TRANSITION METAL COMPLEXES AS CATALYSTS FOR ALCOHOL OXIDATION

Thesis

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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DECLARATION

by the Ph.D. Research Scholar

I hereby ***declare*** that the Research Thesis entitled "**Transition metal complexes as catalysts for alcohol oxidation**" which is being submitted to the ***National Institute of Technology Karnataka, Surathkal*** in partial fulfilment of the requirements for the award of the Degree of ***Doctor of Philosophy*** in ***Chemistry*** is a ***bonafide report of the research work carried out by me.*** The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

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CERTIFICATE

This is to *certify* that the Research Thesis entitled "**Transition metal complexes as catalysts for alcohol oxidation**" submitted by **Sandya Rani** (Register Number: **081048CY08P05**) as the record of the research work carried out by her, is *accepted as the Research Thesis submission* in partial fulfilment of the requirements for the award of degree of **Doctor of Philosophy.**

Dr. B. Ramachandra Bhat
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Date: 09/04/2014

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Chairman-DRPC
Date: 09/04/2014

DEDICATED TO MY PARENTS

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ABSTRACT

Although a great many catalytic reactions of industrial importance are heterogeneous in type, homogeneous catalysis also plays a very vital role in the mechanism of many catalytic reactions. Most advances in industrial homogeneous catalysis are based on the development of coordination compounds as catalysts. Thousands of metal complexes have become known in the last few decades and the rapid development of the organic chemistry of the transition metals has been driven by their potential applications as industrial catalysts. More are being developed in order to find processes that would yield products in greater selectivity, purity and in high yields. Keeping this in mind, the present thesis addresses three major areas namely, designing, developing transition metal complexes using Schiff base and triphenylphosphine ligands. Synthesizing and characterizing all the complexes by established techniques like Elemental analysis, FT-IR, UV-Visible, Mass and NMR spectroscopy. Evaluating the catalytic activities of all the synthesized complexes, for the oxidation of alcohols by gas chromatography using mild oxidants like periodic acid, hydrogen peroxide and aqueous tert-butylhydroperoxide. All the synthesized complexes exhibited good catalytic activity. The mechanism involved in the reaction was also explored by UV visible spectral analysis during the reaction.

Keywords: Coordination complexes, Schiff base complexes, oxidation of alcohols, hydrogen peroxide, aqueous tert-butylhydroperoxide.

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LIST OF ABBREVIATIONS AND SYMBOLS

DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
EDTA	Ethylenediamine tetraacetic acid
ESIMS	Electron spray ionization mass spectra
GC	Gas Chromatography
LMCT	Ligand to metal charge transitions
FT-IR	Fourier Transform Infra red Spectroscopy
NMR	Nuclear Magnetic Resonance
TBHP	Tertiary butylhydroperoxide

CHAPTER 1

1.1 INTRODUCTION

In recent years chemistry has seen a remarkable renaissance. Academic and industrial research in chemistry is growing and the field of coordination chemistry is expanding exponentially, especially the complexation of transition metals with organic ligands. Since Werner's pioneering work of cobalt ammine complexes, coordination chemistry has advanced in a continuous way and has opened up new field of research; today it comprises a large body of inorganic chemistry research. There is an ever increasing academic, commercial and biochemical interest on the metal complexes of organic chelating ligands. Coordination chemistry is the chemistry of metal atoms "coordinated" by atoms, ions or molecules called ligands. As the fundamentals of coordination compounds, their structure and reactivity were realized, new and exciting applications were discovered. This has resulted in the development of allied fields like organometallic chemistry, homogeneous catalysis and bioinorganic chemistry. Hence the coordination compounds have become the backbone of modern inorganic and bio–inorganic chemistry and chemical industry.

1.2 HISTORICAL BACKGROUND

The metal complexes have a long and illustrious history. The earliest examples of coordination chemistry involve dyestuffs. Though there are many examples of coordination compounds, Prussian blue, synthesized in 1704, was the first officially recognized and well characterized metal complex. But the discovery of transition metal complexes are often credited to Taessert, who in 1798 prepared the first known cobalt ammonia salts which resulted in the synthesis of series of complexes. His work inspired and lead a revolution in coordination chemistry and thereby in inorganic chemistry. At the turn of the nineteenth century, amidst the fascinating developments of organic chemistry, the striking colors of the metal ammines and their unusual characteristics captivated the interest of chemists. This resulted in the synthesis of plenty of similar complexes of cobalt, iridium and platinum over the next 50 years. These coordination compounds put forward many challenges to the inorganic chemists as the nature of these inorganic species remained a mystery. However, the systematic studies in the field of coordination chemistry commenced in the latter part of 19th century. As new complex ions were synthesized, several bonding theories were postulated. Among the various theories, two most convincing and debated theories are "the Blomstrand–Jorgensen chain theory" proposed by Sophus Mads Jørgensen and "coordination theory" proposed by Alfred Werner. Although there was considerable controversy between Werner and Jørgensen regarding the interpretation of their experimental results on the structures of coordination compounds, one can now conclude that Werner's interpretation of his results is 'correct'. The pioneering contribution of Werner to the study of coordination chemistry fetched him the Nobel Prize in Chemistry in 1913. Soon after the reports by Werner and Jørgensen, there have been different approaches towards the study of bonding in metal complexes.

1.3 COORDINATION COMPOUNDS AND LIGANDS

Coordination compounds are formed by almost all transition metals, lanthanides and some of the non metals like silicon etc. A complex is a species that contains a central metal ion or atom (M), surrounded by atoms, ions or molecules called ligands (L).

$$M + nL \longrightarrow ML_n$$

Among the various metals, transition metals form a large number of complexes with variety of molecules. This is mainly because of their ability to exhibit variable oxidation states, coordination geometry and low energetic vacant d-orbitals. Although partial substitution may take place at the metal center, the complex tends to retain its identity in solution.

The atoms, ions, or molecules which act as the ligands have the property that can stabilize the metal ion. Ligands bind to the metal center through electron pair donation called coordination bond. The atom in the ligand that forms the bond to the central metal atom is called the donor atom, because it donates the electrons used in bond formation. Variety of elements function as donor atoms towards metal ions, but the most commonly encountered are nitrogen, phosphorus, oxygen, sulfur and the halides. In addition, a large number of compounds are known which contain carbon donor atoms; these are known as organometallic compounds.

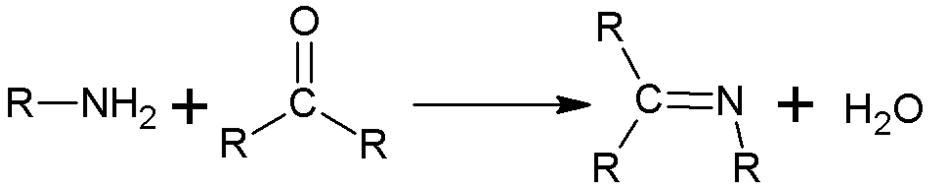
The nature of a bond between metal ion and a donor atom in a coordination compound depends upon various factors like the nature of the metal ion, oxidation state of metal ions, nature of donor atoms, structure of the ligands, steric factors and metal ligand orbital interaction. Similarly the coordination number and geometry varies depending on the nature of the metal ion, as well as on the nature of the ligand. With a given number of ligands, each metal complex adopts one of a number of energetically favorable geometries. Robust complexes have a complex ion metal and the primary coordination sphere of ligands that remain as one entity in solution (Marusak et al. 2007).

A huge variety of ligands appear in coordination complexes. The majority of ligands are either neutral or anionic. Those which coordinate to a metal ion through a single atom are described as monodentate or unidentate ligands. Examples of such ligands include water, ammonia, chloride etc. Where two donor atoms can be used to bind to a metal ion, as with $H_2NCH_2CH_2NH_2$, the ligand is said to be bidentate, and where several donor atoms are present in a single ligand as with $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate. When a bi- or polydentate ligand uses two or more donor atoms to bind to a single metal ion, it is said to form a chelate complex. Cyclic compounds which contain donor atoms oriented so that they can bind to a metal ion and which are large enough to encircle it are known as macro cyclic ligands. Some of these systems have given the names cryptand or sepulchrate, which reflect their ability to wrap up and entomb the metal ion. Sometimes ligands can bind to more than one metal ion in a bridging arrangement. Certain polydentate ligands are particularly good at linking togeother several metal ions and are referred to as polynucleating ligands.

The search for appropriate ligands for effectively controlling the stability and reactivity of metal complexes has been an important topic of coordination and organometallic chemistry research. Among the various ligands, Schiff base and phosphine ligands are the important ligands which have been studied extensively because of their attractive chemical, physical properties and their wide range of applications in numerous scientific areas.

1.3.1 Schiff base ligands

Schiff bases are organic compounds containing azomethine group with a general formula RHC=N-R', where R and R' are alkyl, aryl, cyclo alkyl or heterocyclic groups. Schiff base was first reported by Hugo Schiff in 1864 (Carey, 2003). Schiff bases can be prepared by condensing carbonyl compounds and an aliphatic or aromatic amine accompanied by the elimination of water molecules. The presence of a dehydrating agent normally favours the formation of Schiff bases (Scheme 1.1).



R=Aliphatic or aromatic

Scheme 1.1: Synthesis of Schiff bases

Schiff bases containing aromatic substituents are generally more stable and are more readily synthesized than alkyl substituents. Presence of a lone pair of electrons in a sp^2 hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical importance and impart excellent chelating ability. Hence Schiff bases usually act as bi-, tri- or poly-dentate ligands and form stable complexes with transition metals. This chelating ability of the Schiff bases combined with the ease of preparation and flexibility in varying the chemical environment about the C=N group makes it an interesting ligand in coordination chemistry. These ligands can coordinate from a monodentate (Tian et al., 1997) to a nonadentate (Archibald et al., 1994) fashion to a metal ion.

For several reasons, Schiff bases have been found to be among the most convenient and attractive ligands for transition metal complexes. Schiff base complexes find significant interest due to their biological activity, luminescence properties and catalytic activity. Hence they have played an important role in the development of modern coordination chemistry.

1.3.2 Phosphine ligands

Phosphine ligands (PR_3) are another very important class of ligands. They are probably the most widely used ligands in catalysis field. Their electronic and steric properties can be modified over a wide range by varying the R groups. Tertiary phosphines stabilize a wide variety of metal complexes. They coordinate to the metals in relatively high to low oxidation states. Phosphines have a lone pair of electrons on central P atom that can be donated to a metal. These ligands are strong σ donor and weak π-acceptor. π-acidity varies depending on the R group. Alkyl phosphines have weak π acidity, whereas aryl, dialkylamino, and alkoxy groups are successively more effective in promoting π acidity. The electronic flexibility of PR_3 is the reason it forms so many complexes. Traditional phosphine complexes of metals, particularly those of palladium, have played an extremely important role in the development of homogeneous catalysis. They have shown high catalytic activity and selectivity. But most of the phosphine complexes are relatively less air stable.

Hence, recently, extensive research efforts have been invested in the development of catalysts based on the Schiff base and triphenylphosphine transition metal complexes. This would result in complexes with higher air stability along with good catalytic activity.

1.4 IMPORTANCE AND APPLICATIONS OF COORDINATION COMPOUNDS

Coordination compounds are important not only because of their interesting chemistry, but because of their numerous applications. These compounds are widely present in the minerals, plants, animals and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. Coordination compounds are the basis for a number of therapeutic drugs, chemical sensors, coloring agents etc.

Naturally occurring coordination compounds are vital to living organisms. They are most commonly seen as an integral component to proteins, especially the class of proteins that can perform chemical reactions, termed enzymes. It is estimated that approximately half of all the proteins contain a metal. The pigment chlorophyll which is responsible for photosynthesis is a coordination complex of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase.

The coordination compounds find wide spread applications in chemistry and technology. The brilliant and intense colors of many coordination compounds, such as Prussian blue, make them of great value as dyes and pigments. Phthalocyanine complexes (e.g., copper phthalocyanine), containing large-ring ligands closely related to the porphyrins, constitute an important class of dyes for fabrics.

A major application of coordination compounds is their use as catalysts, which serve to alter the rate of many industrially important chemical reactions. For example, in the oxo reaction, $Co_2(CO)_8$ acts as catalyst in the addition of H_2 and CO to olefins to give aldehydes. Wilkinson's catalyst, $\{RhCl(PPh_3)_3\}$, used for the hydrogenation of alkenes, is of great importance in the manufacture of pharmaceuticals. Ziegler-Natta catalyst is used in the polymerization of alkenes. At present coordination compounds/organometallic compounds are used as catalysts for many industrial processes.

Several important hydrometallurgical processes utilize metal complexes for extraction and purification of several valuable metals. Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $\{Au(CN)_2\}^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc. Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

Coordination compounds find use in many qualitative and quantitative chemical analyses. The familiar colour reactions given by metal ions with a number of ligands especially chelating ligands, as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.

Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $\{Ag(CN)_2\}^-$ and $\{Au(CN)_2\}^-$ than from a solution of simple metal ions. Increasingly, coordination compounds are being used to provide functionality, as well as decorative effect in coatings and surface finishes.

There is growing interest in the use of chelate therapy in medicinal chemistry. Medicinal application of metals can be traced back to almost 5000 years (Orvig and Abrams 1999). The development of modern medicinal inorganic chemistry, stimulated by the discovery of cis- dichlorodiammine platinum(II) (cisplatin) and its subsequent use as a drug in the treatment of several human tumors (Rosenberg et al. 1969, Rosenberg and Vancamp 1970), has been facilitated by the inorganic chemist's extensive knowledge of the coordination and redox properties of metal ions. Metal centers, being positively charged, are favored to bind to negatively charged biomolecules. The constituents of proteins and nucleic acids offer excellent ligands for binding to metal ions. The pharmaceutical use of metal complexes therefore has excellent potential. Apart from therapeutic application of metal complexes, it also finds application in biomedical imaging.

Coordination complexes in the development of new architectural materials such as nano structures and in environmental applications e.g., “green” catalysts and bioremediation; are on the frontiers of research in inorganic chemistry in the twenty-first century. Applications of complexes under the subject of preliminary research include application in photocatalysis, optical information transfer and storage, analytical sensing and harvesting of solar energy. Thus complexes are finding their way into a wide field of medicine, solid state chemistry and nanotechnology. Applications and roles of new metal coordination complexes continue to expand daily.

1.5 CATALYSIS AND COORDINATION COMPLEXES

The continuing sophistication in and ever changing landscape of molecular targets for countless applications ranging from biology to material science requires a continuing evolution of synthetic methods. A key goal must be efficient in synthetic transformation of readily available starting materials to the final target. The development of the science and practice of catalysis has opened up new vistas for the fast and selective production of desired chemical molecules. This scientific revolution has triggered the advent of molecular design techniques which have unlimited scope and potential to provide for the most basic of all human needs like health, food, energy and materials. The rule that underlines all catalyst research is the development of cost effective methods that have an inherent commitment to environmental sustainability.

The term catalysis was coined by Berzelius around 1836 (Laidler K.J. 1982) after observing changes in substances when they came into contact with small amounts of species called “ferments”. The word catalysis comes from Greek: it means ‘down’ or ‘loosen’. Other early chemists involved in catalysis were Alexander Mitscherlich referred to contact processes and Johann Wolfgang Döbereiner who spoke of contact action and whose lighter based on hydrogen and a platinum sponge became a huge commercial success in the 1820’s. Humphrey Davy discovered the use of platinum in catalysis. In the 1880s, Wilhelm Ostwald at Leipzig University started a series of systematic investigations into reactions that were catalyzed by the presence of acids and bases, and found that chemical reactions occur at finite rates which can be used to determine the strengths of acids and bases.

Many years later in 1895 Ostwald came up with a definition “A catalyst is a substance that changes the rate of a chemical reaction without itself appearing into the products” according to which a catalyst could also slow down a reaction. Nowadays, the definition in use is “A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved”. Ostwald was awarded the 1909 Nobel Prize in Chemistry for his contribution in this field (Roberts M.W. 2000). Thus catalysts are substances that accelerates the rates of chemical reactions by effectively lowering the activation barrier for the reaction by providing a new reaction path way. Thus it facilitates the establishment of equillibria and is capable of greatly enhancing the product selectivity. Catalysts allow chemical transformations to be performed with the increased efficiency, minimal waste and reduced energy consumption.

It is not surprising therefore that the vast majority of products in the chemical industry involve a catalyst at some stage in their manufacture. This applies to bulk chemicals produced on a large scale as the starting materials for innumerable end products, such as alcohols, ketones, carboxylic acids, hydrocarbon and fine chemicals and pharmaceuticals. Catalysis is the phenomenon of a catalyst in action, wherein lowering of the activation energy is a fundamental principle that applies to all forms of catalysis – homogeneous, heterogeneous or enzymatic. The numerous catalysts known today can be classified according to various criteria: structure, composition, area of application, or state of aggregation.

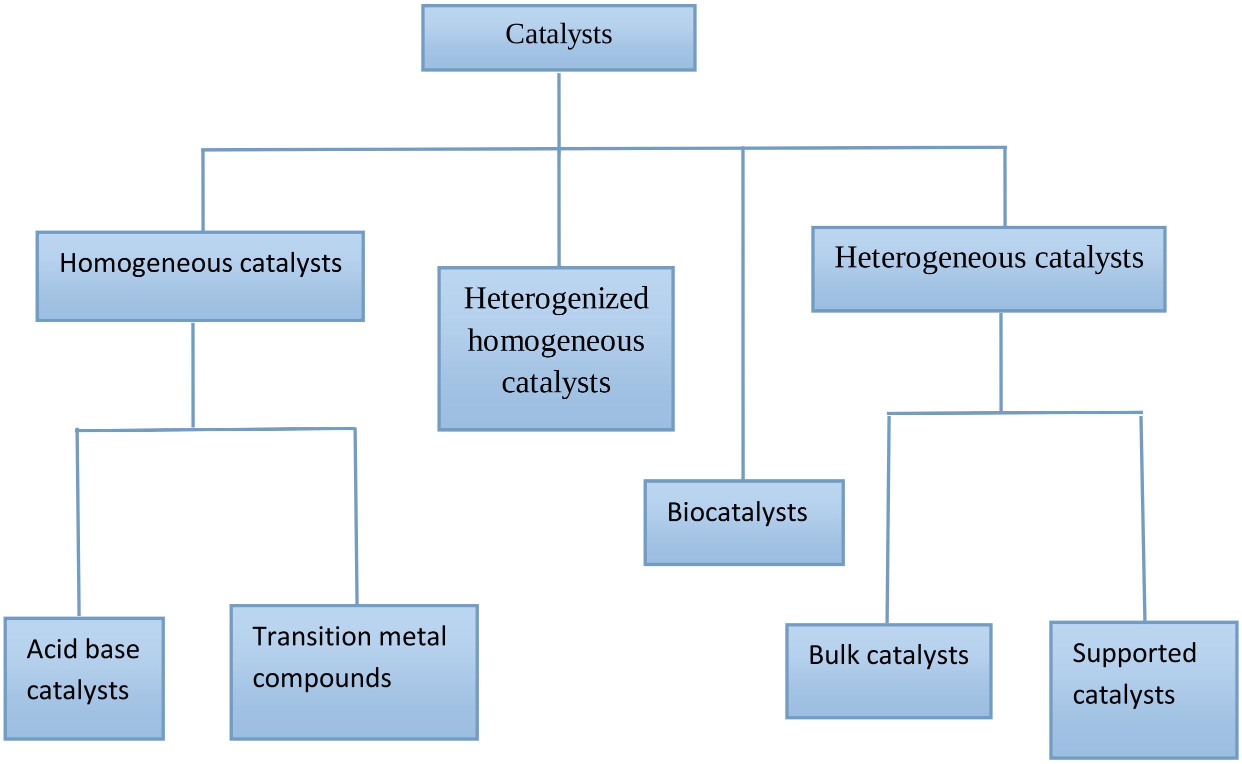


Fig. 1.1: Types of catalysts

Broadly catalysts can be classified into 2 groups according to the state of aggregation in which they act. They are heterogeneous catalysts and homogeneous catalysts. There are also intermediate forms such as homogeneous catalysts attached to solids known as immobilized catalysts and biocatalysts.

In homogeneous catalysis, both the catalyst and the reactant are in the same phase. Generally, in homogeneous catalysts, catalytic processes take place in a uniform gas or liquid phase. Homogeneous catalysts are generally well defined chemical compounds or coordination compounds, which, together with the reactants, are molecularly dispersed in the reaction medium. Metal complexes and organometallic compounds are the important homogeneous catalysts. These catalysts are soluble in the reaction medium and are used in the production of high purity, high value chemicals.

Usually, homogeneous catalytic reactions are very complex and proceed as a closed cycle of linked chemical reactions which involve different intermediate species. However, they exhibit high efficiency and selectivity and operate at milder conditions of temperature and pressure. Moreover, homogeneous catalysts of definite stoichiometry and structure can be easily made with more reproducibility.

Heterogeneous catalysis takes place between several phases. Generally the catalyst is a solid, and the reactants are gases or liquids. Heterogeneous catalysis is based on surface phenomena where atoms that are available at the surface of a solid are those which activate the substrates. Examples of heterogeneous catalysts are Pt/Rh for the oxidation of ammonia to nitric acid (Ostwald process), supported catalysts such as nickel on kieselgurh for fat hardening. They are mainly used for the production of large scale commodity chemicals and in petrochemical industry. One attractive feature of heterogeneous catalysts is their high stability which makes it suitable for wide range of operating conditions.

Both homogeneous and heterogeneous catalysts were extensively used in industry since the beginning of the twentieth century. But, heterogeneous catalysis has grown at a faster rate than homogeneous catalysis in industry. The main technical problem in the use of homogeneous systems is the separation of catalysts from reactants and products, which is practically very easy in the case of heterogeneous catalysts. The deactivation of homogeneous catalysts by the self aggregation of the active sites may also restrict its application in industrial processes, whereas heterogeneous catalysts are relatively more stable. The above mentioned facts may be the reason for the slow growth of homogeneous catalyst systems in industry. However, the ability of homogeneous systems to catalyze a variety of specifically designed chemical transformations promises lot of scope for future developments.

Biocatalysts are substances, such as an enzyme or hormone that activates or speeds up a biochemical reaction. These are very specific in comparison to other catalysts. Biocatalysts can be thought of as a mixture of a homogenous and heterogeneous catalyst. This is because the enzyme is in solution itself, but the reaction takes place on the enzyme surface.

An electrocatalyst is a catalyst that participates in electrochemical reaction. Electrocatalyst are a specific form of catalysts that function at electrode surfaces or may be the electrode surface itself. An electrocatalyst can be heterogeneous such as a platinum surface or nanoparticles, or homogeneous like a coordination complex or enzyme. The electrocatalysts assists in transfer of electron between the electrode and reactants and/or facilitates an intermediate chemical transformation described by an overall half-reaction. This finds major application in fuel cell engineering (Jens Hagen 2006).

Since the discovery of the catalysis phenomenon, catalysts are serving the purpose of selective chemical processing. Most of the industrial reactions are catalytic. Catalysis plays a key role in production of such a wide variety of products, which are having applications in food, clothing, drugs, plastics, agrochemicals, detergents, fuels etc. In addition to these, it plays an ever-expanding role in the balance of ecology and environment by providing cleaner alternative routes for stoichiometric technologies by the conversion of polluting emissions to harmless streams. Thus the importance of catalysis to society is obviously based on its great economic impact in the production of broad range of commodity products that improve our standards of living and quality of life.

1.5.1 Why transition metals are chosen as catalysts?

Transition metals and their compounds are often good catalysts. Transition metal catalysts can be homogeneous catalysts or heterogeneous catalysts. Transition metals and transition metal oxides tend to be used as heterogeneous catalysts, their ions and complexes are usually employed as catalysts in homogeneous contexts.

Typical common features of transition metals and their compounds are the presences of d electrons, and in many of them, and their incompletely filled d orbitals. As a result, transition metals form compounds with variable oxidation states. Thus, these metals and their compounds can act as electron banks that lend out electrons at appropriate time and store them for chemical species at other times. This kind of ability is the basis for the catalytic activity of certain transition metal complexes to a great extent. Upon coordination to a metal ion, changes take place in the electronic distribution in a ligand, which result in the modification of the reactivity of the ligand molecule, at times dramatically.

1.5.2 Homogeneous catalysis by coordination compounds

By definition, catalytic processes that take place in a uniform gas or liquid phase are classified as homogeneous catalysis. Transition metal catalyzed reactions are the basis of many important industrial processes, such as hydrogenation, carbonylation reactions, and the low pressure polymerization of ethylene and propene. Whereas transition metals and transition metal oxides tend to be used as heterogeneous catalysts, their ions and complexes are usually employed as catalysts in homogeneous contexts.

Some of the important commercial applications of homogeneous catalysis are: hydroformylation of olefins to aldehydes/alcohols, carbonylation of methanol to acetic acid, synthesis of L-dopa by asymmetric hydrogenation, oxidation of p-xylene to terephthalic acid, hydrocyanation of butadiene to adiponitrile, ethylene oligomerization etc. (Emeleus and Sharpe 1973). Though homogeneous catalysis plays an extremely important role in highly efficient processes, yet there are some serious drawbacks, mainly in terms of catalyst-product separation from the reaction mixture and re-usability of the catalyst.

One of the first industrially applied homogeneous processes is Oxo process discovered by Otto Roelen in 1938. In this process, the hydroformylation of olefins occurs in presence of carbon monoxide and hydrogen at 140-180ºC and a pressure of 200-300 atm over cobalt hydride carbonyl complexes. Later, this catalyst was modified with trialkyl phosphine to lower the reaction pressures and to obtain higher selectivity.

Another interesting achievement in this field was the use of Reppe reactions for the commercial production of various chemicals. This reaction involves the addition of a base to olefinic or acetylenic C-C bond with simultaneous insertion of CO. The synthesis of acrylic acid from acetylene, CO and water with activated nickel carbonyl catalyst. HNi(CO)X, is one of such reactions. Reppe carbonylations also include reactions such as propionic acid from ethylene and water, and acetic acid from methanol.

Another significant discovery in the field of homogeneous catalysis was the development of Wacker process for the production of acetaldehyde from ethylene. Soluble metal complex salts like palladium(II) chloride were used as catalysts for this process. This catalyst operates at 10.5 atm and 125-130ºC to obtain a yield of 95%. Wacker process is widely accepted in industry as it replaced expensive acetylene with cheap ethylene for the manufacture of acetaldehyde.

There has been an increase of research in the area of catalysis by transition metal complexes since the 1940s. The demand for cheaper and more efficient processes in the industry necessitated a major explosion of research in the area of synthetic chemistry to develop new systems that can act as catalysts. This also resulted in a rapid development of newer process technologies which are relevant to industrial scale reactions for the production of organic compounds. The notable contributions of Ziegler K and Natta G and Fischer E O and Wilkinson G in this area of chemistry fetched them the Nobel prizes in 1963 and 1973 respectively. Their pioneering work is the stepping stone for the development of homogeneous catalysis.

A great number of soluble metal complexes are now being utilized in industry as catalysts for the generation of a variety of useful compounds. More are being developed in order to find processes that would yield products in greater selectivity and purity and in high yields (Balaji R Jagirdar 1999).

Homogeneous catalysis by soluble metal complexes has a wide range of applications in a variety of reactions such as hydrogenation, oxidation, carbonylation, epoxidation, hydroformylation etc. The unique features of these catalysts are their high selectivity and activity at milder operating conditions and better understanding on a molecular level. The demand for optically active drugs, agrochemicals and food products, has enhanced the importance of homogeneous catalysis.

Most advances in industrial homogeneous catalysis are based on the development of organometallic catalysts. Thousands of organometallic complexes (i.e., compounds with metal–carbon bonds) are known in the last few decades. The rapid development of the organic chemistry has been driven by the transition metals and their potential applications as industrial catalysts (Hagen 2006).

Many types of chemical reactions follow a homogeneous catalytic mechanism. Some of them are listed and shown in as a schematic diagram below.

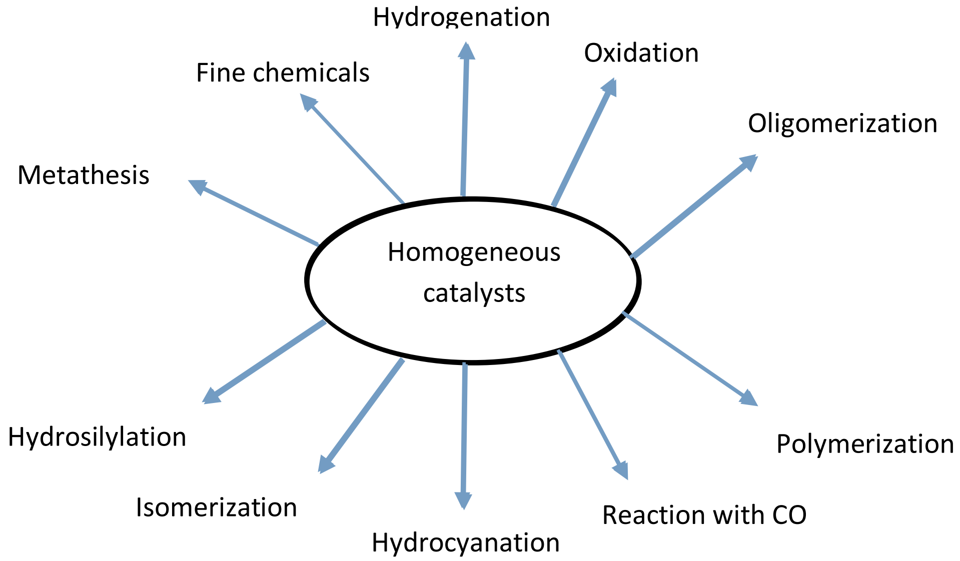


Fig.1.2: Various reactions catalyzed by homogeneous catalysts

1.6 CATALYTIC OXIDATION OF ALCOHOLS

The oxidation of alcohols is of great value in organic synthesis and as the products aldehyde, ketone or carboxylic acids are the important intermediates in the synthesis of other organic compounds (Sheldon and Kochi 1981). Many classical oxidation procedures available for this purpose employ toxic chromium reagents, potassium persulfate, oxone, benzoyl peroxide, cupric oxide, mercuric acetate, thalliumtriacetate, ammonium ceric nitrate, lead dioxide, nitrous anhydride, nitric acid, sulfuric acid, selenium dioxide, molybdenum hexacarbonyl, chromiumtrioxide, potassium permanganate, potassium ferricyanide, nickel peroxide etc., which are highly hazardous and environmentally polluting. These reagents are highly corrosive. In reduced form, many of them contain highly toxic heavy metals. In most of these classical methodologies, a series of oxidation/reduction reactions generate large amounts of inorganic salts. Other classical non-green methods are based on the use of high valent iodine compounds or involve the stoichiometric use of DMSO. However, the method is not a good choice from the point of view of environmental safety and economical point of view. These are expensive and these processes generate organic and heavy metal wastes (Anastas and Warner 1997). Thus, there is a constant need to develop inexpensive oxidation methodology which minimizes inevitable co-products, is inexpensive and environment friendly.

Among such newly developed methodologies, metal catalyzed oxidations are drawing much attention in recent years. Such methods employing metal-containing catalysts will avoid the use of such toxic reagents (Lei et al. 2005). Hence transition metal catalyzed oxidation methods have seen a rapid growth in recent years. In such methodology, the reaction proceeds in fewer steps generating smaller amount of inorganic salts. Such metal catalyzed reactions are more compatible with environmental mandates. Such type of oxidation reactions can proceed by any of the following mechanism. They are,

a) Free radical auto oxidation: In this type, the metal ion induces the decomposition of alkyl peroxides into radicals. Oxidation of this type has poor selectivity.

b) Oxidation of coordinated substrates: In this type, a metal ion oxidizes a coordinated substrate.

c) Oxygen transfer from an oxygen donor: In this type the oxidation proceeds through oxo metal or peroxo metal path way in the presence of a metal catalyst.

Recently extensive research efforts have been invested in the development of metal catalyzed oxidation of alcohols. Metal complexes of ruthenium, cobalt, copper, nickel, vanadium etc., have been investigated extensively in this regard. Numerous catalytic methods have been developed recently which can be used to oxidize alcohols. Ideal environmentally benign oxidation methodology should operate at room temperature in an environmental friendly solvent system like water and should make use of oxidants such as oxygen (air), hydrogen peroxide and organic hydroperoxides or mild oxidants like N-methylmorpholine-N-oxide.

An ideal oxidant for any large scale oxidation reaction should be easily accessible, cheap and non-toxic. The best oxidant to fit this description is dioxygen. The only byproduct produced from its decomposition is water. Though oxygen has high oxidation potential, it is not very reactive towards organic molecules. Also of great concern in oxygen mediated oxidations is that, such reactions proceed through radical mechanism, which is hard to control. Hence the catalyst should activate the dioxygen molecule and mediate the oxidation potential for the correct reaction.

Low valent late transition metal catalyzed aerobic oxidation of alcohols involve an oxidative dehydrogenation mechanism involving alkoxy metal species. These reactions are promoted by bases which act as co-catalysts. These facilitate the formation of the alkoxy metal intermediate. Currently dioxygen is used in several oxidation reactions, in particular heterogeneous reactions. Most of these reactions operate at high temperatures and high pressures. Hence are not suitable for fine chemical synthesis. Hence recently, extensive research has been carried out in the field of oxygen mediated oxidation reactions catalyzed by metal complexes under homogeneous conditions. Air is obviously attractive as an oxidant, but reactions are often nonselective and no generally applicable methods exist so far, despite very recent and interesting results (Elingset et al. 1998).

Another attractive oxidant from the environmental and economical point of view is hydrogen peroxide. As in the case of oxygen, in hydrogen peroxide also, water will be the only byproduct formed. Moreover, hydrogen peroxide is easy to handle and it has higher oxidation potential than oxygen. But the main drawback of this oxidant is the unavoidable presence of water, since water is both the reaction product and the solvent of commercial hydrogen peroxide. The other major drawback of hydrogen peroxide is its lower stability with respect to radical decomposition. The activation of hydrogen peroxide by metal can take place by the following mechanisms.

a) By the formation of metal peroxy or metal hydroperoxy species: where metal peroxy bond remains intact. Many d^0 metal complexes and d^8 metal complexes catalyze the oxidation by this path way.

b) By the formation of metal oxo species: this behaviour is typical of biomimetic systems based. Mostly Fe(II), Ru(II) and Mn(II) proceed through this type of mechanism.

c) By radical decomposition of hydrogen peroxide with one electron redox couples like Fe(II)/Fe(III) or Ti(III)/Ti(IV). However this type of reaction path way is not very selective.

In the peroxo metal path way the metal ion remains in the same oxidation state throughoout the catalytic cycle and no stoichiometric oxidation is observed in the absence of the peroxide. In contrast, oxometal pathways involve a two-electron change in the oxidation state of the metal ion, and a stoichiometric oxidation is observed, with the oxidized form of the catalyst. Although there are varieties of catalytic systems developed for the oxidation of alcohols, it has not yet paralleled the remarkable growth of application of alkylhydroperoxides. Hydrogen peroxide oxidations are expected to be more suitable, but a large excess is generally needed because of competitive dismutation of the oxidant.

Other oxidants of interest to chemistry are the alky hydroperoxides because of their low cost. Alkyl hydroperoxides, particularly tert-butylhydroperoxide, have the advantage of being freely soluble in organic media. Hence they can be used in strictly nonaqueous solvents. The alcohol product resulting can be easily recovered. Oxo metal path way is more probable for TBHP mediated oxidations.

Similarly many other mild oxidants such as N-methyl-morpholine-N-oxide (NMO), periodic acid, sodium periodate are also finding application in metal catalyzed oxidation of alcohols. Use of solid acids in organic transformations has many advantages as, ease of handling, decreased corrosion problems and allows more environmentally safe disposal.

Recently the catalytic oxidation in aqueous solutions has drawn much attention. This is because from the point of environmental safety. By using molecular oxygen as the oxidant and aqueous reaction medium the amount of waste produced in the process can be minimized (Lahtinen 2005). Many water soluble complexes have been developed to catalyze the oxidation of alcohols in aerobic oxidations in water. Use of water as a solvent often imposes a non-banal reformulation of oxidation catalysts, since the active species are metal complexes in high oxidation states, typically strongly coordinated by water and in competition with the less polar organic substrates.

Similarly one more type of methodology involves solvent free oxidation methods. This methodology is quite interesting due to its simple process, easy work-ups, low cost and reduction in harmful waste materials.

Application of ionic liquids in chemical processes has blossomed in recent decades. High specificity, high efficiency, negligible vapour pressure, potential to be used and recycled makes it ideal solvent for chemical reactions. But most of such ionic solvents are very expensive.

Extensive research is currently under way to develop the means to use enzymatic reactions commercially. This is because of their high specificity and selectivity. In a number of cases this has been successful. Major drawbacks are that the enzymes (a) must be isolated from natural sources, (b) are often present only in minute quantities, and (c) are generally contaminated with a wide variety of other materials, some of which also have enzymatic activity of a different kind. Enzymes are effective in living systems, where they can be excreted once they have done their job and can be regenerated biochemically. They may not be as effective and desirable in manufacturing. However, in industry it has been tried to mimic enzymatic activity by immobilizing a transition metal complex within a polymer matrix. This can stabilize the catalytic site and impart selectivity by restricting the size and shape of the site and attracting the substrate to that site. When the reaction is complete, the catalyst should be readily removed.

Metal catalyzed reactions are and will continue to play an important role in designing environmentally benign technologies in the production of chemicals. Metal catalyzed reactions result in the cost effective manufacture of chemicals as well as in a large reduction of pollutants in the environment. Metal catalyzed oxidation of alcohols is the field where the largest contribution of homogeneous catalysis is found. In this field, homogeneous catalysts compete effectively with heterogeneous ones.

CHAPTER 2

2.1 LITERATURE REVIEW

Coordination compounds are the backbone of modern inorganic, bio–inorganic chemistry and chemical industries. The search for appropriate ligands for effectively controlling the selectivity and reactivity of metal complexes has been an important topic of coordination chemistry. By changing the ligand one can change the properties of a complex. Among the various ligands, Schiff bases are most convenient and attractive. Schiff base complexes have been vigorously explored in recent years and such studies have been the subject of many papers and reviews.

2.1.1 Schiff base complexes

Schiff bases have played a key role as chelating ligands in main group and transition metal coordination chemistry. This is due to their ease of synthesis, stability under various reaction conditions and their structural variability along with their diverse applications. Schiff bases and their metal complexes have been studied extensively for their biological activities such as antibacterial agents (Shujah et al. 2011; Mandal et al. 2011; Singh and Biyala, 2006; Chohan et al. 2006), antifungal agents (Chohan et al. 2010; Shanker etal. 2009; Parekh et al. 2006), anti tumour drugs (Pradeepta et al. 2013; Adsule et al. 2006; Zhong et al. 2006; Garcia-Friaza et al. 2006) and in coordination chemistry (Vigato et al. 2007; Lewinski et al. 2005; Che and Huang 2003).

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, such as their ability to bind oxygen (Jones et al. 1979), catalytic activity in the hydrogenation of olefins (Henrici-Olive and Olive 1984), transfer of an amino group (Dugas and Penney 1981), photochromic properties (Akitsu and Itoh 2010; Margerum and Miller 1971), complexing ability towards some toxic metals (Sawondny and Riederer 1977) and so on. Schiff base complexes, especially those of Zn(II), are now a days used as electroluminescent materials (Yu te al. 2007). Schiff base metal complexes have emerged as potential building blocks for nonlinear optical materials (Anita et al. 2012; Kumar et al. 2010; Lenoble et al. 1998; Averseng et al. 1999). A ruthenium(III) Schiff base complex was used in the fabrication of chloride PVC-based membrane sensor (Ganjali et al. 2004). Many Schiff bases are known to be medicinally important and used to design medicinal compounds (Patole et al. 2006; Khan et al. 2008; Iqbal et al. 2009) Schiff bases are widely used as analytical reactants since they allow simple and inexpensive determination of several organic and inorganic substances (Cimernman et al. 1997).

