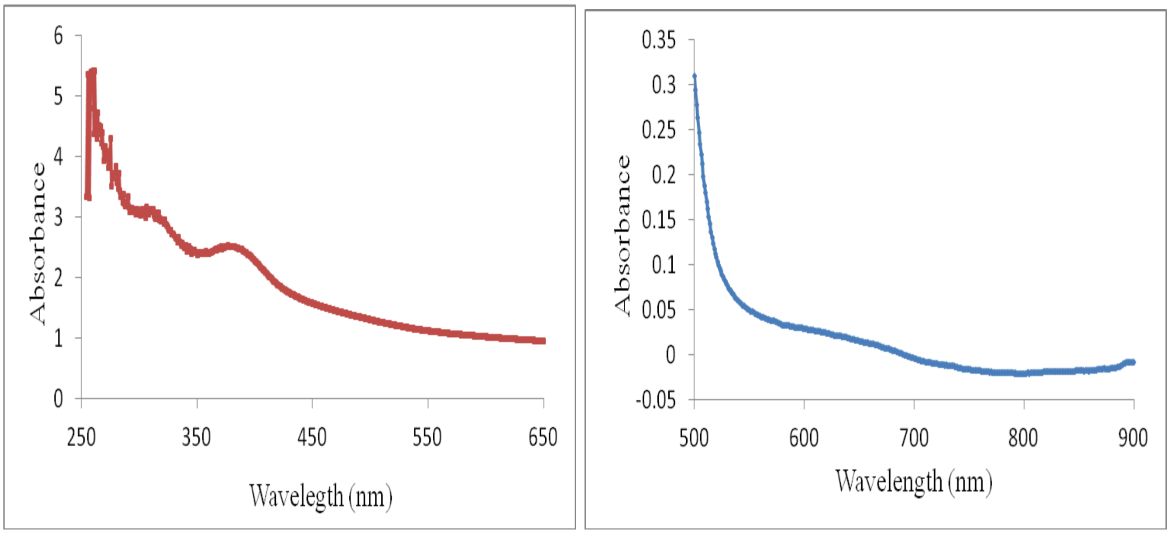


Figure 4. 19 Electronic spectra of copper catalyst Cu(II) in the UV (left) and Vis. (right) region.

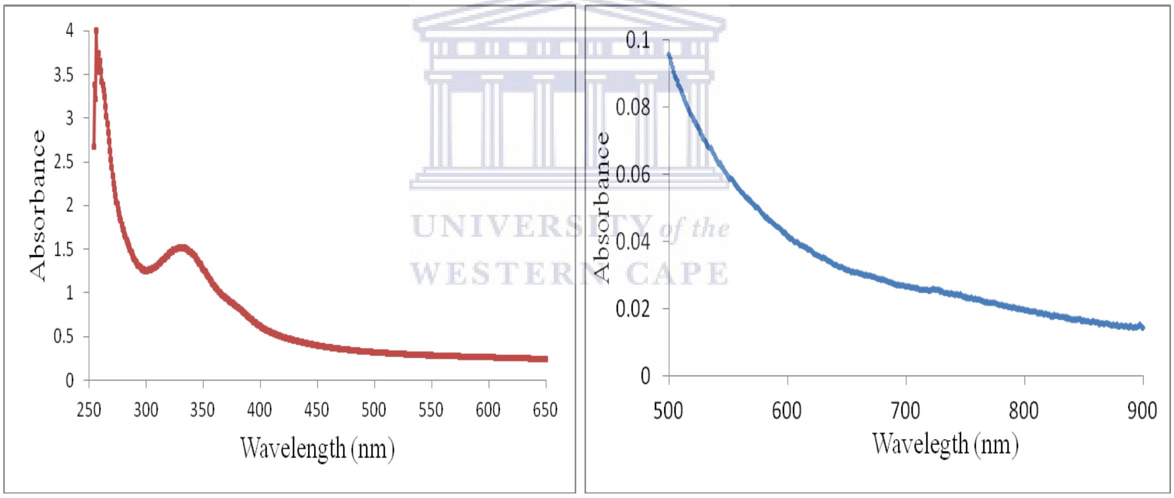


Figure 4. 20 Electronic spectra of vanadium catalyst VO(IV) in the UV (left) and Vis. (right) region.

4.2.4 Scanning electron microscopy of L2, Cu(II) and VO(IV) complexes

The SEM analysis was carried out to check the surface morphology of the ligand and complexes, and the micrographs obtained are given in Fig 4.21. The micrograph of the polymeric Schiff base ligand is given in Fig 4.21 (a & b), it can be seen as porous material with a flower-like appearance with a numerous territorial patches. These facts revealed the amorphous nature of the ligand [28]. On the other hand, the micrographs of copper and vanadium complexes (Fig 4.21 (C & d)) indicates the presence of well defined crystals, free from metal ions on the external surface [29].

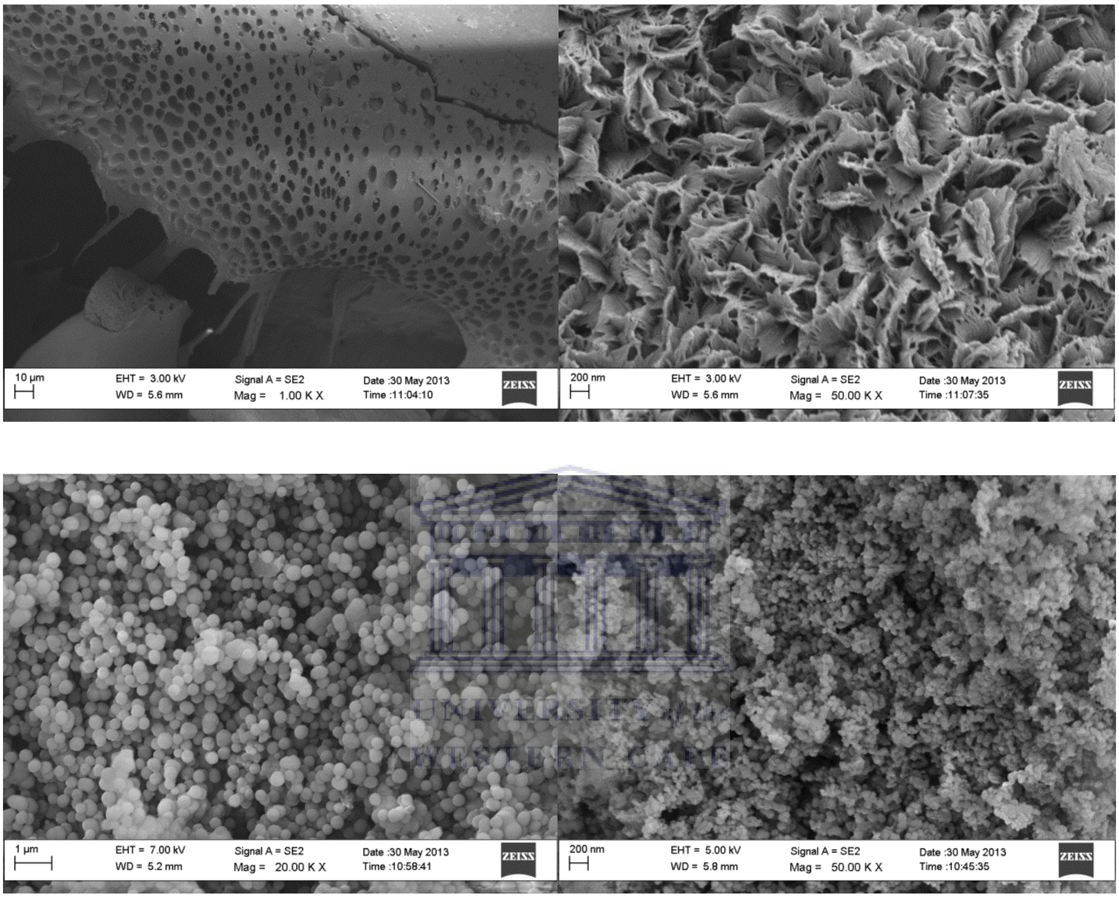


Figure 4. 21 Scanning electron micrographs of (a, b) ligand, (c) Cu(II) complex and (d) VO(IV) complex.

4.2.5 Magnetic susceptibility measurements for L2 Complexes

The room temperature magnetic moments (μ_{eff}) value of the copper(II) complex (L2) is 1.53 B.M. This value indicates a high degree of antiferromagnetic interaction between the metal centres. This further indicate a square planar geometry around each Cu(II) of the binuclear complexes, and a degree of association [30].

The observed moment (μ_{eff}) value of the oxovanadium(IV) complex at room temperature is 1.75 B.M. This value is normally expected for the spin-only moment of a d^1 system [31].

4.2.6 Thermal analyses of L2 and it is complexes

The TGA curve of L2 (Fig. 4.22) shows two step decomposition patterns and no water loss, which indicates proper drying of the sample. In the temperature range from 280-340 ^oC, 10% (ca 9.08) weight loss was observed due to the loss of CH_2-CH_2 from the aliphatic part. The second step shows 23% (ca. 22.5) weight loss from 360-560 ^oC temperature range, which may be due to the loss of ($CH=NCH_2CH_2$) and the polymeric linker (CH_2).