2.1.2 Schiff base complexes in homogeneous catalysis

Schiff base complexes play a central role in various homogeneous catalytic reactions and the activity of these complexes varies with the type of ligands, coordination sites and metal ions. Hence Schiff base complexes have been widely investigated in this regard. The important reactions and the complexes used for the reaction under homogeneous conditions are listed in Table 2.1

Table 2.1: Schiff base complexes in catalysis

Authors	**Reaction studied**	**Catalyst**	**Remarks**
Grivani et al. 2012	Epoxidation of cyclooctene	Oxovanadium Schiff base complex containing bidentate *N*-salicylidin-2-chloroethylimine ligand	The active and selective epoxidation of cyclooctene by TBHP was described with the mechanism involved.
Lu et al. 2006	Epoxidation of styrene with H_2O_2	Salen type complexes of Mn, Co, Cu and Fe	Among all the complexes studied in the reaction Mn complexes showed

			highest yield.
Soriente et al. 2005	Epoxidation of allylic alcohols by TBHP	Octahedral titanium complex bearing a binaphthyl-bridged Schiff base ligand	The epoxyalcohols were obtained in very high regio- and chemoselective way by the Microwave exposure of the mixture in solvent free-conditions.
Li et al. 2005	Asymmetric epoxidation by PhIO	Binaphthyl Schiff base complex of Cr(III) complex	The catalytic ability of the complexes, the effects of reaction conditions on the catalytic activity has been reported.
Ambroziak et al. 2004	Epoxidation of olefins by TBHP as oxidant	Dioxomolybdenum(VI) complexes of Schiff-base derivatives of *trans*-1,2-diaminocyclohexane and aromatic 2-hydroxyaldehydes	The catalytic activities of the complexes in the epoxidation of cyclohexene and 1-octene were studied.
Zolezzi et al. 2003	Epoxidation of styrene with iodosylbenzene	Copper(II) complexes with salen Schiff-base ligands derived from ethylenediamine or (S,S)-1,2-diphenylethylenediamine and salicyladehyde and its derivatives	Catalytic activity of the complexes, kinetics of the reaction and possible mechanism has been described.
Khureshy	Asymmetric	Dissymmetric Mn(III) and	Catalytic activities of

et al. 1996	epoxidation by PhIO	Ru(III) chiral Schiff base complexes	the complexes were studied.
Sood et al. 2013	Ethene polymerization	Mn(II) complexes with bidentate N,Nˈ-imine-pyridine and N,Nˈ-imine-quinoline-type donor ligands	Catalytic activities of the complexes were studied which indicated single-site polymerization behavior.
Yao et el. 2012	Ring opening polymerization	Zinc complex with $\{(CH_3)_2NCH_2CH_2NCHC_6H_3(OH)(OMe)\}$	Described the kinetic study of l-lactide polymerization with the complex
Strianese et el. 2006	Polymerization of ethylene and propene	Binaphthyl-bridged Schiff base complexes of Titanium	The catalytic activity of the complexes was tested and compared with earlier reported related Zr and Ti complexes.
Liu et al 2006	Ethylene polymerization	Cr(III) with 2,2ˈ-iminodiphenylsulfide ligands	Catalytic behavior towards ethylene polymerization was studied.
Clercq and Verpoort 2002	Radical polymerization	Ruthenium Schiff base complexes	Polymerization of norbornene and cyclooctene were reported.
Bera et al. 2012	Asymmetric oxidation of	Titanium complexes of chiral amino alcohol derived Schiff	The paper demonstrated a

	prochiral sulfides	bases	significant role of steric influence of the substituent attached on both aryl and alkyl moiety on the enantioselectivity. It also focused on catalytic study and kinetic studies.
Himeda et al. 2003	Asymmetric reduction	{CpRh(bpy)Cl}Cl	Reported the efficient catalytic activity in the transfer hydrogenation of a wide variety of ketones in aqueous formic acid solution under mild reaction conditions.
Kwong et al. 1999	Asymmetric transfer hydrogenation	Ru(II) complex bearing chiral P,N,O Schiff base ligands	Reported the catalytic activity with best enantioselectivity.
Takenaka et al. 2002	Diels alder reaction of 1,2-dihydropyridine	Cr(III) salen complexes	Reported the enantioselective Diels–Alder reactions between 1, 2-dihydropyridine and *N*-acryloyloxazolidinone.
Maruyama et al. 1995	Aldol reaction	Co(III) Schiff base complex	Reported aldol reaction of dibenzoylmethanes with formaldehyde

Shahnaz et al. 2013	Suzuki–Miyaura cross-coupling reactions	Palladium complex derived from a bidentate Schiff-base ligand	Reported the excellent yields of biaryls.
Pasa et al. 2013	Suzuki reaction	Pd(II) complex with N,N´-bis(2-hydroxy-1-naphtaldehydene)-1,4-bis(o-amino phenilthio)butane	Reported the catalytic activity of the complex towards Suzuki cross coupling reaction with mechanism.
Kumar et al. 2009	Heck and Suzuki reaction	Pd(II) with chalcogenated Schiff bases of 2-hydroxybenzophenone	Described the application of synthesized ligands in the coupling reaction under aerobic condition.
Uchida et al. 2001	Baeyer-Villeger oxidation	Co(III)(salen) complex	Reported the efficient catalytic activity reaction of 3-substituted cyclobutanone using hydrogen peroxide terminal oxidant.

In addition to the homogeneous catalytic reaction, supported transition metal Schiff base complexes also find wide application in catalysis. Among these polymer supported (Gupta et al. 2009; Gupta and Sutar 2007; Syamal and Singh 1993) and zeolite encapsulated Schiff base complexes are the most widely used in heterogeneous catalysis (Jin et al 2006; Mostafa et al. 2005).

2.1.3 Phosphine complexes in homogeneous catalysis

Phosphine complexes find wide application in catalysis. The important reactions and the complexes used for the reaction under homogeneous conditions are listed in Table 2.2.

Table 2.2: Metal phopshine complexes in catalysis

Authors	**Reaction studied**	**Catalyst**	**Remarks**
Xu et al. 2012	Suzuki reaction	N-heterocyclic carbene (NHC)-phosphine palladium(II) complexes	Complexes exhibited efficient catalytic activity.
Deb et al. 2011	Carbonylation reaction	Rhodium(I) carbonyl complexes of tetradentate chalcogen functionalized phosphines	Carbonylation of methanol to acetic acid and its esters were reported wwith high turn over frequency.
Li et al. 2010	Hydrosilylation	Rhodium complexes e mploying 2-imidazolium phosphin e ligands	Reported the excellent catalytic activity and selectivity for hydrosilylation of olifins.
Aizawa et al. 2007	C-C couling reaction	Palladium(II) complex with bidentate phosphine sulfide ligands	Catalytic activity of the complexes for Heck reaction were evaluated and compared with the conventional phosphine Pd(0) complex.
Wolf et	Kumada-Corriu	Zwitter ionic	Reported the catalytic activity

al. 2006	coupling	Nickel(II) bifunctional phosphine–imidazolium complexes	of the complexes.
Jackson et al. 2006	Dehydrocoupling of di-n-hexylsilane	Rhodium(I) bis(phosphine) complexes	The catalytic activity of several rhodium complexes were investigated and discussed in the context of the coordination numbers and geometries.
Tsai et al. 2005	Oxidation of alcohols	Copper complexes containing pyridine, amine and phosphine oxide donor systems	Complexes efficiently converted alcohols to carbonyls in presence base under O_2 at reflux condition.
Horvath et al. 2004	Hydrogenation of bicarbonates	Water soluble (η^6-arene)ruthenium(II)-phosphine complexes	Catalytic activity of the complexes was discussed.
Li et al. 2002	Hydrogenation of C=O group in cinnamaldehyde	Iridium complexes containing bidentate phosphine ligands	The hydrogenation activities and selectiveness of the complexes for the carbonyl group of citral and cinnamaldehyde were discussed.
Moldes et al. 1998	Hydrogenation of styrene and phenylacetylene	Ruthenium(II) complexes containing both arene and functionalized phosphines	Examined the activities of the complexes.
Matteoli et al. 1995	Hydrogenation of olefins	Phosphine-substituted ruthenium carbonyl	The catalytic activity of the complex was tested in the

		carboxylates	reduction of internal and terminal olefins, of the carbonyl double bond and of both free and esterified carboxylic groups.
Fogg et al. 1994	Imine hydrogenation	Ruthenium ditertiary phosphine complexes	Studied the catalytic activity for the reaction.

2.1.4 Oxidation of alcohols

The selective oxidation of alcohols has been of great value in organic synthesis and represents an important entry to essential functional groups, such as ketones, aldehydes, and carboxylic acids (Sheldon and Kochi 1981) is a highly desirable and much sought after transformation in industrial chemistry due to the wide-ranging utility of these products as important precursors and intermediates for many drugs, vitamins and fragrances. Many standard oxidation procedures have been available for this purpose. These are expensive and generate organic and heavy metal wastes (Anastas and Warner 1997). Thus, there is a constant need to develop inexpensive oxidants, preferably operating under catalytic conditions, to minimize inevitable co-products, which represents an environmental problem. Catalytic conditions involve transition metal complexes in combination with oxidants such as $NaIO_4$, NaOCl, *tert*-BuOOH, *N*-oxides, *S*-oxides, etc. Some important catalytic systems are listed in Table 2.3.

Table 2.3: Homogeneous oxidation of alcohols

Authors	**Catalyst**	**Oxidant**	**Remarks**
Dileep and Bhat 2011	Copper (II)–N–(2-pyridyl)–N'–(5-R-salicylidene) hydrazine triphenylphosphine complexes	Periodic acid	Evaluated the catalytic activity of primary and secondary alcohols acetonitrile under reflux condition. Mechanistic aspect of the reaction was also given.

Ganesamoorthy et al. 2009	$[Ru(acac)_2(CH_3CN)_2]PF_6$	Periodic acid	Reported the catalytic reaction in water at room temperature.
Xu and Trudell 2003	Chromium(III) acetylacetonate	Periodic acid	Demonstrated the efficient catalytic oxidation with 1.5 equivalents of periodic acid at room temperature in acetonitrile.
Yang et al. 2007	Ru(III) complexes with 1,10-phenanthroline, 8-hydroxy-quinoline, and 2,2ˈ-bipyridine	PhIO	Reported the oxidation at room temperature in high efficiency in acetonitrile.
Raja and Ramesh 2012	Cationic arene ruthenium(II) complexes bearing N, S chelating thiocarboxamides	NMO	Reported the oxidation in dichloromethane under reflux in good yields. Mechanism was also discussed.
Tamizh et al. 2012	$\{Ru(L)(CO)(PPh_3)_2\}$ with L = binegative tridentate ONS donor ligand	NMO	Reported the oxidation in dichloromethane at room temperature in good yields.
Thilagavati and Jayabalakrishnan 2010	Ruthenium(III)- 3,4-dihydropyrimidin-2(1H)-one/thione complexes.	NMO	Examined the catalytic efficiency.
Gunasekaran and Karvembu 2010	Ru(III) complexes containing N-{di(alkyl/aryl)carbamothioyl}benzamide derivatives and	NMO	Reported the oxidation in dichloromethane at room temperature in good yields.

	triphenylphosphine/triphenylarsine		
Kumar et al. 2008	Half-sandwich para-cymene ruthenium(II)naphthylazo phenolato complexes	NMO	Reported the oxidation in dichloromethane at reflux condition.
Bahramian et al. 2006	Water soluble Manganese(III) salen complex	Sodium periodate	Potential catalysis in the oxidation of alcohols with sodium periodate in 1:1 CH_3CN/H_2O mixture at room temperature was explored.
Pearson and Kwak 2005	Iron carbonyl complex	Trimethylamine-*N*-oxide	Described the oxidation in benzene at room temperature.
Gunasekaran et al. 2012	Tris-chelate cobalt(III) complexes	TBHP	Reported the reaction in acetonitrile medium at reflux condition. Reaction proceeded but with long duration and required 3 equivalents of oxidant.
Bose et al. 2011	Manganese(III) corrole	TBHP	Reported the efficient and selective oxidation under mild condition in benzene.
Chakravorty and Das 2010	Cobalt(II) 4-nitrobenzoates	TBHP	Reported the oxidation at reflux condition in acteonotrile. It was observed that reaction resulted in the formation of both aldehyde and acid depending on the substrate.
Kirillova et al.	Water soluble tetracopper(II)	TBHP	Reported the oxidation of alkene and alcohol in water/acetonitrile.

2010	triethanolaminate complex		
Boudreau et al. 2006	Water soluble Copper complex	TBHP	Reported the efficient and selective oxidation of secondary 1-heteroaryl alcohols under mild conditions in aqueous media.
Ferguson et al. 2003	Water soluble Copper complex	TBHP	Described the selective oxidation of secondary benzylic, allylic and propargylic alcohols under solvent free conditions at room temperature.
Zhou et al. 2013	Ruthenium-bis(benzimidazole)pyridinedicarboxylate complex	H_2O_2	Reported the reaction under solvent free condition at 60° C in good yield.
Kharat et al. 2011	Cobalt (II) and cobalt (III) complexes of a terpyridine based ligand	H_2O_2	Tested the catalysts for the oxidation of a variety of aliphatic and aromatic alcohols utilizing aqueous hydrogen peroxide in water media and showed Co(II) complexes to be more active than similar Co(III) complexes.
Golchoubian and Babaei 2010	Mn(III) Schiff-base complex	H_2O_2	Aliphatic and aromatic alcohols are efficiently oxidized to ketones or carboxylic acids under solvent-free conditions.
Ye et al. 2009	Hexadentate 8-quinolinolato manganese(III) complexes	H_2O_2	The catalysts exhibited efficient catalytic activity in acetone. Mechanism was also proposed.
Liu et al.	Pd (OAc)$_2$−sodium	H_2O_2	Reported the reaction under solvent

2008	oxalate (SO)		free condition at 70^{o} C in good yield. Probable mechanism was also given.
Mardani and Golchoubian 2006	Manganese(III) Schiff-base complex	H_2O_2	A variety of alcohols were oxidized efficiently into the corresponding ketones and carboxylic acids in excellent yields under solvent-free and mild conditions.
Balogh-Hergovich and Speier 2005	Dinuclear iron complexes	H_2O_2	Reported the reaction in acetone at room temperature in good yield. Mechanistic aspect of the reaction was also discussed.
Das and Punniyamurthy 2003	Co(II) salen complex	H_2O_2	Reported the conversion to acid/ketone in acetonitrile media at 80^{o} C in good yield.
Rahim et al. 2011	Copper (II) meso-tetra phenyl porphyrin	O_2	The oxidation of benzyl alcohols was studied in the presence of isobutyraldehyde as co-catalyst in o-xylene.
Ahmad et al. 2009	bis(3,5-di-*tert*-butylsalicylaldimine)copper(II) complexes	O_2	Reported the good conversion at 60°C in combination with TEMPO.
Shimazu et al. 2008	Palladium(II)–alkylamine complexes	O_2	Reported the good conversion with excellent turn over frequency.
Ji et al. 2007	Ruthenium (III) *meso*-tetraphenylporphyrin	O_2	Efficient selective oxidation of alcohols to carbonyl compounds by

	chloride		molecular oxygen with isobutyraldehyde as cocatalyst was reported.
Veluswamy et al. 2006	Cu(II) salen complex	O_2	Reported the selective oxidation of primary alcohols to aldehydes in high yields by atmospheric oxygen in the presence of TEMPO in toluene at 100°C.
Egami et al. 2005	(nitrosyl)Ru(salen) complex	O_2	Chemoselective aerobic oxidations of primary alcohols in the presence of activated secondary alcohols were effected under irradiation of visible light was reported.
Sharma et al. 2004	cobalt (II) Schiff base complexes	O_2	A variety of secondary alcohols were efficiently oxidized in acetonitrile at room temperature.
Kervinen et al. 2003	Cobalt salen-type complexes	O_2	Described the oxidation of veratryl alcohol in basic aqueous solution.
Sharma et al. 2003	Cobalt phthalocyanine	O_2	A variety of activated and non-activated secondary alcohols were efficiently oxidized in presence of KOH in xylene under reflux condition.
Miyata et al. 2001	(nitrosyl)Ru(salen) complex	O_2	In the presence of secondary alcohols, primary alcohols were selectively oxidized to aldehydes under irradiation of visible light at room

			temperature.
Rong et aal. 2012	Salicylic amino acid Schiff base manganese complex	H_2O_2	A selective oxidation was reported in the ionic liquid [bmim]BF_4 at room temperature.
Dileep et al. 2010	Ni(II)-schiff base-triphenylphosphine complex	NaOCl	A selective oxidation was reported in an ionic liquid.
Jiang et al. 2007	$VO(acac)_2$/DABCO	O_2	A selective oxidation was reported in the ionic liquid [bmim]PF_6.
Chhikara et al. 2005	(tris(imidazolium)-tetrakis(diperoxotungsto)phosphate	H_2O_2	An efficient and environmentally friendly procedure was described by imidazolium ion-based phosphotungstate complex at 90°C in ionic liquid.

2.2 SCOPE AND OBJECTIVES

Metal complexes play a central role in many organic transformations as versatile catalyst due to their reversible and accessible oxidation states along with their ability to exhibit variable coordination number. Particularly transition metal complexes containing triphenylphosphine and triphenylarsine ligands have been used as catalysts since very long time in many reactions of industrial importance such as hydrogenation, hydroformylation, oxidation, carbonylation, decarbonylation etc. But most of such complexes are found to be less air stable. It has also been observed from literature that the metal complexes with the Schiff base ligands play an important role in coordination chemistry, mainly due to their stability, ease of preparation and structural variability. This stimulated us to incorporate both Schiff bases and triphenylphosphine as ligands in the synthesis of transition metal complexes and to investigate their catalytic efficiency in the oxidation of alcohols using various oxidants. Although there is a wealth of information available on such Schiff base complexes, it is largely confined to their biological studies. Moreover, relatively little work has been done on the synthesis of metal complexes incorporating both Schiff bases and triphenylphosphines of iron, vanadium, cobalt etc.

Hence, this study is intended to synthesize Fe(III), V(IV) and Co(III) complexes containing triphenylphosphine and Schiff base ligands. The catalytic efficiency of the synthesized complexes was examined for the oxidation of alcohols to aldehydes/ ketones using various oxidants in mild conditions.

The objectives of the research work are as follows:

- To synthesize a series of Schiff base ligands Salicylidene-2-aminothiophenol/Salicylidene-2-aminophenol and also their derivatives from the condensation of aminophenol/aminothiophenol with salicylaldehyde/substituted salicylaldehydes.
- To synthesize a series of metal complexes of iron, vanadium and cobalt containing above synthesized ligands and triphenylphosphine (PPh_3) / triphenylphosphineoxide.
- To characterize the synthesized ligands and complexes by analytical, spectral (NMR, Mass, UV-Vis, and FT-IR) and magnetic studies.
- To use the synthesized complexes as homogeneous catalysts for the oxidation of alcohols using various oxidants and to analyze reaction products by gas chromatographic technique.
- To study the effect of solvent, temperature, catalyst concentration, oxidant concentration and time on the yield of carbonyl compounds.
- To investigate the effect of substrate on the oxidation reaction.
- To study the effect of variations in ligand frame work on the catalytic activity.

- To investigate the mechanism involved in the oxidation reaction by UV visible spectra of the reaction mixture and hence to propose the probable mechanism involved in the reaction.

CHAPTER 3

EXPERIMENTAL METHODS, SYNTHESIS OF LIGANDS AND COMPLEXES

3.1 INTRODUCTION

The Schiff base-triphenylphosphine-transition metal complexes are expected to be attractive catalysts because of their chemical and thermal stability. Considerable attention has been paid in recent years for the synthesis of these complexes because they are considered to constitute potential biological and catalytic activity.

3.2 EXPERIMENTAL

3.2.1 Materials

All the chemicals used were of analytical grade. Solvents were purified and dried according to standard procedure (Vogel 1989). $FeCl_3$, $CoCl_2.6H_2O$, VCl_3, o-aminophenol, o-aminothiophenol, salicyladehyde, 2-hydroxy-1-naphthaldehyde, 5-chloro-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde, 2-hydroxy-5-methoxy benzaldehyde, were purchased from Sigma Aldrich and were used without further purification.

3.2.2 Physical measurements

A variety of physico-chemical methods were employed to characterize the structure of organic Schiff base ligands and their metal complexes. A brief account of these methods is given below.

The C, H, N and S contents were determined by Thermoflash EA1112 series elemental analyzer.

The magnetic susceptibility measurements were done at room temperature on a Sherwood UK magnetic balance. The solid sample was tightly packed into a weighed sample tube to suitable length (l) and noted the sample weight (m). Then the packed sample tube was placed into tube guide of the balance and noted the reading (R). The magnetic susceptibility, χ_g, is calculated using the formula,

$$\chi_g = [\, C_{bal} \times l \times (R - R_0)] \div [10^9 \times m]$$

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

$$\mu_{eff} = 2.83\sqrt{T \times X_A}$$

where X_A is the corrected molar susceptibility.

^{1}H NMR spectra were recorded in Bruker AMX 400 instrument using TMS as internal standard. The spectra of the ligands were recorded in $CDCl_3$ and that of the complexes were recorded in DMF. ^{31}P NMR spectra were recorded in Bruker AMX 400 instrument in $CDCl_3$ with H_3PO_4 as a reference.

FT-IR spectra were recorded on a Thermo Nicolet Avatar FT-IR spectrometer as KBr powder in the frequency range 400-4000 cm^{-1}.

Electronic spectra of ligands and complexes were measured on Analytikjena S-600 UV – Vis spectrophotometer in the 200 – 1000 nm range.

TG-DTA-DTG analysis of the complexes was carried out under air and nitrogen at a heating rate of 10°C min^{-1} using Exstar 6000 TG/DTA analyser.

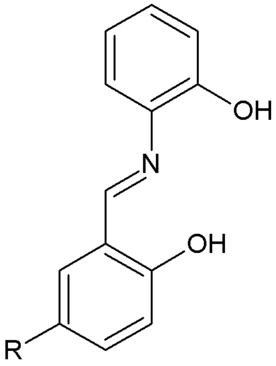
Electron Spray Ionization Mass spectra of the complexes were recorded on API4000 ABSciex ionization mass spectrometer.

The reaction product analysis was carried out using GC (Shimadzu 2014, Japan); the instrument has a 5% diphenyl and 95% dimethyl siloxane Restek capillary column (30 m length and 0.25 mm diameter) and a flame ionization detector (FID).

3.3 SYNTHESIS OF LIGANDS

3.3.1 N-(2-aminophenyl)salicylideneimine and its derivatives (L_1-L_5)

The ligands L_1-L_5 were synthesized according to the reported procedure (Jesmin et al. 2008) by refluxing 1:1 ratio of salicylaldehyde/its derivatives and o-aminophenol in ethanol for 4-6 hours, followed by cooling to room temperature (Fig. 3.1). The precipitated products were collected by filtration and washed with cold ethanol. The product was purified by recrystallization from ethanol and dried in *vacuo.* Yield: 80-90%.

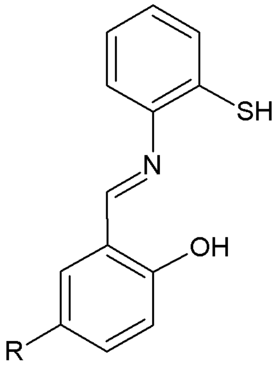


L_1: R=H, L_2: R= Cl, L_3: R=Br, L_4: R=NO_2, L_5: R=OCH_3

Fig. 3.1: Structure of N-(2-aminophenyl)salicylideneimine and its derivatives

3.3.2 N-(2-mercaptophenyl)salicylideneimine, its derivatives and N-(2-mercaptophenyl) naphthylideneimine (L_6-L_{10})

The ligands L_6-L_{10} were synthesized according to the reported procedure (Tamizh et al. 2009). Salicylaldehyde/its derivatives or 2-hydroxy-1-naphthaldehyde and 2-mercaptoaniline were refluxed in 1:1 ratio in ethanol for 4-6 hours. It was then cooled to room temperature. The precipitated products were collected by filtration and washed with cold ethanol. The product was purified by recrystallization from ethanol and dried in *vacuo*. Yield: 70-80%. The structure of the molecule is given below.



L_6: R=H, L_7: R= Cl, L_8: R=Br, L_9: R=NO_2

Fig. 3.2: Structure of N-(2-mercaptophenyl)salicylideneimine and its derivatives

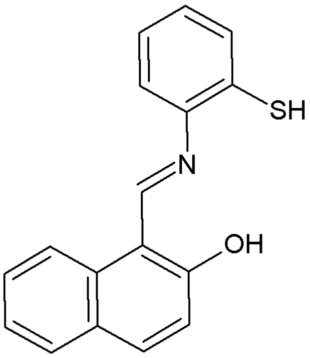
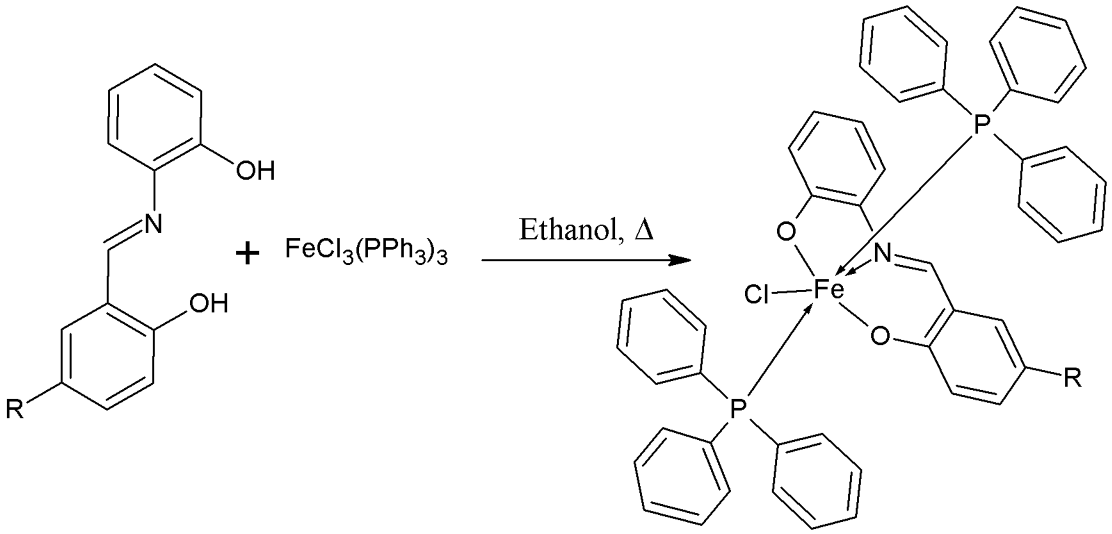


Fig. 3.3: Structure of N-(2-mercaptophenyl)naphthylideneimine (L_{10})

3.4 SYNTHESIS OF COMPLEXES

3.4.1 Synthesis of Fe(III) complexes FeL_1-FeL_5

The precursor complex $[FeCl_3(PPh_3)_3]$ was prepared by the reaction between $FeCl_3$ and triphenylphosphine in glacial acetic acid (Rao et al. 2000). All the complexes were prepared by refluxing an ethanolic solution of $[FeCl_3(PPh_3)_3]$ and ligand in a 1:1 molar ratio for 4 hrs (Scheme 3.1). The red colored complex was filtered, washed with diethyl ether and dried in *vacuo*. The formation of the complex was checked by TLC. Yield: 70–80 %.

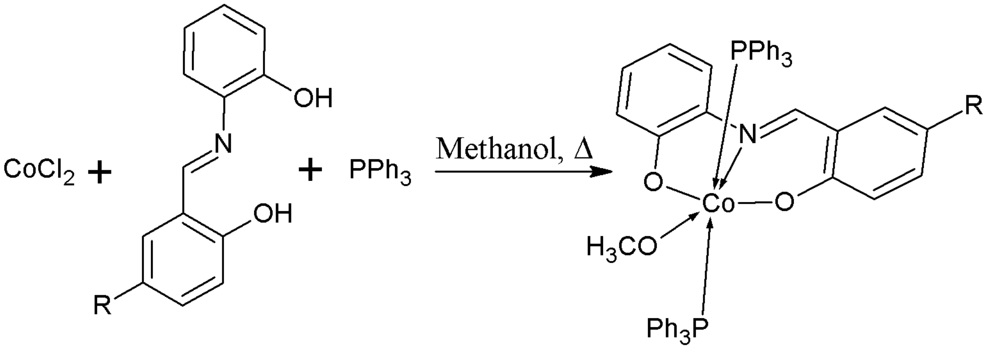


FeL_1: R=H, FeL_2: R= Cl, FeL_3: R=Br, FeL_4: R=NO_2, FeL_5: R=OCH_3

Scheme 3.1: Synthesis of Fe (III) complexes.

3.4.2 Synthesis of Co(III) complexes CoL_1-CoL_5

The cobalt complexes were prepared by refluxing a methanolic solution of $CoCl_2.6H_2O$, the synthesized ligand and triphenylphosphine in a 1:1:3 molar ratios for 4-5 hrs (Scheme 3.2). The formed greenish colored complex was filtered, washed with diethyl ether and dried in *vacuo*. The formation of the complex was checked by TLC. Yield: 70–80 %.

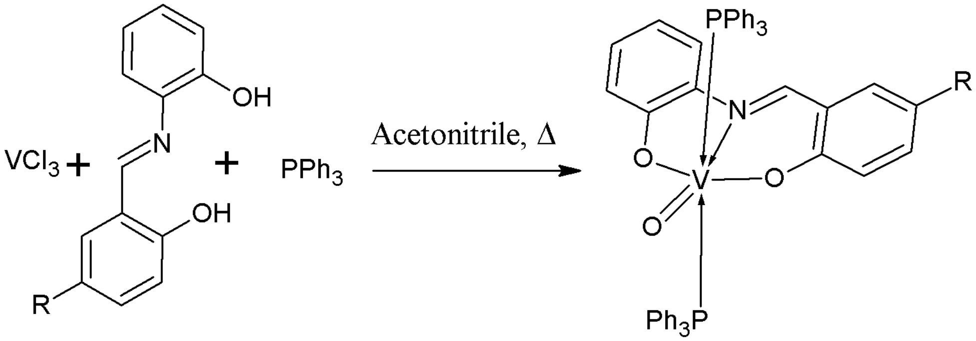


CoL$_1$: R=H, CoL$_2$: R= Cl, CoL$_3$: R=Br, CoL$_4$: R=NO_2: CoL$_5$: R=OCH_3

Scheme 3.2: Synthesis of Co(III) complexes

3.4.3 Synthesis of V(IV) complexes VL$_1$-VL$_5$

The complexes were prepared by refluxing a solution of VCl_3, the synthesized ligand and triphenylphosphine in a 1:1:4 molar ratios for 4-5 hrs in acetonitrile (Scheme 3.3). The formed brown colored complex was filtered, washed with diethyl ether and dried in *vacuo*. The formation of the complex was checked by TLC. Yield: 70–80 %.

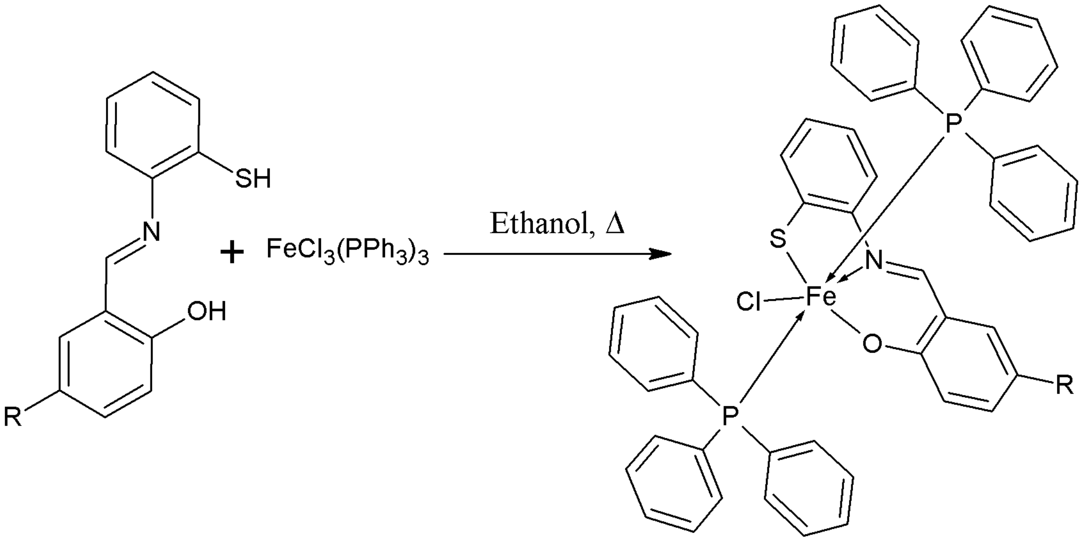


VL$_1$: R=H, VL$_2$: R= Cl, VL$_3$: R=Br, VL$_4$: R=NO_2: VL$_5$: R=OCH_3

Scheme 3.3: Synthesis of V(IV) complexes.

3.4.4 Synthesis of Fe(III) complexes FeL$_6$-FeL$_{10}$

The complexes were prepared by refluxing an ethanolic solution of $[FeCl_3(PPh_3)_3]$ and corresponding ligand in a 1:1 molar ratio for 4 h (Scheme 3.4) The red colored complex was filtered, washed with diethyl ether and dried in *vacuo*. The formation of complex was checked by TLC. Yield: 70–80 %.

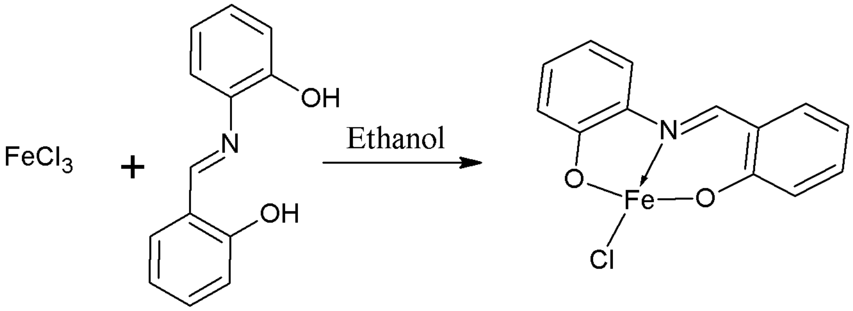


FeL$_6$: R=H, FeL$_7$: R= Cl, FeL$_8$: R=Br, FeL$_9$: R=NO$_2$

Scheme 3.4: Synthesis of FeL$_6$-FeL$_{10}$ complexes.

3.4.5 Synthesis of Fe(III) complex FeL$_{11}$

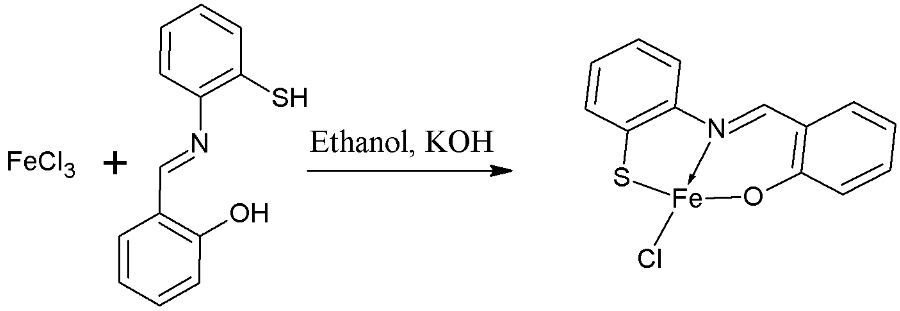
FeL$_{11}$ was prepared by stirring ferric chloride with N-(2-aminophenyl)salicylideneimine in 1:1 ratio in ethanolic medium (Scheme 3.5). The formed complex was filtered and washed with diethyl ether and dried in *vacuo*. The formation of complex was checked by TLC. Yield: 80–90 %.



Scheme 3.5: Synthesis of FeL$_{11}$ complex

3.4.6 Synthesis of Fe(III) complex FeL$_{12}$

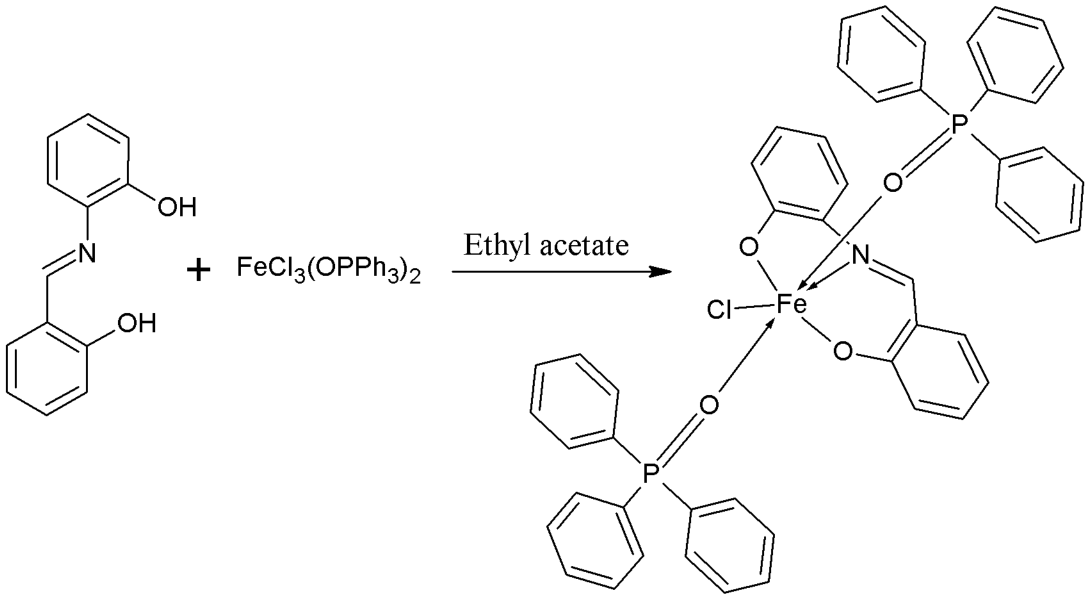
FeL$_{12}$ was prepared by stirring ferric chloride with N-(2-mercaptophenyl)salicylideneimine in 1:1 ratio in ethanolic medium (Scheme 3.6). The formed complex was precipitated by adding potassium hydroxide and filtered, washed with diethyl ether and dried in *vacuo*. The formation of complex was checked by TLC. Yield: 80–90 %.



Scheme 3.6: Synthesis of FeL$_{12}$ complex.

3.4.7 Synthesis of Fe(III) complex FeL$_{13}$

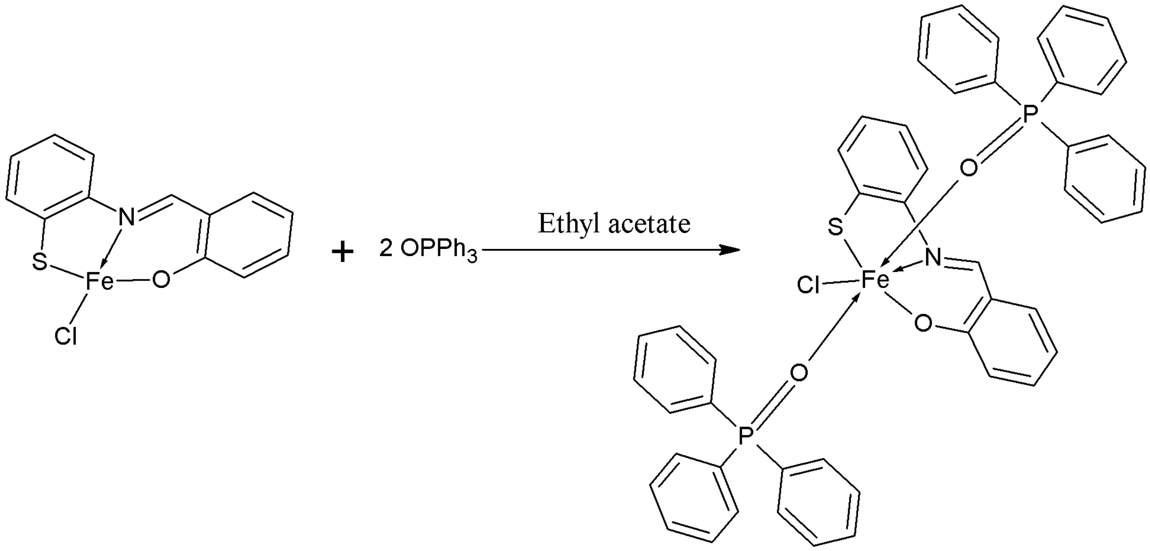
The precursor complex [FeCl$_3$(OPPh$_3$)$_2$] was prepared by the reaction between FeCl$_3$ and triphenylphosphineoxide in 1:3 ratio in ethanol according to the reported procedure (Ondrejkovicova et al. 1991). FeL$_{13}$ was prepared by the reaction between the precursor and N-(2-aminophenyl)salicylideneimine in ethyl acetate at room temperature (Scheme 3.7). The formed complex was filtered and washed with diethyl ether and dried in *vacuo*. The formation of complex was checked by TLC. Yield: 80%.



Scheme 3.7: Synthesis of FeL_{13} complex

3.4.8 Synthesis of Fe(III) complex FeL_{14}

FeL_{14} was prepared by stirring FeL_{12} and triphenylphosphineoxide in 1:2 ratio in ethyl acetate at room temperature for 4-5 hours (Scheme 3.8). The formed complex was filtered and washed with diethyl ether and dried in *vacuo*. The formation of the complex was checked by TLC. Yield: 70%.



Scheme 3.8: Synthesis of FeL_{14} complex

3.5 GENERAL PROCEDURE FOR OXIDATION OF ALCOHOLS

3.5.1 Oxidation using periodic acid

A solution of complex in 5 cm^3 CH_3CN was added to the solution of substrate (1 mmol) and H_5IO_6 (0.75 mmol). The solution mixture was refluxed for requisite time and analyzed by GC using dichlorobenzene as internal standard.