The copper complexes (Fig. 4.22) show weight loss of about 1.5% at 90 ^oC due to presence of water, and continues weight loss ~4% (ca .3.8) from 150-250 ^oC which may assigned to loss of CH_2 group indicating the breaking of the chelating polymeric repeating unit [24]. However, the major weight lost occured in the last step 27.6% (ca. 26.9%) from 300-570^oC which is due to the loss of the aliphatic parts of the ligand ($CH=N$-CH_2-CH_2-CH_2-CH_2-N).

The TGA curve of VO-complex shows three decomposition steps (Fig 4.22). The first step shows weight loss of ~1.5% at 90 ^oC due to the presence of water moisture. The second step shows 4% (ca. 4.2%) at 110-180 ^oC weight loss due to decomposition of oxygen molecules. The last step shows 25% (ca. 25.7) weight loss from 240-520 ^oC due to the loss of $C=N$-CH_2CH_2-CH_2-CH_2 and decomposition of CH_2 group [26].

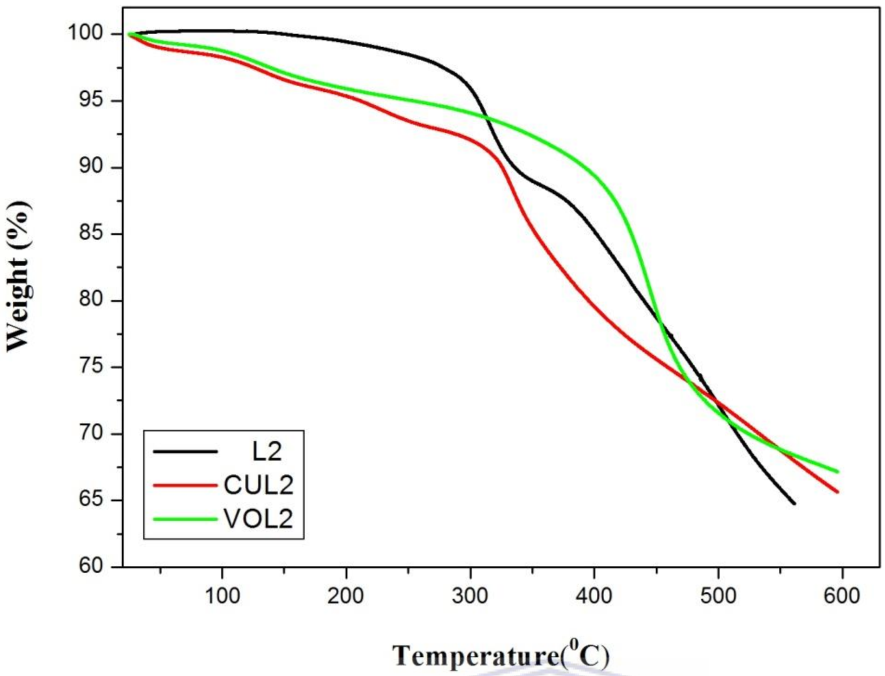


Figure 4. 22 The TGA thermograms of L2 and its complexes

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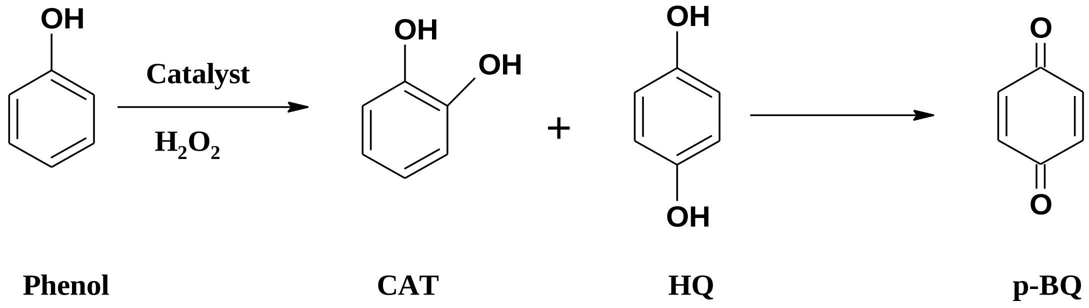
CHAPTER 5

This chapter deals with the catalytic activity of N,N′-1,2-phenylene bis(5-methylenesalicylidenamine) complexes and determination of the optimum reaction conditions for the oxidation of phenol, benzene, styrene and cyclohexene. These catalysts are discussed below.

5.1 Oxidation reactions

5.1.1 Hydroxylation of phenol

Catalytic oxidation of phenol gives catechol and hydroquinone as well as parabenzoquinone as minor product due to further oxidation of hydroquinone in some cases [1] as shown in Scheme 5.1. These products are important fine chemicals and are widely used as flavouring agents, perfumes, antioxidants, photographic developers, and pharmaceutical industries.



Scheme 5. 1 Oxidized products resulying from the hydroxylation of phenol

In order to achieve suitable reaction conditions for the maximum hydroxylation of phenol the following parameters were studied in detail, using the Cu (L1) catalyst:

5.1.1.1 Effect of H_2O_2: phenol molar ratio

5.1.1.2 Effect of volume of solvent

5.1.1.3 Effect of amount of catalyst

5.1.1.4 Effect of temperature

5.1.1.5 Effect of solvents

The percentages substrate conversion and product selectivity were calculated from data obtained from GC analysis using the following formulae:

$$\%\ \text{Conversion of substrate} = \frac{Amount\,of\ products}{Amount\ substrate + Amount\,of\ products} \times 100$$

$$\%\ \text{Selectivity of a product} = \frac{Amount\ of\ a\ product}{Total\,amount\ of\ products} \times 100$$

The quantifications were made on the basis of the relative peak area of the substrate and their corresponding products.

5.1.1.1 Effect of H_2O_2: Phenol molar ratio

The effect of H_2O_2: phenol molar ratios on the oxidation of phenol as a function of time is shown in Fig 5.1. Three different molar ratios of H_2O_2:phenol (0.3:1, 1:1and 2:1 mol) were studied, keeping the other parameters constant; phenol (2.34g) and catalyst (0.01g) in 3 ml MeCN at 70 °C . It was found that the percentage of phenol conversion increased from 8.4 to 26.9% after 5h reaction time, giving an increase of 18.5% when the molar ratios of H_2O_2 increases from 0.3 to 1 mol. This may be as a result of increasing hydroxyl radicals generated from H_2O_2, which can react with an excess of phenol to generate the intermediate [2]. However, doubling the H_2O_2 concentration increases the phenol conversion by only 9% and produces by-product, i.e. *p*-BQ which affects the selectivity of the main product. Hence, it was decided to use 1:1 molar ratio as it was more efficiencies efficient, reduces the oxidant consumption, and give high conversion and selectivity to the products.

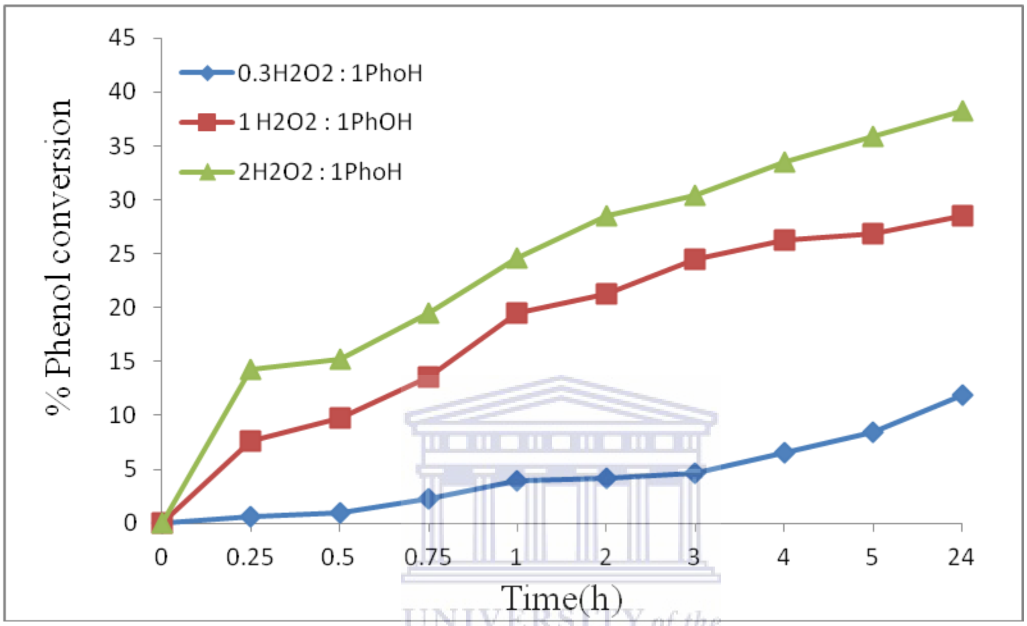


Figure 5. 1 % Phenol conversion using different H_2O_2: PhOH molar ratios

Table 5. 1 Effect of H_2O_2:PhOH molar ratio on phenol hydroxylation[a] and product selectivity

H_2O_2/ PhOH (molar ratio)	% Phenol conversion	% Product selectivity		
		CAT	HQ	*P*-BQ
0.3:1	8.4	100	-	-
1:1	26.9	73.3	26.7	-
2:1	35.9	66.0	30.2	3.8

[a] Reaction conditions : phenol 2.35 g, Cu(L1) 0.010 g, MeCN 3 ml, 70 °C, 5h

5.1.1.2 Effect of solvent volume

In order to study the influence of volume on the reaction medium, the reaction was performed in various volumes of solvent (CH_3CN), Fig 5.2. It was concluded that the volume of the solvent does not significantly affect the % phenol conversion. Using 3 ml of MeCN was found to be sufficient to perform the reaction as well as to give best phenol conversion. On the other hand, increasing the amount of solvent to 5 ml and 7 ml decreases the % conversion of phenol compared to 3 ml, which may be due to increased solvent volume, which will decrease reactant concentration in the reaction mixture which causes poor catalytic performance [3]. Hence, 3ml of (CH_3CN) was used as optimal reaction volume in all the experiments, as it reduces consumption of the solvent and gives best conversion.