3.5.2 Oxidation using hydrogen peroxide

Oxidation of alcohols to carbonyl compounds were carried out as follows. To a solution containing substrate (1mmol) and complex, H_2O_2 (30%) was added. The reaction mixture was stirred for requisite time duration. It was then extracted with minimal volume of ether and dried over $MgSO_4$. The ether solution was then analyzed by GC using 1,2-dichlorobenzene as internal standard.

3.5.3 Oxidation using aqueous tert-Butyl hydroperoxide (TBHP)

A solution of the complex in 3 cm^3 acetonitrile was added to the solution of substrate (1 mmol) and aqueous TBHP (70%). The reaction mixture was stirred at 80°C. After completion of the reaction, the excess of sodium metabisulphite was added into the reaction mixture and water was poured into it. Then the reaction mixture was extracted with dichloromethane and dried over $MgSO_4$. The solution was then analyzed by GC using 1,2-dichlorobenzene as internal standard.

3.6 GENERAL PROCEDURE FOR PRODUCT ANALYSIS

The initial column temperature was increased from 60ºC to 150ºC at the rate of 10ºC/min and then to 220ºC at the rate of 40°/min. Nitrogen was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 150ºC and 250ºC respectively during product analysis. The retention time for different compounds was determined by injecting pure compounds under identical gas chromatography conditions. GC conversion was calculated using dichloromethane as internal standard.

CHAPTER 4

CHARACTERIZATION AND CATALYTIC ACTIVITY STUDY

4.1 CHARACTERIZATION OF COMPLEXES FeL_1-FeL_5

The reaction of equimolar ratios of the respective ligand (L_1, L_2, L_3, L_4 or L_5) and $[FeCl_3(PPh_3)_3]$ yielded the new complexes of the general formula $[Fe(L)Cl(PPh_3)_2]$ in moderate to good yield. All the present complexes were red in color. They were found to be soluble in CH_2Cl_2, CH_3CN, DMF and DMSO. The analytical data for these complexes were in good agreement with the molecular formula. In all the reactions, it was observed that the Schiff base behaves as a tridentate ligand.

4.1.1 Electronic spectra and Analytical data

The electronic spectra of the ligands and complexes were recorded in dimethyl formamide (Fig. 4.1). The electronic spectra of the all the complexes in DMF showed four bands in the region 240–518 nm. The bands appearing in the region 245-302 nm have been assigned to intra ligand transitions (Sureshan and Bhattacharya 1998). Bands in the range 406-425 nm corresponds to ligand to metal charge transfer band (Garcia et al. 2004). Low intense bands observed in the range of 475-518 nm must be due to d-d transition which confirms the presence of high spin octahedral iron (III) complexes (Bhattacharjee et al. 2012). The analytical data for the complexes are given in Table 4.1.

Table 4.1: Analytical and Electronic spectral data of Fe(III) complexes

	Elemental Analysis data*			Electronic spectral data			Magnetic moment
Complex	C	H	N	Intra ligand transitions	Charge transfer transition	d-d transition	μ_{eff} (BM)
FeL_1	71.05	4.79	1.59	245, 286	406	483	5.98
	(71.16)	(4.75)	(1.69)				
FeL_2	68.45	4.43	1.67	248, 299	409	498	5.72
	(68.31)	(4.45)	(1.63)				
FeL_3	64.80	4.29	1.59	249, 302	411	500	5.77
	(64.96)	(4.23)	(1.55)				
FeL_4	67.55	4.23	3.23	246,291	400	475	5.68
	(67.48)	(4.39)	(3.21)				
FeL_5	70.12	4.98	1.70	248, 294	425	518	5.90
	(70.07)	(4.82)	(1.63)				

*Found (Calculated)

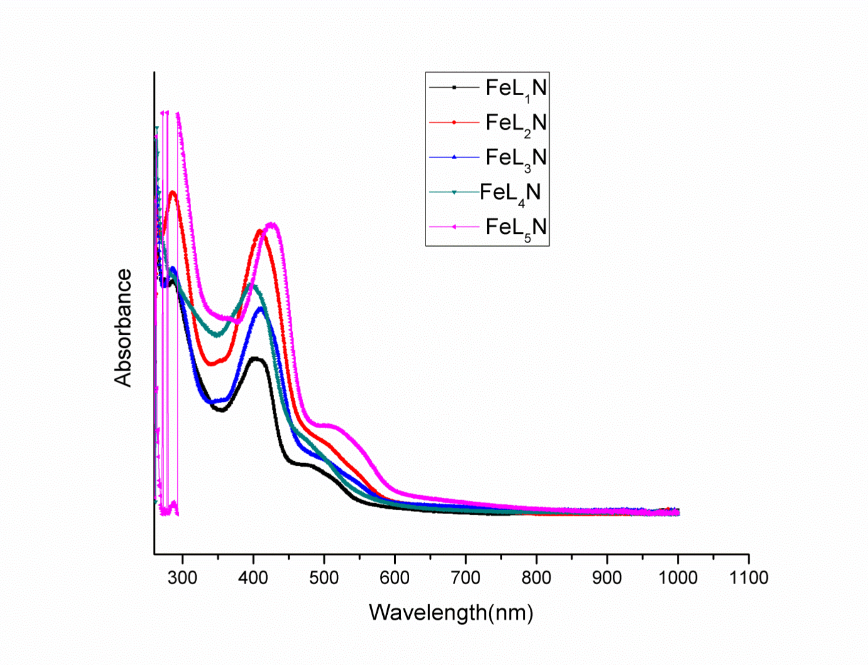


Fig. 4.1: UV-visible spectra of FeL_1-FeL_5 complexes

4.1.2 FTIR spectra

Selected FTIR bands of ligands and complexes are listed in Table 4.2. The FTIR spectra of the ligands exhibit a strong band around 1611-1625 cm^{-1}, which is assigned to ν(C=N) vibration. As a result of coordination, this band is shifted to lower wave number in complexes. The band in the region 1250-1271 cm^{-1} which is assigned to phenolic ν(C–O) in the free ligand, is shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion (Latif et al 2007, Deligonul and Tumer, 2006). The bands around 530 cm^{-1} and 500 cm^{-1} in the complex is assigned to ν(M–O) and ν(M–N) respectively. Bands due to triphenylphosphine also appeared in the expected region (Tamizh et al 2009) (Fig. 4.2 and Fig. 4.3).

Table 4.2: FTIR spectral data (cm^{-1}) for ligands and its Fe(III) complexes

Compound	$\nu_{(C=N)}$	$\nu_{(C-O)}$	$\nu_{(Fe-O)}$	$\nu_{(Fe-N)}$	Bands due to PPh_3
L_1	1618	1271	-	-	-
L_2	1625	1269	-	-	-
L_3	1623	1267	-	-	-
L_4	1611	1270	-	-	-
L_5	1625	1250	-	-	-
FeL_1	1599	1297	532	512	1434, 1083, 688
FeL_2	1592	1300	535	505	1435, 1078, 695
FeL_3	1593	1294	533	509	1437, 1083, 686
FeL_4	1598	1309	538	512	1436, 1084, 688
FeL_5	1602	1293	532	510	1437, 1083, 688

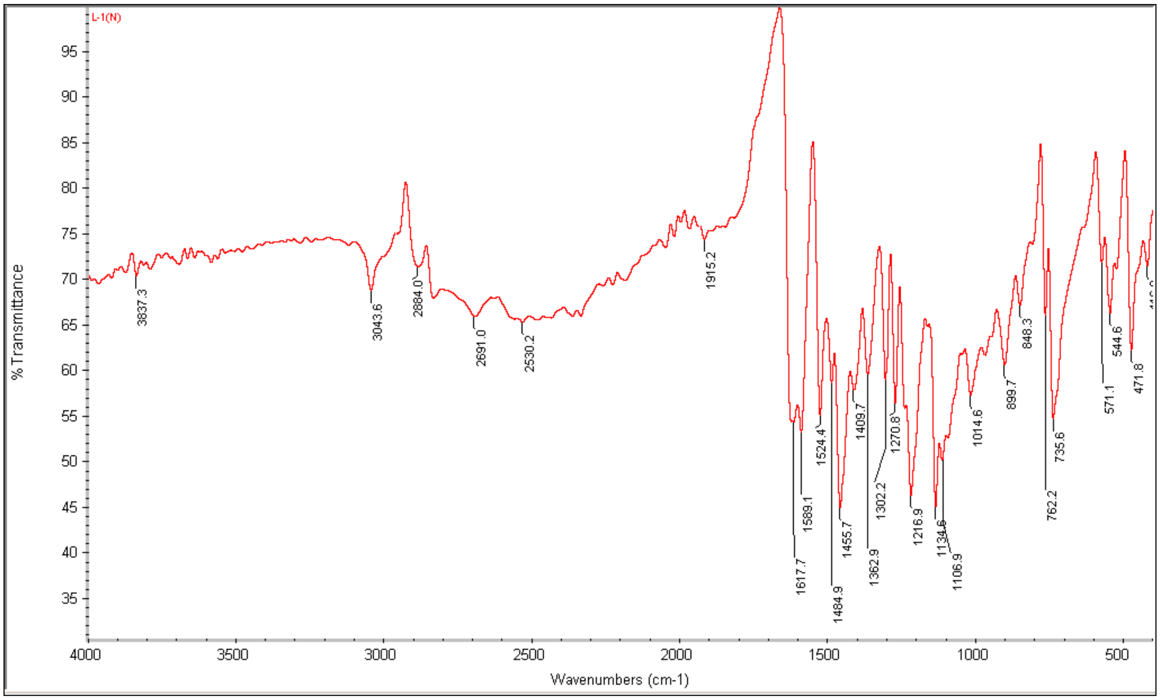


Fig. 4.2: FTIR spectra of ligand L_1

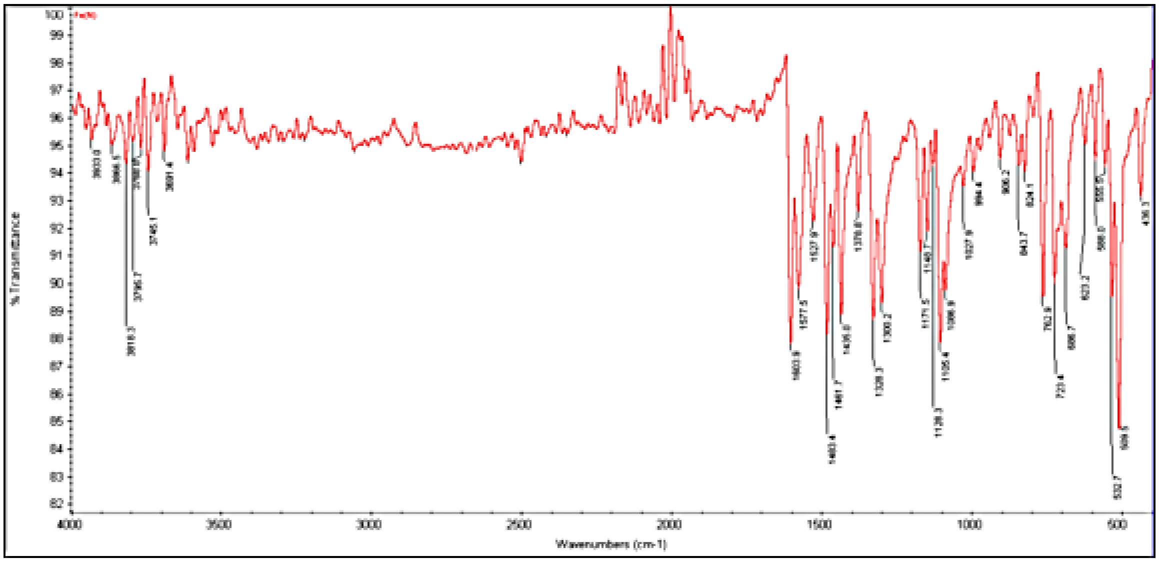


Fig. 4.3: FTIR spectra of FeL_1 complex

4.1.3 ESI Mass Measurements

In the mass spectra of the complexes, the molecular weight of the complexes correspond to the presence of the tridentate ligand, two triphenylphosphine ligands and chloride group in the synthesized complexes confirming the assumed structure. The ESIM spectra of the complex FeL_1 is shown in the Figure 4.4. Similarly expected molecular weight and the observed molecular weight of the complexes are given in the Table 4.3.

Table 4.3: ESIMS data of Iron complexes

Complex	Expected mass	Observed mass
FeL_1	827.2	828.3
FeL_2	861.5	862.2
FeL_3	906.0	907.2
FeL_4	872.1	873.4
FeL_5	856.9	857.3

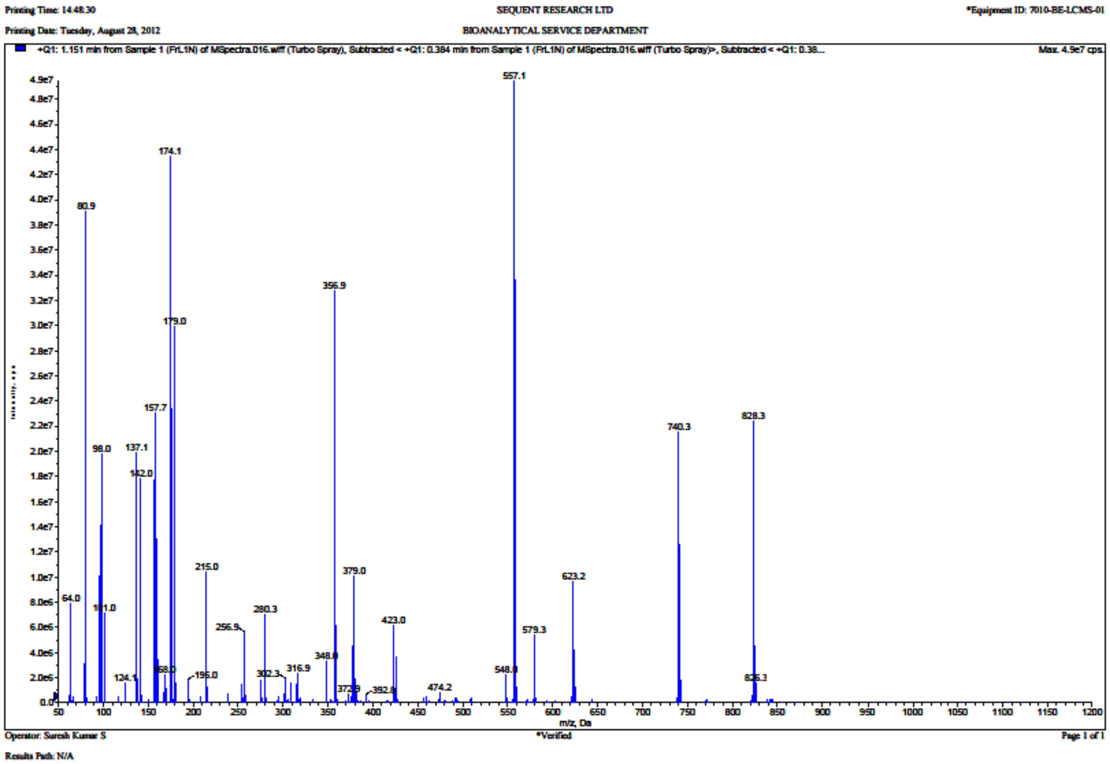


Fig. 4.4: ESIM spectra of FeL_1 complex

4.1.4 Magnetochemical measurements

In order to obtain further structural information, the magnetic moments of the complexes were measured. All iron (III) complexes showed magnetic moments in the range 5.68-5.98 B.M, confirms the high spin octahedral iron (III) complexes (Sallam et al 2002).

4.1.5 Thermal measurements

The thermograms of Fe(III) complexes showed 3 stages of decomposition. First stage of decomposition at around 200°C which corresponds to the loss of chloride, second stage of decomposition at around 350°C which indicates the loss of triphenylphosphine and third stage of decomposition in the range of 420-750°C which occurs in multistep indicating the loss of ligand molecule (Fig. 4.5).

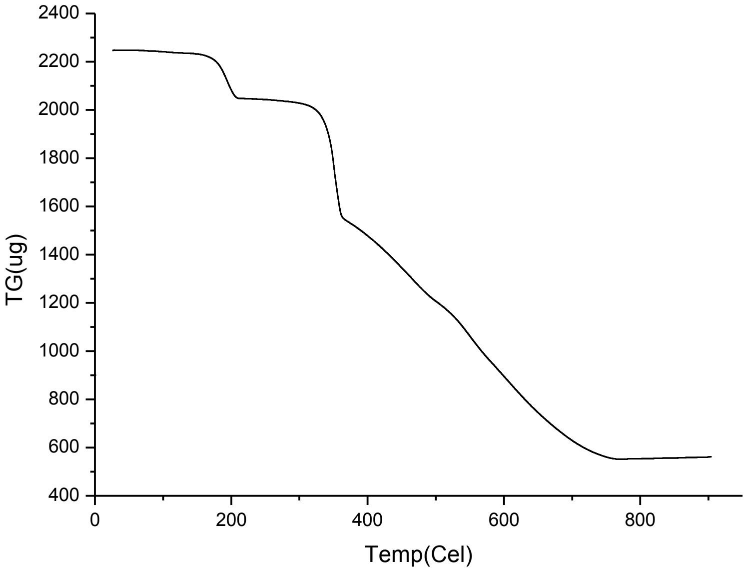


Fig. 4.5: TG diagram of FeL_1

4.2 CATALYTIC ACTIVITY OF COMPLEXES FeL_1-FeL_5

The present work describes the catalytic oxidation of primary and secondary alcohols by the synthesized complexes using mild oxidants like periodic acid, hydrogen peroxide and aqueous tert-butylhydroperoxide. All the synthesized iron complexes were found to catalyze the oxidation of alcohol to corresponding carbonyls but the yields were found to vary with different catalysts.

The oxidation of benzyl alcohol, as a standard substrate, was first investigated in order to optimize the reaction variables such as solvent, temperature, alcohol/oxidant molar ratio and length of the reaction time. The activity of FeL_1 was studied in different solvents (methanol, acetonitrile, and acetone) using H_5IO_6, H_2O_2 and aqueous TBHP as the oxidants. In case of H_5IO_6 and aqueous TBHP, best conversions were observed in acetonitrile, whereas H_2O_2 system showed the best conversion under solvent less condition. The activity of FeL_1 was studied at different temperature by taking benzyl alcohol as the model substrate in all the 3 above mentioned systems. It was observed that at 80°C, the system showed higher conversions in case of H_5IO_6 and aqueous TBHP while in H_2O_2 system, the reaction occurred at room temperature. The optimization of other reaction conditions mentioned below, were studied by taking benzyl alcohol as the substrate with FeL_1 in all the 3 systems.

i. Effect of time

ii. Effect of catalyst concentration

iii. Effect of oxidant concentration

4.2.1 Effect of time

In order to study the effect of time on the activity, the product analysis was done at regular intervals of time, under similar reaction conditions.

In the case of CH_3CN-H_5IO_6, it was observed that the total reaction time was 90 minutes at 80°C. The experiments were conducted at regular intervals of time beyond 90 minutes. The results show that the conversion remains constant at about 96% after a reaction time of 90 minutes (Table 4.4).

In the case of H_2O_2 system, it was found that the reaction was complete in 20 minutes (Table 4.5).

Similarly the effect of time was studied for TBHP system, in which case it was observed that total reaction time of 120 minutes was needed for highest catalytic conversion (Table 4.6).

Table 4.4: Effect of time on benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system

Sl. No.	Time (min)	% Yield[a] CH_3CN-H_5IO_6 system
1	2	10.3
2	15	58.6
3	30	74.6
4	45	79.6
5	60	84.3
6	75	89.6
7	**90**	**96.3**
8	105	96.3
9	120	95.8
10	135	96.1

[a]GC yield, average of 3 trials

Table 4.5: Effect of time on benzyl alcohol to benzaldehyde in H_2O_2 system

Sl. No.	Time (min)	% Yield[a] H_2O_2 system
1	2	28.5
2	5	45.6
3	10	68.3
4	15	78.4
5	**20**	**86.7**
6	25	86.7
7	30	86.5

[a]GC yield, average of 3 trials

Table 4.6: Effect of time on benzyl alcohol in CH_3CN- aq TBHP system

Sl. No.	Time (min)	% Yield[a] CH_3CN-aq TBHP system
1	2	9.8
2	15	21.5
3	30	33.6
4	45	40.8
5	60	47.5
6	75	56.8
7	90	63.8
8	105	69.3
9	**120**	**80.7**
10	135	80.7
11	150	80.6

[a]GC yield, average of 3 trials

4.2.2 Effect of catalyst concentration

In order to study the effect of the concentration of catalyst with respect to substrate and oxidant, the reaction was carried out at different catalyst concentrations. From the results it is confirmed that the oxidants used will bring about the oxidation of alcohols in negligible amount without the presence of the catalyst. The results are summarized in the Table 4.7.

A minimum quantity of 0.02 mmol of the catalyst was sufficient for the effective transformation of benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system. While in case of H_2O_2 and CH_3CN-aq. TBHP systems 0.03 mmol and 0.01 mmol of catalyst was sufficient to bring about the conversions respectively (Fig. 4.6).

Table 4.7: Effect of catalyst concentration on benzyl alcohol

Sl. No.	Catalyst concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 system	H_2O_2 system	CH_3CN-aq TBHP system
1	0	12.0	2.0	15.4
2	0.01	75.6	67.9	**80.7**
3	0.02	**96.1**	86.6	80.6
4	0.03	95.7	**86.9**	80.7
5	0.04	95.4	86.4	80.5

[a] GC yield, average of 3 trials

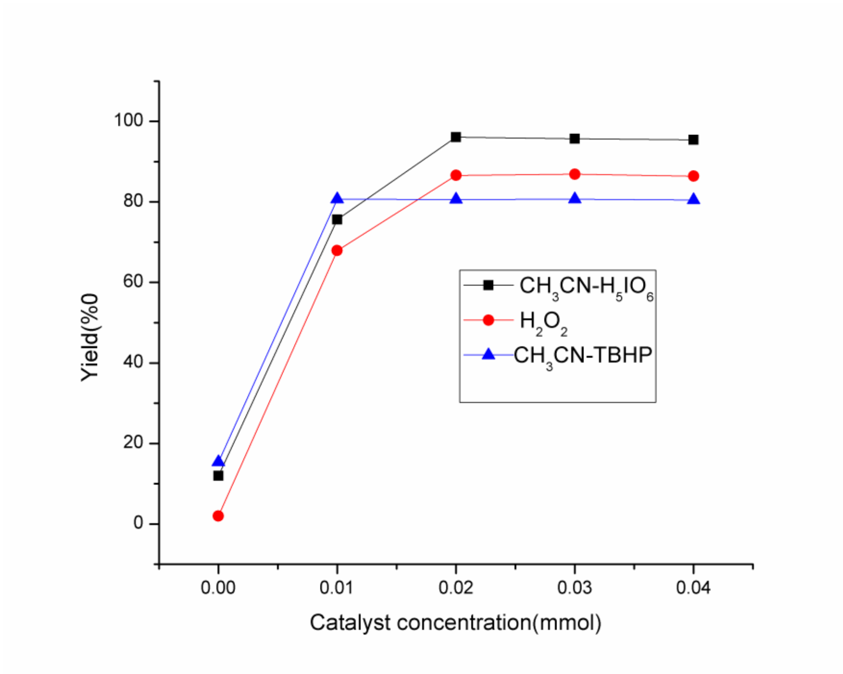


Fig. 4.6: Effect of catalyst concentration on benzyl alcohol

4.2.3 Effect of oxidant concentration

The reactions were studied with respect to substrate and catalyst at different oxidant concentrations. The results are summarized in Table 4.8. A minimum quantity of 0.75mmol, 3 mmol, 2 mmol of the oxidants were required in CH_3CN-H_5IO_6, H_2O_2,

CH_3CN-aq. TBHP systems respectively for the effective oxidation of benzyl alcohol to benzaldehyde (Fig. 4.7).

Table 4.8: Effect of oxidant concentration on benzyl alcohol

Sl. No.	Oxidant concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 system	H_2O_2 system	CH_3CN-aq. TBHP system
1	0	3.7	3.6	3.8
2	0.5	82.3	15.6	39.2
3	0.75	**96.2**	32.6	52.7
4	1.0	96.2	56.8	69.7
5	2.0	96.1	72.6	**80.7**
6	3.0	96.4	**86.6**	80.6
7	4.0	96.3	86.7	80.6
8	5.0	96.5	86.5	80.7

[a] GC yield, average of 3 trials

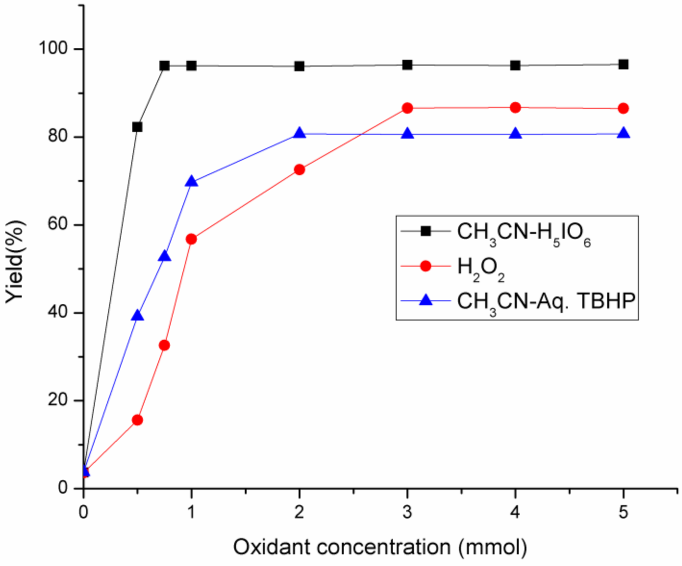


Fig. 4.7: Effect of oxidant concentration on benzyl alcohol

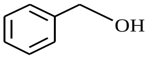
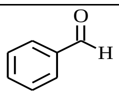
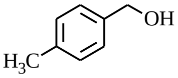
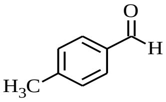
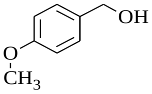
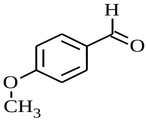
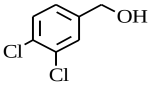
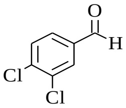
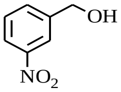
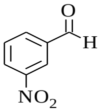
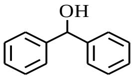
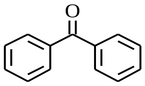
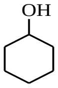
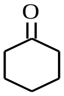
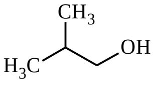
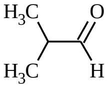
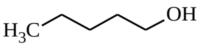
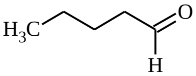
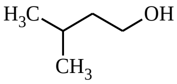
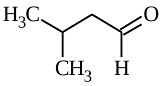
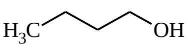
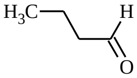
The oxidation was extended to a variety of alcohols including primary and secondary, aromatic, aliphatic and cyclic alcohols using the optimized reaction conditions. The results for the oxidation of a variety of alcohols are summarized in Tables 4.9, 4.10, 4.11 respectively in CH_3CN-H_5IO_6, H_2O_2, CH_3CN-aq. TBHP systems.

Among the three systems studied, in CH_3CN-H_5IO_6 and H_2O_2, selectivity towards aldehyde remains more than 95%. The over oxidation to carboxylic acid was ruled out by derivative test. While in CH_3CN-aq. TBHP, primary alcohols are oxidized to corresponding acids with high yield. No oxidation was observed in the aromatic ring of benzylic substrates hence the catalytic systems are selective towards the alcoholic group.

In CH_3CN-H_5IO_6 and CH_3CN-aq. TBHP systems, no significant conversion was observed even after 24 hr, at room temperature. The need of higher temperature may increase the solubility of the oxidant and assist in the deprotonation of the substrate which is considered to be the initial step in the oxidation of alcohols.

Among the various alcohols studied those containing aromatic substituents were found to be more reactive than alicyclic and aliphatic alcohols. This can be attributed to the higher reactivity of aromatic systems due to its delocalization. Lower reactivity of aliphatic alcohols is because of the lesser reactivity of the substrates. Similarly electron donating groups were found to slow down oxidation, whereas electron withdrawing groups accelerate it. Para or ortho substituents with electron releasing or electron withdrawing properties do not induce any change on the selectivity. It was also observed that electron donating group on the ligand enhanced the catalytic activity whereas; electron withdrawing substituents decreased the catalytic activity of the complexes. As the ligand becomes more electron donating, the increased electron density makes the metal centre in the complex easier to oxidize. This is in agreement with earlier reported observations (Sharma et al., 2004).

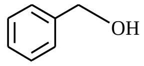
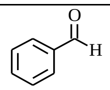
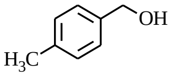
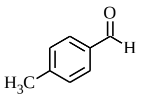
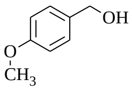
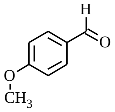
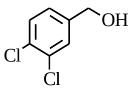
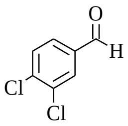
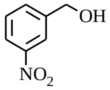
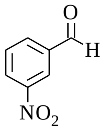
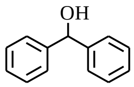
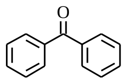
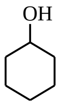
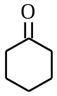
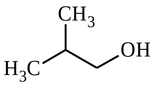
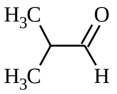
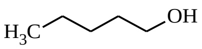
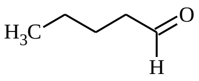
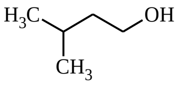
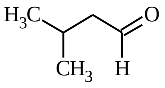
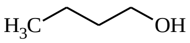
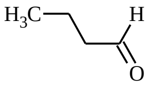
Table 4.9: Oxidation of alcohols by Fe(III) complexes[a] in CH_3CN-H_5IO_6 system

Alcohols	Product	% Yield of carbonyl compound[b]				
		FeL_1	**FeL_2**	**FeL_3**	**FeL_4**	**FeL_5**
		96.1	88.4	90.3	89.9	97.8
		85.3	80.3	82.4	81.7	84.7
		81.4	76.3	78.2	78.9	82.7
		80.6	77.8	78.9	79.1	81.4
		98.1	90.9	91.6	91.3	98.3
		84.5	78.1	82.6	81.9	86.7
		75.6	71.5	73.9	72.8	76.2
		65.8	61.4	59.8	62.4	66.8
		57.6	53.5	52.7	53.1	58.1
		54.3	50.6	52.8	52.7	54.7
		51.4	47.6	46.7	46.8	52.9

[a] 1 mmol alcohol, 0.75 mmol H_5IO_6, 0.02 mmol Fe (III) complex, 3 mL CH_3CN, stirring at 80°C.

[b] GC yield, average of 3 trials.

Table 4.10: Oxidation of alcohols catalyzed by Fe(III) complexes[a] in H_2O_2 system

Alcohols	Product	% Yield of carbonyl compound[b]				
		FeL₁	**FeL₂**	**FeL₃**	**FeL₄**	**FeL₅**
		86.6	82.4	82.9	82.7	87.9
		82.4	77.6	78.5	80.3	83.3
		80.3	75.6	77.9	78.2	81.2
		84.6	82.4	81.3	82.7	85.8
		87.6	83.6	85.9	84.7	88.1
		72.4	65.8	67.8	66.9	73.3
		60.3	54.6	57.8	58.4	60.9
		34.5	30.1	30.8	30.6	34.4
		32.8	25.4	27.2	28.4	30.8
		27.1	22.9	24.6	25.9	26.3
		22.5	15.3	18.4	18.7	19.2

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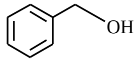
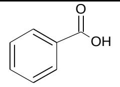
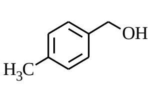
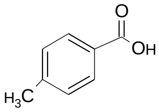
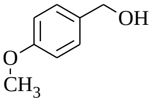
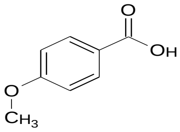
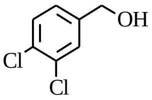
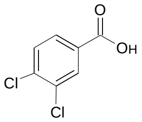
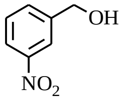
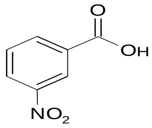
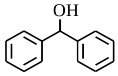
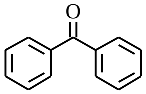
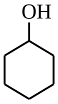
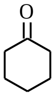
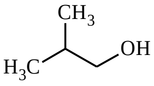
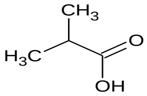
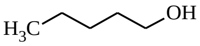
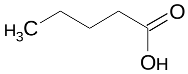
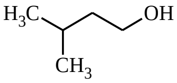
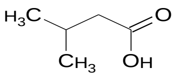
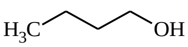
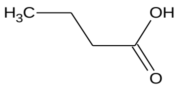
[a] 1 mmol alcohol, 5.0 mmol H_2O_2, 0.02 mmol Fe (III) complex.

[b] GC yield, average of 3 trials.

Table 4.11: Oxidation of alcohols by Fe(III) complexes[a] in CH_3CN-aq. TBHP system

Alcohols	Product	% Yield of carbonyl compound[b]				
		FeL_1	**FeL_2**	**FeL_3**	**FeL_4**	**FeL_5**
		80.7	76.3	77.5	78.3	82.1
		71.3	66.9	67.4	68.7	73.1
		72.2	68.8	69.7	70.1	74.9
		73.2	69.8	71.6	72.5	72.8
		81.5	77.9	78.3	78.6	82.4
		65.2	62.2	60.8	64.9	66.2
		54.9	50.0	51.2	52.6	53.9
		35.2	30.6	32.0	32.7	35.8
		32.9	25.6	26.1	28.8	32.6
		21.8	17.9	18.6	19.5	20.0
		16.2	10.8	11.7	13.0	17.2

[a] 1 mmol alcohol, 2.0 mmol aq. TBHP, 0.01 mmol Fe (III) complex, 1 mL CH_3CN, stirring at 80°C.

[b] GC yield, average of 3 trials.

4.2.4 Mechanistic study

To study the mechanism involved in the reaction, UV spectra of the reaction mixture before and after the addition of the oxidant were examined (Fig. 4.8, 4.9 and 4.10).

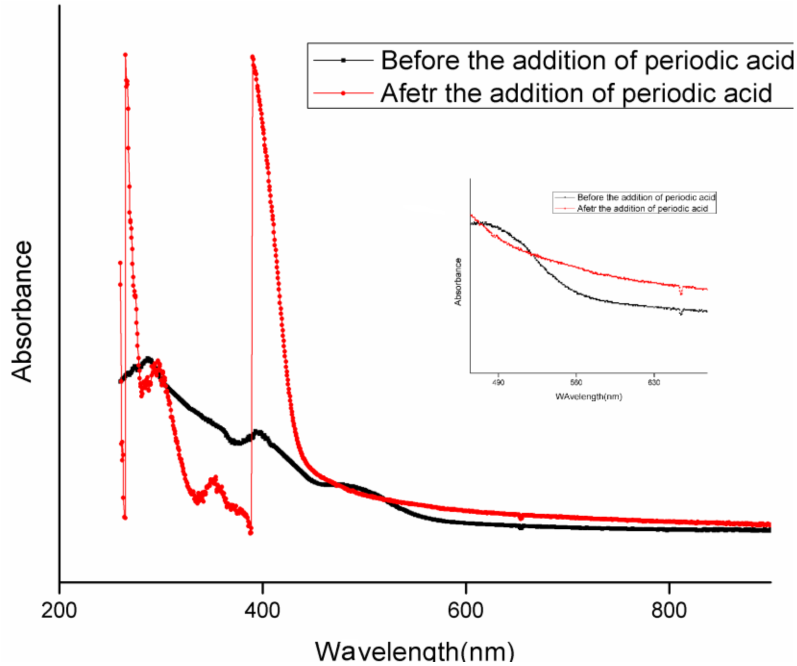


Fig. 4.8: UV-visible spectra of the reaction mixture in CH_3CN-H_5IO_6 system catalyzed by FeL_1 complex

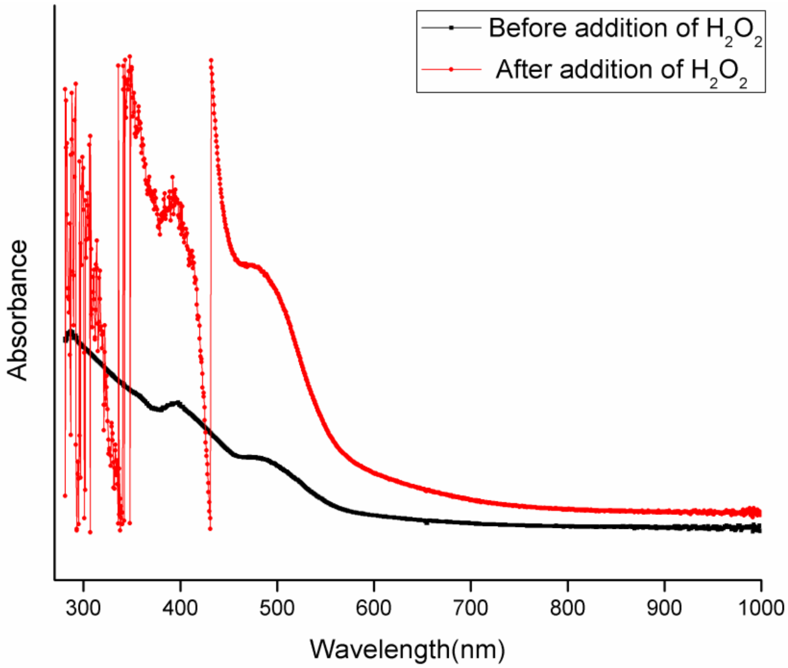


Fig. 4.9: UV-visible spectra of the reaction mixture in H_2O_2 system catalyzed by FeL_1 complex

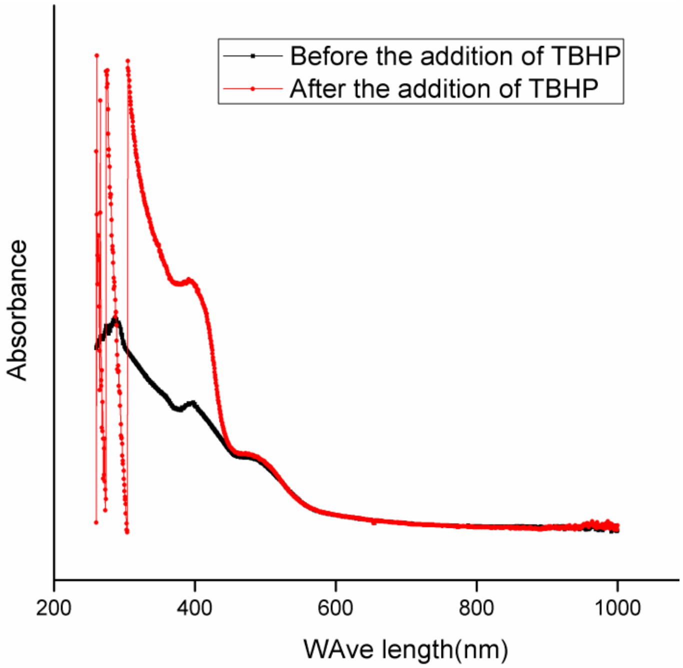
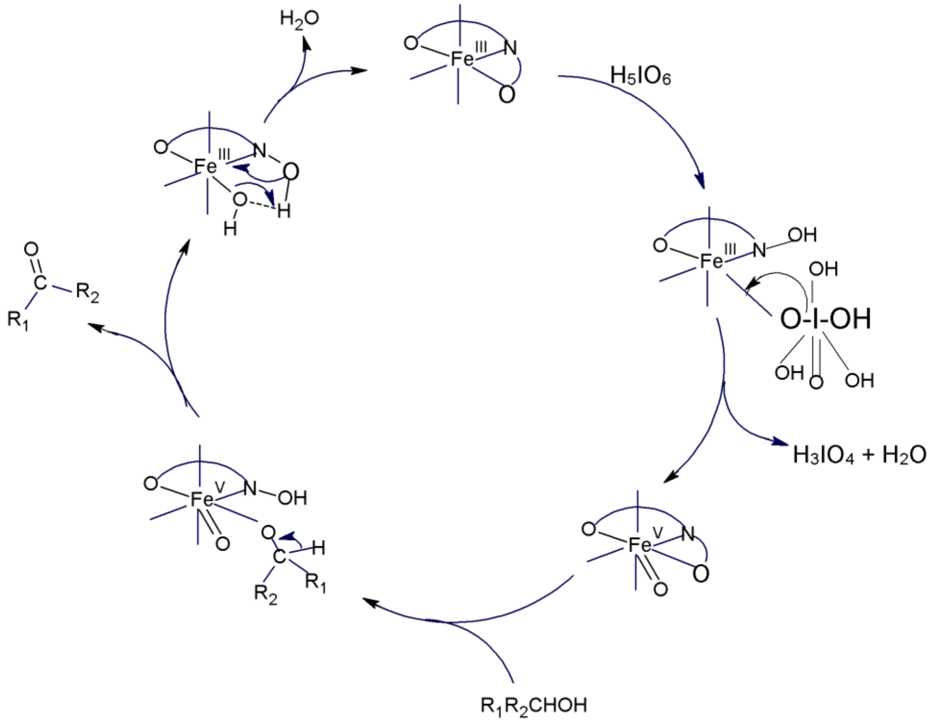


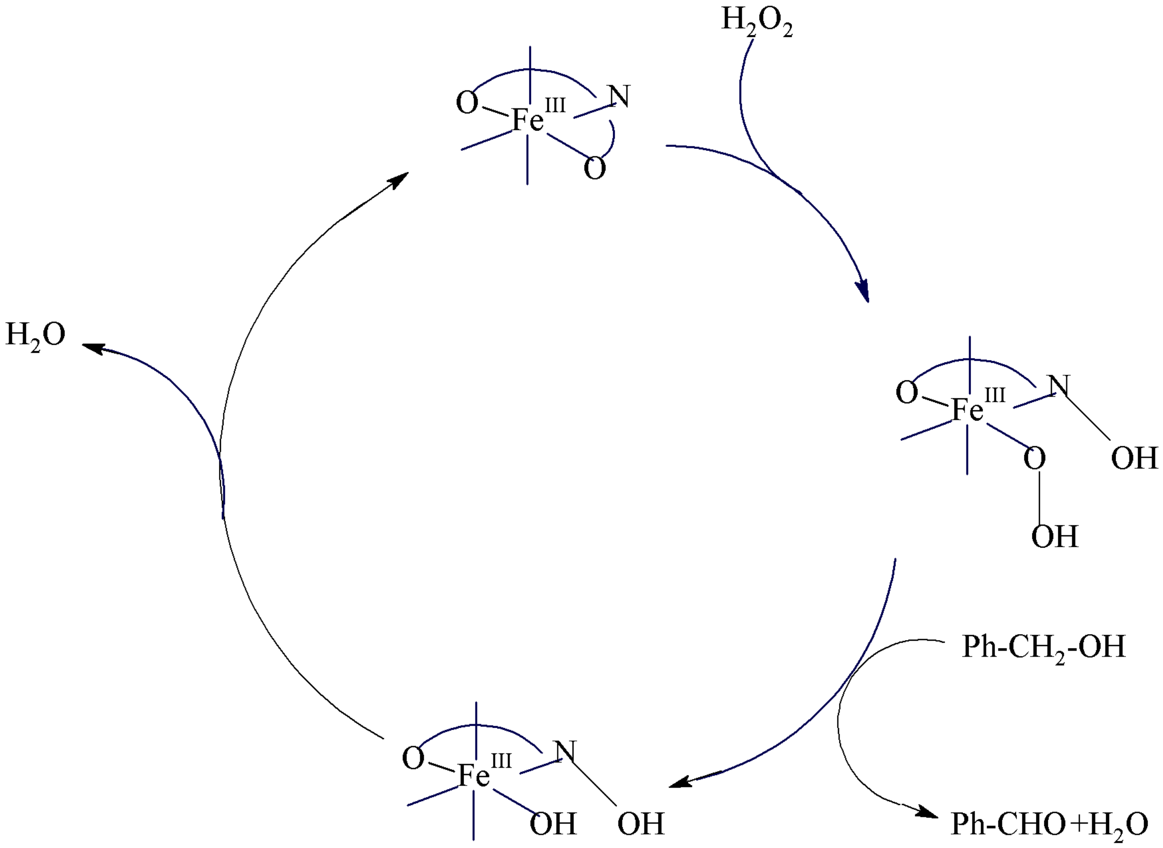
Fig. 4.10: UV-visible spectra of the reaction mixture in aq. TBHP system catalyzed by FeL_1 complex

In the UV-visible spectra of the reaction mixture of periodic acid system, an increase in the intensity of intra ligand band and charge transfer band was observed suggesting the interaction between the oxidant and the complex. Similarly, the d-d band disappeared after the addition of the oxidant. This indicates the formation of high valent iron oxo species ($Fe^{V}=O$) (Balogh-hergovicha and Speier 2005, Upadhyay et al. 1992). Based on these results, oxometal pathway is more likely to be involved in the alcohol oxidation reaction in periodic acid system. Hence the following mechanism has been proposed for the oxidation of alcohols in CH_3CN-H_5IO_6 system (Scheme 4.1). The high conversion can be attributed to formation of strong and highly active oxidant $Fe^{V}=O$.



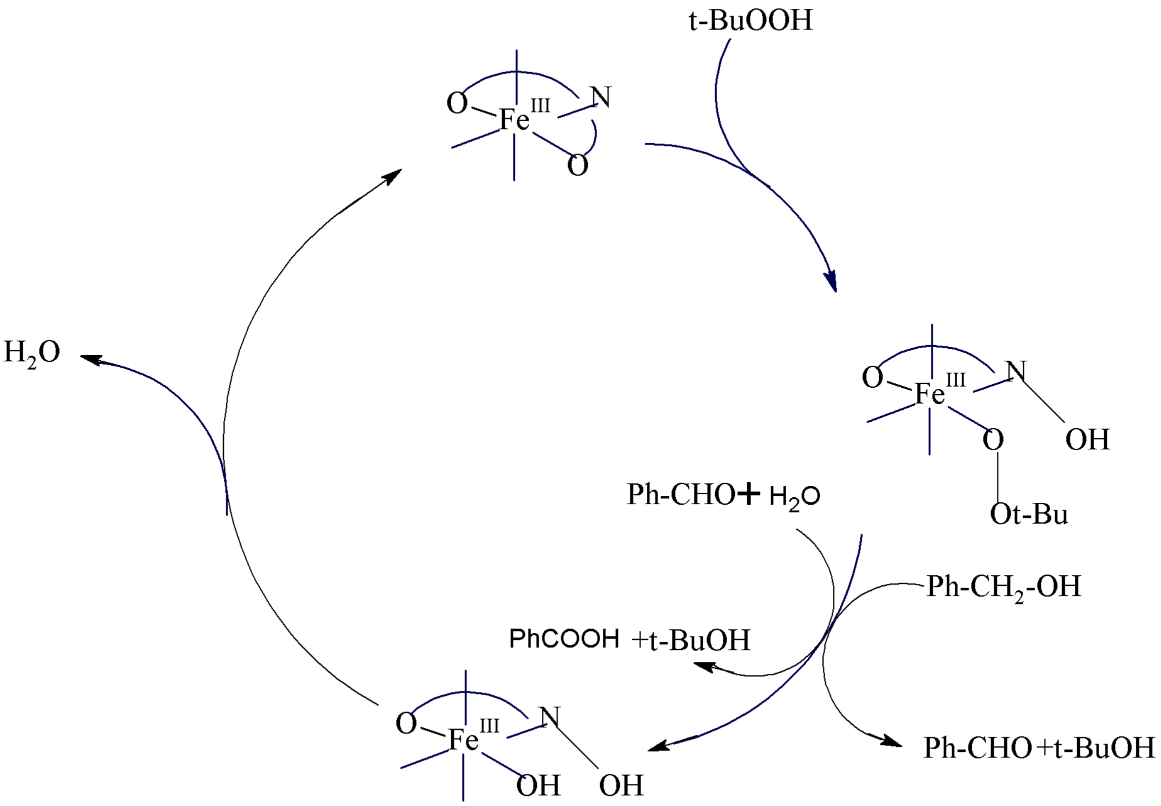
Scheme 4.1: Mechanism of oxidation of alcohols in CH_3CN-H_5IO_6 system

In H_2O_2 system, an increase in the intensity of intra ligand band and charge transfer band was observed suggesting the interaction between the oxidant and the complex. Along with that, a sharp increase in intensity at around 355 nm was observed which is assignable to the LMCT band of hydroperoxide to the metal centre (Yamaguchi and Masuda 2005). This clearly indicates the involvement of hydroperoxo metal species in the mechanism. Also since there is no change with respect to d-d transition, the oxidation state of the complex does not change during the reaction. Hence the following mechanism has been proposed for the oxidation of alcohols in H_2O_2 system (Scheme 4.2).



Scheme 4.2: Mechanism of oxidation of alcohols in H_2O_2 system

In TBHP system, only increase in intensity of Intra ligand and LMCT band is observed indicating the interaction between the metal and oxidant. Since there is no change in d-d band, the oxidation state of the metal does not change. Hence the reaction must be proceeding through peroxo mechanism similar to H_2O_2 system (Scheme 4.3). Formed aldehyde further reacts with water and gets protonated. The protonated aldehyde gets oxidized to acid following the same mechanism. Among the three oxidant systems, periodic acid system showed higher conversion. This must be due to strong oxidant formed during the reaction, $Fe^{V}=O$.



Scheme 4.3: Mechanism of oxidation of alcohols in CH_3CN-aq. TBHP system

4. 3 SYNTHESIS OF COMPLEXES CoL_1-CoL_5

The reaction of solution of $CoCl_2$, the synthesized ligand and triphenylphosphine in a 1:1:3 molar ratios yielded the new complexes of the general formula $[CoOCH_3(L)(PPh_3)_2]$ (L = Schiff base ligand) in moderate to good yield. All the synthesized complexes were green in color. They were found to be soluble in CH_3CN, C_6H_6, DMSO, DMF and $CHCl_3$.

4.3.1. Electronic Spectra and Analytical data

The analytical data for these complexes are in good agreement with the above molecular formula. In all the reactions, it has been observed that the Schiff base behaves as a tridentate ligand. The electronic spectra of the ligands and complexes were recorded in dimethylformamide. The electronic spectra of the all the complexes showed two bands in the region 250–270 nm and around 450 nm. The former band has been assigned to intra ligand transitions. The band appearing in the region of 450 nm is associated to charge transfer transition (Fig 4.11). The analytical data for the complexes are given in Table 4.12.

Table 4.12: Analytical and Electronic spectral data of Co(III) complexes

Complex	Elemental composition *Found (Calculated)			Electronic spectral data		Magnetic moment μ_{eff} (BM)
	C	H	N	Intra ligand transition	charge transfer transition	
CoL_1	72.70 (72.73)	5.10 (5.13)	1.60 (1.70)	264	439	Diamagnetic
CoL_2	69.71 (69.81)	4.72 (4.80)	1.59 (1.63)	264	446	Diamagnetic
CoL_3	66.30 (66.38)	4.59 (4.57)	1.55 (1.55)	264	446.5	Diamagnetic
CoL_4	68.90 (68.97)	4.66 (4.75)	3.18 (3.21)	265	417.5	Diamagnetic
CoL_5	70.57 (70.58)	5.10 (5.18)	1.58 (1.64)	265	459.5	Diamagnetic

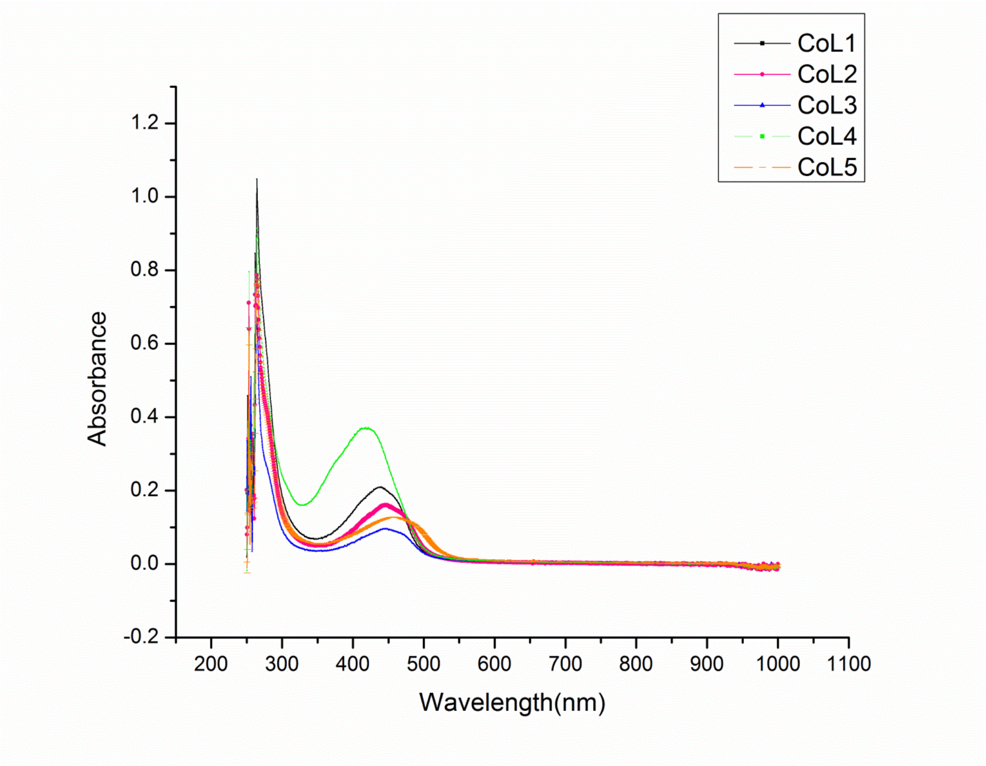


Fig. 4.11: UV spectra of complexes CoL_1-CoL_5.

4.3.2 FTIR Spectra

Selected FTIR bands of ligands and complexes are listed in Table 4.13. The ν(C=N) vibration is shifted to lower frequency in complexes as a result of coordination. The band in the region 1234-1271 cm^{-1} which is assigned to phenolic ν(C–O) in the free ligand, is shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion as discussed under section 4.1.2. The bands around 535 cm^{-1} and 500 cm^{-1} in the complex is assigned to ν(M–O) and ν(M–N) respectively. Bands due to triphenylphosphine also appeared in the expected region (Fig. 4.12) (Table 4.13).

Table 4.13: FTIR spectral data (cm^{-1}) for ligands and its Co(III) complexes

Compound	$\nu_{(C=N)}$	$\nu_{(C-O)}$	$\nu_{(Co-O)}$	$\nu_{(Co-N)}$	Bands due to PPh_3
H_2L_1	1617	1271	-	-	-
H_2L_2	1625	1269	-	-	-

H_2L_3	1623	1267	-	-	-
H_2L_4	1611	1234	-	-	-
H_2L_5	1625	1250	-	-	-
CoL_1	1602	1299	543	498	1433, 1090, 691
CoL_2	1600	1290	535	505	1435, 1078, 695
CoL_3	1596	1293	545	497	1432, 1088, 691
CoL_4	1598	1251	530	498	1432, 1096, 692
CoL_5	1592	1293	532	510	1437, 1083, 688

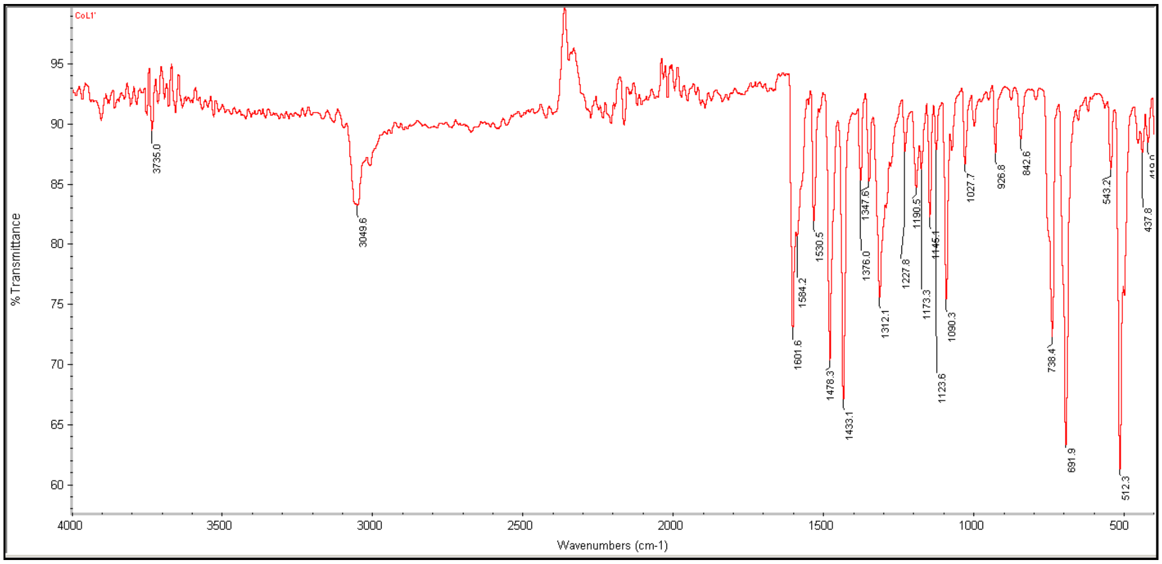


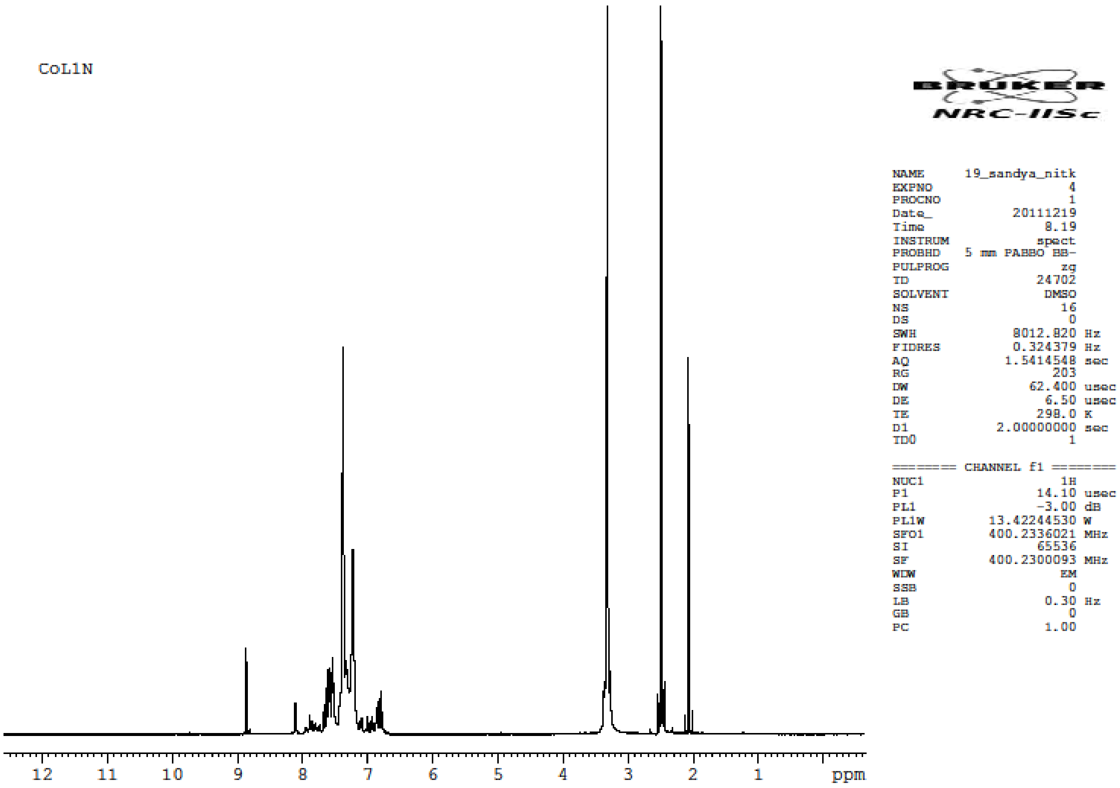
Fig. 4.12: FTIR spectra of CoL_1

4.3.3 NMR Spectra

The ^1H NMR spectra of all the complexess resonances at 6.2–8.2 ppm as set of multiplets which are assigned to the aromatic protons that of coordinated striphenylphosphine groups present in the complexes and that of the Schiff base ligand. $^{31}P\{^1H\}$ NMR spectra of the complexes (Table 4.14) exhibit a sharp singlet in the range 42-43 ppm supporting the presence of the triphenylphosphine groups in *trans*-positions. The ^1H NMR and $^{31}P\{^1H\}$ NMR spectra of the complexes **CoL_1** are shown in the Figure 4.13 and 4.14 respectively.

Table 4.14: ^{1}H NMR and ^{31}P NMR chemical shifts of the complexes

Complex	Chemical shift (ppm)	
	^{1}H	^{31}P
CoL₁	6.3-8.2	43.3
CoL₂	6.1-8.0	43.5
CoL₃	6.2-8.2	43.7
CoL₄	6.0-7.8	42.3
CoL₅	6.4-8.4	43.8



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NAME       19_sandya_nitk
EXPNO                   4
PROCNO                  1
Date_            20111219
Time                 8.19
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG                zg
TD                  24702
SOLVENT              DMSO
NS                     16
DS                      0
SWH              8012.820 Hz
FIDRES           0.324379 Hz
AQ              1.5414548 sec
RG                    203
DW                 62.400 usec
DE                   6.50 usec
TE                  298.0 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.10 usec
PL1                 -3.00 dB
PL1W          13.42244530 W
SFO1          400.2336021 MHz
SI                  65536
SF            400.2300093 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Fig. 4.13: ^{1}H NMR spectra of CoL1

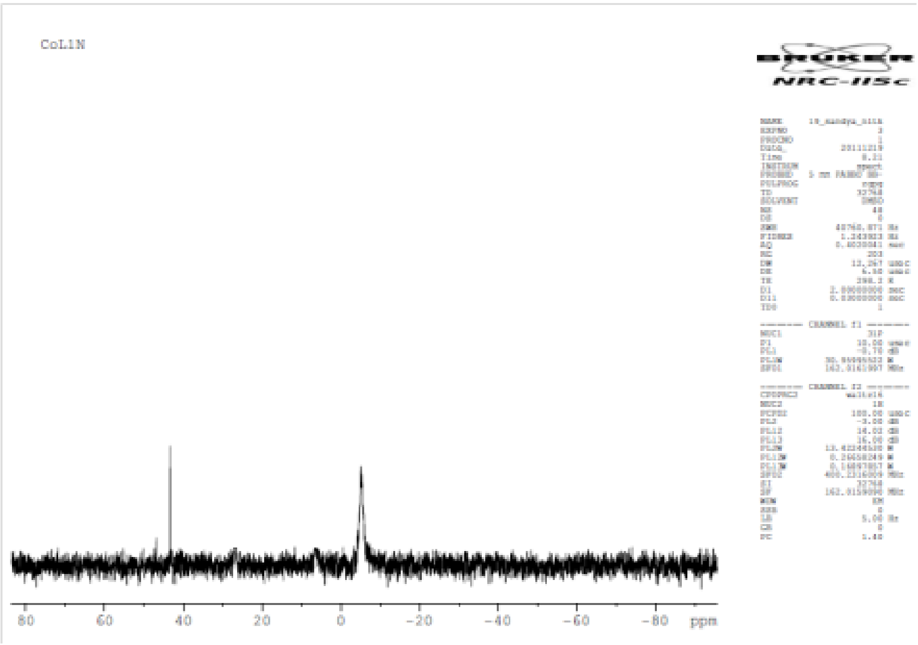


Fig. 4.14: ^{31}P NMR spectra of CoL1

4.3.4 ESI Mass Measurements

In the mass spectra of the complexes, the molecular weight of the complexes correspond to the presence of the tridentate ligand, two triphenylphosphine ligands and methoxy group in the synthesized complexes confirming the assumed structure. The LCMS spectra of the complex CoL_1 is shown in the Figure 4.15. Similarly expected molecular weight and the observed molecular weight of the complexes are given in the Table 4.15.

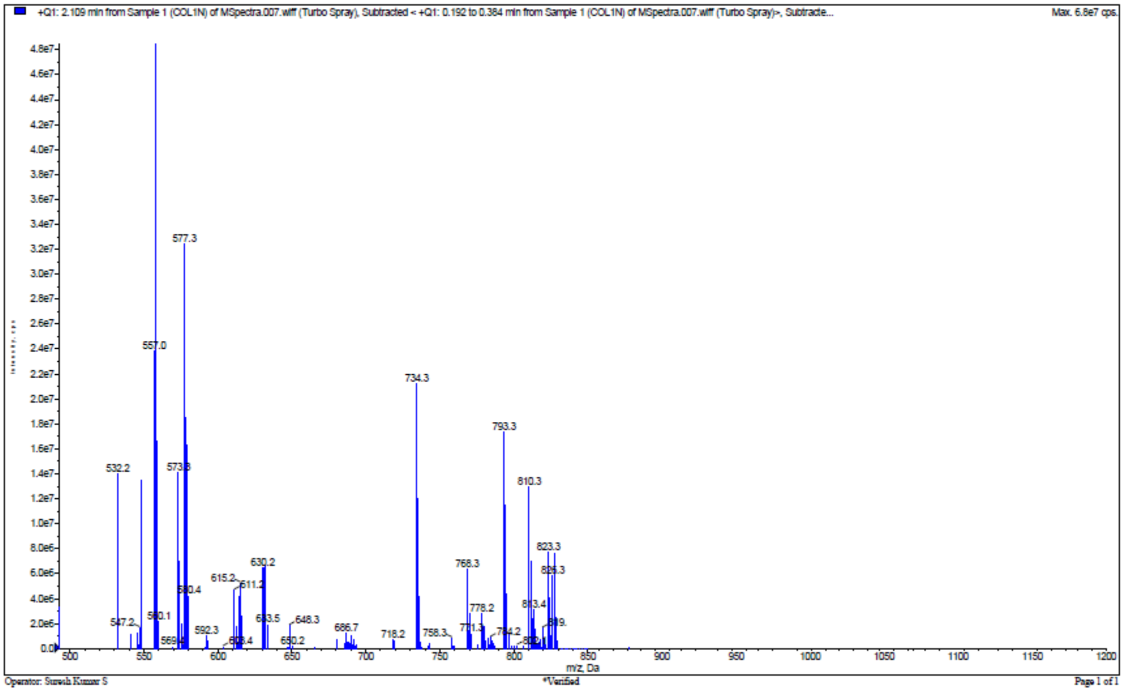


Fig. 4.15: ESIM spectra of CoL1

Table 4.15: ESIMS data of Cobalt complexes

Complex	Expected mass	Observed mass
CoL$_1$	825.7	826.3
CoL$_2$	860.2	861.2
CoL$_3$	905.7	906.2
CoL$_4$	871.78	872
CoL$_5$	855.78	856.8

4.3.5 Magnetochemical measurements

In order to obtain further structural information, the magnetic moments of the complexes were measured. All cobalt complexes showed diamagnetic behavior further confirming the d^6 configuration which can be due to +3 oxidation state of cobalt ion with low spin state.

4.3.6 Thermal measurements

The thermograms of Co(III) chelates showed 3 stages of decomposition (Fig. 4.16). First stage of decomposition at around 200ºC which corresponds to the loss of methoxy group, second stage of decomposition from 220-350ºC corresponds to the loss of triphenylphosphine and third stage of decomposition in the range of 380-700ºC indicates the loss of ligand molecule. This further supports our assumed structure.

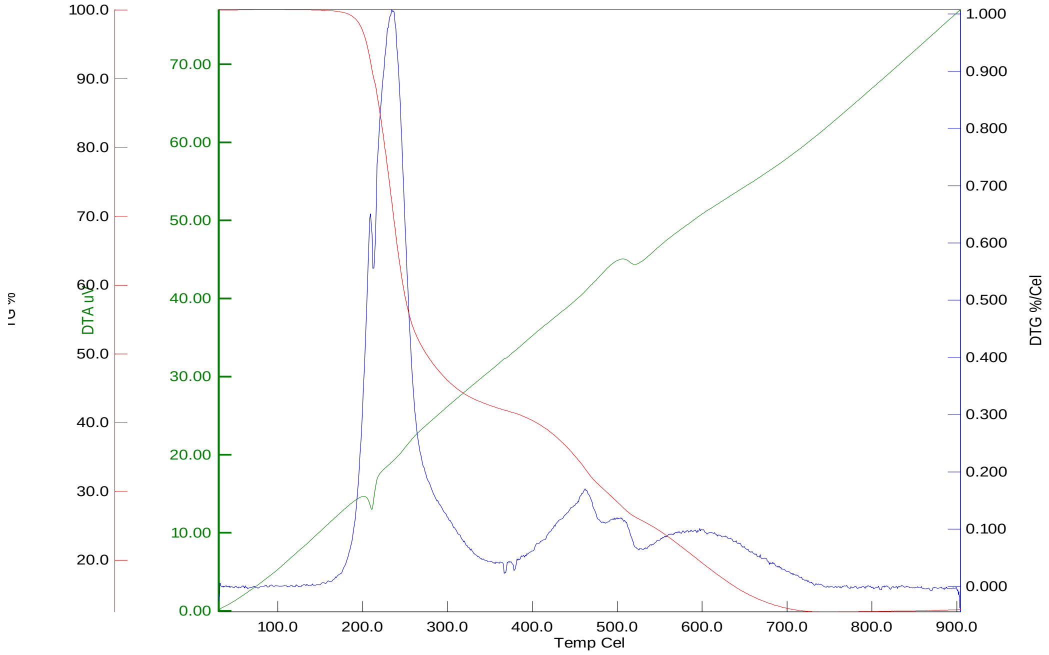


Fig. 4.16: TG and DTG graph of **CoL_1**

4.4 CATALYTIC ACTIVITY OF COMPLEXES CoL_1-CoL_5

Cobalt mediated oxidations are finding increasing application due to the unique properties of this extremely versatile transition metal and more economic nature of this metal. The oxidation of benzyl alcohol, as a standard substrate, was first investigated in order to optimize the reaction variables such as solvent, temperature, alcohol/oxidant molar ratio and length of the reaction time as discussed under section 4.2 in three oxidant systems namely H_5IO_6, H_2O_2, aq. TBHP.

Initially, the activity of CoL_1 was investigated in different solvents (methanol, acetonitrile, and acetone) using H_5IO_6, H_2O_2, TBHP as the oxidants. All systems showed the best yield in acetonitrile medium. All catalytic systems showed higher yield at reflux condition, which was tested by taking benzyl alcohol as the model substrate.

The optimization of other reaction conditions mentioned below, were studied by taking benzyl alcohol as the substrate and CoL_1 as the catalyst in all the 3 systems.

i. Effect of time

ii. Effect of catalyst concentration

iii. Effect of oxidant concentration

4.4.1 Effect of time

In order to study the effect of time on the activity, the product analysis was done at regular intervals of time, under similar reaction conditions.

In the case of CH_3CN-H_5IO_6, it was observed that the total reaction time was 150 minutes at 80ºC. The experiments were conducted at regular intervals of time beyond 150 minutes. The results show that the yield remains constant at about 89% after a reaction time of 150 minutes (Table 4.16).

In the case of CH_3CN-H_2O_2 system, it was found that the reaction was complete in 240 minutes with maximum yield of 59% (Table 4.17).

Similarly the effect of time was studied for aq. TBHP system, in which case it was observed that total reaction time of 120 minutes was needed for highest catalytic yield of 92% (Table 4.18).

Table 4.16: Effect of time on benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system

Sl. No.	Time (min)	% Yield[a] CH_3CN-H_5IO_6 system
1	30	45.26
2	60	60.51
3	90	69.75
4	120	75.98
5	130	82.68
6	140	85.09
7	**150**	89.2
8	160	88.98
9	170	89.10
10	180	88.42

[a] GC yield, average of 3 trials.

Table 4.17: Effect of time on benzyl alcohol to benzaldehyde in H_2O_2 system

Sl. No.	Time (min)	% Yield[a] CH_3CN-H_2O_2 system
1	60	14.99
2	120	25.28
3	180	33.15
4	200	49.45
5	220	58.4
6	**240**	59.5
7	260	59.5
8	280	59.1
9	300	59.2

[a] GC yield, average of 3 trials

Table 4.18: Effect of time on benzyl alcohol in CH_3CN- aq. TBHP system

Sl. No.	Time (min)	% Yield[a] CH_3CN-aq. TBHP system
1	20	36.0
2	40	45.3
3	60	64.7
4	80	74.5
5	100	88.8
6	110	92.0
7	**120**	92.3
8	130	92.0
9	140	92.2

[a]GC yield, average of 3 trials

4.4.2 Effect of catalyst concentration

In order to study the effect of the concentration of catalyst with respect to substrate and oxidant, the reaction was carried out at different catalyst concentrations. From the results it is confirmed that the oxidants used will bring about the oxidation of alcohols in negligible amount without the presence of the catalyst. The results are summarized in the Table 4.19.

A minimum quantity of 0.03 mmol of the catalyst was needed for the effective transformation of benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system. While in case of H_2O_2 and CH_3CN-aq. TBHP systems 0.02 mmol of catalyst was sufficient to bring about the conversions (Fig. 4.17).

Table 4.19: Effect of catalyst concentration on benzyl alcohol

Sl. No.	Catalyst concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 System	H_2O_2 system	CH_3CN-aq. TBHP system
1	0	12.0	2.0	15.4
2	0.01	76.8	34.6	79.2
3	0.02	89.05	**59.5**	**92.3**
4	0.03	**88.98**	58.6	92.3
5	0.04	89.10	58.4	92.0
6	0.05	88.95	58.5	91.8

[a] GC yield, average of 3 trials

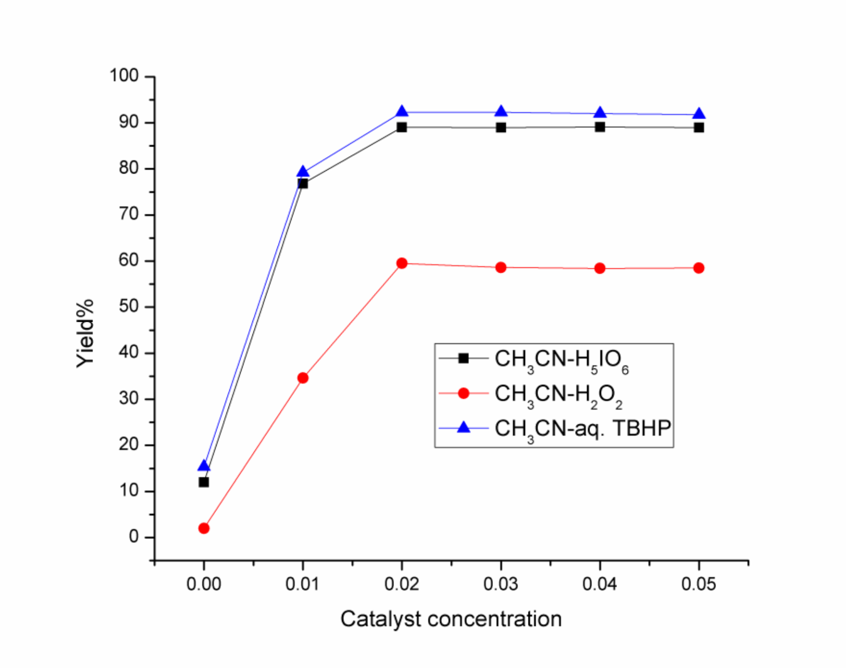


Fig. 4.17: Effect of catalyst concentration on benzyl alcohol

4.4.3 Effect of oxidant concentration

The reactions were studied with respect to substrate and catalyst at different oxidant concentrations. The results are summarized in Table 4.20. A minimum quantity of 0.75 mmol, 5 mmol, 2 mmol of the oxidants were required in CH_3CN-H_5IO_6, H_2O_2, CH_3CN-aq. TBHP systems respectively for the effective oxidation of benzyl alcohol (Fig. 4.18).

Table 4.20: Effect of oxidant concentration on benzyl alcohol

Sl. No.	Oxidant concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 System	H_2O_2 system	CH_3CN-aq. TBHP system
1	0	3.7	3.6	3.2
2	0.5	75.6	5.4	32.5
3	0.75	**88.9**	12.6	38.9
4	1.0	88.9	16.7	42.3
5	2.0	88.7	24.5	**92.3**
6	4.0	88.2	46.5	92.3
7	5.0	88.3	**59.5**	92.4
8	6.0	88.5	59.3	92.1
9	7.0	88.5	59.4	91.9

[a]GC yield, average of 3 trials

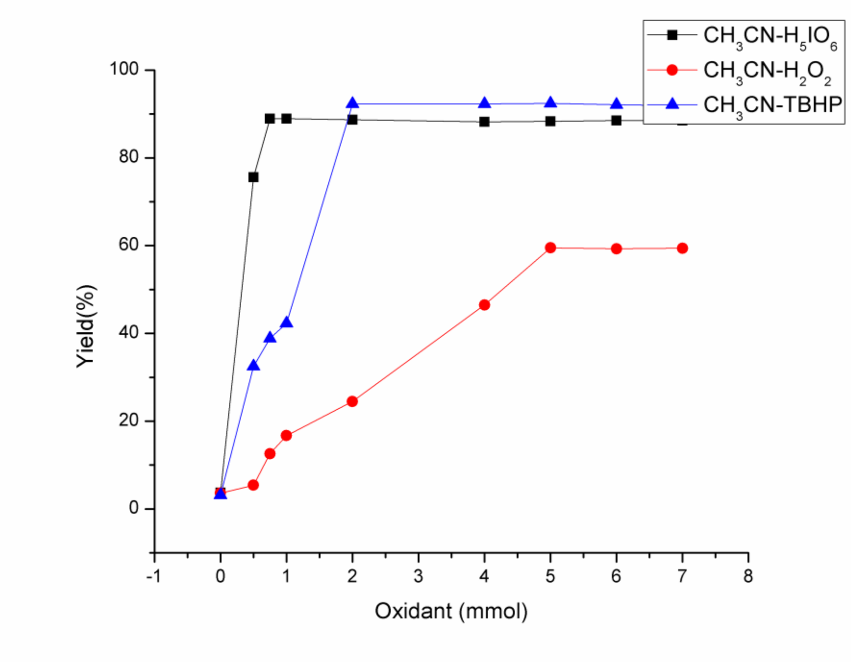


Fig. 4.18: Effect of oxidant concentration on benzyl alcohol

The oxidation was extended to a variety of alcohols including primary and secondary, aromatic, aliphatic and cyclic alcohols using the optimized reaction conditions. The results for the oxidation of a variety of alcohols are summarized in Tables 4.21, 4.22, 4.23 respectively in $CH_3CN-H_5IO_6$, $CH_3CN-H_2O_2$, CH_3CN-aq. TBHP systems.

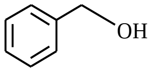
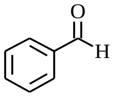
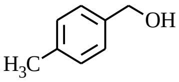
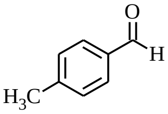
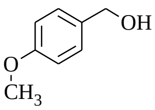
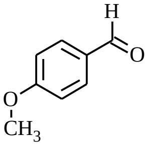
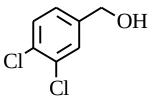
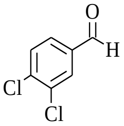
All the benzylic primary and secondary alcohols studied were oxidized smoothly to give aldehydes and ketones respectively in $CH_3CN-H_5IO_6$, $CH_3CN-H_2O_2$. Whereas in CH_3CN-aq. TBHP medium, the primary alcohols and secondary were oxidized to carboxylic acids or ketones respectively in high yields similar to FeL_1-FeL_5 complexes. No oxidation was observed in the aromatic ring of benzylic substrates.

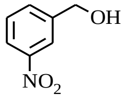
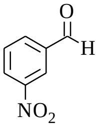
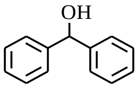
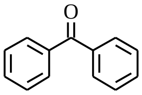
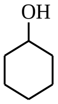
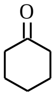
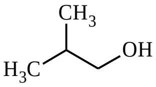
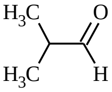
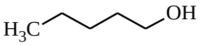
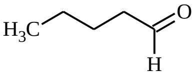
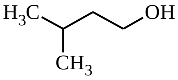
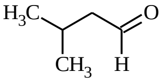
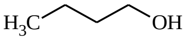
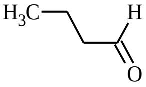
In all of the above systems, at room temperature no significant yield was observed even after 24 hr. However, the yield increased remarkably at the reflux temperature. Thus we choose reflux condition as the standard reaction temperature for our study.

Among the three systems studied, in CH_3CN-H_5IO_6 and CH_3CN-H_2O_2, selectivity towards aldehyde remains almost more than 95%. The over oxidation to carboxylic acid was ruled out by derivative test. While in CH_3CN-aq. TBHP, primary alcohols were oxidized to corresponding acids with high yield.

To examine the versatility of the synthesized Co(III) complexes, a wide variety of alcohols were used as substrates. Among the various alcohols studied those containing aromatic substituent were found to be more reactive than alicyclic and aliphatic alcohols. Similarly electron donating groups were found to slow down oxidation, whereas electron withdrawing groups accelerate it. Para or ortho substituents with electron releasing or electron withdrawing properties do not induce any change on the selectivity. It was also observed that electron donating group on the ligand enhanced the catalytic activity. And also electron withdrawing substituents decreased the catalytic activity of the complexes. This is in agreement with earlier reported observations.