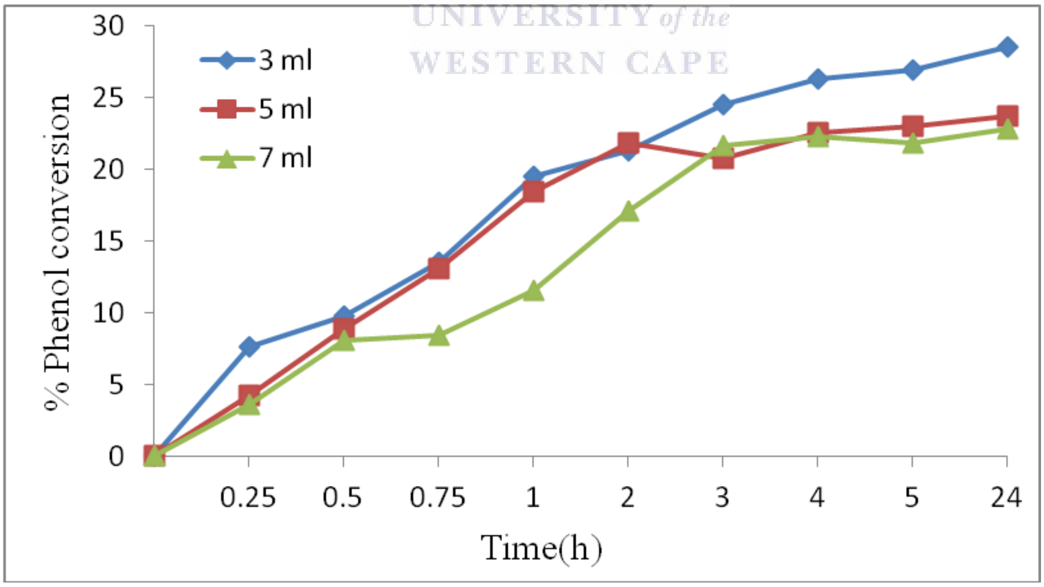


Figure 5. 2 % Phenol conversion using different volumes of the solvent CH_3CN.

Table 5. 2 Effect of volume of solvent on phenol conversion [a] and product selectivity

Volume (ml)	%Phenol Conversion	% Product Selectivity	
		CAT	HQ
3	26.9	73.3	26.7
5	23.0	64.8	35.2
7	21.8	87.0	13.0

[a] Reaction conditions : phenol 2.35 g, H_2O_2 2.83 g, 0.010 g Cu(L1), MeCN, 70 °C, 5h

5.1.1.3 Effect of amount of catalyst

The effect of the amount of catalyst on the rate of reaction is representated in Fig 5.3, i.e. three amounts (5, 10 and 20 mg) of the catalyst used for the fixed amount of substrate (2.35 g phenol) and oxidant (2.83 g H_2O_2) in 3 ml MeCN at 70 °C. The result shows the conversion of phenol using 10 mg reaches 24% after 3h from the time of reaction starting, while it took after 24h on using 5 mg. However, increasing the catalyst amount to 20 mg gave only 2% increase in the conversion. Hence, in order to reduce the amount of catalyst and obtain high conversion at the same time, 10 mg of catalyst was used in all experiments. The very slight increase in activity at higher amounts of catalyst may possibly be due to the availability of large surface area, which favours the dispersion of more active species. Therefore, accessibility of large numbers of reactant molecules to the catalyst is favoured [4].

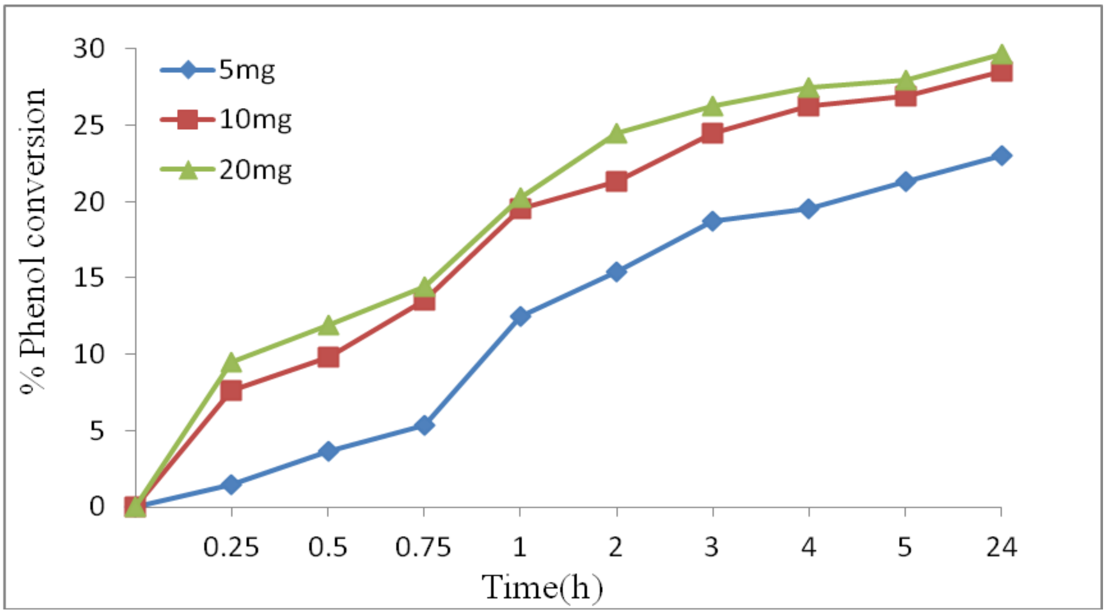


Figure 5. 3 % Phenol conversion with amount of catalyst

Table 5. 3 Effect of catalyst amount on % phenol conversion [a] and selectivity

Wt catalyst (g)	**% Phenol Conversion**	**% Product selectivity**	
		CAT	**HQ**
0.005	19.5	69.9	30.1
0.01	26.9	73.3	26.7
0.02	27.9	63.3	36.7

[a] Reaction conditions : phenol 2.35 g, 30 % H_2O_2 2.83 g, Cu(L1), MeCN 3 ml, 70 °C, 5h

5.1.1.4 Effect of temperature

The performance of the catalysts was investigated at three different temperatures, *viz.* 60, 70 and 80 °C. Selection of this particular temperature range was to avoid the enhanced H_2O decomposition [5] and further oxidation of dihydroxybenzene to quinones and then to tar formation [6]. Whilst keeping all the other parameters constant over a period of 24h (Fig 5.4), it was observed that phenol conversion increases as the temperature increases.

When the temperature increases from 60 to 70 °C the phenol conversion increases by 8%. However further increase of temperature gives only a 2% difference at 80 °C. For this reason it was decided that the best temperature to work at was 70°C.

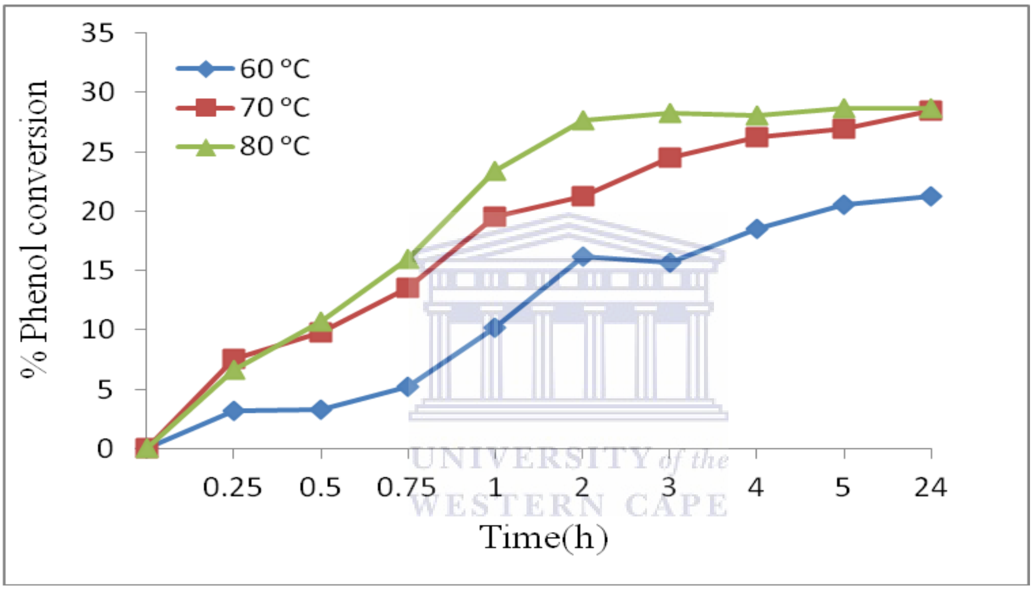


Figure 5. 4 Effect of reaction temperature on % phenol conversion over time

Table 5. 4 Effect of reaction temperature on phenol conversion [a] and product selectivity.

Reaction Temperature (°C)	% Phenol Conversion	% Product selectivity	
		CAT	HQ
60	18.5	95.8	4.2
70	26.9	73.3	26.7
80	28.6	63.4	36.7

[a] Reaction conditions : Phenol 2.35 g, H_2O_2 2.83 g, Cu(L1), 0.010 g, MeCN 3 ml, 5h

5.1.1.5 Effect of solvents

It is known that solvents have an important influence on reactions, i.e. on yields, product formation and reaction kinetics [7]. The influence of solvent on the catalytic activity of the hydroxylation of phenol was investigated using three different solvents ranging from polar, MeCN and ethanol to non-polar, DCM, while keeping all the other reaction parameters constant. The % conversion and the selectivity towords expected products of phenol oxidation unsing three solvents are present in Table 5.5.

DCM and ethanol shows moderate activity for hydroxylation of phenol, i.e. ~12% and ~16% respectively. The MeCN shows the highest (~27%) conversion within 5h, which could be explained as MeCN being a better coordinating solvent, hence, forming a five-coordinated complex with MeCN. The trend for the solvent type for oxidation efficiency of phenol under these experimental conditions, was MeCN> DCM> EtOH.

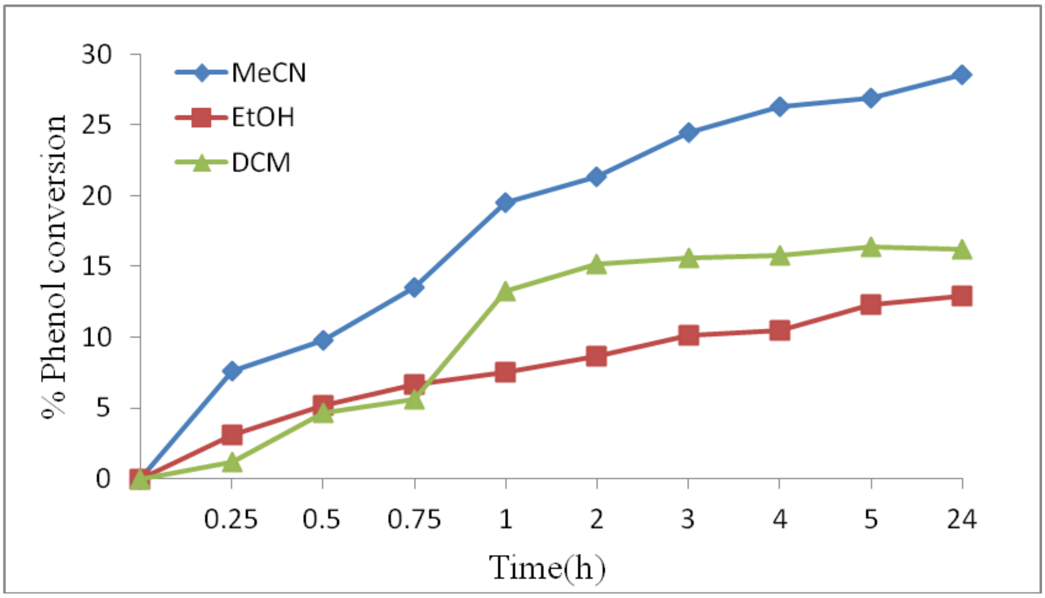


Figure 5. 5 Effect of different solvents on the % phenol conversion

Table 5. 5 Effect of solvents on phenol hydroxylation [a], and product selectivity

Solvent	% Phenol Conversion	% Product selectivity	
		CAT	HQ
DCM	16.4	95.8	4.2
MeCN	26.9	73.3	26.7
EtOH	12.3	63.4	36.7

[a] Reaction conditions: phenol 2.35 g, 30 % H_2O_2 2.83 g, 0.010 g Cu(L1), CH_3CN 3 ml, 70°C, 5h

5.1.2 Comparison studies between Cu (L1) and VO (L1)

The catalytic activity of the copper and vanadium catalysts towards phenol oxidation under optimized conditions (phenol (0.025 mol), H_2O_2: phenol molar ratio is 1:1, catalyst (0.01g), CH_3CN (3 ml) and temperature 70 °C) are shown in Fig 5.6 and Table 5.6.

The progress of the reaction was monitored by gas chromatography. The two expected products, namely catechol and hydroquinone, were observed along with phenol during the reaction > 99% [8]. These are the expected products due to the directing effect of the phenolic OH group. Both these two coordination polymer catalysts are more selective for catechol formation. It was observed that the Cu-complex displayed a slightly higher activity than the vanadium complex with maximum conversions of 26.2 and 20.15% after 4h, respectively. However, increasing the reaction time from 5h to 24h, only negligible change in % phenol conversion and product selectivity was observed. On the other hand a blank reaction carried out under the same optimum conditions showed no reactivity.

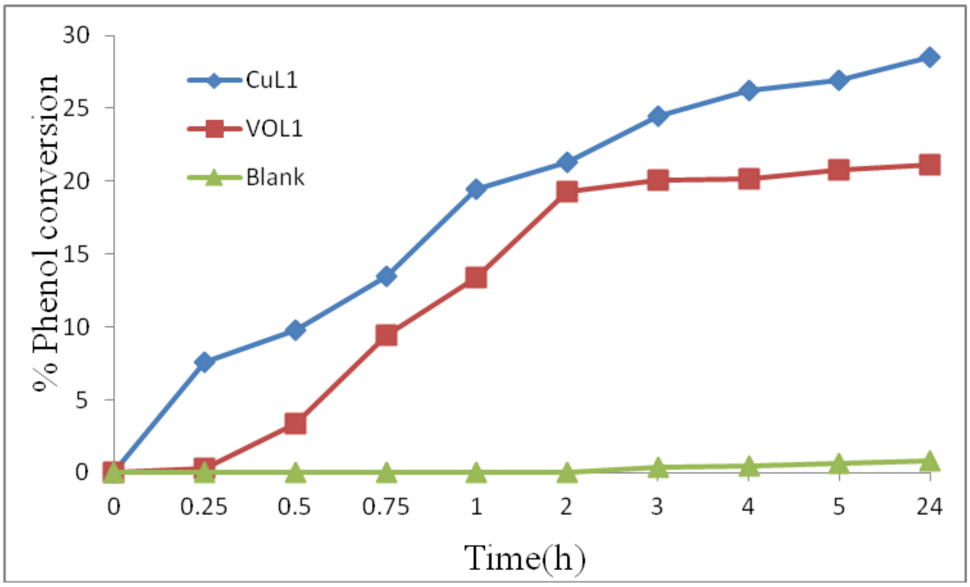


Figure 5. 6 % Phenol conversion for catalysts over time

Table 5. 6 % Phenol conversion [a] and product selectivity

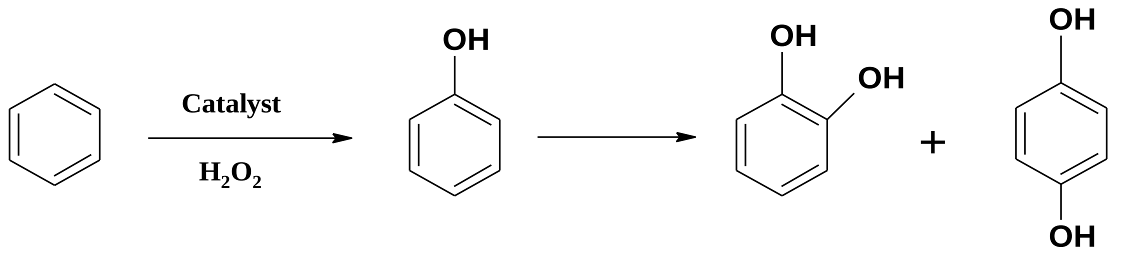
Catalyst	% phenol conversion	% Product Selectivity	
		CAT	HQ
Cu(L1)	26.9	73.3	26.7
VO(L1)	20.8	75.1	42.9
Blank	0.5	94.2	5.8

[a] Reaction conditions : Phenol 2.35 g, H_2O_2 2.83 g, 0.010 g catalyst, CH_3CN 3 ml, 70 °C, 5h

5.1.3 Hydroxylation of benzene

Direct oxidation of benzene to phenol is of great interest not only for its industrial importance, but also for its scientific value. The lack of studies on oxidation of benzene is largely due to the fact that activation of the C–H bond in benzene is difficult due to its resonance stability [9,10]. Nonetheless, oxidation of benzene produced phenols and benzoquinones [11].