Table 4.21: Oxidation of alcohols by Co(III) complexes[a] in CH_3CN-H_5IO_6 system

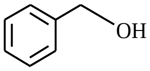
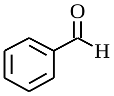
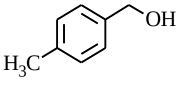
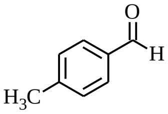
Alcohols	Product	% Yield[b]				
		CoL_1	**CoL_2**	**CoL_3**	**CoL_4**	**CoL_5**
		89.2	83.4	82.7	80.8	92.1
		79.5	77.5	74.3	68.6	81.3
		77.5	77.1	74.8	73.2	81.8
		86.5	85.7	83.2	83.8	89.4

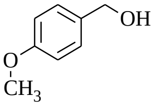
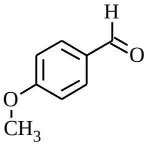
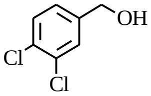
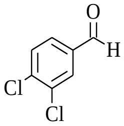
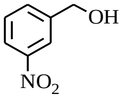
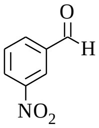
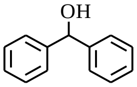
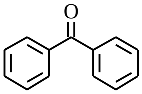
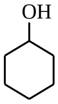
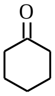
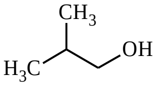
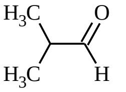
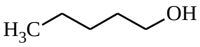
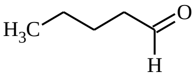
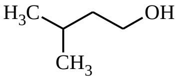
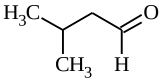
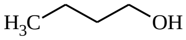
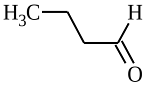
		90.8	87.6	85.9	86.7	91.2
		79.7	77.2	74.0	73.1	86.3
		69.3	64.5	63.6	60.1	70.3
		54.8	52.6	51.2	48.1	54.8
		44.3	41.5	40.0	39.6	46.2
		42.1	41.6	39.6	38.1	43.5
		30.6	26.9	21.6	19.1	32.5

[a] 1 mmol alcohol, 0.75 mmol H_5IO_6, 0.04 mmol Co (III) complex, 3 mL CH_3CN, stirring at 80°C.

[b] GC yield, average of 3 trials.

Table 4.22: Oxidation of alcohols catalyzed by Co(III) complexes[a] in H_2O_2 system

Alcohols	Product	% Yield[b]				
		CoL$_1$	**CoL$_2$**	**CoL$_3$**	**CoL$_4$**	**CoL$_5$**
		59.4	58.6	57.8	56.2	61.3
		55.3	53.2	52.6	50.2	56.7

		53.2	52.5	51.6	50.7	55.6
		54.3	51.9	50.9	49.2	53.9
		64.6	60.1	62.6	61.6	65.3
		43.7	41.1	41.8	40.2	44.0
		38.3	35.7	33.7	32.6	39.7
		19.2	17.6	14.2	12.1	20.7
		18.6	17.5	14.0	12.6	21.8
		15.3	12.4	11.6	10.2	18.6
		15.7	14.3	12.6	10.1	16.4

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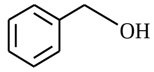
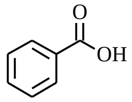
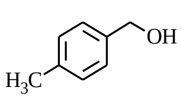
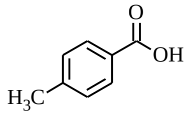
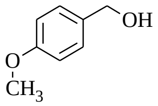
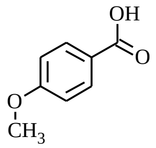
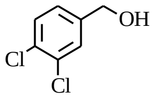
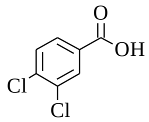
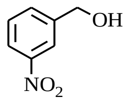
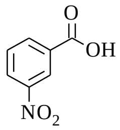
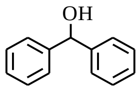
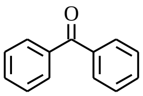
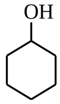
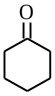
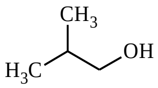
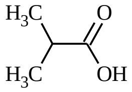
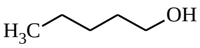
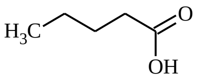
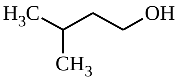
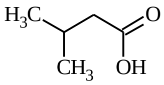
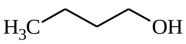
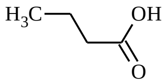
[a] 1 mmol alcohol, 5.0 mmol H_2O_2, 0.02 mmol Co(III) complex under reflux condition.

[b] GC yield, average of 3 trials.

Table 4.23: Oxidation of alcohols by Co(III) complexes[a] in CH_3CN-aq. TBHP system

Alcohols	Product	% Yield[b]				
		CoL_1	**CoL_2**	**CoL_3**	**CoL_4**	**CoL_5**
		92.3	90.1	88.9	87.3	94.6
		90.1	88.5	86.9	84.6	92.7
		88.6	86.1	83.0	81.5	92.1
		89.6	88.6	86.9	83.4	92.8
		93.4	87.4	86.3	82.9	95.7
		83.8	81.4	79.8	76.7	84.0
		74.3	70.6	68.5	66.8	75.1
		60.9	58.8	57.7	56.2	64.0
		53.7	51.4	50.7	47.1	55.5
		49.8	48.6	46.2	42.8	52.4
		40.2	39.5	38.6	35.1	43.7

[a] 1 mmol alcohol, 2.0 mmol aq. TBHP, 0.01 mmol Co(III) complex, 1 mL CH_3CN, stirring at 80°C.

[b] GC yield, average of 3 trials.

4.4.4 Mechanistic study

To study the mechanism involved in the reaction, UV spectra of the reaction mixture before and after the addition of the oxidant was examined (Fig. 4.19, 4.20 and 4.21).

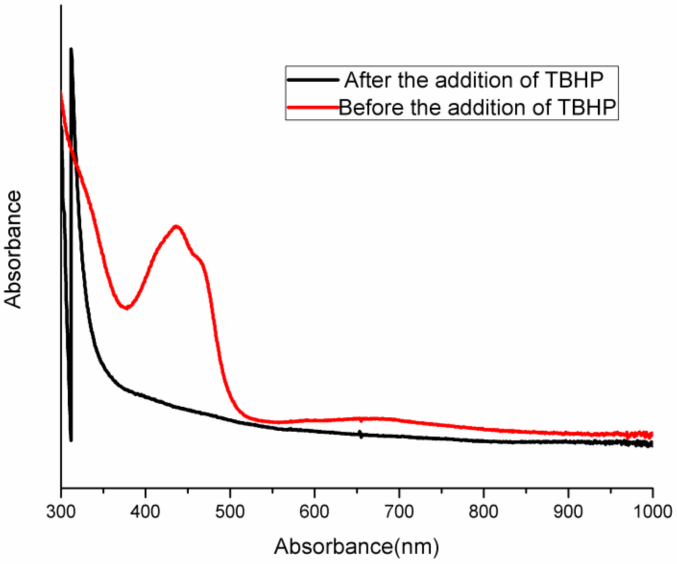


Fig. 4.19: UV-visible spectra of reaction mixture of CoL_1 catalyzed reaction in periodic acid system

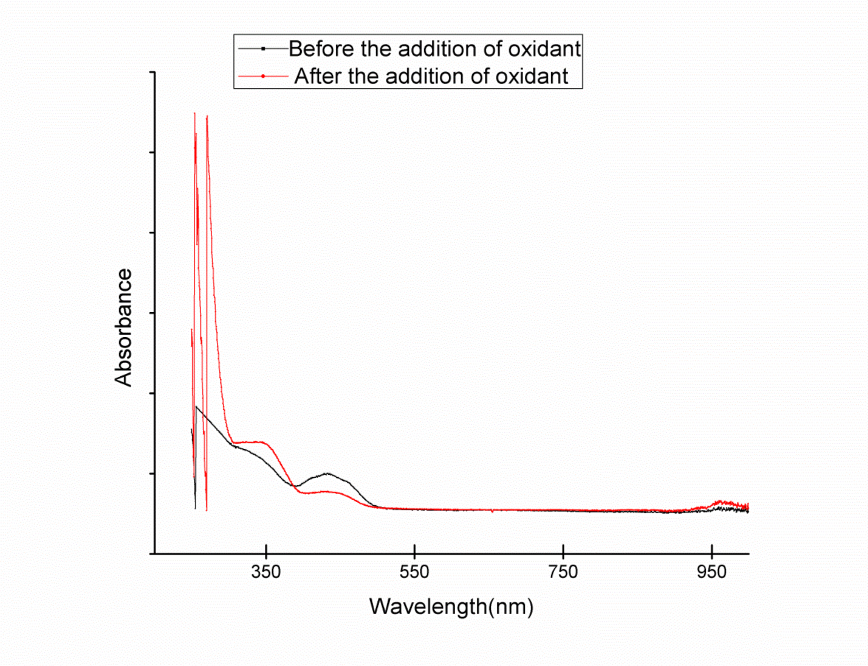


Fig. 4.20: UV-visible spectra of reaction mixture of in CH_3CN-H_2O_2 system

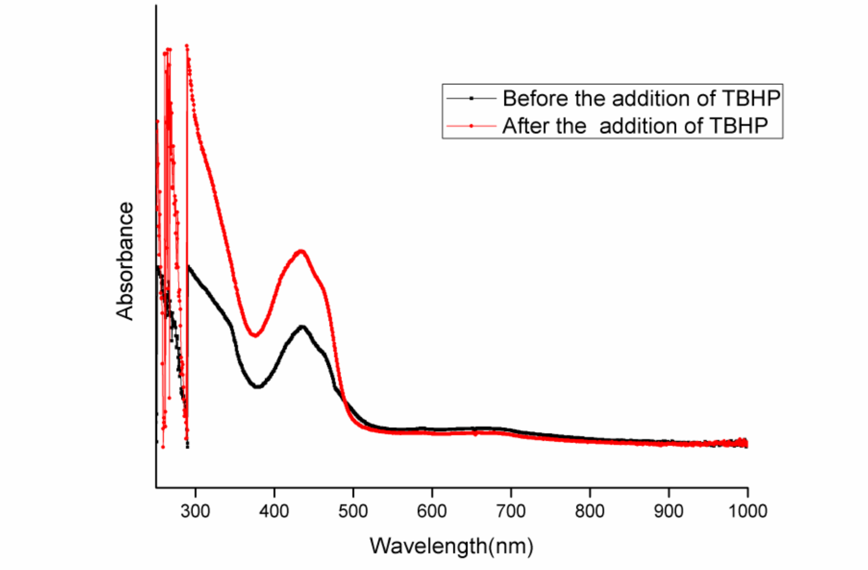
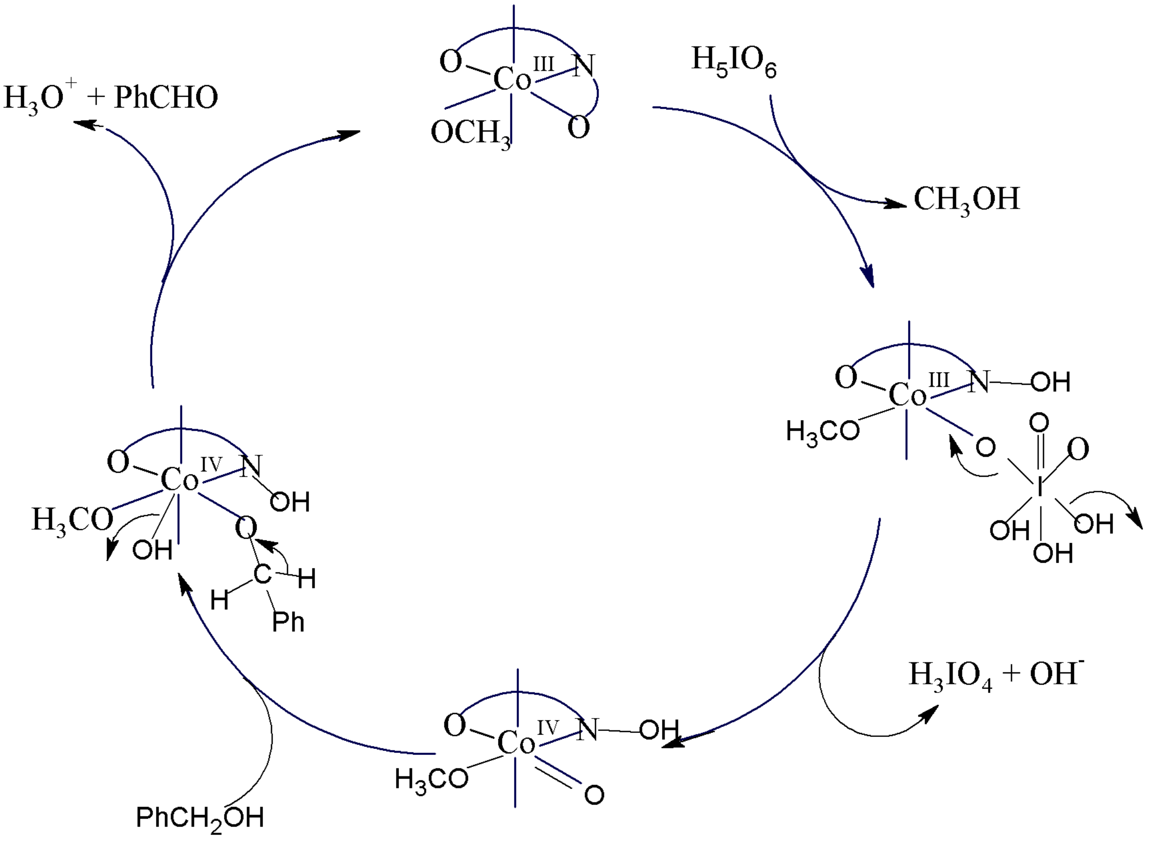


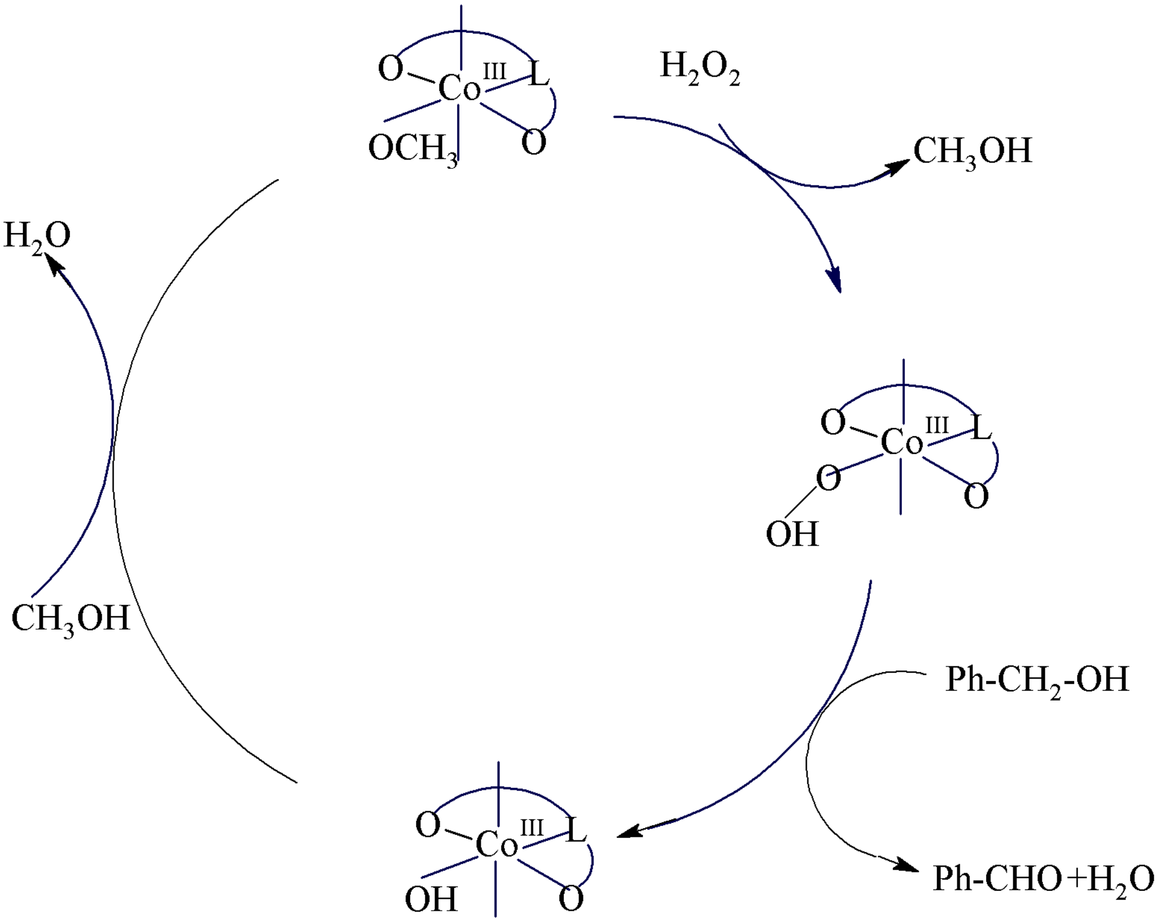
Fig. 4.21: UV-visible spectra of reaction mixture in CH_3CN-aq.TBHP system

In the UV-visible spectra of the reaction mixture of periodic acid system, an increase in the intensity of intra ligand band was observed suggesting the interaction between the oxidant and the complex. Further charge transfer band disappeared after the addition of the oxidant. This indicates the oxidation of the metal. Based on these results, oxometal pathway is more likely to be involved in the alcohol oxidation reaction in periodic acid system. Hence the following mechanism has been proposed for the oxidation of alcohols in periodic acid system (Scheme 4.4).



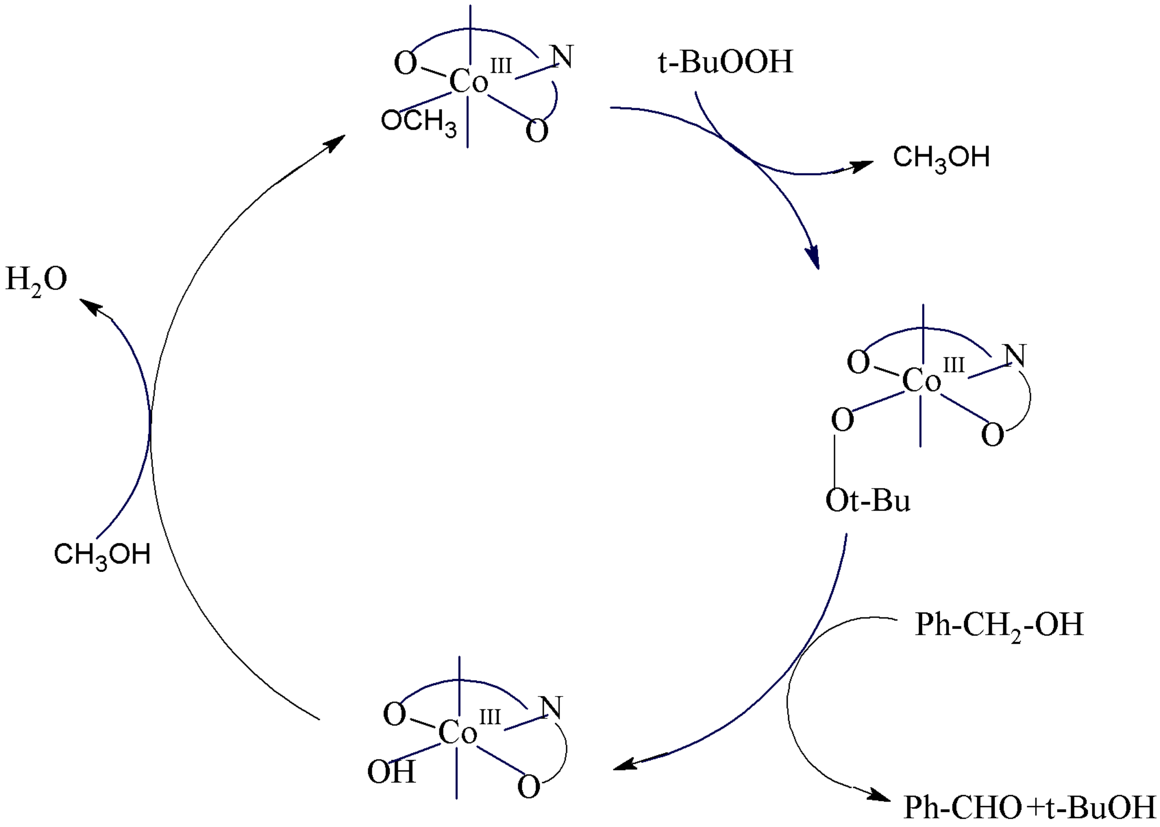
Scheme 4.4: Possible mechanism of oxidation of alcohol catalyzed CoL$_1$ in periodic acid system

In H_2O_2 system, an increase in the intensity of intra ligand band and charge transfer band was observed suggesting the interaction between the oxidant and the complex. Along with that, a sharp increase in intensity at around 355 nm was observed which is assignable to the LMCT band of hydroperoxide to the metal centre. This clearly indicates the involvement of hydroperoxo metal species in the mechanism. Hence the following mechanism has been proposed for the oxidation of alcohols in H_2O_2 system (Scheme 4.5).



Scheme 4.5: Mechanism of oxidation of alcohol catalyzed CoL_1 in H_2O_2 system

When the UV spectrum of the complex along with aq. TBHP was examined, an increase in intensity of intra ligand band and LMCT band is observed indicating the interaction between the metal and oxidant. Hence the mechanism must be proceeding through peroxo mechanism similar to TBHP mechanism discussed under section 4.2.4.



Scheme 4.6: Mechanism of oxidation of alcohol catalyzed CoL_1 in aq. TBHP system

Cobalt complexes showed lower conversion compared to similar Fe(III) complexes as well as earlier reported similar Co(II) complexes (Kharat et al. 2011). The lower reactivity of the complex must be due to the lower lability of Co-OCH_3 bond in the present system.

4.5 CHARACTERIZATION OF VL_1-VL_5

The reaction of solution of VCl_3, the synthesized ligand and triphenylphosphine in a 1:1:4 molar ratios yielded the new complexes of the general formula $[VO(L)(PPh_3)_2]$ in moderate to good yield. All the synthesized complexes were brown in color. They were found to be soluble in CH_3CN, DMSO, DMF and $CHCl_3$.

4.5.1. Electronic Spectra and Analytical Data

The analytical data for these complexes are in good agreement with the above molecular formula. In all the reactions, it has been observed that the Schiff base behaves as a tridentate ligand. The electronic spectra of the ligands and the complexes were recorded in dimethylformamide (Fig. 4.22). The electronic spectra of the all the complexes showed bands in the region 250–300 nm and 350-470 nm which can be due to intra ligand transitions, ligand to metal charge transfer transitions. Very low intense bands at 623-650 nm and 900-950 nm observed which is due to ligand field transitions indicating the presence of V(IV) metal ion in the octahedral environment (Bastos et al. 2008). The analytical data for the complexes are given in Table 4.1.

Table 4.24: Analytical and Electronic spectral data of V(IV) complexes

Complex	Elemental composition Found (Calculated)			Electronic spectral data (nm)	Magnetic moment μ_{eff} (BM)
	C	H	N		
VL_1	73.30	4.80	1.65	297, 431,620,924	1.72
	(73.32)	(4.90)	(1.74)		
VL_2	70.19	4.52	1.69	290, 438, 640, 920	1.74
	(70.30)	(4.58)	(1.67)		
VL_3	66.70	4.39	1.55	287, 443, 648, 918	1.74
	(66.75)	(4.34)	(1.59)		
VL_4	69.32	4.48	3.20	296, 353,425,632, 926	1.75
	(69.42)	(4.52)	(3.30)		
VL_5	72.20	4.90	1.58	286, 460, 613, 921	1.71
	(72.11)	(4.96)	(1.68)		

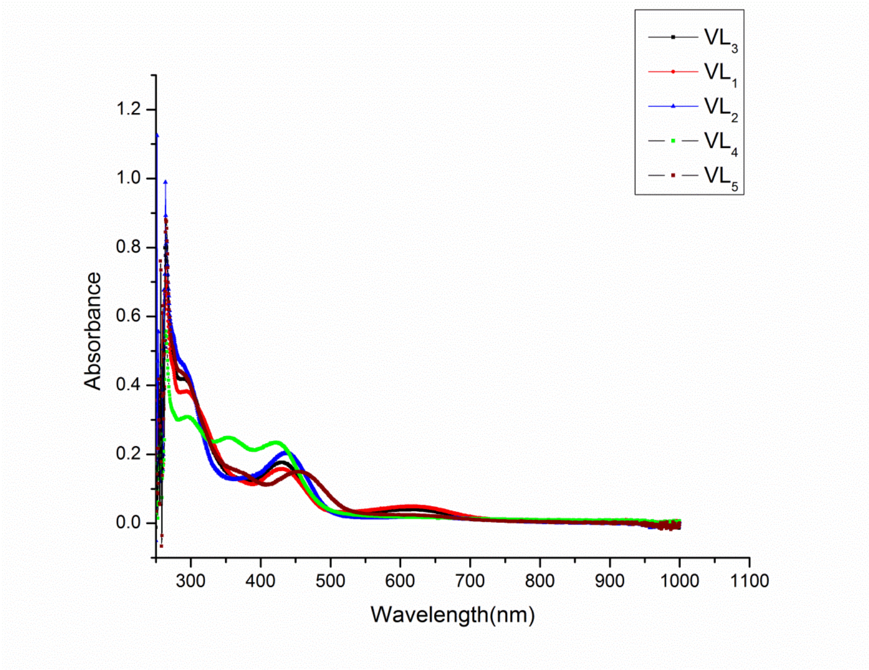


Fig. 4.22: UV spectra of complexes VL_1-VL_5

4.5.2 FTIR Spectra

Selected FTIR bands of ligands and complexes are listed in Table 4.25. In the FTIR spectra of the complexes, the strong band of ν(C=N) vibration is shifted to lower wavenumber due to coordination. The band in the region 1234-1271 cm^{-1} which is assigned to phenolic ν(C–O) in the free ligand, is shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion. The bands around 590 cm^{-1} and 440 cm^{-1} in the complex is assigned to ν(V–O) and ν(V–N) respectively. Bands due to triphenylphosphine are also appeared in the expected region. The sharp band at around 960 confirms the octahedral environment around vanadium metal ion (Fig. 4.23) (Ghosh and Bandyopadhyay 2004).

Table 4.25: FTIR spectral data (cm^{-1}) for ligands and its V(IV) complexes

Compound	$\nu_{(C=N)}$	$\nu_{(C\text{-}O)}$	$\nu_{(V\text{-}O)}$	$\nu_{(V\text{-}N)}$	$\nu_{(V=O)}$	Bands due to PPh_3
L_1	1617	1271	-	-		-
L_2	1625	1269	-	-		-
L_3	1623	1267	-	-		-
L_4	1611	1234	-	-		-
L_5	1625	1250	-	-		-
VL_1	1614	1299	592	449	964	1436, 1079, 688
VL_2	1604	1289	590	438	962	1436, 1078, 687
VL_3	1602	1281	590	434	963	1436, 1078, 687
VL_4	1603	1251	590	430	951	1436, 1096, 689
VL_5	1620	1299	585	440	965	1435, 1085, 690

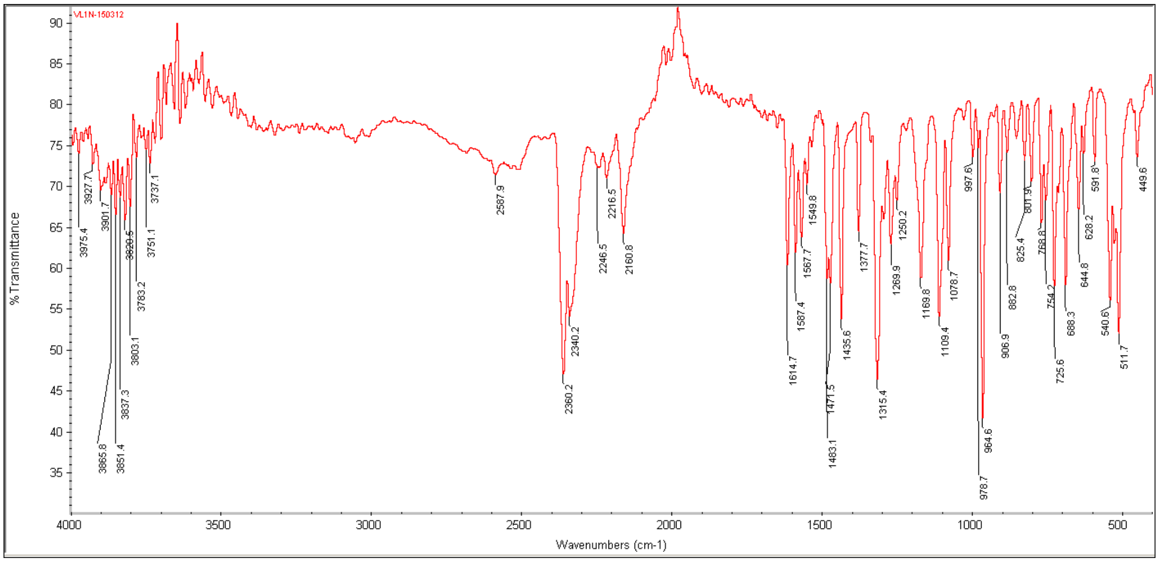


Fig. 4.23: FTIR spectra of VL_1

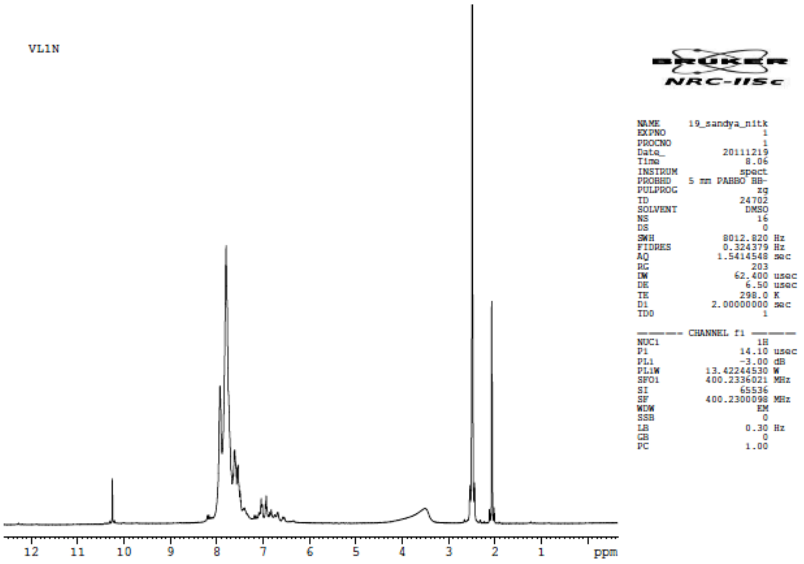
4.5.3 NMR Spectra

The ^{1}H NMR spectra of all the complexes showed resonance at 6.2–8.2 ppm as set of multiplets which has been assigned to the aromatic protons that of coordinated triphenylphosphine groups present in the complexes and that of the Schiff base ligand.

$^{31}P\{^{1}H\}$ NMR spectra of the complexes (Table 4.26) exhibit a sharp singlet in the range 23 ppm supporting the presence of the triphenylphosphine groups in *trans*-position (Raveendran 2005). The ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectra of the complexes VL_1 are shown in the Figure 4.24 and 4.25 respectively.

Table 4.26**:** ^{1}H NMR and ^{31}P NMR chemical shifts of the complexes

Complex	Chemical shift (ppm)		
	^{1}H		^{31}P
VL_1	6.9-7.9	10.2	23.1
VL_2	6.7-7.8	10.0	23.3
VL_3	6.8-7.9	10.1	23.4
VL_4	6.6-7.5	9.8	22.6
VL_5	7.0-8.0	10.0	23.8



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NAME        19_sandya_nitk
EXPNO                    1
PROCNO                   1
Date_             20111219
Time                  8.06
INSTRUM              spect
PROBHD      5 mm PABBO BB-
PULPROG                 zg
TD                   24702
SOLVENT               DMSO
NS                      16
DS                       0
SWH               8012.820 Hz
FIDRES            0.324379 Hz
AQ               1.5414548 sec
RG                     203
DW                  62.400 usec
DE                    6.50 usec
TE                   298.0 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.10 usec
PL1                  -3.00 dB
PL1W           13.42244530 W
SFO1           400.2336021 MHz
SI                   65536
SF             400.2300098 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

Fig. 4.24: ^{1}H NMR spectra of VL_1

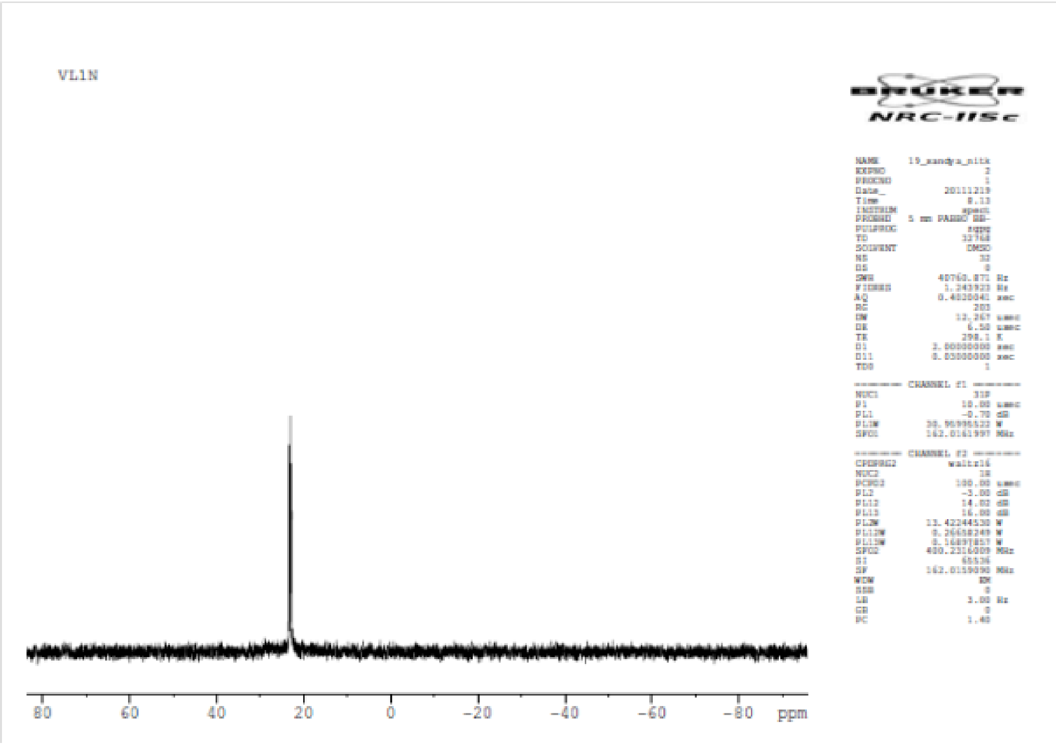


Fig. 4.25: ^{31}P NMR spectra of VL_1

4.5.4 ESI Mass Measurements

In the mass spectra of the complexes, the molecular weight of the complexes correspond to the presence of the tridentate ligand, two triphenylphosphine ligands and oxygen group in the synthesized complexes confirming the assumed structure. The ESIMS spectra of the complex VL_1 is shown in the Figure 4.26. Similarly expected molecular weight and the observed molecular weight of the complexes are given in the Table 4.27**.**

Table 4.27**:** ESIMS datas of Vanadium complexes

Complex	Expected mass	Observed mass($M+NH_4^+$)
VL_1	802.73	821.1
VL_2	837.17	855

VL_3	881.62	899.6
VL_4	847.73	865.3
VL_5	832.75	850.7

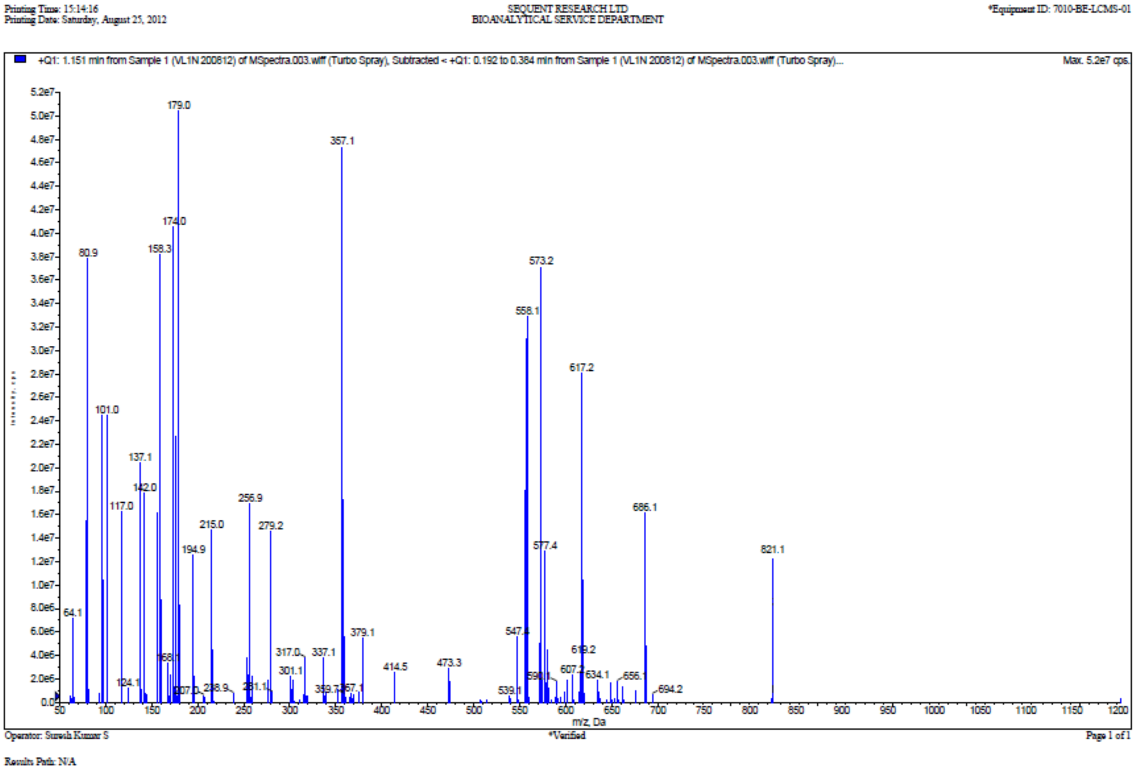


Fig. 4.26: ESIMS spectra of VL_1

4.5.5 Magnetochemical Measurements

In order to obtain further structural information, the magnetic moments of the complexes were measured. All vanadium complexes showed magnetic moment in the range of 1.7 BM confirming the presence of I unpaired electron supporting the assumed structure.

4.5.6 Thermal Measurements

The thermograms of V(IV) chelates showed 2 stages of decomposition (Fig. 4.27). First stage of decomposition from 220-450°C corresponds to the loss of triphenylphosphine and second stage of decomposition in the range of 470-700°C indicates the loss of ligand molecule. This further supports our assumed structure.

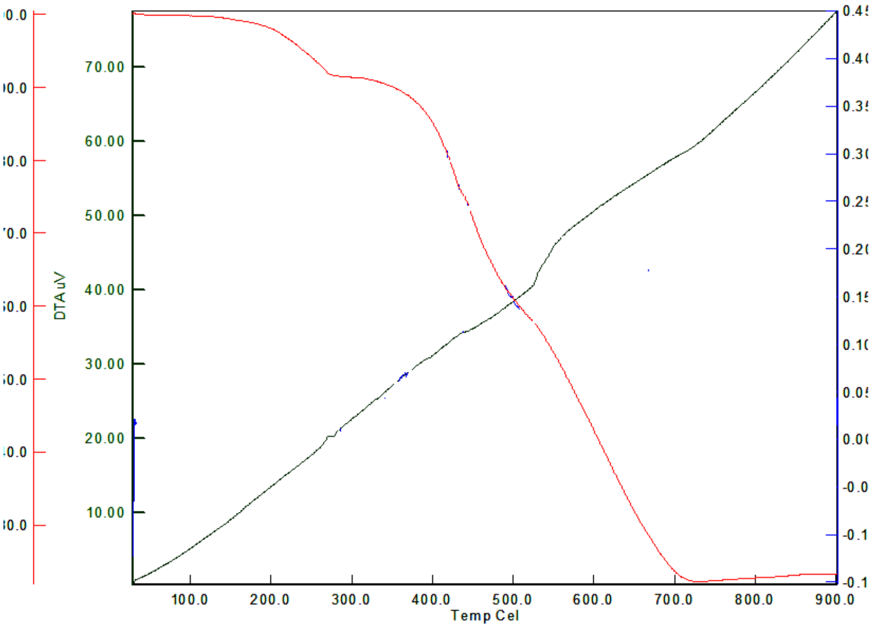


Fig. 4.27: TG and DTA graph of VL_1

4.6 CATALYTIC ACTIVITY OF COMPLEXES VL_1-VL_5

Vanadium mediated oxidations are finding increasing application due to the unique properties of this extremely versatile transition metal. The catalytic activity of all the synthesized vanadium complexes was studied using the mild oxidants like periodic acid, hydrogen peroxide and aqueous tert-butylhydroperoxide. All complexes were found to catalyze the oxidation of alcohol to corresponding carbonyls but the yields were found to vary with different catalysts.