Hydroxylation of benzene was carried out under the same optimized conditions for phenol. The oxidation products for this reaction are presented in Scheme 5.2.



Benzene Phenol Catechol Hydroquinone

Scheme 5. 2 Oxidized products for the oxidation of benzene

The results point out that conversion of benzene increased with reaction time for both catalysts and attained a steady state after ~5 h. In case of the VO-based catalyst, benzene conversion was initially (2h) low, but improved with time and reached the steady state at ~5h, thereafter, only a very slow conversion was observed up to 24 h, which may be due to inefficient product desorption from the catalyst surface rather than deactivation of the catalyst [12,13]. The Cu-based catalyst shows better performance (~7.8%) than VO-based catalyst (~2.01%) after 5h, under reaction conditions benzene: H_2O_2 (1:1 molar ratio), catalyst (10 mg); solvent, CH_3CN (3 ml) at 70 °C as shown in Table 5.7. Both catalysts showed 100% selectivity for producing phenol, without any by-product being detected by GC. The selectivity towards phenol formation remained unchanged over a period of 24 h.

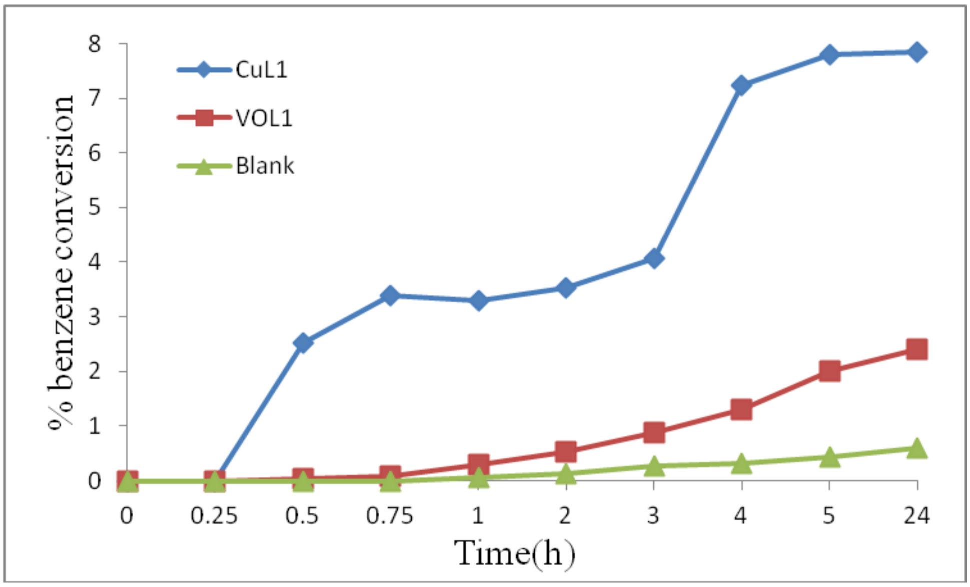


Figure 5. 7 Catalytic benzene conversion over time.

Table 5. 7 % Benzene conversion and product selectivity [a]

Catalyst	**% Benzene Conversion**	**% Product selectivity**
		PhOH
Cu(L1)	7.8	100
VO(L1)	2.0	100
Blank	0.4	100

[a] Reaction conditions : benzene 1.93 g, H_2O_2 2.83 g, catalyst 0.010 g, CH_3CN 3 ml, 70 °C, 5h

5.1.4 Oxidation of styrene

Oxidation of styrene using hydrogen peroxide (H_2O_2) as an oxidant, can lead to various reaction products, depending on the catalyst and reaction conditions. These products are styrene oxide, benzaldehyde, benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol as major products and a small amount of other unidentified products were also obtained (Scheme 5.3) [12,13].

Styrene oxidation with oxovanadium(IV) and copper(II) polymeric complexes, using H_2O_2 as oxidant was carried out in MeCN, and gave five products; styrene oxide, benzaldehyde, benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol. These products were observed under the reaction conditions with a mass balance of about ~93% and ~98% for Cu(II) and VO(IV) catalysts respectively, as shown in Table 5.8. The other unidentified products which formed could be due to further oxidation of these five products [14].

The blank reaction shows poor activity towards styrene conversion under similar reaction conditions, which indicates that the use of the catalyst is essential for the reaction. The catalytic activity of copper catalyst was gradually increased by ~3% untill reached steady state at 5h. However, increasing the reaction time to 24h shows insignificant change. The results also clearly indicate that oxovanadium complex efficiently catalyse styrene, giving 26 % conversion after 5h under the similar reaction conditions.

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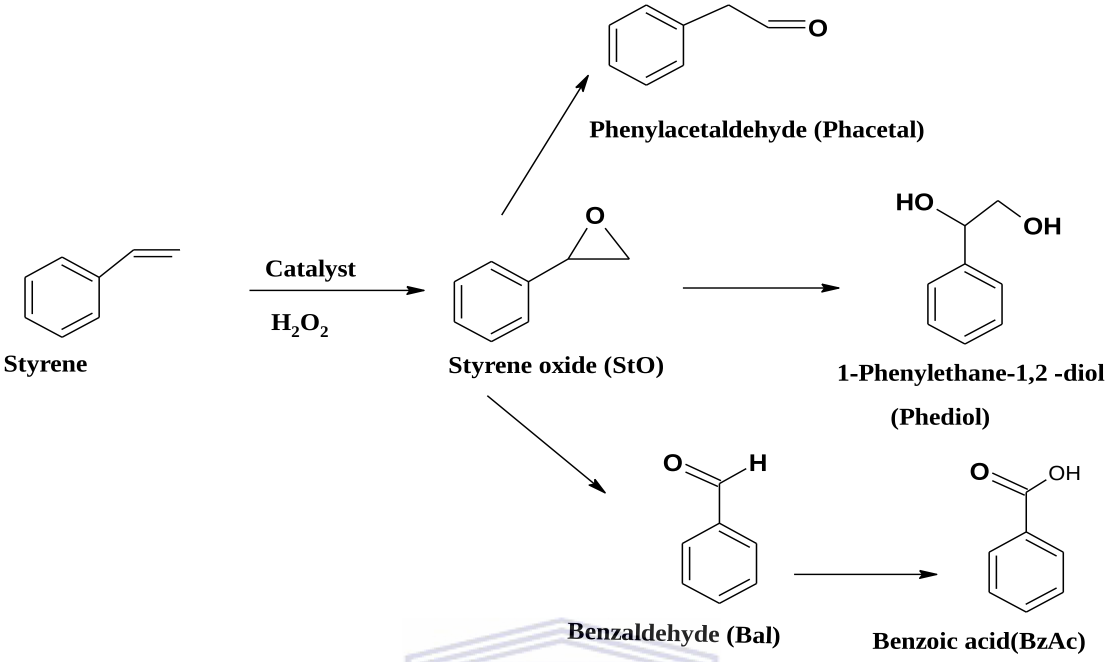


Scheme 5. 3 Oxidized products from the oxidation of styrene

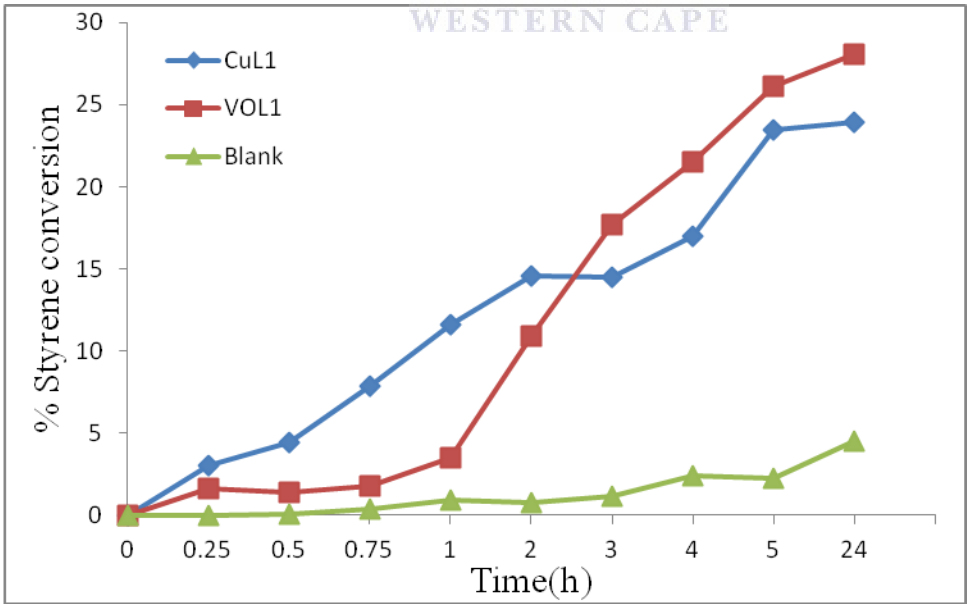


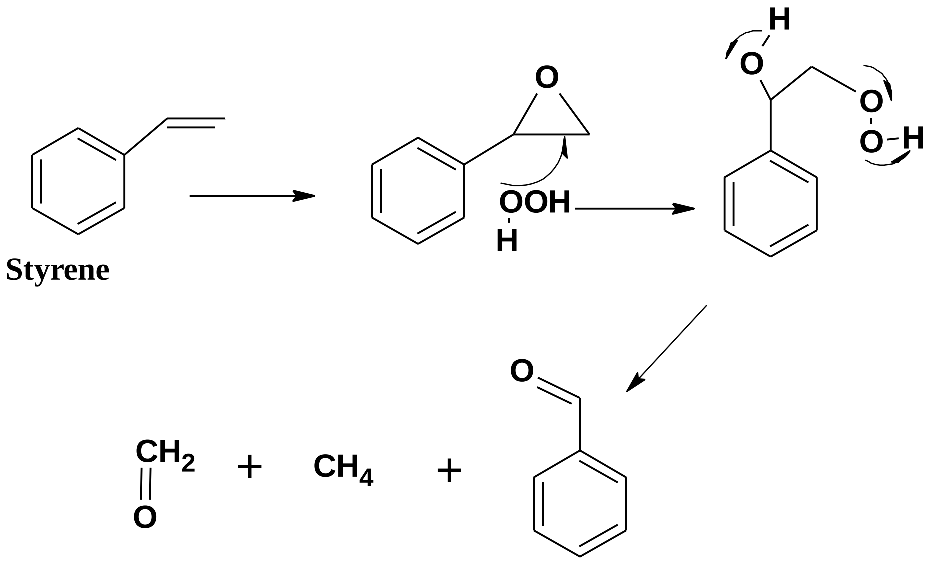
Figure 5. 8 Calalytic styrene conversion over time

Table 5. 8 Styrene conversion[a] and product selectivity

Catalysts	**% Styrene conversion**	**% Product selectivity**					
		Bal	**Phacetal**	**Sto**	**Phediol**	**BzAc**	**Other**
Cu(L1)	23.5	71.9	2.5	3.1	8.3	8.8	5.4
VO(L1)	26.1	70.9	3.0	4.5	5.9	13.8	2.0
Blank	2.2	89.1	3.1	4.0	3.6	-	0.2

[a] Reaction conditions: Styrene 2.60 g, H_2O_2 2.83 g, 0.010 g catalyst, CH_3CN 3ml, 70 °C, 5h

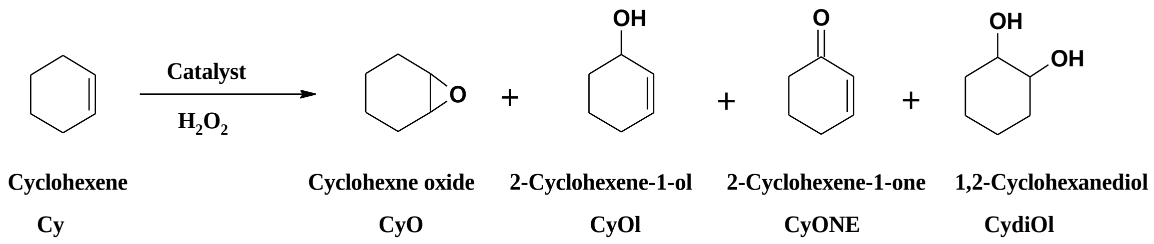
Table 5.8 shows that the benzelaldehyde product was in highest yield obtained (70-72)%. This is possibly due to the conversion of most of the styrene oxide (formed in the first step) to benzaldehyde, which occurred *via* nucleophilic attack of H_2O_2 on styrene oxide, followed by the cleavage of the intermediate hydroperoxystyrene (Scheme 5.4) [15]. Formation of benzaldehyde may also occur through direct oxidative cleavage of the styrene side chain double bond *via* the radical reaction mechanism [16]. The comparable yields of all the other products are also in low quantities. The formation of phenylacetaldehyde is very low for all catalysts and its formation possibly produces via isomerization of styrene oxide [17]. The selectivity of all styrene oxidation product for both complexes has a similar trend, as follows: benzaldehyde > benzoic acid > 1-phenylethane-1, 2-diol > styrene oxide > phenylacetaldehyde.



Scheme 5. 4 Mechanism for the formation of benzaldehyde from styrene oxide

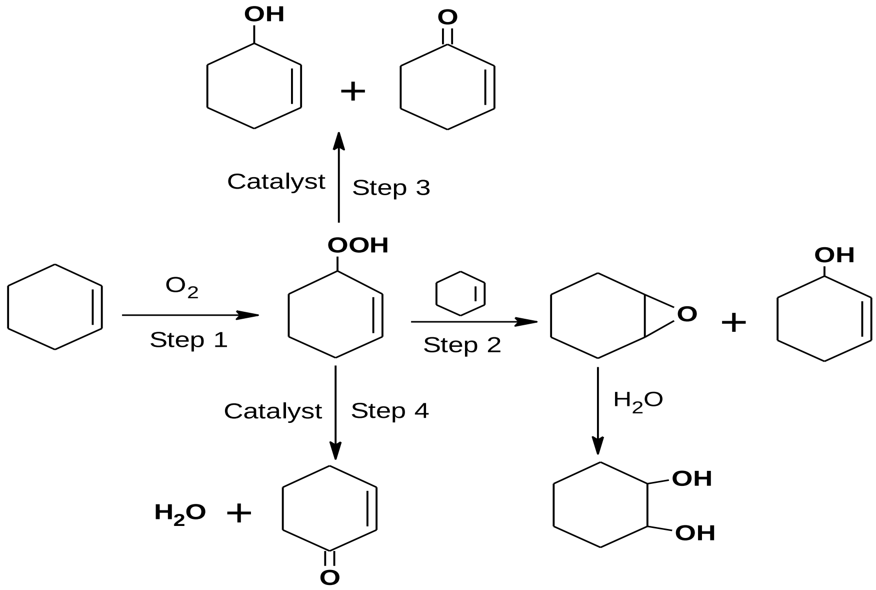
5.1.5 Oxidation of cyclohexene

Oxidation of cyclohexene generally yields various products, such as cyclohexene oxide, cyclohexene-1-ol, 2-cyclohexene-1-one and 1,2-cyclohexanediol as main products (Scheme 5.5) [18]. However, the selectivity towards these products depends on various parameters, like reaction conditions, central metal ion, solvent, oxidant agent, nature of the catalyst, etc. A blank reaction experiment was carried out without catalyst under identical conditions; H_2O_2 (1:1 molar ratio), catalyst (10 mg); solvent, CH_3CN (3ml) at 70 °C. Only a very low amount of substrate was converted in the blank reaction (below 5%), suggesting that our complex is functioning as a catalyst for the cyclohexene oxidation reaction [19]. Allylic oxidation products such as cyclohexenol and cyclohexenone were formed as the major products, along with cyclohexene oxide as the minor product [20]. Major formation of cyclohexene oxide may be due to the oxidation reaction occurring mainly at the double bond [21].



Scheme 5. 5 Oxidized products for the oxidation of cyclohexene

Literature reports [22] indicated that the oxidation of cyclohexene with molecular oxygen forms 2-cyclohexene1-hydroperoxide, as shown in Step 1, Scheme 5.6. As 2-cyclohexene-1-hydroperoxide is not stable, it was converted to 2-cyclohexene-1-ol and 1,2-cyclohexenediol throughout Step 2. However in the presence of catalyst, 2-cyclohexene-1-hydroperoxide was converted to 2-cyclohexene-1-ol and 2-cyclohexene-1-one at Step 3, and to 2-cyclohexene-1-one and water at Step 4. The conversion of cyclohexene is controlled by the rate of Step 1 in Scheme 6 and selectivity for cyclohexene oxide and 1,2-cyclohexanediol is controlled by the ratio of the rate at Step 2 to the rates at Steps 3 and 4 [23,9].



Scheme 5. 6 Oxidation of cyclohexene

The catalytic activities of Cu and VO complexes, as well as the blank reaction are shown in Fig 5.9. It is clear from the graphs that the blank reaction gives very poor activity, which indicates the importance use of the catalyst. The catalytic activity under similar reaction conditions for copper and oxovanadium catalysts were increased gradually untill reached steady state at 5h, with a maximum conversion of 68% and 92% respectively. However, increasing the reaction time to 24h showed insignificant improvement.

The selectivity for the different reaction products for both catalysts follows the order: cyclohexene oxide > cyclohexene-1-ol > 2-cyclohexene-1-one > cyclohexane-1,2-diol.