The oxidation of benzyl alcohol, as a standard substrate, was first investigated in order to optimize the reaction variables such as solvent, temperature, alcohol/oxidant molar ratio and length of the reaction time as discussed under section 4.2.

All system showed the best yields in acetonitrile medium among the various solvents tested. The activity of VL_1 was studied at different temperature by taking benzyl alcohol as the model substrate in all the 3 above mentioned systems. It was observed that under reflux, the system showed higher conversions.

4.6.1 Effect of time

In order to study the effect of time on the activity, the product analysis was done at regular intervals of time, under similar reaction conditions.

In the case of CH_3CN-H_5IO_6 , it was observed that the total reaction time was 120 minutes at 80ºC. The experiments were conducted at regular intervals of time beyond 120 minutes. The results show that the yield remains constant at about 97% after a reaction time of 120 minutes (Table 4.28).

In the case of CH_3CN-H_2O_2 system, it was found that the reaction was complete in 120 minutes with maximum yield of 90.9% (Table 4.29).

Similarly the effect of time was studied for CH_3CN-aq. TBHP system, in which case it was observed that total reaction time of 60 minutes was needed for highest catalytic conversion of 89% (Table 4.30).

Table 4.28: Effect of time on benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system

Sl. No.	Time (min)	% Yield[a] CH_3CN-H_5IO_6 system
1	30	49.6
2	60	57.8
3	90	79.4
4	100	88.6
5	110	94.5
6	**120**	97.3
7	130	97.3
8	140	97.1

[a]GC yield, average of 3 trials.

Table 4.29: Effect of time on benzyl alcohol in CH_3CN-H_2O_2 system

Sl. No.	Time (min)	% Yield[a] CH_3CN-H_2O_2 system
1	30	45.8
2	60	56.2
3	90	69.5
4	100	81.4
5	110	87.6
6	**120**	90.9
7	130	90.8
8	140	90.5

[a]GC yield, average of 3 trials

Table 4.30: Effect of time on benzyl alcohol to benzoic acid in CH_3CN- aq. TBHP system

Sl. No.	Time (min)	% Yield[a] CH_3CN-aq. TBHP system
1	10	36.0
2	20	45.3
3	30	64.7
4	40	79.6
5	50	88.8
6	**60**	89.2
7	70	89.2
8	80	89.2

[a]GC yield, average of 3 trials

4.6.2 Effect of catalyst concentration

In order to study the effect of the concentration of catalyst with respect to substrate and oxidant, the reaction was carried out at different catalyst concentrations. From the results it is confirmed that the oxidants used will bring about the oxidation of alcohols in negligible amount without the presence of the catalyst. The results are summarized in the Table 4.31.

A minimum quantity of 0.02 mmol of the catalyst was sufficient for the effective transformation of benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system. While in case of CH_3CN-H_2O_2 and CH_3CN-aq TBHP systems 0.04 mmol of catalyst was necessary to bring about the conversions respectively (Fig. 4.28).

Table 4.31: Effect of catalyst concentration on benzyl alcohol

Sl. No.	Catalyst concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 System	CH_3CN-H_2O_2 system	CH_3CN-aq. TBHP system
1	0	12.0	2.0	15.4
2	0.01	76.8	34.6	61.9
3	0.02	**97.3**	67.3	72.9
4	0.03	97.2	75.6	83.2
5	0.04	97.3	**90.9**	**89.2**
6	0.05	97.3	90.9	89.1

[a]GC yield, average of 3 trials

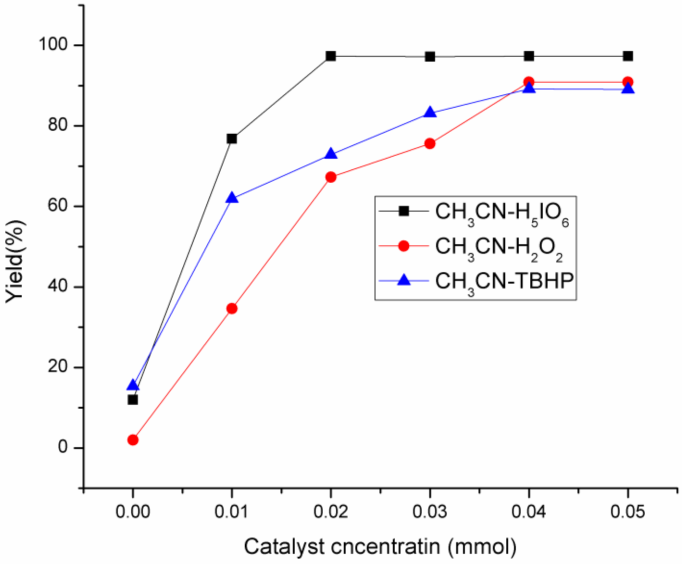


Fig. 4.28: Effect of catalyst concentration on benzyl alcohol

4.6.3 Effect of oxidant concentration

The reactions were studied with respect to substrate and catalyst at different oxidant concentrations. The results are summarized in Table 4.32. A minimum quantity of 0.75mmol, 5 mmol, 2 mmol of the oxidants were required in CH_3CN-H_5IO_6, CH_3CN-H_2O_2, CH_3CN-aq. TBHP systems respectively for the effective oxidation of benzyl alcohol (Fig. 4.29).

Table 4.32: Effect of oxidant concentration on benzyl alcohol

Sl. No.	Oxidant concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 System	CH_3CN-H_2O_2 system	CH_3CN-aq. TBHP system
1	0	4.1	3.6	3.0
2	0.5	72.3	4.4	26.5
3	0.75	**97.3**	11.6	39.2
4	1.0	97.2	38.3	76.3
5	2.0	97.3	52.3	**89.2**
6	4.0	97.3	86.2	89.2
7	5.0	97.3	**90.9**	89.1
8	6.0	97.3	90.6	89.2
9	7.0	97.3	90.8	89.2

[a] GC yield, average of 3 trials

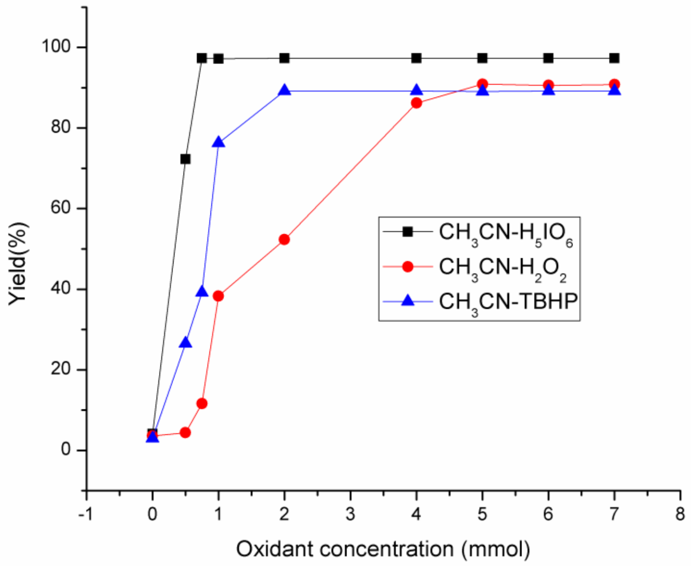


Fig. 4.29: Effect of oxidant concentration on benzyl alcohol

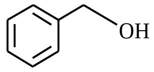
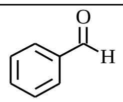
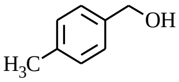
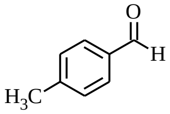
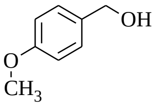
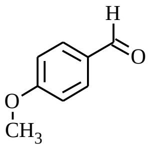
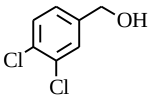
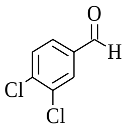
The oxidation was extended to a variety of alcohols including primary and secondary, aromatic, aliphatic and cyclic alcohols using the optimized reaction conditions. The results for the oxidation of a variety of alcohols are summarized in Tables 4.33, 4.34, 4.35 below respectively in $CH_3CN-H_5IO_6$, $CH_3CN-H_2O_2$, CH_3CN-aq. TBHP systems.

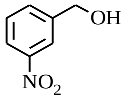
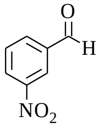
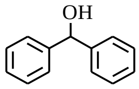
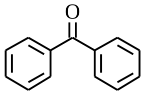
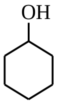
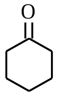
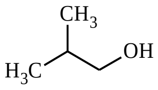
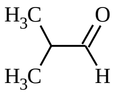
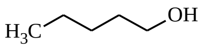
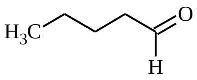
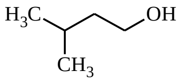
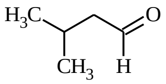
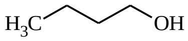
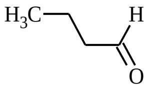
All the benzylic primary and secondary alcohols studied were oxidized smoothly to give aldehydes and ketones respectively in $CH_3CN-H_5IO_6$, $CH_3CN-H_2O_2$. Whereas in CH_3CN-aq. TBHP medium, the alcohols were oxidized to carboxylic acids or ketones respectively in high yields. In all of the above systems, at room temperature no significant conversion was observed even after 24 hr. However, the yield increased remarkably at the reflux temperature. Thus we choose reflux condition as the standard reaction temperature for our study.

Among the three systems studied, in $CH_3CN-H_5IO_6$ and $CH_3CN-H_2O_2$, selectivity towards aldehyde remains almost more than 95%. The over oxidation to carboxylic acid was ruled out by derivative test. While in CH_3CN-aq. TBHP, primary alcohols are oxidized to corresponding acids with high yield similar to iron and cobalt complexes.

Among the various alcohols studied those containing aromatic substituent were found to be more reactive than alicyclic and aliphatic alcohols. Similarly electron donating groups were found to slow down oxidation and electron withdrawing groups accelerated it. Para or ortho substituents with electron releasing or electron withdrawing properties did not induce any change on the selectivity. It was also observed that electron donating group on the ligand enhanced the catalytic activity. And also electron withdrawing sustituents decreased the catalytic activity of the complexes. As the ligand becomes more electron donating, the increased electron density makes the metal centre in the complex easier to oxidize. This is also in agreement with earlier reported observations.

Table 4.33: Oxidation of alcohols catalyzed by V(IV) complexes[a] in $CH_3CN-H_5IO_6$ system

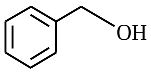
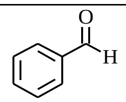
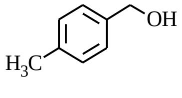
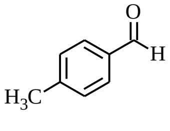
Alcohols	Product	% Yield[b]				
		VL_1	**VL_2**	**VL_3**	**VL_4**	**VL_5**
		97.1	94.3	93.7	90.8	98.1
		95.6	94.2	91.3	89.6	96.4
		94.2	92.8	90.7	88.6	96.3
		90.3	86.4	85.7	83.1	92.3

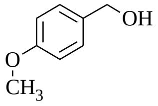
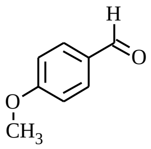
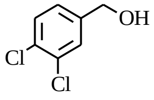
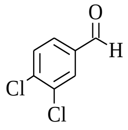
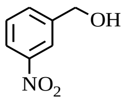
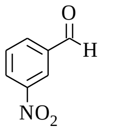
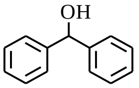
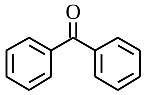
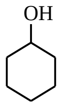
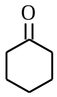
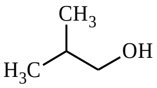
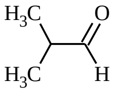
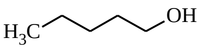
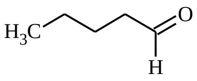
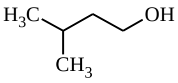
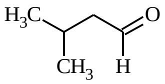
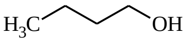
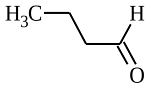
		98.6	92.3	90.1	89.5	98.9
		95.8	93.8	92.0	91.6	96.1
		85.6	80.5	79.6	75.1	87.3
		70.2	57.6	55.2	52.1	72.0
		64.3	61.5	60.0	59.1	68.2
		62.3	60.3	58.6	56.1	64.5
		59.8	56.9	54.6	51.1	63.5

[a] 1 mmol alcohol, 0.75 mmol H_5IO_6, 0.4 mmol V(IV) complex, 3 mL CH_3CN, stirring at 80°C.

[b] GC yield, average of 3 trials.

Table 4.34: Oxidation of alcohols catalyzed by V(IV) complexes[a] in H_2O_2 system

Alcohols	Product	% Yield[b]				
		VL_1	**VL_2**	**VL_3**	**VL_4**	**VL_5**
		90.9	90.4	87.6	85.9	91.9
		88.5	86.9	83.7	81.4	90.3

		84.8	82.0	79.8	76.8	87.4
		82.6	79.4	76.9	74.2	83.8
		92.7	90.1	88.8	86.2	94.0
		84.9	82.8	81.3	78.8	86.2
		80.3	78.7	76.7	73.6	83.7
		58.1	53.6	51.2	50.1	60.7
		54.7	51.5	49.0	43.6	57.8
		49.8	48.4	47.6	46.2	51.6
		35.7	33.5	32.6	31.1	38.4

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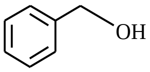
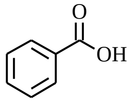
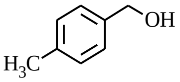
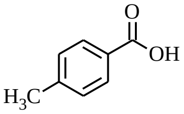
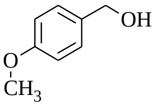
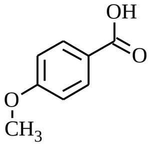
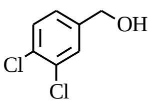
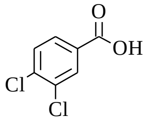
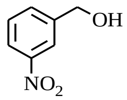
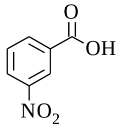
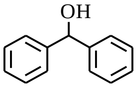
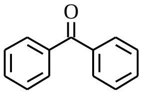
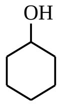
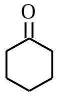
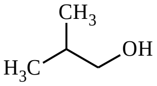
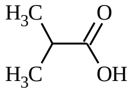
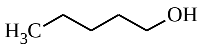
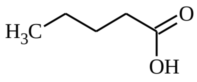
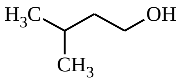
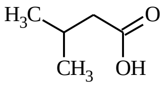
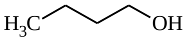
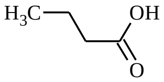
[a] 1 mmol alcohol, 5.0 mmol H_2O_2, 0.02 mmol V(IV) complex under reflux condition.

[b] GC yield, average of 3 trials.

Table 4.35: Oxidation of alcohols catalyzed by V(IV) complexes[a] in CH_3CN-aq. TBHP system

Alcohols	Product	% Yield[b]				
		VL$_1$	**VL$_2$**	**VL$_3$**	**VL$_4$**	**VL$_5$**
		89.8	85.4	84.9	83.3	92.1
		85.4	83.4	82.6	80.2	87.0
		83.1	81.8	80.9	78.5	84.1
		81.4	76.2	73.7	70.4	83.8
		93.8	92.4	90.3	89.9	95.7
		82.3	80.4	77.8	78.7	85.0
		74.3	70.6	68.5	67.8	75.1
		50.9	43.8	41.7	38.2	53.0
		43.7	39.4	37.7	35.1	46.5
		39.8	34.6	32.2	30.8	41.4

		30.2	27.5	25.6	26.1	32.7

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[a] 1 mmol alcohol, 2.0 mmol aq. TBHP, 0.01 mmol V(IV) complex, 1 mL CH_3CN, stirring at 80°C.

[b] GC yield, average of 3 trials.

4.6.4 Mechanistic aspeect

To study the mechanism involved in the reaction, UV spectra of the reaction mixture before and after the addition of the oxidant was examined (Fig. 4.30, 4.31 and 4.32).

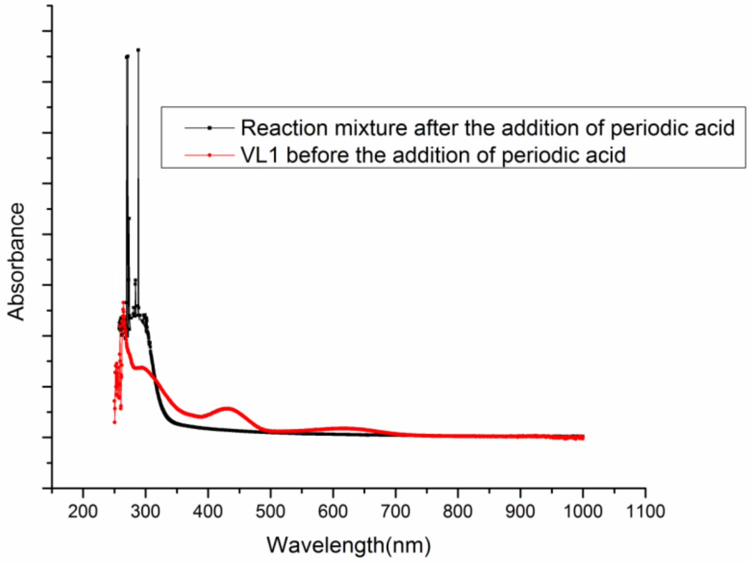


Fig. 4.30: UV-visible spectra of the reaction mixture in periodic acid system catalyzed by VL_1 complex

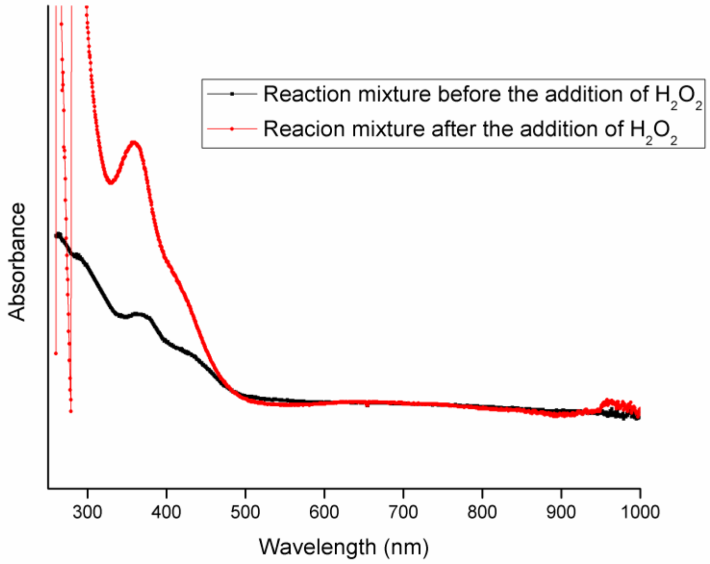


Fig. 4.31: UV-visible spectra of the reaction mixture in CH_3CN-H_2O_2 system

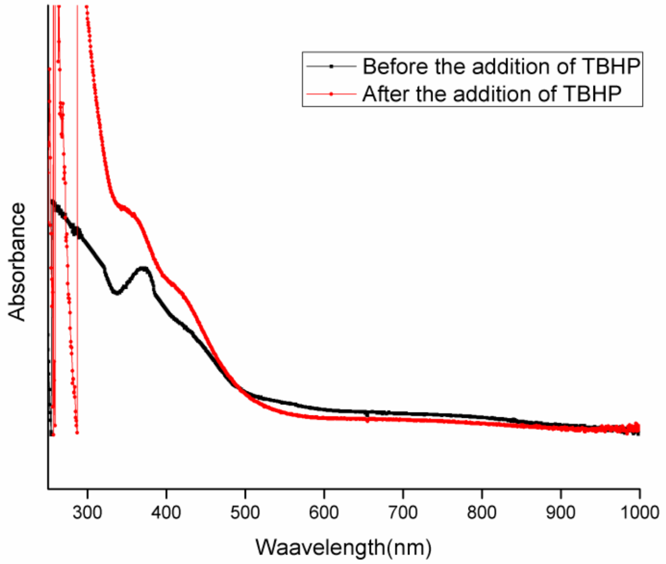
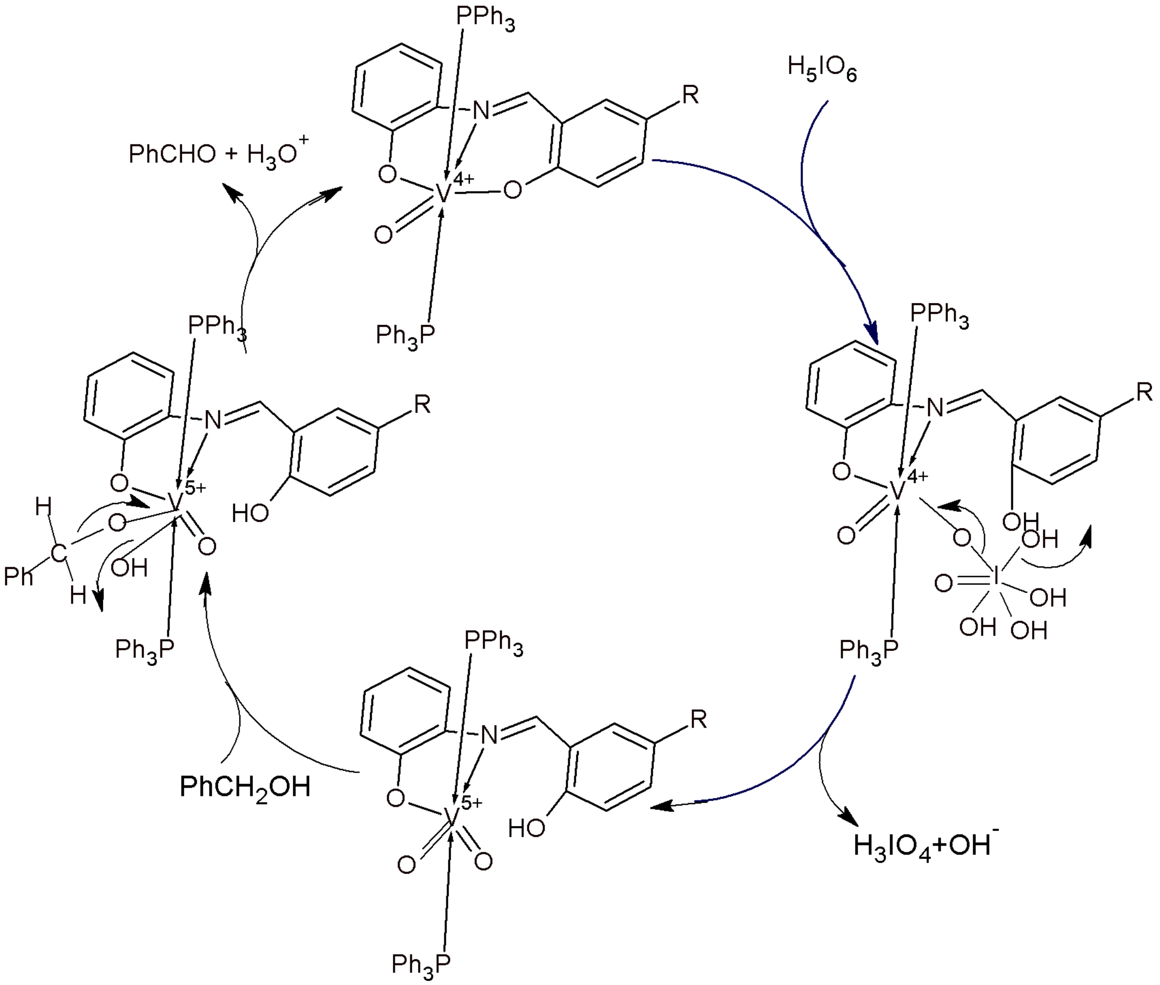


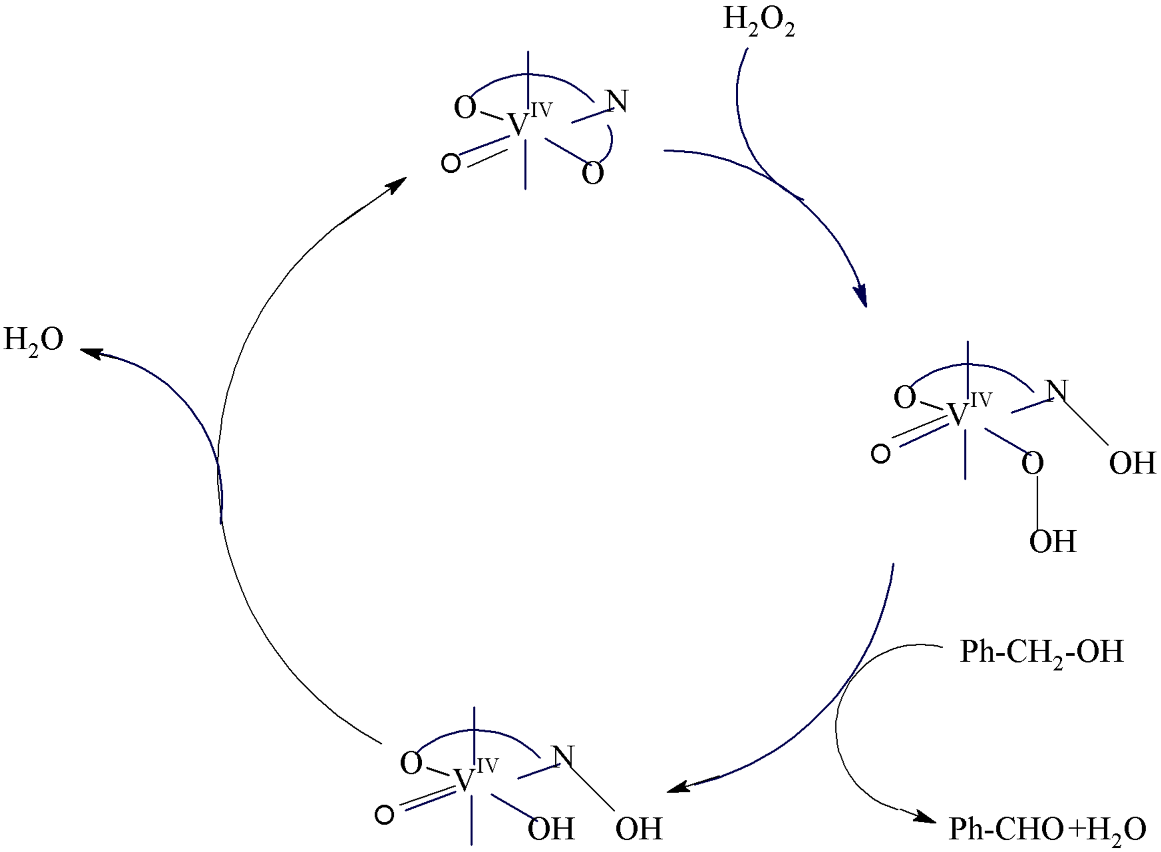
Fig. 4.32: UV-visible spectra of the reaction mixture in CH_3CN-aq. TBHP system

When the UV spectrum of the reaction mixture was examined in the presence of periodic acid, all the d-d bands as well as the charge transfer bands disappeared after the addition of the oxidant. Also, intra ligand transition band gained intensity. This clearly indicates that the metal ion under goes oxidation to +5 state which then assists in the oxidation of the substrate. This implies that the alcohol oxidation reaction mediated by V(IV) complexes proceeds through oxo mechanism in presence of periodic acid. Hence the possible mechanism for the oxidation of alcohols is as given in scheme 4.7.



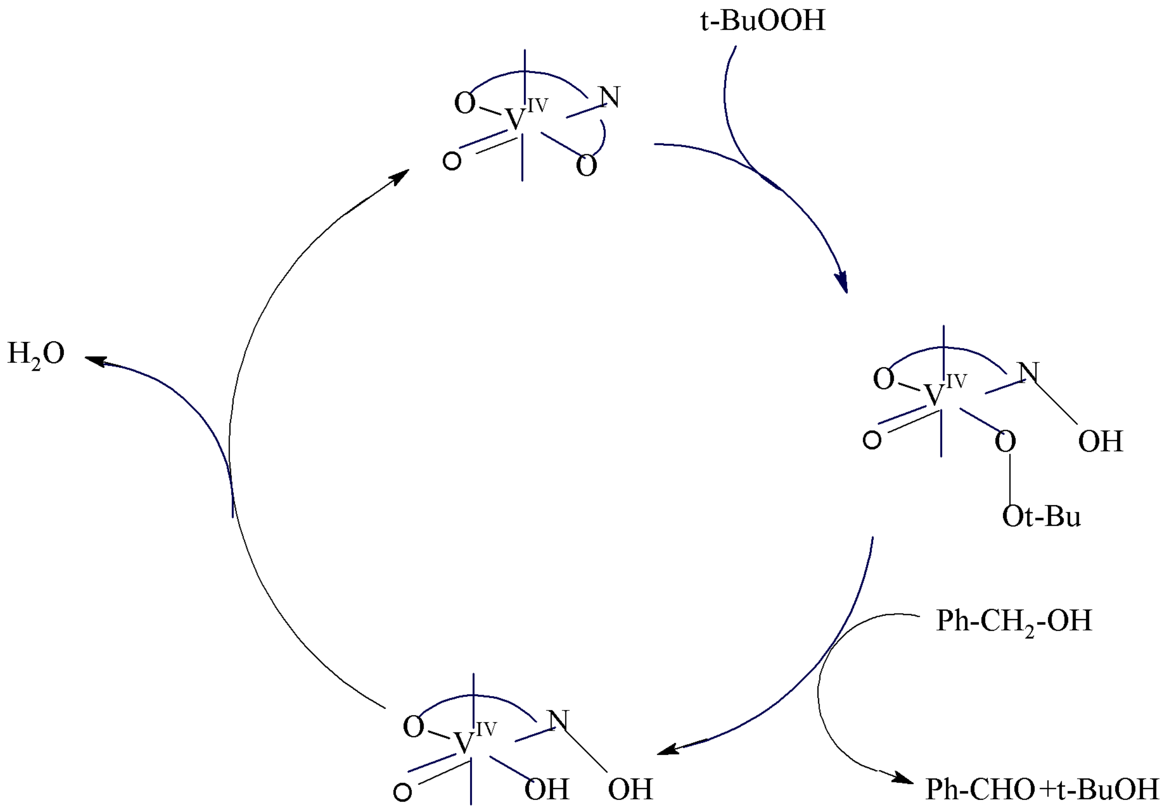
Scheme 4.7: Mechanism of oxidation of alcohols in periodic acid system

In H_2O_2 system, an increase in the intensity of intra ligand band and charge transfer band was observed suggesting the interaction between the oxidant and the complex. Along with that, a sharp increase in intensity at around 360 nm was observed which is assignable to the LMCT band of hydroperoxide to the metal centre. This clearly indicates the involvement of hydroperoxo metal species in the mechanism. Also there was no change in d-d band. Thus, we believed that here also peroxometal pathway is likely to be involved in the alcohol reactions mediated by V(IV) complexes. Hence the possible mechanism for the oxidation of alcohols is as given in scheme 4.8



Scheme 4.8: Mechanism of oxidation of alcohols in H_2O_2 system

In TBHP system, only increase in intensity of Intra ligand and LMCT band is observed indicating the interaction between the metal and oxidant. Also there was no change in d-d band, indicating no change in the oxidation state of the metal during the reaction. Hence the reaction must be proceeding through peroxo mechanism similar to H_2O_2 system (Scheme 4.9). Formed aldehyde further reacts with water and gets protonated. The protonated aldehyde gets oxidized to acid following the same mechanism as discussed under section 4.2.3.



Scheme 4.9: Proposed mechanism for alcohol oxidation in Aq. TBHP

4.7 CHARACTERIZATION OF COMPLEXES FeL$_6$-FeL$_{10}$

The reaction of equimolar ratios of the respective ligand (L$_6$, L$_7$, L$_8$, L$_9$ or L$_{10}$) and [FeCl$_3$(PPh$_3$)$_3$] yielded the new complexes of the general formula [Fe(L)Cl(PPh$_3$)$_2$] in moderate to good yield. All the present complexes were red in color. They were found to be soluble in CH$_2$Cl$_2$, CH$_3$CN, DMF and DMSO. The analytical data for these complexes were in good agreement with the above molecular formula. In all the reactions, it was observed that the Schiff base behaves as a tridentate ligand.

4.7.1 Electronic spectra and Analytical data

The electronic spectra of the ligands and complexes were recorded in acetonitrile. The electronic spectra of the all the complexes in CH_3CN showed three bands in the region 240–420 nm. The bands appearing in the region 245-295 nm have been assigned to intra ligand transitions. A band in the range 380-420 nm corresponds to ligand to metal charge transfer band. No bands observed in the d-d transition range as for six co-ordinate iron(III) complexes d-d transitions are generally forbidden and hence absorption bands are generally not observed (Aneetha et al, 1996) (Fig. 4.33). The analytical data for the complexes are given in Table 4.36.

Table 4.36: Analytical and Electronic spectral data of Fe(III) complexes

Complex	Elemental analysis data*				Electronic spectral data(nm)		d-d band	Magnetic moment μ_{eff} (BM)
	C	H	N	S	Intra Ligand transitions	Charge transfer transition		
FeL_6	69.69 (69.80)	4.60 (4.66)	1.60 (1.66)	3.69 (3.80)	248, 294	381, 446	538	6.05
FeL_7	63.61 (63.83)	4.12 (4.15)	1.49 (1.52)	3.39 (3.48)	247, 288	388, 442	540	5.92
FeL_8	67.00 (67.06)	4.29 (4.36)	1.55 (1.60)	3.59 (3.65)	248, 294	380, 441	555	5.96
FeL_9	66.20 (66.26)	4.26 (4.31)	3.59 (3.61)	3.10 (3.15)	246,288	394, 439	535	5.82
FeL_{10}	67.67 (68.78)	4.72 (4.73)	1.58 (1.60)	3.60 (3.67)	248, 288	378, 438	534	6.00

*Found (Calculated)

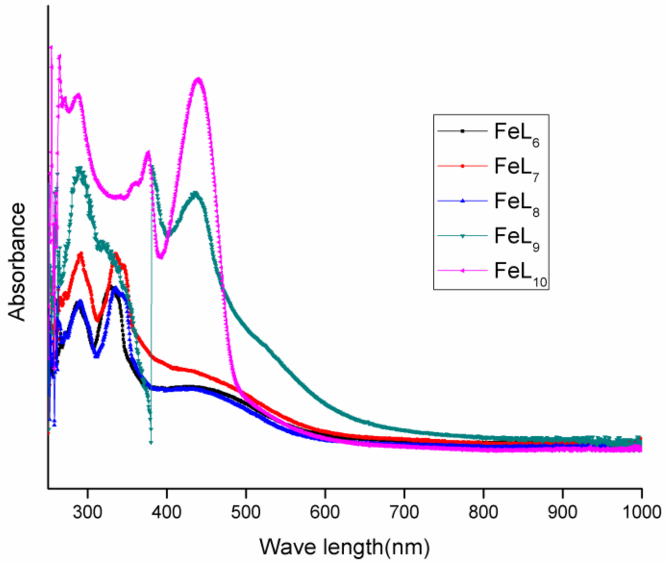


Fig. 4.33: UV-visible spectra of FeL_6-FeL_{10} complexes

4.7.2 FTIR spectra

Selected FTIR bands of ligands and complexes are listed in Table 4.37. The FTIR spectra of the ligands exhibit a strong band around 1608-1644 cm^{-1}, which is assigned to ν(C=N) vibration. As a result of coordination, this band is altered in complexes. The band in the region 1265-1315 cm^{-1} which is assigned to phenolic ν(C–O) in the free ligand, is shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion. A weak band observed at around the region 1240 cm^{-1}, corresponding to ν (C–S) in the ligands, shifts to a longer wave number (1251-1293 cm^{-1}) which supports sulfur coordination with the iron centre (Arunachalam et al, 2009). The bands around 535 cm^{-1} and 415-434 cm^{-1} in the complex is assigned to ν(M–O) and ν(M–N) respectively. Bands due to triphenylphosphine are also appeared in the expected region (Fig. 4.34 and Fig. 4.35).

Table 4.42: FTIR spectral data (cm^{-1}) for ligands and its Fe(III) complexes

Compound	ν$_{(C=N)}$	ν$_{(C-O)}$	ν$_{(C-S)}$	ν$_{(Fe-O)}$	ν$_{(Fe-N)}$	Bands due to PPh$_3$
L$_6$	1608	1270	1240	-	-	-
L$_7$	1621	1265	1246	-	-	-
L$_8$	1624	1270	1254	-	-	-
L$_9$	1644	1277	1243	-	-	-
L$_{10}$	1610	1315	1248	-	-	-
FeL$_6$	1591	1320	1268	535	415	1438,1073,688
FeL$_7$	1597	1318	1278	533	427	1440, 1080, 690
FeL$_8$	1586	1316	1293	537	426	1464, 1082, 690
FeL$_9$	1600	1327	1280	535	431	1436, 1077, 690
FeL$_{10}$	1593	1322	1251	535	434	1437, 1069, 691

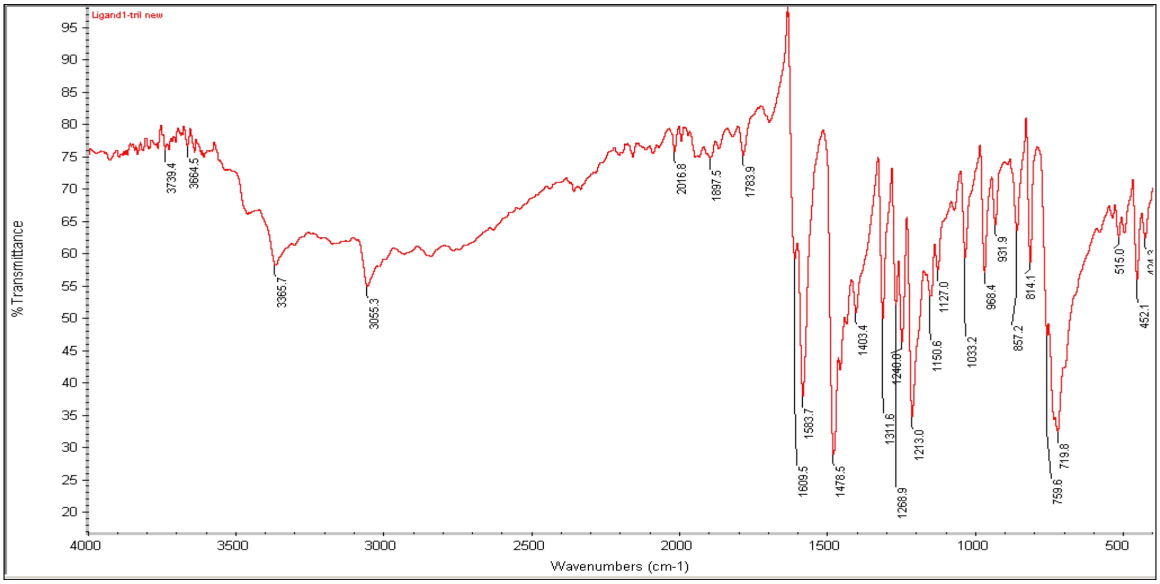


Fig. 4.34: FTIR spectra of L$_6$ ligand

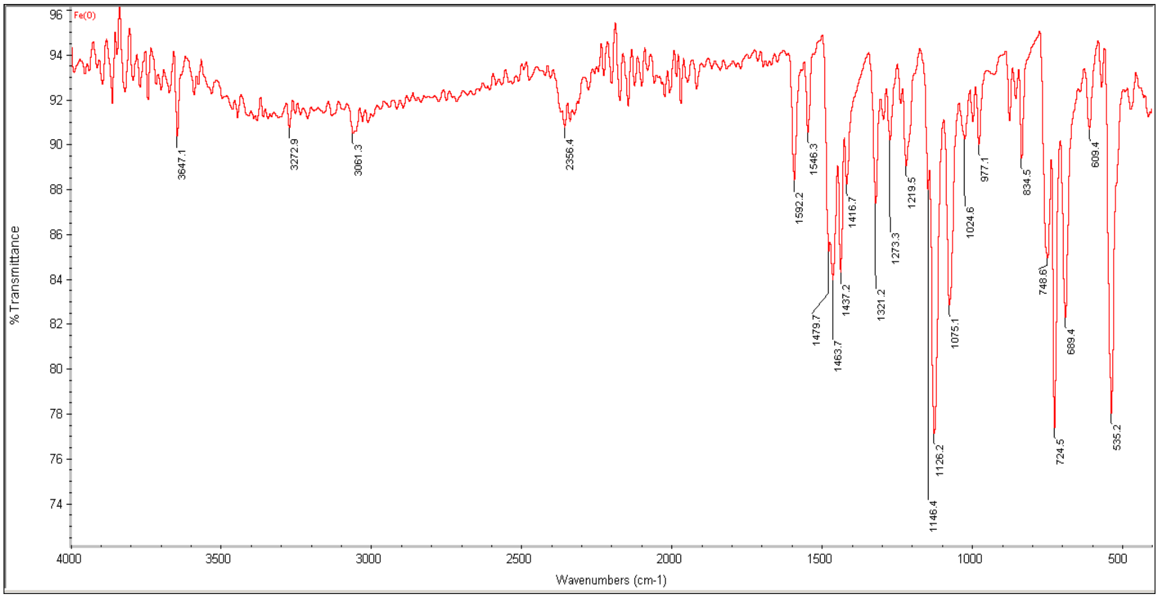


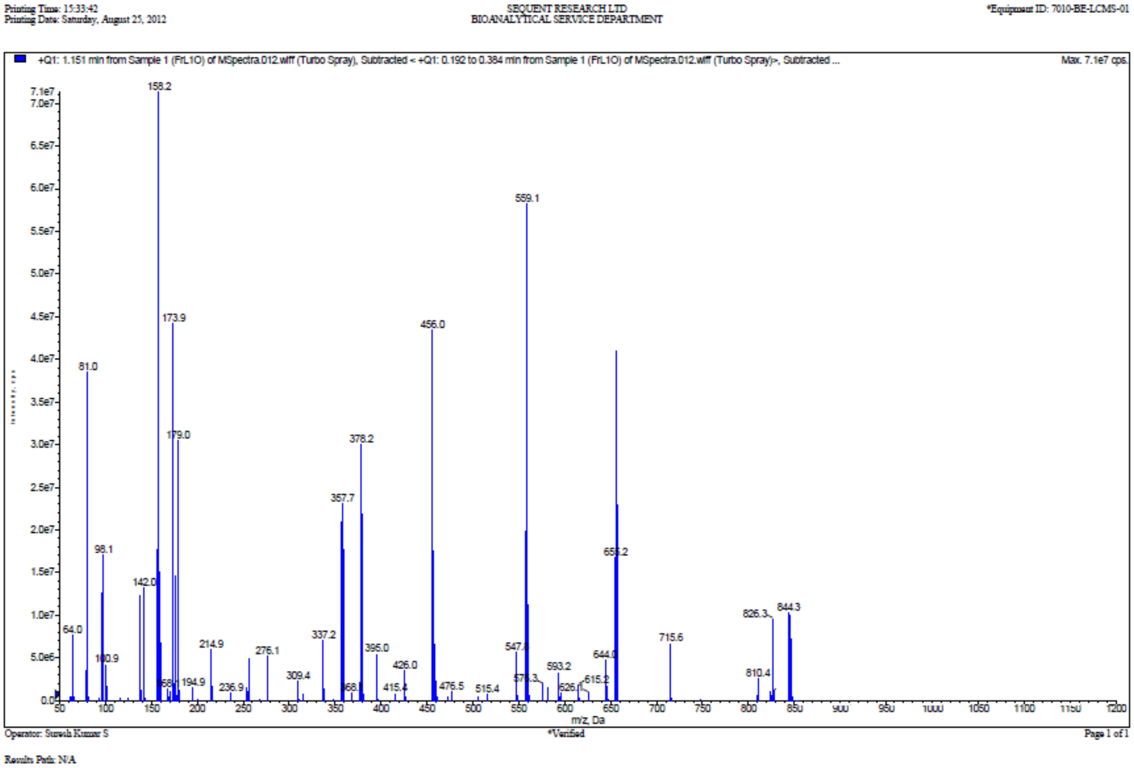
Fig. 4.35: FTIR spectra of FeL_6 complex

4.7.3 ESI Mass Measurements

In the mass spectra of the complexes, the molecular weight of the complexes correspond to the presence of the tridentate ligand, two triphenylphosphine ligands and chloride group confirming the assumed structure. The ESIM spectra of the complex FeL_6 is shown in the Figure 4.36. Similarly expected molecular weight and the observed molecular weight of the complexes are given in the Table 4.38.

Table 4.38: ESIMS datas of Iron complexes

Complex	Expected mass	Observed mass
FeL_6	843.3	844.3
FeL_7	861.5	862.2
FeL_8	906.0	907.2
FeL_9	872.1	873.4
FeL_{10}	856.9	857.3



Printing Time: 15:33:42
Printing Date: Saturday, August 25, 2012

SEQUENT RESEARCH LTD
BIOANALYTICAL SERVICE DEPARTMENT

*Equipment ID: 7010-BE-LCMS-01

+Q1: 1.151 min from Sample 1 (FrL1O) of MSpectra.012.wiff (Turbo Spray), Subtracted < +Q1: 0.192 to 0.384 min from Sample 1 (FrL1O) of MSpectra.012.wiff (Turbo Spray)>, Subtracted ...

Max. 7.1e7 cps.

Operator: Suresh Kumar S

*Verified

Page 1 of 1

Results Path: N/A

Fig. 4.36 ESIM Spectra of complex FeL_6

4.7.4 Magnetochemical measurements

In order to obtain further structural information, the magnetic moments of the complexes were measured. All iron (III) complexes show magnetic moments in the range 5.80-6.05 B.M, confirms the high spin octahedral iron (III) complexes.

4.7.5 Thermal measurements

The thermograms of Fe(III) chelates showed 3 stages of decomposition (Fig. 4.37). First stage of decomposition at around 200ºC which corresponds to the loss of chloride, second stage of decomposition at around 350ºC which indicates the loss of triphenylphosphine and third stage of decomposition in the range of 420-750ºC indicating the loss of ligand molecule.

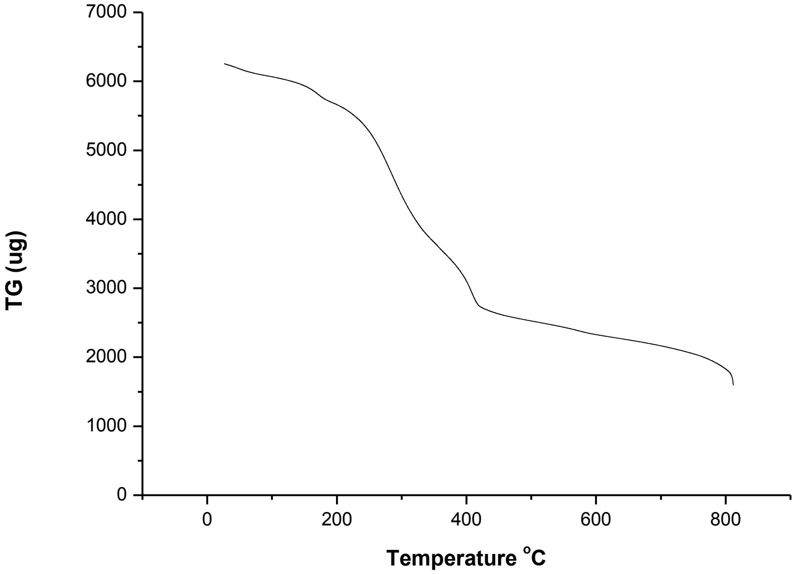


Fig. 4.37: TG diagram of FeL_6

4.8 CATALYTIC ACTIVITY OF COMPLEXES FeL_6-FeL_{10}

The catalytic activities of the complexes were examined for the oxidation of primary and secondary alcohols by the FeL_6-FeL_{10} complexes as discussed under section 4.2 using oxidants periodic acid, hydrogen peroxide and aqueous tert-butylhydroperoxide. All the synthesized iron complexes were found to catalyze the oxidation of alcohol to corresponding carbonyls but the yields were found to vary with different catalysts.

The oxidation of benzyl alcohol, as a standard substrate, was first investigated in order to optimize the reaction variables such as solvent, temperature, alcohol/oxidant molar ratio and length of the reaction time as discussed under section 4.2.

In case of H_5IO_6 and aq. TBHP best yields have been observed in acetonitrile, whereas H_2O_2 system showed the best yield under solvent less condition. The activity of FeL_6 was studied at different temperature by taking benzyl alcohol as the model substrate in all the 3 above mentioned systems. It was observed that at 80°C, the system showed higher yield in case of CH_3CN-H_5IO_6 and CH_3CN-aq. TBHP while in H_2O_2 system, the reaction occurred at room temperature.

4.8.1 Effect of time

In order to study the effect of time on the activity, the product analysis was done at regular intervals of time, under similar reaction conditions. In the case of CH_3CN-H_5IO_6, it was observed that the total reaction time was 90 minutes at 80°C. The experiments were conducted at regular intervals of time beyond 90 minutes. The results show that the yield remains constant at about 86% after a reaction time of 90 minutes (Table 4.39). In the case of H_2O_2 system, it was found that the reaction was complete in 20 minutes (Table 4.40). Similarly the effect of time was studied for CH_3CN-aq. TBHP system, in which case it was observed that total reaction time of 120 minutes was needed for highest catalytic conversion (Table 4.41).

Table 4.39: Effect of time on benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system

Sl. No.	Time (min)	% Yield[a] CH_3CN-H_5IO_6 system
1	2	8.1
2	15	61.5
3	30	74.6
4	45	80.2
5	60	82.5
6	75	83.4
7	**90**	86.4
8	105	86.4
9	120	85.3
10	135	86.4

[a]GC yield, average of 3 trials.

Table 4.40: Effect of time on benzyl alcohol in H_2O_2 system

Sl. No.	Time (min)	% Yield[a] H_2O_2 system
1	2	1.4
2	5	35.8
3	10	52.6
4	15	68.1
5	**20**	75.5
6	25	75.3
7	30	75.2

[a]GC yield, average of 3 trials

Table 4.41: Effect of time on benzyl alcohol in CH_3CN- aq TBHP system

Sl. No.	Time (min)	% Yield[a] CH_3CN-aq TBHP system
1	2	10.2
2	15	32.7
3	30	54.4
4	45	62.8
5	60	70.7
6	75	75.8
7	90	79.6
8	105	84.3
9	**120**	94.2
10	135	94.2
11	150	94.1

[a]GC yield, average of 3 trials

4.8.2 Effect of catalyst concentration

In order to study the effect of the concentration of catalyst with respect to substrate and oxidant, the reaction was carried out at different catalyst concentrations. The results are summarized in the Table 4.42.

A minimum quantity of 0.04 mmol of the catalyst was needed for the effective transformation of benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system. While in case of H_2O_2 and CH_3CN-aq. TBHP systems 0.02 mmol and 0.01 mmol of catalyst was sufficient to bring about the conversions respectively (Fig. 4.38).

Table 4.42: Effect of catalyst concentration on benzyl alcohol

Sl. No.	Catalyst concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 System	H_2O_2 system	CH_3CN-aq. TBHP system
1	0	12.0	2.0	15.4
2	0.01	63.0	59.2	**94.2**
3	0.02	69.5	**75.5**	94.3
4	0.03	79.4	75.7	94.3
5	0.04	**87.3**	74.9	94.2
6	0.05	87.1	74.5	94.2

[a] GC yield, average of 3 trials

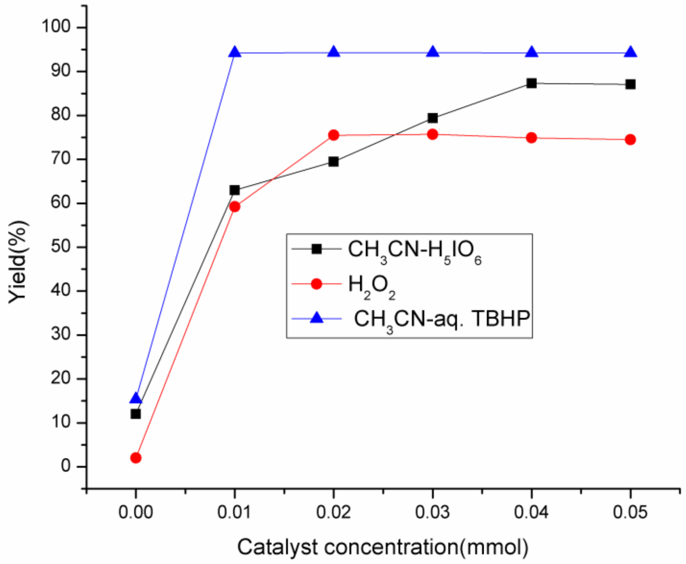


Fig. 4.38: Effect of catalyst concentration on benzyl alcohol

4.8.3 Effect of oxidant concentration

The reactions were studied with respect to substrate and catalyst at different oxidant concentrations. The results are summarized in Table 4.43.

A minimum quantity of 0.75mmol, 5 mmol, 2 mmol of the oxidants were required in CH_3CN-H_5IO_6, H_2O_2, CH_3CN-aq. TBHP systems respectively for the effective oxidation of benzyl alcohol (Fig. 4.39).

Table 4.43: Effect of oxidant concentration on benzyl alcohol

Sl. No.	Oxidant concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 System	H_2O_2 system	CH_3CN-aq. TBHP system
1	0	3.7	3.6	3.8
2	0.5	77.59	5.4	43.7
3	0.75	**86.8**	12.6	56.4
4	1.0	86.4	16.7	81.6
5	2.0	86.5	24.5	**94.2**
6	3.0	86.4	55.5	94.2
7	4.0	86.2	68.9	94.3
8	5.0	86.5	**75.5**	94.3
9	6.0	86.4	75.7	94.3

[a] GC yield, average of 3 trials

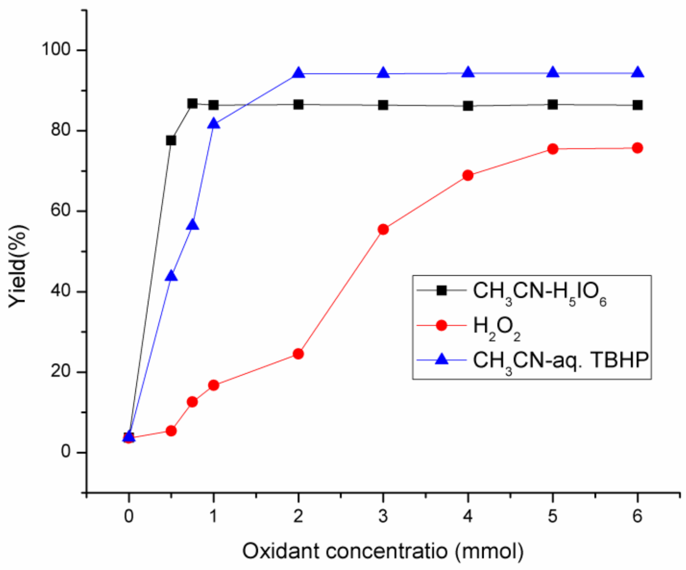


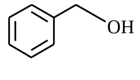
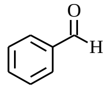
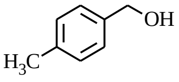
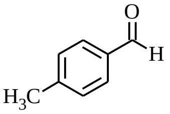
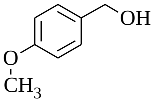
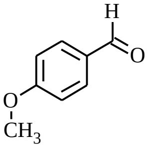
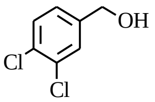
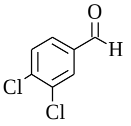
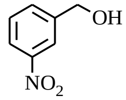
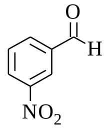
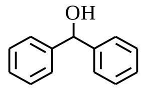
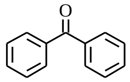
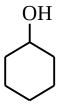
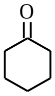
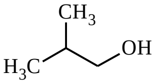
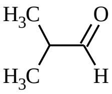
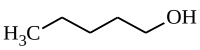
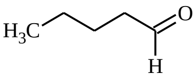
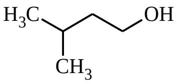
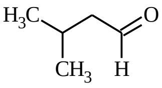
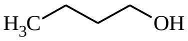
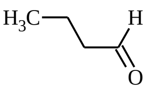
Fig. 4.39: Effect of oxidant concentration on benzyl alcohol

The oxidation was extended to a variety of alcohols including primary and secondary, aromatic, aliphatic and cyclic alcohols using the optimized reaction conditions. The results for the oxidation of a variety of alcohols are summarized in Tables 4.44, 4.45, 4.46 below respectively in CH_3CN-H_5IO_6, H_2O_2, CH_3CN-aq. TBHP systems.

All the benzylic primary and secondary alcohols studied were oxidized smoothly. Among the three systems studied, in CH_3CN-H_5IO_6 and H_2O_2, selectivity towards aldehyde remains almost more than 95%. The over oxidation to carboxylic acid was ruled out by derivative test. While in CH_3CN-aq. TBHP, primary alcohols are oxidized to corresponding acids with high yield. No oxidation was observed in the aromatic ring of benzylic substrates hence the catalytic systems are selective towards the alcoholic group.

In CH_3CN-H_5IO_6 and CH_3CN-aq. TBHP systems, no significant yield was observed even after 24 hr, at room temperature. Among the various alcohols studied those containing aromatic substituent were found to be more reactive than alicyclic and aliphatic alcohols. This can be attributed to the higher reactivity of aromatic systems due to its delocalization. Lower reactivity of aliphatic alcohols is because of the lesser reactivity of the substrates. Similarly electron donating groups were found to slow down oxidation, whereas electron withdrawing groups accelerate it. Para or ortho substituents with electron releasing or electron withdrawing properties do not induce any change on the selectivity. It was also observed that electron donating group on the ligand enhanced the catalytic activity. And also electron withdrawing substituents decreased the catalytic activity of the complexes. As the ligand becomes more electron donating, the increased electron density makes the metal centre in the complex easier to oxidize. This is in agreement with earlier reported observations.

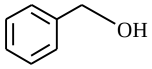
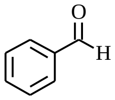
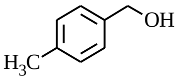
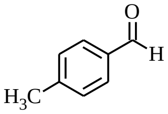
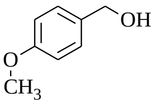
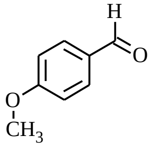
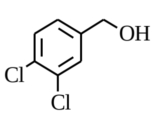
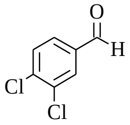
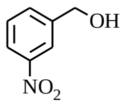
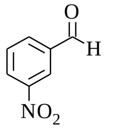
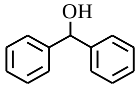
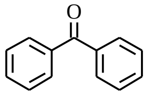
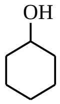
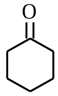
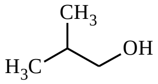
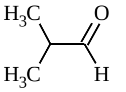
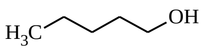
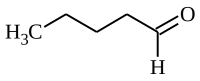
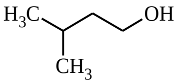
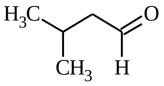
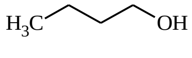
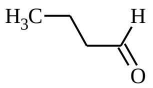
Table 4.44: Oxidation of alcohols by Fe(III) complexes[a] in CH_3CN-H_5IO_6 system

Alcohols	Product	% Yield[b]				
		FeL_6	**FeL_7**	**FeL_8**	**FeL_9**	**FeL_{10}**
		86.4	82.3	83.7	80.8	87.1
		79.5	77.5	78.2	78.6	74.4
		77.5	77.1	74.8	76.2	71.8
		76.5	75.7	73.2	73.8	70.4
		88.8	87.6	85.9	86.7	89.2
		79.7	77.2	74.0	76.1	81.3
		72.6	70.5	67.6	70.1	73.3
		64.8	60.6	56.2	61.1	65.0
		54.3	51.5	49.0	52.6	55.2
		52.1	49.6	45.6	48.1	52.5
		50.6	46.9	41.6	45.1	51.5

[a] 1 mmol alcohol, 0.75 mmol H_5IO_6, 0.4 mmol Fe (III) complex, 3 mL CH_3CN, reflux.

[b] GC yield, average of 3 trials.

Table 4.45: Oxidation of alcohols catalyzed by Fe(III) complexes[a] in H_2O_2 system

Alcohols	Product	% Yield[b]				
		FeL_6	**FeL_7**	**FeL_8**	**FeL_9**	**FeL_{10}**
		75.5	71.4	72.2	74.3	76.7
		73.5	70.5	72.2	72.8	74.2
		71.8	69.0	69.8	70.8	72.4
		78.6	76.4	76.9	77.2	79.8
		77.9	71.8	72.3	74.8	78.2
		63.7	60.1	61.8	62.2	64.0
		54.3	49.7	52.7	53.6	55.7
		28.1	23.6	24.2	26.1	29.7
		24.7	21.5	23.0	23.6	25.8
		19.8	15.4	17.6	18.2	20.6
		15.7	10.5	11.6	12.1	17.4

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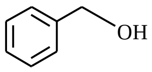
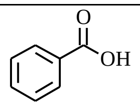
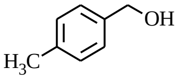
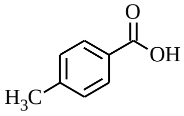
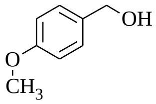
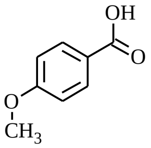
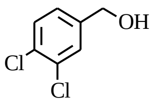
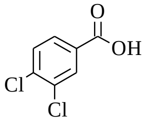
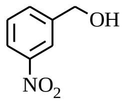
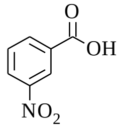
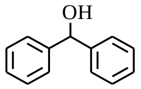
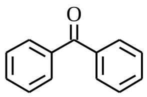
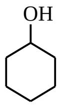
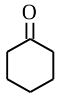
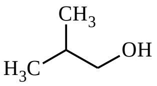
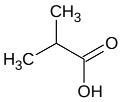
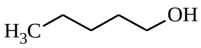
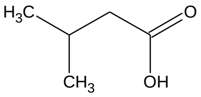
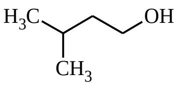
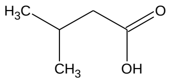
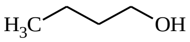
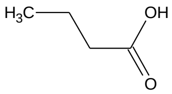
[a] 1 mmol alcohol, 5.0 mmol H_2O_2, 0.02 mmol Fe (III) complex.

[b] GC yield, average of 3 trials.

Table 4.46: Oxidation of alcohols by Fe(III) complexes[a] in CH_3CN-aq. TBHP system

Alcohols	Product	% Yield[b]				
		FeL_6	**FeL_7**	**FeL_8**	**FeL_9**	**FeL_{10}**
		94.2	90.4	88.9	87.3	95.1
		85.4	81.4	82.6	84.2	86.0
		83.1	79.8	80.9	81.5	84.1
		93.4	90.2	91.7	92.4	94.8
		95.8	91.4	88.3	88.9	96.7
		82.3	79.4	79.8	81.7	83.0
		74.3	70.6	72.5	73.8	75.1
		50.9	43.8	45.7	46.2	52.0
		43.7	39.4	40.7	42.1	44.5
		39.8	34.6	36.2	36.8	40.4
		30.2	27.5	28.6	29.1	31.7

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[a] 1 mmol alcohol, 2.0 mmol aq. TBHP, 0.01 mmol Fe (III) complex, 1 mL CH_3CN, stirring at 80°C.

[b] GC yield, average of 3 trials.

4.8.4 Mechanistic study

To study the mechanism involved in the reaction, UV spectra of the reaction mixture before and after the addition of the oxidant was examined (Fig. 4.40, 4.41 and 4.42).

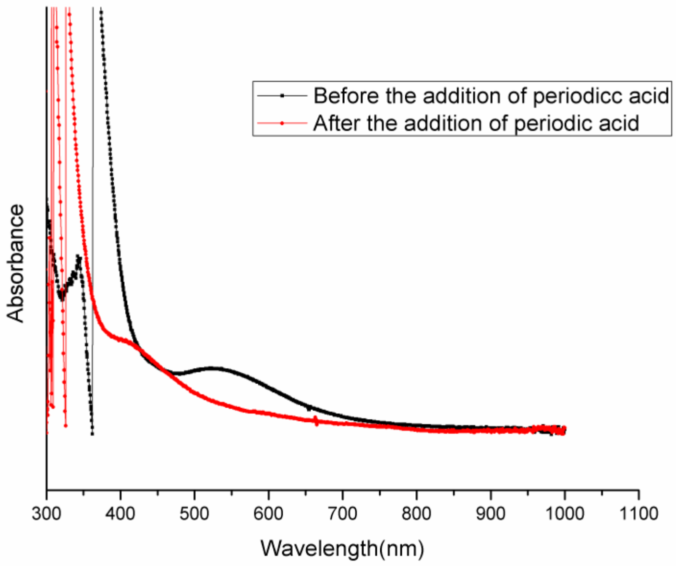


Fig. 4.40: UV-visible spectra of the reaction mixture in CH_3CN-H_5IO_6 acid system catalyzed by FeL_6 complex

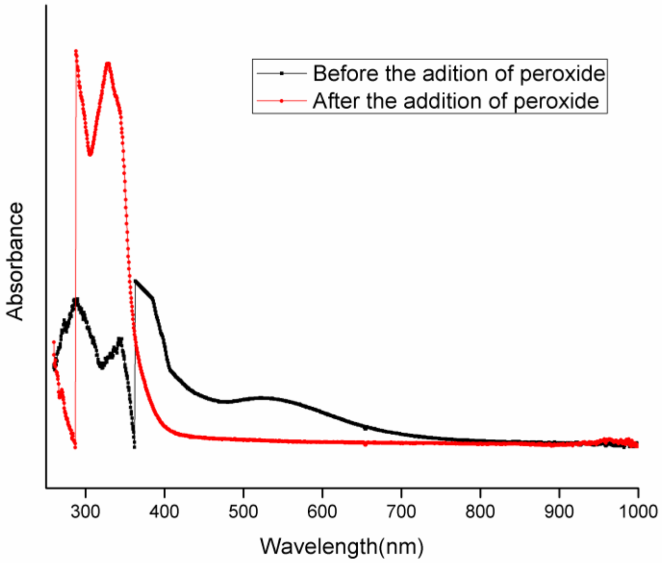


Fig. 4.41: UV-visible spectra of the reaction mixture in H_2O_2 system catalyzed by FeL_6 complex

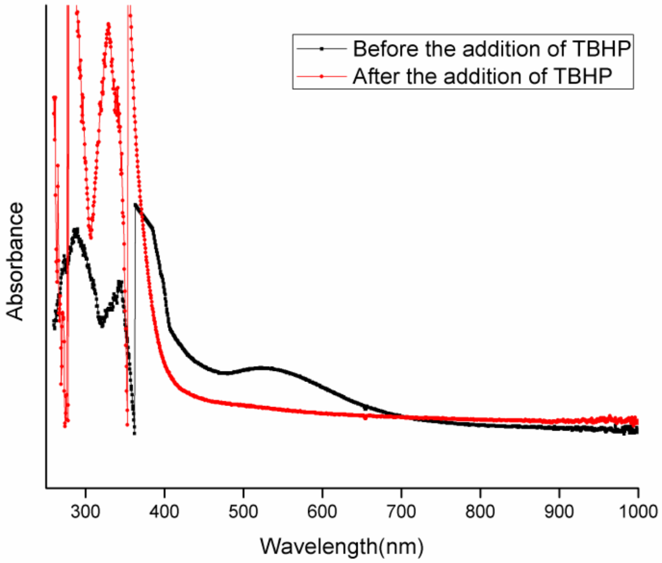


Fig. 4.42: UV-visible spectra of the reaction mixture in CH_3CN-aq. TBHP system catalyzed by FeL_6 complex

In the UV-visible spectra of the reaction mixture of periodic acid system, an increase in the intensity of intra ligand band and charge transfer band was observed suggesting the interaction between the oxidant and the complex. Similarly, the d-d band disappeared after the addition of the oxidant. This indicates the formation of high valent iron oxo species ($Fe^{V}=O$) similar to the periodic system discussed under section 4.2.3. Based on these results, oxometal pathway is more likely to be involved in the alcohol oxidation reaction in periodic acid system. Hence the following mechanism has been proposed for the oxidation of alcohols in periodic acid system is similar to the mechanism of oxidation by periodic acid discussed under section 4.2.3

In both H_2O_2 and CH_3CN-aq.TBHP systems, an increase in the intensity of intra ligand band and charge transfer band was observed suggesting the interaction between the oxidant and the complex. The d-d band disappeared after the addition of the oxidant. Hence the reaction must be proceeding through oxo pathway unlike the peroxo path way involved in the reaction catalyzed by FeL_1-FeL_5 complexes. Hence the mechanism involved in the reaction is similar to the mechanism involved in periodic system catalyzed by FeL_1-FeL_5 complexes discussed under section 4.2.3 except that the oxidant involved is H_2O_2 and aq. TBHP.

4.9 CHARACTERIZATION OF COMPLEXES FeL_{11}-FeL_{14}

FeL_{11} and FeL_{12} were obtained by stirring a solution of $FeCl_3$ and L_1 or L_6 in ethanol and alcoholic ethanol respectively in 1:1 ratio. The general formula of the complex is [Fe(L)Cl] (L = Schiff base ligand. FeL_{13} was obtained by the reaction of L_1 with $FeCl_3(OPPh_3)_2$ in ethylacetate at room temperature. Similarly FeL_{14} was obtained by treating FeL_{12} with $OPPh_3$ in 1:2 ratio at room temperature. All the synthesized complexes were red in color. They were found to be soluble in CH_3CN, C_6H_6, DMSO, DMF and $CHCl_3$.

4.9.1Electronic Spectra and Analytical data

The analytical data for these complexes are in good agreement with the above molecular formula. In all the reactions, it has been observed that the Schiff base behaves as a tridentate ligand. The electronic spectra of the ligands and complexes were recorded in dimethylformamide. The electronic spectra of the all the complexes showed bands in the region 260-501nm. The band observed around 260-315nm has been assigned to intra ligand transitions. The band appearing in the region of 303-404 nm is associated with ligand to metal charge transfer bands. The very low intensity d-d band appeared in the range of 475-501 nm (Fig. 4.43 and Fig. 4.44).

Table 4.47: Analytical and Electronic spectral data of Fe(III) complexes

Complex	Elemental composition *Found (Calculated)			Electronic spectral data	Magnetic moment μ_{eff} (BM)
	C	H	N		
FeL_{11}	51.54 (51.61)	2.96 (3.00)	4.62 (4.63)	265, 288,403, 501	5.88
FeL_{12}	48.88 (49.01)	2.83 (2.85)	4.35 (4.40)	263, 276, 334, 498	5.82
FeL_{13}	68.45 (68.51)	4.52 (4.58)	1.55 (1.63)	264, 271, 289, 404, 500	6.10
FeL_{14}	67.20 (67.25)	4.36 (4.49)	1.53 (1.60)	271, 312, 360, 475	6.04

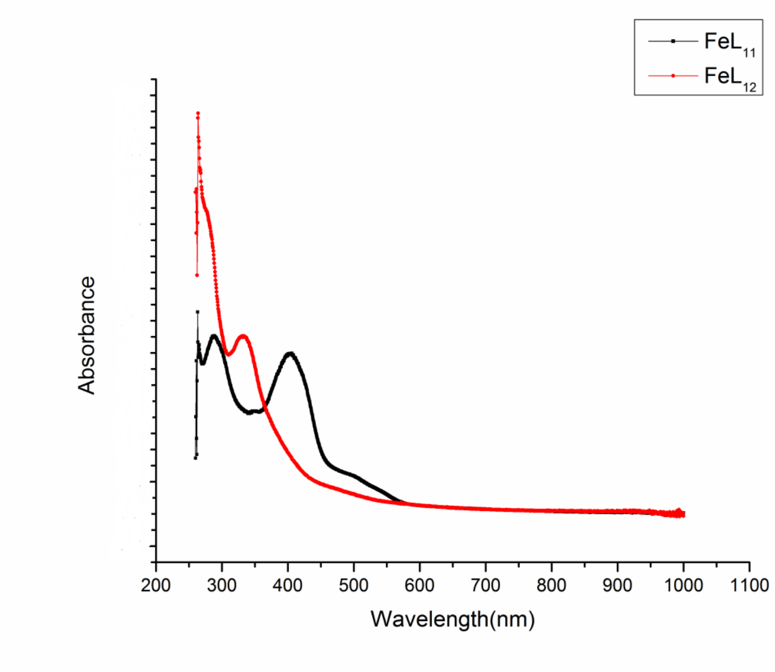


Fig. 4.43: UV-visible spectra of FeL$_{11}$-FeL$_{12}$ complexes

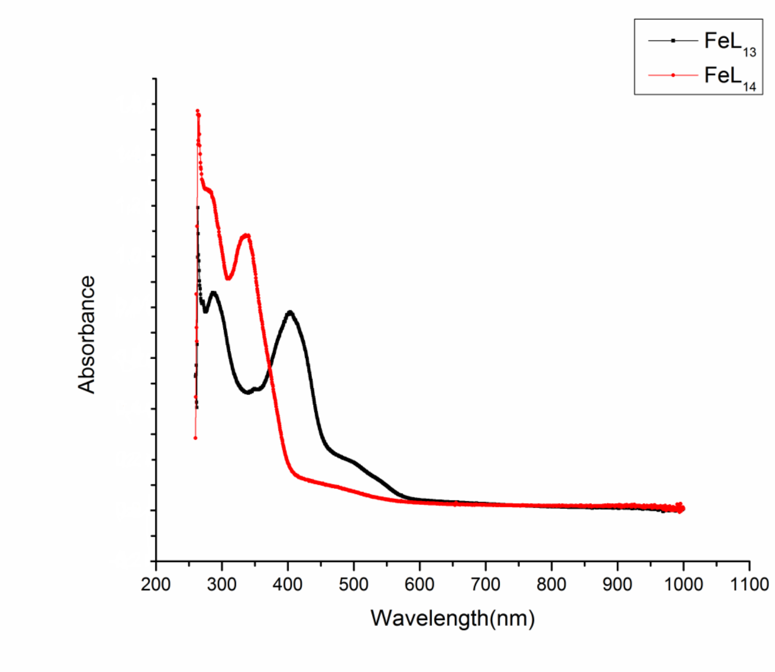


Fig. 4.44: UV-visible spectra of FeL$_{13}$-FeL$_{14}$ complexes

4.9.2 FTIR Spectra

Selected FTIR bands of ligands and complexes are listed in Table 4.48. The ν(C=N) vibration of the ligands which appeared at around 1608-1625 cm^{-1} was shifted to 1592-1600 cm^{-1}, lower frequency in complexes due to its coordination to the metal. The band in the region 1270 cm^{-1} which is assigned to phenolic ν(C–O) in the free ligand, was shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion. The bands around 560-620 cm^{-1} and 530-450 cm^{-1} in the complex can be assigned to ν(M–O) and ν(M–N) respectively. Bands due to triphenylphosphineoxide were also appeared in the expected region (Fig. 4.45 and Fig. 4.46).

Table 4.48: FTIR spectral data (cm^{-1}) for ligands and its Fe(III) complexes

Compound	$\nu_{(C=N)}$	$\nu_{(C-O)}$	$\nu_{(Fe-O)}$	$\nu_{(Fe-N)}$	Bands due to $OPPh_3$
L_1	1625	1271	-	-	-
L_2	1608	1270	-	-	-
FeL_{11}	1592	1297	621	532	-
FeL_{12}	1595	1294	564	448	-
FeL_{13}	1600	1297	570	460	1149, 1124, 1035 749, 622, 534
FeL_{14}	1593	1321	611	456	1145, 1127, 1074, 725, 691, 537

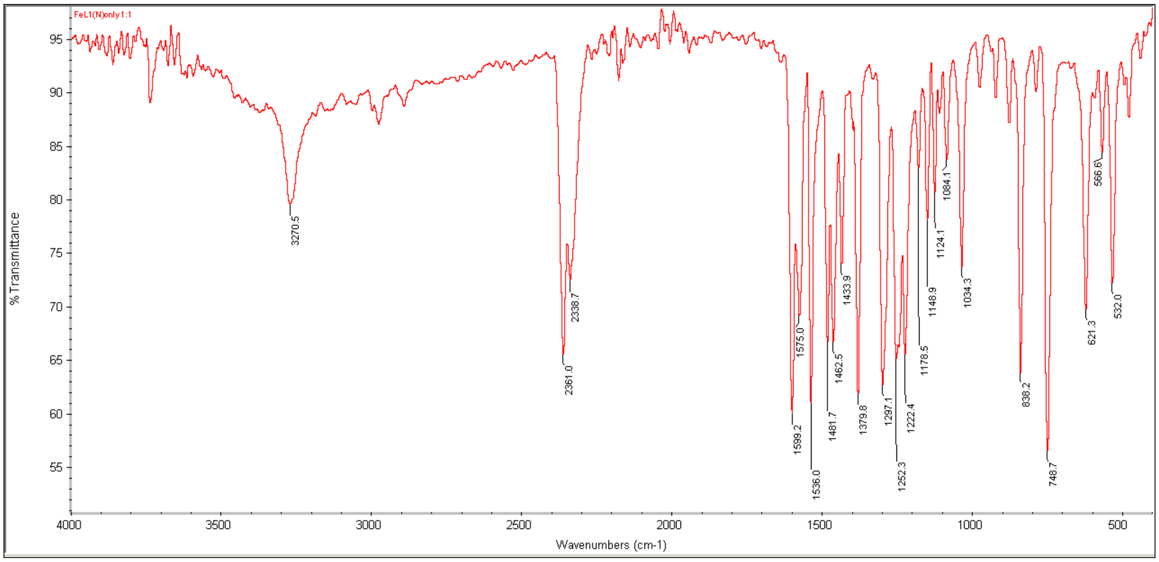


Fig. 4.45: FTIR spectra of FeL_{11} complex

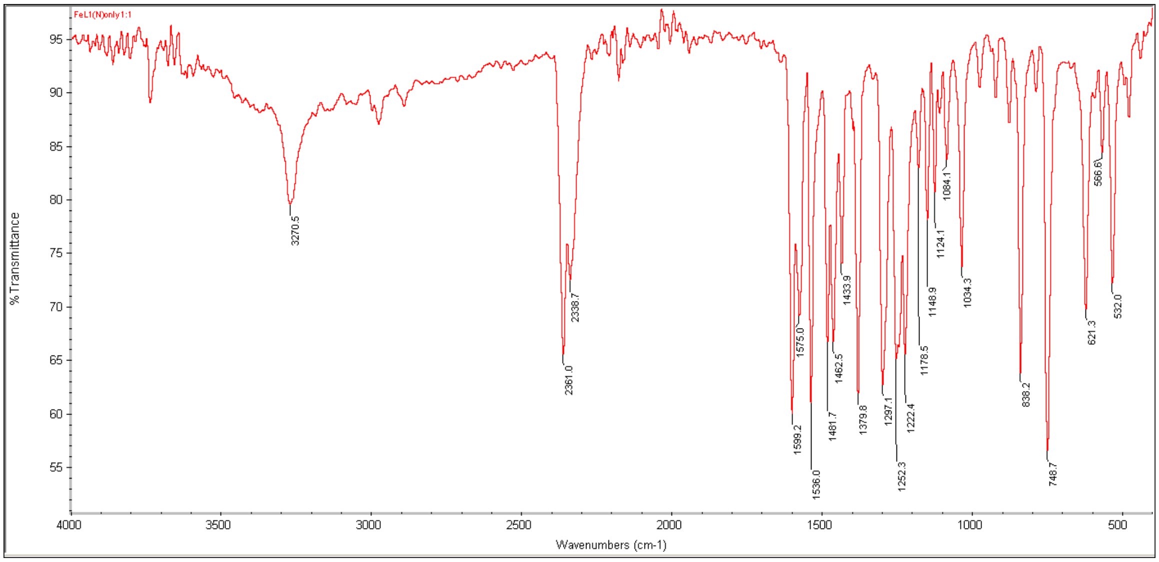


Fig. 4.46: FTIR spectra of FeL_{14} complex

4.9.3 NMR Specta

The ^{31}P NMR spectra of FeL_{13} and FeL_{14} complexes showed single resonance peak at around 25 ppm which has been assigned to the coordinated triphenylphosphineoxide present in the complexes in trans- position. The $^{31}P\{^{1}H\}$ NMR spectra of the complexes are shown in the Figure 4.47 and 4.48 respectively.