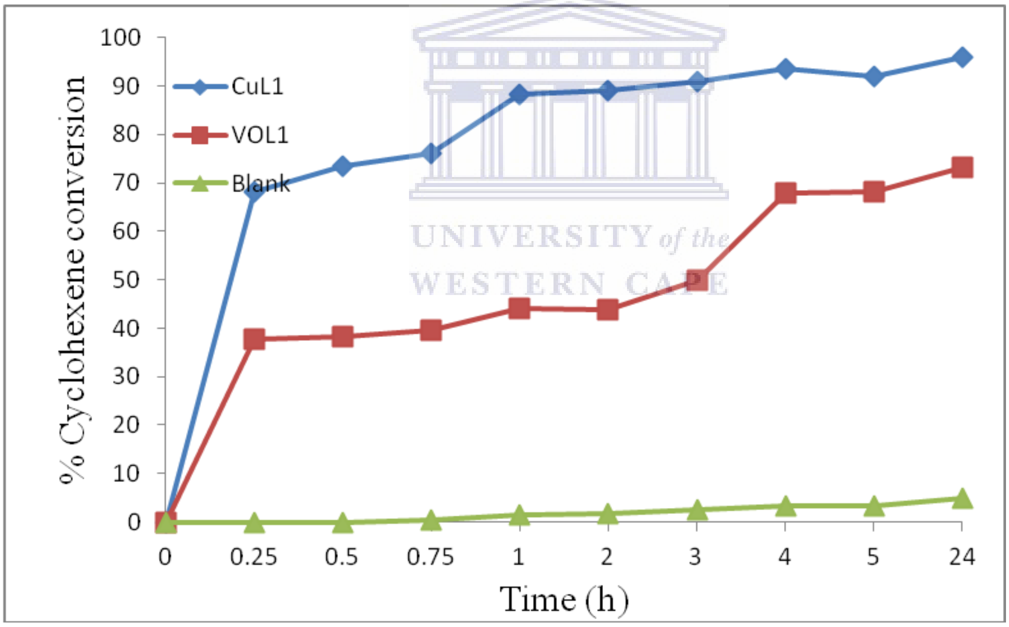


Figure 5. 9 Cyclohexene conversion for catalysts over time

Table 5. 9 Cyclohexene conversion [a] and product selectivity

Catalyst	**% Cyclohexene conversion**	**% Product selectivity**				
		CyO	**CyOl**	**CyONE**	**CydiOl**	**Other**
Cu(L1)	92.1	50.3	24.8	18.4	4.0	2.5
VO(L1)	68.3	45.6	27.3	22.7	2.6	1.8
Blank	4.5	42.2	34.4	17.8	5.7	-

[a] Reaction conditions : Cyclohexene 2.06 g, H_2O_2 2.83 g, catalyst 0.010 g, CH_3CN 3 ml, 70°C, 5h

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CHAPTER 6

6. Catalytic activity studies of Cu(II) and VO(IV) (L2) catalysts for oxidation reactions

6.1 Introduction

Schiff base transition metal complexes, in particular N_2O_2 Schiff base complexes, have been extensively studied because of their potential use as catalysts in a wide range of oxidation reactions [1-4]. However, not all complexes are catalytically active. The formation of octahedral complexes with no vacant coordination sites or absence of labile ligands could be a possible reason. One of the attractive features of the N_2O_2 Schiff base complexes is that it is possible to tune the electronic and steric properties of the complexes by making alterations at the Schiff base portion. The introduction of bulky substituents near coordination sites may lead to low symmetry complexes and enhanced catalytic properties. Furthermore, by suitable incorporation of donating/accepting groups, it may be possible to tune the electronic environment around the metal centre and alter the catalytic properties. A variety of Schiff base complexes of copper(II) and oxovanadium(IV) ion have been shown to catalyze a wide range of oxidation reactions [5-11].

Oxovanadium(IV) ion can readily coordinate four, five and six donor atoms to form VOL4, VOL5 and VOL6-type complexes. Most of the oxovanadium(IV) complexes with N_2O_2 Schiff base ligands are reported to have mononuclear structures having square pyramidal geometries whereas very few have a binuclear structure [12-14].

In this study, new copper(II) and oxovanadium(IV) coordination metal complexes of tetradentate ligands were synthesised by condensation of 1,4-diaminebutane with salicylaldehyde. The catalytic activities of these complexes during oxidation of phenol, benzene, styrene and cyclohexene were investigated below using H_2O_2 as oxidant [15].

6.2 Oxidation reactions

6.2.1 Hydroxylation of phenol

Catalytic hydroxylation of phenol to catechol and hydroquinone using environmentally friendly oxidants such as dioxygen, hydrogen peroxide and alkyl hydroperoxide is an active area of research, especially in the fine chemicals industry [16]. Among these oxidants, hydrogen peroxide is easy to handle and ecofriendly, as it produces only water as the by-product [17]. Over the past few decades, numerous reports appeared on the hydroxylation of phenol with hydrogen peroxide as oxidant [18-21].

Fig 6.1 shows the comparison of the activity of the Cu(II) and VO(IV) complexes and the blank reaction towards the hydroxylation of phenol. Both catalysis shows high phenol conversion, 27.5% with Cu(II) and 26% with VO(IV) after 5h while, the blank reaction showed no activity. Increasing the reaction time to 24h showed no significant change on the phenol conversion, as well as the catechol and hydroquinone selectivity.

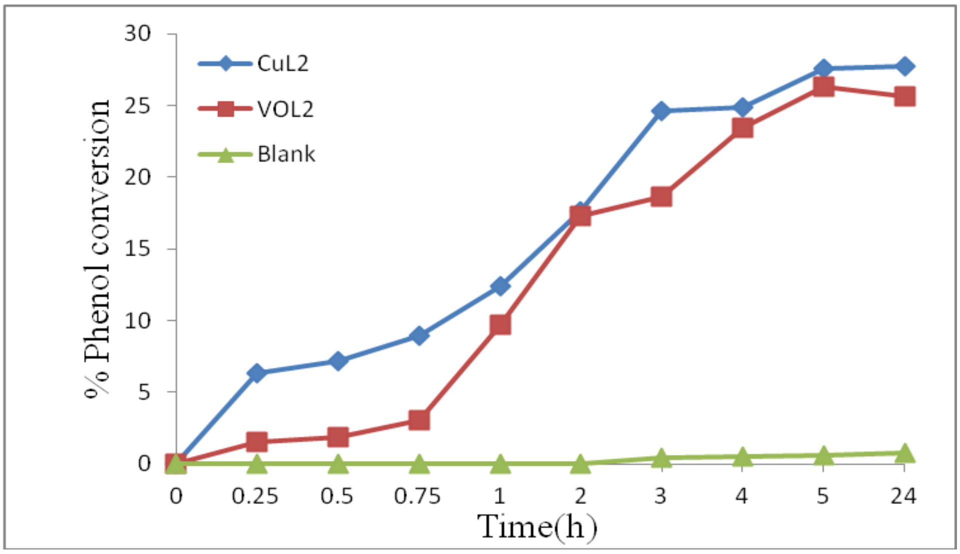

Figure 6. 1 Catalytic phenol conversion over time

Table 6. 1 The % phenol conversion [a] and product selectivity

Catalyst	% phenol conversion	% Product Selectivity	
		CAT	HQ
Cu(L2)	27.5	64.6	35.4
VO(L2)	26.3	57.6	42.4
Blank	0.5	94.2	5.8

[a] Reaction conditions : phenol 2.35 g, 30 % H_2O_2 2.83 g, catalyst 0.010 g, MeCN 3 ml, 70°C, 5h

6.2.2 Hydroxylation of benzene

Hydroxylation of benzene is usually carried out in three steps, to give low phenol yield and other products such as acetone and α-methylstyrene by using the cumene process. This process is a highly energy-consuming three step reaction and also produce by product. One-step oxidation of benzene to phenol through direct hydroxylation of an aromatic ring by the green chemistry oxidant would be a good option for the chemical industry, as it is more energy efficient and produce only phenol.

The catalytic activity of benzene hydroxylation (Fig 6.2 & Table 6.2) shows 100% selectivity toward phenol as well as benzene conversion. The blank reaction shows poor activity toward benzene conversion, which indicates that the use of catalyst is important in this reaction. Copper catalyst shows high activity, ~11% at 5h, compared to oxovandium catalyst, ~5 % over the same time. Both catalysts show low conversion at the start of the reaction, which a graduall increase was observed untill reaches almost steady state at 5h. However, increasing the reaction time to 24h shows only a slight increase in conversion.

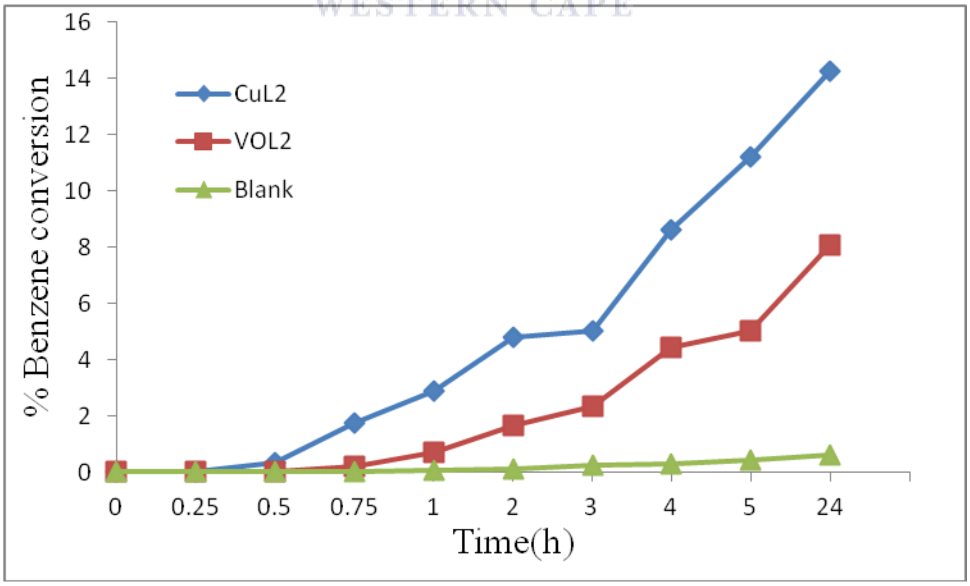

Figure 6. 2 Catalytic benzene conversion over time

Table 6. 2 The % benzene conversion and product selectivity [a]

Catalyst	% Benzene Conversion	% Product selectivity
		PhOH
Cu(L2)	11.2	100
VO(L2)	5.0	100
Blank	0.4	100

[a] Reaction conditions : benzene 2.35 g, 30 % H_2O_2 2.83 g, catalyst 0.010 g, MeCN 3ml, 70 °C, 5h

6.2.3 Oxidation of styrene

The catalytic oxidation of styrene using hydrogen peroxide (H_2O_2) as an oxidant can lead to various reaction products as shown in chapter 5. The oxovanadium coordination polymers complexes display low activity at the beginning of the reaction, but increased over time and achieved maximum conversion, around 33% at ~5h. On the other hand, the catalytic activity of copper catalyst was moderate, increased gradually, and reach the steady state of 25% conversion at ~5h. Leaving the reaction time to 24h did not change conversion, as shown in Fig 6.3.

Selectivity towards the products, using Cu(II) and VO(IV) catalytic systems, are follows the trend, in this order: benzaldehyde >> styrene oxide > 1-phenylethane-1, 2-diol > phenylacetaldehyde.

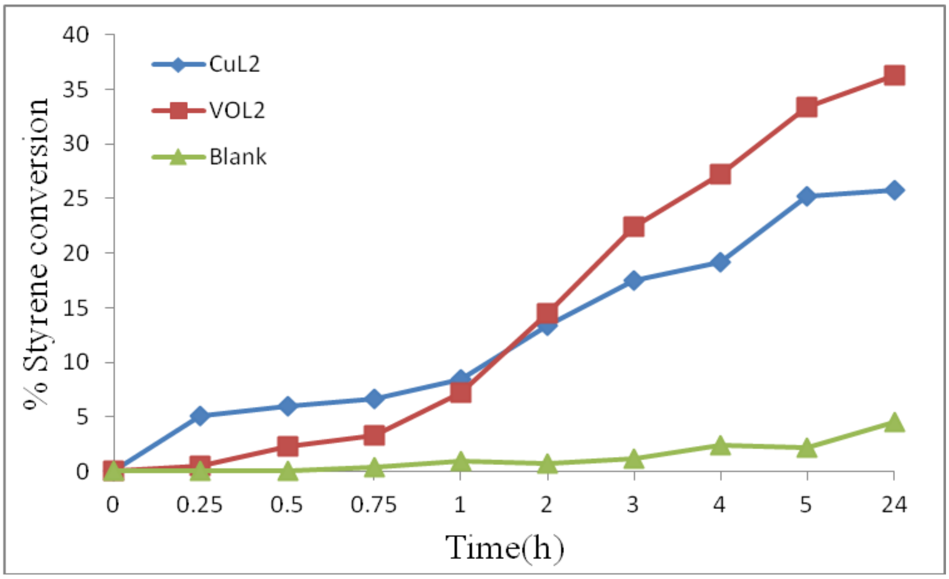

Figure 6. 3 Catalytic styrene conversion over time

Table 6. 3 The % styrene conversion [a] and product selectivity

Catalysts	**% Styrene conversion**	**% Product selectivity**					
		Bal	**Phacetal**	**Sto**	**Phediol**	**BzAc**	**Other**
Cu(L2)	25.2	75.3	3.7	6.3	7.5	4.6	2.7
VO(L2)	33.4	78.1	2.6	3.5	8.7	5.7	1.5
Blank	2.2	89.1	3.1	4.0	3.6	-	0.2

[a] Reaction conditions : styrene 2.60 g, H_2O_2 2.83 g, 0.010 g catalyst, MeCN 3 ml, 70 °C, 5h

6.2.4 Oxidation of cyclohexene

The catalytic activity of cyclohexene as a function of time, with copper and oxovanadium catalysts under similar reaction conditions as for phenol, are presented in (Fig 6.4) and Table 6.4, illustrating the % conversion and selectivity after 6h reaction time.

Under these reaction conditions, copper and oxovanadium catalysts display high activity compared to the blank reaction and respectively gave 85% and 73% conversion after 5h reaction time. The catalytic activities of both catalysts were gradually increased over time. The copper catalyst shows slightly higher activity toward cyclohexene conversion.

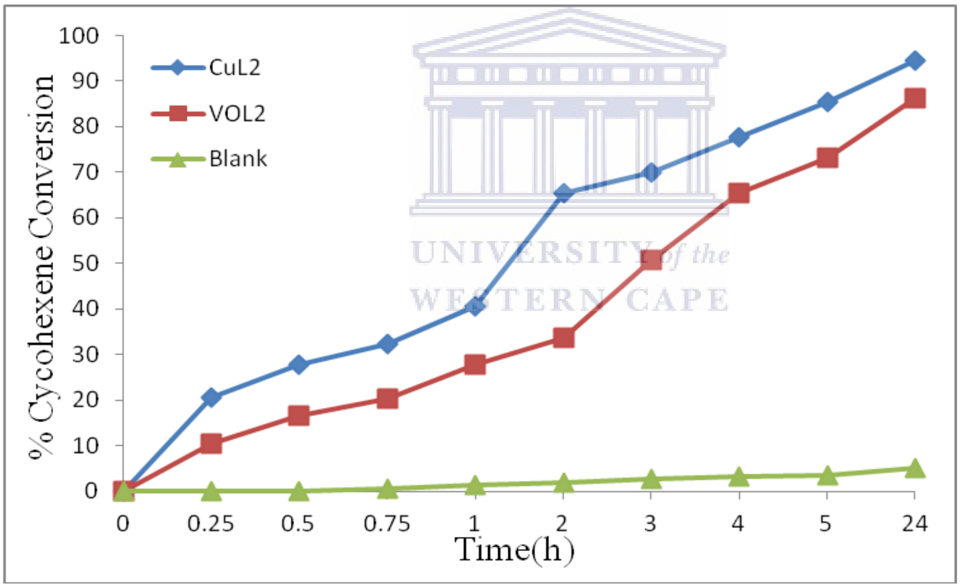

Figure 6. 4 Catalytic cyclohexene conversion over time

The selectivity for the different reaction products from copper and oxovanadium catalysts follows the order: cyclohexene-1-ol > cyclohexene oxide > 2-cyclohexene-1-one > cyclohexane-1,2-diol. Major formation of the allylic oxidation products indicates preferential attack of the activated C−H bond over the C=C bond [22].

Table 6. 4 The % cyclohexene conversion [a] and product selectivity

Catalyst	**% Cyclohexene conversion**	**% Product selectivity**				
		CyO	**CyOl**	**CyONE**	**CydiOl**	**Other**
Cu(L2)	85.3	26.9	34.5	27.7	8.6	2.3
VO(L2)	73.2	24.8	37.1	26.5	7.4	4.3
Blank	4.5	42.2	34.4	17.8	5.7	-

[a] Reaction conditions : Cyclohexene 2.06 g, H_2O_2 2.83 g, catalyst 0.010 g, MeCN 3 ml, 70°C, 5h

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CHAPTER 7

7. Conclusion and future work

7.1 Conclusion

The synthesis of new Cu(II) and VO(IV) coordination metal complexes of tetradentate ligands formed by condensation of o-phenylenediamine and 1,4-diaminobutane with salicylaldehyde have been prepared succssfuly.

Various physico-chemical techniques such as Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR), Ultraviolet-Visible spectroscopy (UV-Vis), and thermogravimetric Analysis (TGA) were used to confirm the structures of these synthesised complexes.

These coordinated polymer complexes were assessed as catalysts for liquid phase hydroxylation of phenol, benzene, styrene and cyclohexene, using a green oxidant (H_2O_2).

The exprimental parameters (molar ratio of substrate to oxident, temperature, solvents, and volume of solvent and of amount of catalyst) have been optimized for hydroxylation of phenol. Hence, the molar ratio of substrate to oxidant is 1:1, temperature 70 °C, solvent type MeCN, volume of solvent 3 ml and the amount of catalyst 10 mg were identified to be most suitable conditions for the oxidation reactions.

The catalytic potential towards the oxidation of phenol, benzene, cyclohexene and styrene using the Cu-based catalysts are higher than the VO-based catalysts for both ligands (L1and L2). The percentage conversion of phenol, benzene, styrene and cyclohexene are (~27- 20.8%), (7.8-2.0%), (24-26.1%) and (92.1-68.3%) for Cu and VO based catalysts respectively.

7.2 Future work and recommendations

In future, investigations of the catalytic activity of these complexes toward other oxidation reactions such as benzoin and methyl phenyl sulphide oxidation may be done.

The study may also be extended to using different metals to study the effect of the active sites on catalytic activity.