Table 4.49: $^{31}P\{^{1}H\}$ NMR of FeL_{13} and FeL_{14}

Complex	Chemical shift (ppm)
	^{31}P
FeL_{13}	25.8
FeL_{14}	25.6

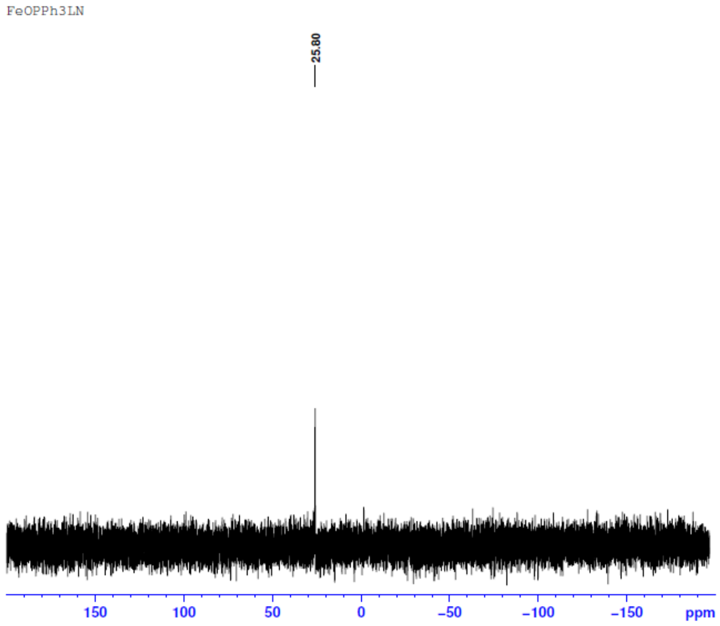


Fig. 4.47: $^{31}P\{^{1}H\}$ NMR spectra of FeL_{13} complex

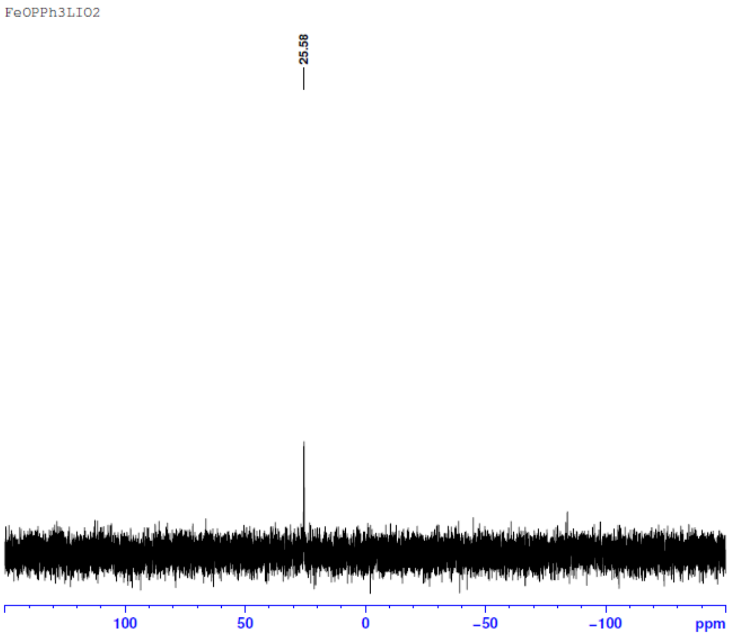


Fig. 4.48: $^{31}P\{^1H\}$ NMR spectra of FeL_{14} complex

4.9.4 ESI Mass Measurements

In the mass spectra of the complexes, the molecular weight of the complexes corresponds to the assumed structure. The ESIM spectra of the complex FeL_{11} is shown in the Figure 4.49. Similarly expected molecular weight and the observed molecular weight of the complexes are given in the Table 4.50**.**

Table 4.50: ESIMS data of Iron complexes

Complex	Expected mass	Observed mass
FeL_{11}	302.5	320.6 ($M+NH_4^+$)
FeL_{12}	318.6	336.9 ($M+NH_4^+$)
FeL_{13}	859.1	860.3
FeL_{14}	875.1	876.1

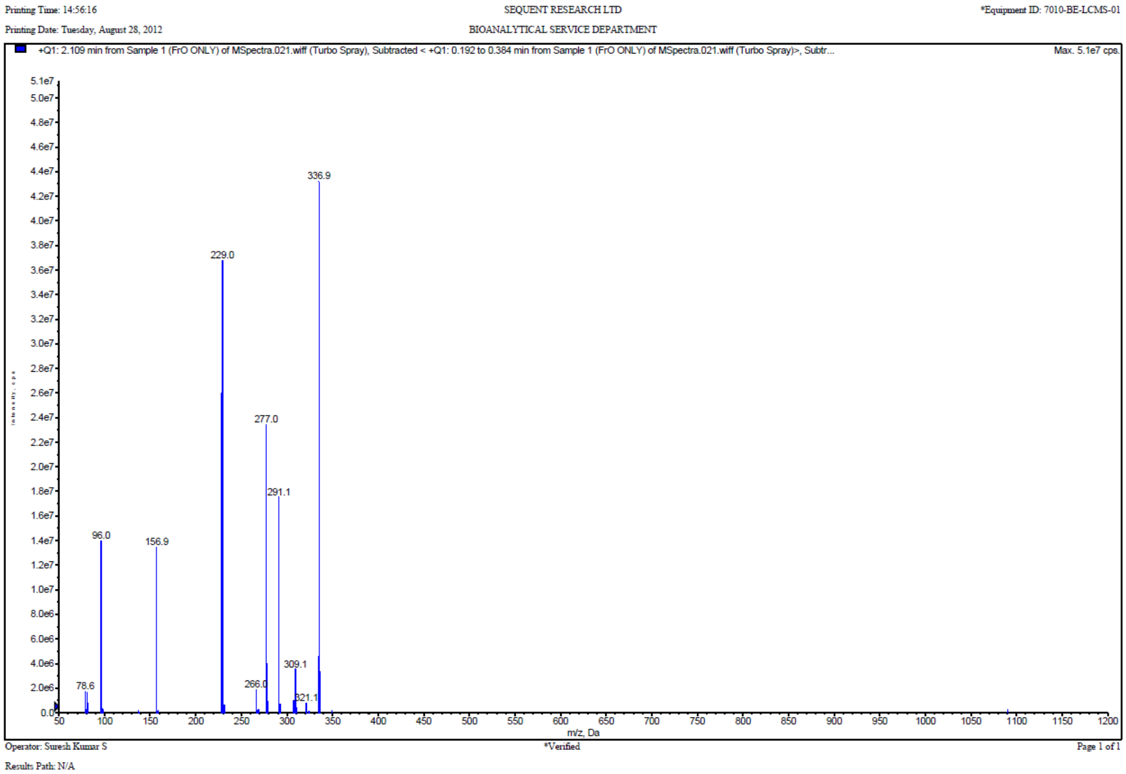


Fig. 4.49: ESIM spectra of FeL_{12}

4.9.5 Magnetochemical measurements

All iron complexes showed magnetic moment in the range of 5.82-6.10 BM confirming the presence of high spin complex. This further confirms the tetrahedral geometry of FeL_{11}, FeL_{12} and octahedral geometry of FeL_{13} and FeL_{14}.

4.10 CATALYTIC ACTIVITY OF Fe(III) COMPLEXES (FeL_{11}-FeL_{14})

The catalytic activities of the complexes were examined for the oxidation of primary and secondary alcohols by the FeL_{11}-FeL_{14} complexes as discussed under section 4.2 using oxidants periodic acid, hydrogen peroxide and t-butylhydroperoxide. All the synthesized iron complexes were found to catalyze the oxidation of alcohol to corresponding carbonyls but the yields were found to vary with different catalysts.

The oxidation of benzyl alcohol, as a standard substrate, was first investigated in order to optimize the reaction variables such as solvent, temperature, alcohol/oxidant molar ratio and length of the reaction time as discussed under section 4.2.

In case of H_5IO_6 and TBHP best yields have been observed in acetonitrile, whereas H_2O_2 system showed the best yield under solvent less condition. The activity of FeL_{11} was studied at different temperature by taking benzyl alcohol as the model substrate in all the 3 above mentioned systems. It was observed that at 80°C, the system showed higher yield in case of H_5IO_6 and aqueous TBHP while in H_2O_2 system, the reaction occurred at room temperature.

4.10.1 Effect of time

In order to study the effect of time on the activity, the product analysis was done at regular intervals of time, under similar reaction conditions.

In the case of H_5IO_6, it was observed that the total reaction time was 150 minutes at 80°C. The experiments were conducted at regular intervals of time beyond 150 minutes. The results show that the conversion remains constant at about 71.2% after a reaction time of 150 minutes (Table 4.51).

In the case of H_2O_2 system, it was found that the reaction was complete be complete in 20 minutes (Table 4.52).

Similarly the effect of time was studied for TBHP system, in which case it was observed that total reaction time of 180 minutes was needed for highest catalytic conversion (Table 4.53).

Table 4.51: Effect of time on benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 system

Sl. No.	Time (min)	% Yield[a] CH_3CN-H_5IO_6 system
1	2	7.8
2	30	26.5
3	60	41.9
4	90	52.7
5	120	66.3
6	**150**	**71.2**
7	180	71.2
8	210	71.2

[a]GC yield, average of 3 trials

Table 4.52: Effect of time on benzyl alcohol H_2O_2 system

Sl. No.	Time (min)	% Yield[a] H_2O_2 system
1	2	9.00
2	5	48.6
3	10	66.9
4	15	77.2
5	**20**	**84.4**
6	25	84.2
7	30	84.0

[a]GC yield, average of 3 trials

Table 4.53: Effect of time on benzyl alcohol CH_3CN-aq. TBHP system

Sl. No.	Time (min)	% Yield[a] CH_3CN-aq. TBHP system
1	2	7.3
2	30	21.7
3	60	38.5
4	90	41.0
5	120	46.8
6	150	56.3
7	**180**	**58.3**
8	210	58.3
9	240	58.2

[a]GC yield, average of 3 trials

4.10.2 Effect of catalyst concentration

In order to study the effect of the concentration of catalyst with respect to substrate and oxidant, the reaction was carried out at different catalyst concentrations as discussed under section 4.2.2. The results are summarized in the Table 4.54.

A minimum quantity of 0.06 mmol of the catalyst was sufficient for the effective transformation of benzyl alcohol to benzaldehyde in CH_3CN-H_5IO_6 and CH_3CN-Aq TBHP systems. While in case of H_2O_2 0.08 mmol of catalyst was sufficient to bring about the conversions respectively (Fig. 4.50).

Table 4.54: Effect of catalyst concentration on benzyl alcohol

Sl. No.	Catalyst concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 system	H_2O_2 system	CH_3CN-aq. TBHP system
1	0	12.0	2.0	15.4
2	0.02	45.1	54.6	46.2
3	0.04	66.4	64.5	53.0
4	0.06	**71.2**	73.2	**58.3**
5	0.08	71.2	**84.4**	58.1
6	0.10	71.2	84.1	58.0

[a]GC yield, average of 3 trials

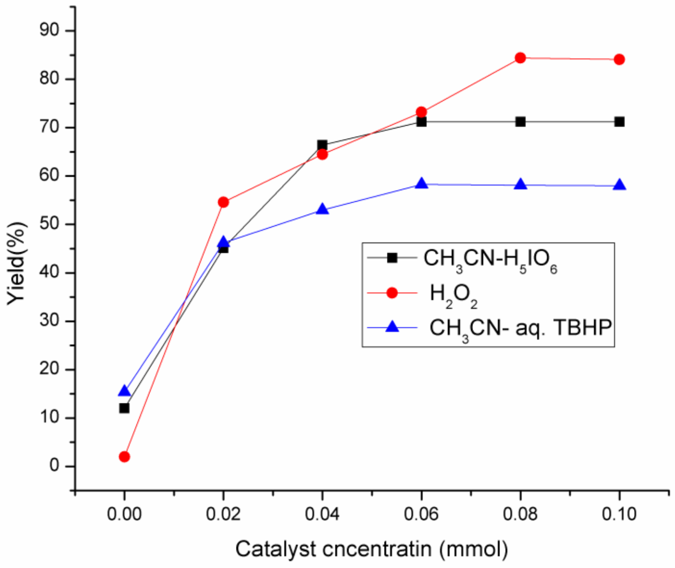


Fig. 4.50: Effect of catalyst concentration on benzyl alcohol

4.10.3 Effect of oxidant concentration

The reactions were studied with respect to substrate and catalyst at different oxidant concentrations. The results are summarized in Table 4.55. A minimum quantity of 0.75mmol, 3 mmol, 2 mmol of the oxidants were required in CH_3CN-H_5IO_6, H_2O_2, CH_3CN-aq. TBHP systems respectively for the effective oxidation of benzyl alcohol to benzaldehyde (Fig. 4.51).

Table 4.55: Effect of oxidant concentration on benzyl alcohol

Sl. No.	Oxidant concentration (mmol)	% Yield[a]		
		CH_3CN-H_5IO_6 System	H_2O_2 system	CH_3CN-Aq TBHP system
1	0	3.7	3.6	3.8
2	0.5	58.6	10.3	32.2
3	0.75	**71.2**	41.0	45.6
4	1.0	71.2	56.3	49.4
5	2.0	71.2	78.9	**58.3**
6	3.0	71.3	**84.4**	58.2
7	4.0	71.0	84.4	58.0

[a] GC yield, average of 3 trials

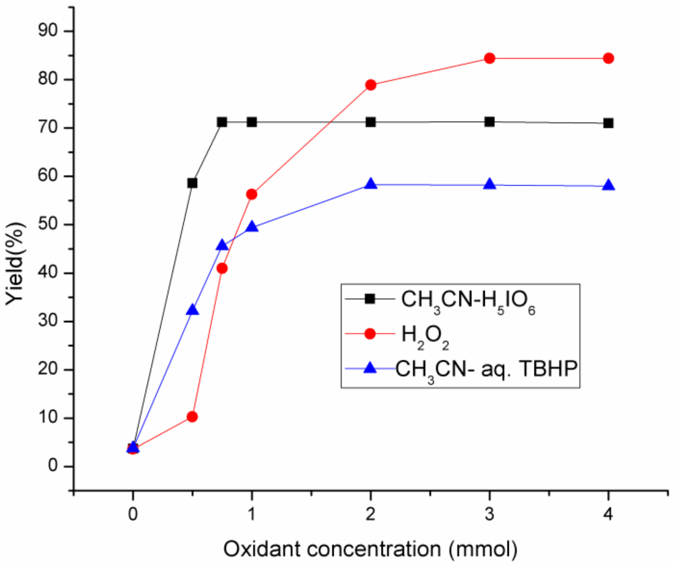


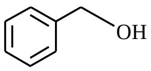
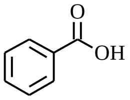
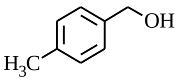
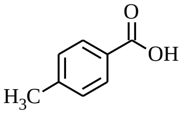
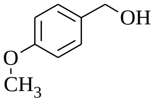
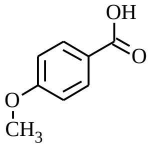
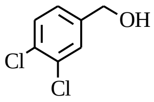
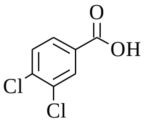
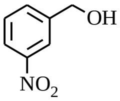
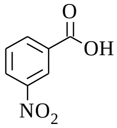
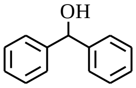
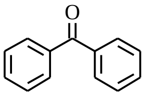
Fig. 4.51: Effect of oxidant concentration on benzyl alcohol

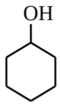
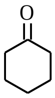
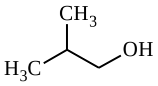
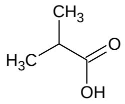
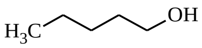
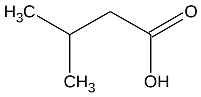
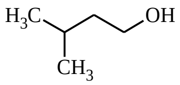
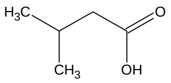
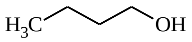
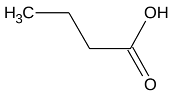
The oxidation was extended to a variety of alcohols including primary and secondary, aromatic, aliphatic and cyclic alcohols using the optimized reaction conditions. The results for the oxidation of a variety of alcohols are summarized in Tables 4.56, 4.57, 4.58 below respectively in $CH_3CN-H_5IO_6$, H_2O_2, CH_3CN-aq. TBHP systems.

Among the three systems studied, in $CH_3CN-H_5IO_6$ and H_2O_2, selectivity towards aldehyde remains almost more than 95%. The over oxidation to carboxylic acid was ruled out by derivative test. While in CH_3CN-aq. TBHP, primary alcohols are oxidized to corresponding acids with high yield. No oxidation was observed in the aromatic ring of benzylic substrates hence the catalytic systems are selective towards the alcoholic group. In $CH_3CN-H_5IO_6$ and CH_3CN-aq. TBHP systems, no significant conversion was observed even after 24 hr, at room temperature.

Among the various alcohols studied those containing aromatic substituent were found to be more reactive than alicyclic and aliphatic alcohols. This can be attributed to the higher reactivity of aromatic systems due to its delocalization. Lower reactivity of aliphatic alcohols is because of the lesser reactivity of the substrates. Similarly electron donating groups were found to slow down oxidation, whereas electron withdrawing groups accelerate it. Para or ortho substituents with electron releasing or electron withdrawing properties do not induce any change on the selectivity. It was also observed that electron donating group on the ligand enhanced the catalytic activity. And also electron withdrawing substituents decreased the catalytic activity of the complexes. As the ligand becomes more electron donating, the increased electron density makes the metal centre in the complex easier to oxidize. This is in agreement with earlier reported observations.

Table 4.56: Oxidation of alcohols by Fe(III) complexes[a] in CH_3CN-H_5IO_6 system

Alcohols	Product	% Yield[b]			
		FeL_{11}	**FeL_{12}**	**FeL_{13}**	**FeL_{14}**
		71.2	80.2	84.9	87.3
		65.4	75.4	82.6	84.2
		63.1	69.8	76.9	78.5
		68.4	70.2	81.7	82.4
		75.8	78.4	86.3	88.9
		62.3	69.4	79.8	81.7

		54.3	57.6	62.5	63.8
		50.9	43.8	45.7	46.2
		33.7	37.4	38.7	40.1
		31.8	33.6	35.2	36.8
		26.2	27.5	28.6	29.1

[a] 1 mmol alcohol, 0.75 mmol H_5IO_6, 0.06 mmol Fe (III) complex, 3 mL CH_3CN, stirring at 80°C.

[b] GC yield, average of 3 trials.

Table 4.57: Oxidation of alcohols catalyzed by Fe(III) complexes[a] in H_2O_2 system

Alcohols	Product	% Yield[b]			
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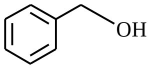
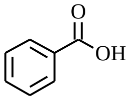
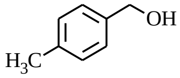
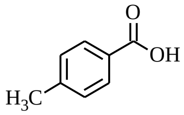
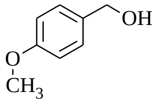
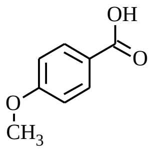
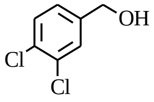
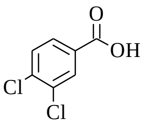
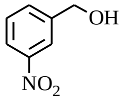
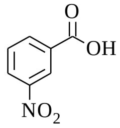
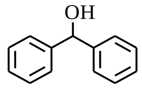
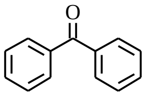
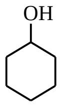
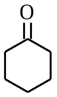
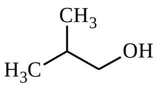
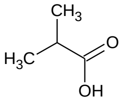
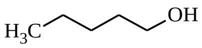
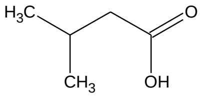
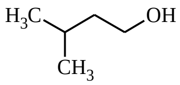
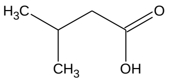
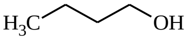
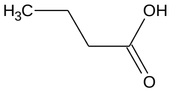
		84.4	72.6	69.3	61.7
		80.3	65.4	62.3	58.6
		75.3	61.3	56.4	52.5
		78.4	70.2	65.7	62.4

		85.4	81.9	70.3	65.9
		72.3	69.4	57.8	52.7
		64.3	57.6	52.5	48.8
		41.9	38.8	32.7	30.2
		38.7	35.4	31.7	29.1
		34.8	30.6	25.2	20.8
		24.2	22.5	20.6	17.1

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[a] 1 mmol alcohol, 0.08 mmol Fe (III) complex, 3 mmol H_2O_2, stirring at room tempeerature.

[b] GC yield, average of 3 trials.

Table 4.58: Oxidation of alcohols by Fe(III) complexes[a] in CH_3CN-aq. TBHP system

Alcohols	Product	% Yield[b]			
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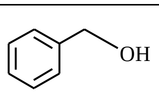
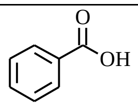
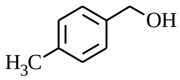
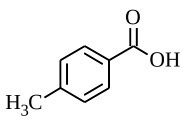
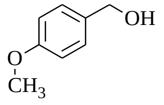
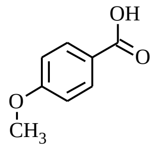
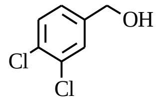
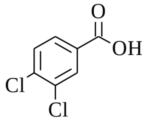
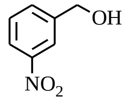
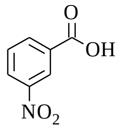
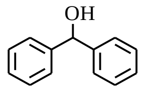
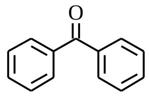
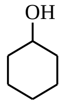
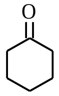
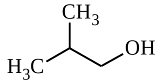
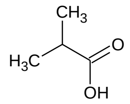
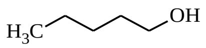
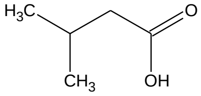
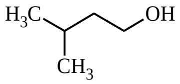
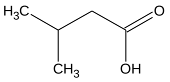
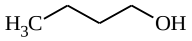
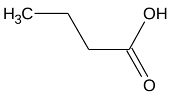
		58.3	57.6	55.6	51.7
		54.3	52.4	50.3	48.6

		53.3	51.3	48.4	45.5
		57.4	55.2	53.7	50.4
		65.4	61.9	60.3	58.9
		72.3	69.4	57.8	52.7
		52.3	50.6	46.5	43.8
		35.9	31.8	28.7	26.2
		33.7	30.4	26.7	24.1
		32.8	27.6	24.2	20.8
		26.2	20.5	18.6	15.1

[a] 1 mmol alcohol, 2.0 mmol aq. TBHP, 0.06 mmol Fe (III) complex, 3 ml CH_3CN, reflux.

[b] GC yield, average of 3 trials.

4.10.4 Mechanistic study

To study the mechanism involved in the reaction, UV spectra of the reaction mixture before and after the addition of the oxidant was examined (Fig. 4.52, 4.53, 4.54 and 4.55). It was observed that in periodic system and in H_2O_2 system the intra ligand transitions gained intensity. LMCT band slowly reduced the intensity and d-d band disappeared indicating that mechanism proceed through oxo- pathway as discussed in periodic system under section 4.2.3.

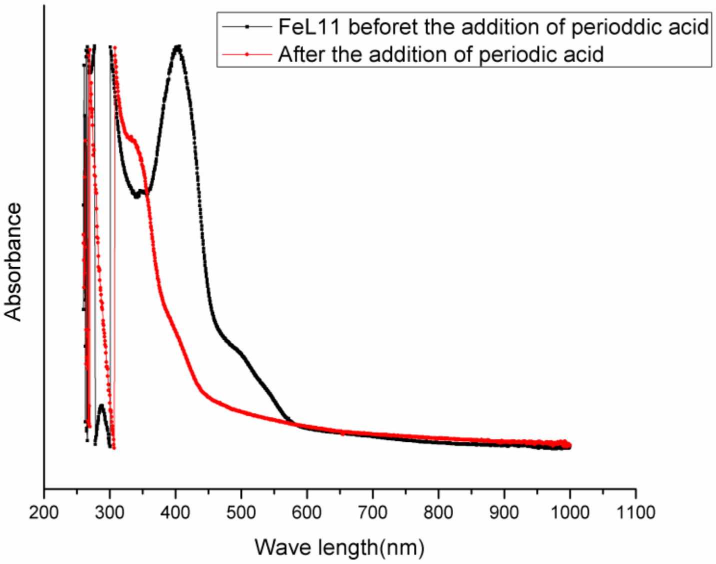


Fig. 4.52: UV-visible spectra of the reaction mixture in periodic system catalyzed by FeL_{11} complex

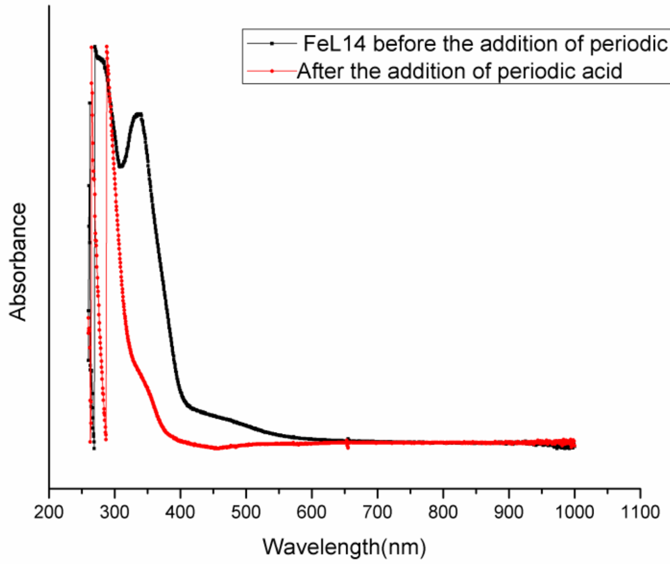


Fig. 4.53: UV-visible spectra of the reaction mixture in periodic system catalyzed by FeL_{14} complex

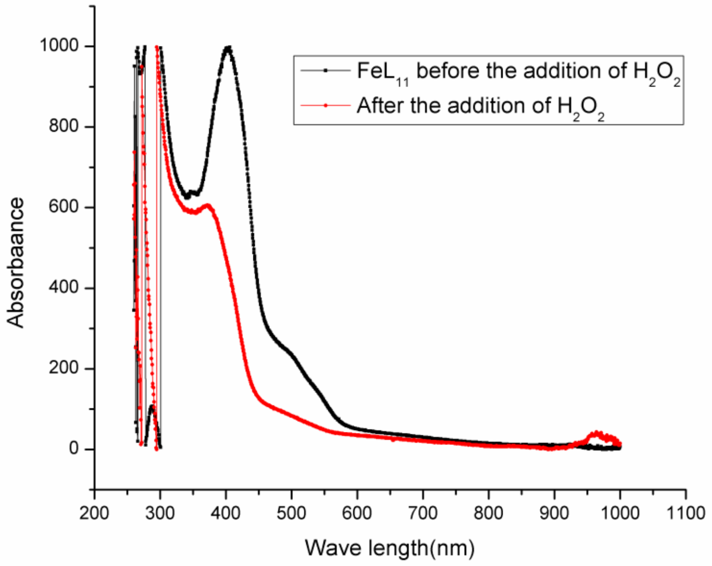
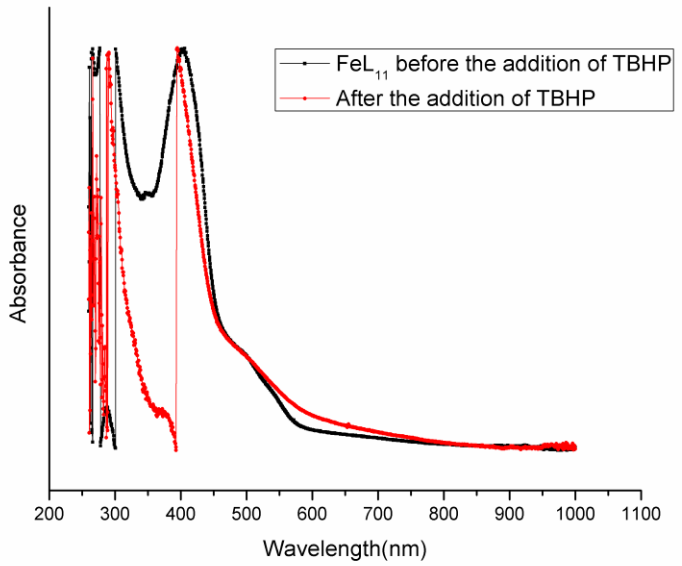


Fig. 4.54: UV-visible spectra of the reaction mixture in H_2O_2 system catalyzed by FeL_{11} complex



4.55: UV-visible spectra of the reaction mixture in TBHP system catalyzed by FeL_{11} complex

Similarly in TBHP system, an increase in the intensity of intra ligand band and charge transfer band was observed suggesting the interaction between the oxidant and the complex. Also since there is no change with respect to d-d transition, the oxidation state of the complex does not change during the reaction. Hence the reaction must be proceeding through peroxo mechanism as discussed under section 4.2.3.

Hence it was observed that when H_5IO_6 was used as oxidant, in all catalytic systems the reaction proceeds through oxo mechanism. This must be because H_5IO_6 being comparatively stronger oxidizing agent, oxidizes metal to high valent species. Since the formed high valent metal oxo intermediate is highly reactive, good yield was observed in all the catalytic systems. Among the studied complexes, vanadium complex showed highest yield. This must be because of the highly active, electron deficient V(V) intermediate formed during the reaction. This favors the product forming reductive elimination step. Similarly, among the iron complexes studied, sulfur containg Schiff base complex showed lower yield compared to the oxygen containing Schiff complex.

Since nucleophillicity of sulfur being more than oxygen, makes the metal centre more electron rich compared to metal attached to oxygen, decreasing the ease of reductive elimination resulting in lower catalytic activity. Replacement of PPh_3 with $OPPh_3$ reduced the catalytic activity in the similar context in iron complex. This may be because, PPh_3 being π-acceptor ligand makes the metal centre electron deficient thus favoring reductive elimination step and better yield. $OPPh_3$ is being only a σ-donor, stabilizes the metal oxo intermediate attenuating its activity.

In case of H_2O_2 oxidant, it was observed that in complexes with salicylidene-2-aminophenol ligands the reaction proceeded through peroxo pathway. Among such complexes cobalt complex showed lower catalytic activity. This may be because, the smaller size of Co^{3+} ion makes M-O bond less labile resulting in lower activity. Among the iron complexes, in case of sulfur containing complex the reaction proceeded through oxo pathway. This must be because of the high nucleophillicity of sulfur makes the metal centre electron rich favouring oxo pathway. Similary in case of electron rich $OPPh_3$ complexes, the reaction proceeded through oxo pathway. It was also observed that in all complexes containing sulfur and $OPPh_3$, the catalytic activity was less as the high nucleophillicity stabilizes the metal oxo intermediate formed reducing the activity. Among all the complexes studied, iron complexes showed good catalytic activity under solvent free condition at room temperature. It is also noteworthy to mention that these complexes showed better performance in terms of time and yield compared to earlier reported similar systems in literature (Golchubian and Babaei 2010; Zhao et al. 2010; Balogh-Hergovich and Speier 2005; Kharat et al. 2011).

In case of aq. TBHP, except aminothiophenol complex, in all catalytic systems the reaction proceeded through peroxo pathway. Among the catalytic systems studied, iron aminothiophenol complex showed highest activity which may be because of the highly active iron oxo intermediate formed.

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 SUMMARY

The metal complexes of iron, cobalt and vanadium with triphenylphosphine and Schiff base ligands were synthesized. The complexation behaviour of a series of salicylidene-2-aminothiophenol and salicylidene-2-aminophenol were studied. The synthesized ligands and complexes were characterized by analytical, spectral (NMR, ESI Mass, UV-Vis, and FTIR) and magnetic studies. The catalytic activities of all the synthesized complexes were examined by using the oxidants like periodic acid, hydrogen peroxide and aqueous tert-butylhydroperoxide for the oxidation of various alcohols. The effect of solvent, temperature on catalytic activity was investigated. The optimization of the reaction parameters with respect to time, catalyst concentration and oxidant concentration were carried out by taking benzyl alcohol as the model substrate for all the complex series. The quantitative analysis of the reaction products were carried out using gas chromatographic technique by internal standard method. The effect of substrate on the oxidation reaction was examined by taking various alcohols in all the studied catalytic systems. The effect of variation in ligand frame work on the catalytic activity was also analyzed. The study on the mechanism involved in the oxidation reaction was carried out by examining the UV visible spectra of the reaction mixture before and after the addition of oxidant in all the catalytic systems. Based on these studies, the probable mechanism for the oxidation of alcohol was proposed.

5.2 CONCLUSIONS

Based on the results of the present investigation, the following important conclusions were drawn:

- Both series of ligands namely, salicylidene-2-aminothiophenol and salicylidene-2-aminophenol and their derivatives behaved as tridentate ligands in Fe(III), Co(III) and V(IV) complexes.

- All the synthesized complexes were found to catalyze the oxidation of alcohol.

- Among the systems studied, in H_5IO_6 and H_2O_2 oxidants, selectivity towards aldehyde remained more than 95%. While in aq. TBHP oxidant, primary alcohols were oxidized to corresponding acids with high yield.

- In H_5IO_6 and aq. TBHP systems, all the complexes showed increase in catalytic activity at reflux condition in acetonitrile medium. However in case of H_2O_2, all the Fe(III) complexes showed good conversion at room temperature in the absence of solvent.

- Among the various alcohols studied those containing aromatic substituent were found to be more reactive than alicyclic and aliphatic alcohols.

- Electron donating groups were found to slow down the oxidation whereas electron withdrawing groups accelerates it.

- Para or ortho substituents with electron releasing or electron withdrawing properties did not induce any change on the selectivity.

- It was also observed that electron donating group on the ligand enhanced the catalytic activity. Electron withdrawing substituents decreased the catalytic activity of the complexes.

- In case of H_5IO_6 oxidant, in all the catalytic systems the oxidation of primary and secondary alcohols was found to proceed through oxo- pathway to give aldehyde/ ketones.

- In case of H_2O_2 oxidant, in all the catalytic systems the oxidation of primary and secondary alcohols was converted to aldehyde and ketones whereas in aq- TBHP oxidant, carboxylic acid and ketone was yielded.

- In case of H_5IO_6 oxidant, all the catalytic systems showed very high catalytic activity. Among all the catalytic systems, vanadium complexes showed higher activity.

- In case of aq. TBHP oxidant, Iron-Schiff base—triphenylphosphine complex with sulphur donor showed maximum conversion.

- In all the oxidants, the Fe(III) complexes with triphenylphosphineoxide as the ancillary ligands and tetra coordinated Fe(III) complexes showed lower conversions.

5.3 SCOPE FOR FUTURE WORK

The following extensions are recommended to the work presented in this thesis,

- The above study can be extended to other structurally related ligands to understand the effect of structure on catalytic activity.

- Study of complexing behavior and catalytic activity of complexes of other first row transition metals for the comparative study.

- Study of complexing behavior and catalytic activity of complexes of other metals of the same group to study the variation of size of metal on the catalytic activity.

- The above complexes can be utilized to explore its catalytic activity in other reactions.

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RESEARCH PUBLICATIONS

(A) Research Papers in International Journals

1. Sandya Rani and Badekai Ramachandra Bhat (2010). "Synthesis, characterization and catalytic activity of Fe(III) complexes containing Schiff base and triphenylphosphine ligands". *Inorg. Chem. Commun.*, 13, 1289–1292.
2. Sandya Rani and Badekai Ramachandra Bhat (2010). "Effective oxidation of alcohols by iron(III)-Schiff base-triphenylphosphine complexes." *Tetrahedron lett.,* 51, 6403–6405.
3. A.S. Ramasubramanian, Badekai Ramachandra Bhat, Ramakrishna Dileep and Sandya Rani (2011). "Transition metal complexes of 5-bromosalicylidene-4-amino-3-mercapto-1,2,4-triazine-5-one: Synthesis, characterization, catalytic and antibacterial studies". *J. of Serb. Chem. Soc.,* 76 (1) 75–83.
4. Sandya Rani and Badekai Ramachandra Bhat "Catalytic oxidation of alcohols by Aq. TBHP using Iron(III) complexes" *Transit. Metal Chem..,* (under review).
5. Sandya Rani and Badekai Ramachandra Bhat "Octahedral V(IV) complexes containing ONO ligands as effective catalysts for the oxidation of alcohols." *Inorg. Chem.Comm.,* (communicated).
6. Sandya Rani and Badekai Ramachandra Bhat "Synthesis characterization and catalytic activity of Co(III) complexes containing ONO- donor Schiff base and triphenylphosphine ligands." *Inorg. Chim. Acta.,* (under review).
7. Sandya Rani and Badekai Ramachandra Bhat "Synthesis, characterization and catalytic activity of Fe(III) complexes containing ONO-Schiff base and triphenylphosphine ligands" *Europ. J. Inorg. Chem.,* (communicated).
8. Sandya Rani and Badekai Ramachandra Bhat "Oxidation of alcohols by Co(III)-Schiff base-triphenylphosphine complexes in presence of aqueous TBHP" *Coord. Chem*. (Manuscript under preparation).

9. **Sandya Rani** and Badekai Ramachandra Bhat "Oxidation of alcohols by iron(III)-Schiff base-triphenylphosphine/triphenylphosphineoxide complexes- Comparitive study" (Manuscript under preparation).
10. **Sandya Rani** and Badekai Ramachandra Bhat "Octahedral V(IV)- Schiff base-triphenylphosphine complexes as effective catalysts for the oxidation of alcohols in presence of Hydrogen peroxide" (Manuscript under preparation).
11. **Sandya Rani** and Badekai Ramachandra Bhat "Oxidation of alcohols by V(IV)-Schiff base-triphenylphosphine complexes in presence of Aq. Tertiarybutylhydroperoxide" (Manuscript under preparation).

(B) Research Papers Presented in National/International Conferences

1. Sandya Rani and B. Ramachandra Bhat (2009). "Synthesis, characterization and catalytic application of Fe(III) complexes with N,S,O- donor Schiff base ligands" *International conference on coordination and organometallic chemistry,* 19-20, March, Bharatihar University, Coimbutore, India.

2. Sandya Rani and B. Ramachandra Bhat (2010). "Iridium-Schiff base-triphenylphosphine complex catalyzed oxidation of alcohols" *International conference on Emerging Trends In Chemistry*, 5-7, January, Pune University, Pune, India.

3. Sandya Rani and B. Ramachandra Bhat (2011). "Catalytic oxidation of alcohols to carbonyl compounds by vanadium (1V) complexes containing NSO donor Schiff base and triphenylphosphine" *National symposium on chemistry and humanity,* 11-12, July, Manipal Institute of Technology, Manipal, Karnataka, India

4. Sandya Rani and B. Ramachandra Bhat (2011). "Cobalt-schiff base-triphenylphosphine complex catalyzed oxidation of alcohols." *International conference on synthetic and structural Chemistry,* 8-10, December, Mangalore University, Mangalore, India.

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Worked as chemist in cosmic laboratories, Bangalore (Oct 2007-June 2008)

Worked as lecturer in Alva’s College, Moodbidri, Mangalore (Oct 2005-Sept2007)

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Research Experience

Various chemical reactions including oxidation, reduction, organometallic reactions, complex synthesis etc.,

Publications

1. Sandya Rani and Badekai Ramachandra Bhat (2010). “Synthesis, characterization and catalytic activity of Fe(III) complexes containing Schiff base and triphenylphosphine ligands”. *Inorganic Chemistry Communications 13 (2010) 1289–1292*
2. Sandya Rani and Badekai Ramachandra Bhat (2010). “Effective oxidation of alcohols by iron(III)-Schiff base-triphenylphosphine complexes”. *Tetrahedron letters 51 (2010) 6403–6405*
3. A.S. Ramasubramanian, Badekai Ramachandra Bhat, Ramakrishna Dileep and Sandya Rani (2011). “Transition metal complexes of 5-bromosalicylidene-4-amino- 3-mercapto-1,2,4-triazine-5-one: Synthesis, characterization, catalytic and antibacterial studies”. *Journal of the Serbian Chemical Society 76 (1) 75–83*

Paper presented in conferences

1. Sandya Rani and B. Ramachandra Bhat “Synthesis, characterization and catalytic application of Fe(III) complexes wit N,S,O- donor schiff base ligands” *International conference on coordination and organometallic chemistry, Bharatihar Universit MARCH 19-20. 2009.*

2. Sandya Rani and B. Ramachandra Bhat “Iridium-schiff base-triphenylphosphine complex catalyzed oxidation of alcohols” *International conference on Emerging Trends In Chemistry, Pune*

University, Jan 5-7 2010.

3. Sandya Rani and B. Ramachandra Bhat "Catalytic oxidation of alcohols to carbonyl compounds by vanadium (1V) complexes containing NSO donor schiff base and triphenylphosphine" *Nation symposium on chemistry and humanity-NSCH 2011 MIT, Manipal July, 11-12.*

4. Sandya Rani and B. Ramachandra Bhat " Cobalt-schiff base-triphenylphosphine complex catalyzed oxidation of alcohols" *International conference on synthetic and structural Chemistry, Mangalore University, Dec 8-10 2011.*

5. Sandya Rani and B. Ramachandra Bhat "Cobalt-Schiff base-triphenylphosphine catalyzed oxidation of alcohols" ICC conference, *Osmania University, Hyderabad,* 28—30 December, 2011.

Awards

Prof. C.P. Bhasin Young scientist award in ICC conference held at Osmania University, Hyderabad, *28*—30 December, 2011.

Technical Skills

- Having good skill of elucidating the structure from FTIR, NMR, TG, Mass and Elemental analysis data.
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