Understanding Redox behavior of 3d Transition Metals on the basis of Thio-Salen Ligands

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BS-MS dual degree in Science

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Certificate of Examination

This is to certify that the dissertation titled "**Understanding the Redox-behavior of 3d-transition metals on the basis of thiosalen ligands"** submitted by **Miss.Harleen Kaur (Reg.No.MS13070)** for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Sugumar Venkataramani **Dr. Samrat Ghosh** **Dr.Debashis Adhikari**

(Supervisor)

Declaration

The work presented in this dissertation has been carried out by me with Dr.Debashis Adhikari at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Harleen Kaur
(Candidate)

Dated: April 20, 2015

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr.Debashis Adhikari
(Supervisor)

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Abstract

Redox-active ligands (RAL) recently attracted tremendous research focus since base metal catalysis can be realized when RAL is electronically tuned with 3d transition metals. Metallosalens have great importance in catalytic reactions because of their redox-active behavior. Despite, the significant amount of research on redox non-innocence of salens, thiosalen have not been investigated thoroughly.

We anticipate electronic structure for thiosalen will differ considerably as compared to their salen congeners, because of the high polarizability, less electro-negativity and more covalency of the sulfur atom as compare to oxygen. Herein, we attempt to synthesize multiple 3d-metal complexes of thiosalen and understand their redox behavior of them to bring a straight comparison with salens. Furthermore, the electronic tuning of the coordination environment will be regulated by making appropriate changes on the ligand backbone.

Chapter 1

THE PRELUDE

1.1 Introduction

Ligands are the molecules, ions or functional groups which are attached to the central metal atom to form complexes. Further they can be classified into different types on the basis of size (bulkiness), charge, denticity or hapticity. On the basis of redox behavior, Ligands can be divided into two types- Redox-inactive (traditional/innocent) ligands and Redox-active (non-innocent) ligands.

1.2 Innocent/Traditional Ligands

These types of ligands play a spectator role and provide a scaffold to the complex. They act as a chelate; do not take part in the electronic structure of the complex. In these types of ligands we can easily predict the oxidation state of metal center because redox changes only take place at the metal center. Whenever there is an oxidation or reduction taking place, it is believed that the metal center may act as a source or sink for the electron transfer. The typical example of innocent ligands is Werner Complexes. In case of Werner complexes, we can confidently do the assignment of oxidation states to the metal center without thinking about any participation from redox-activity of ligands. Cis-$[Co(NH_3)_4Cl_2]$ is the well known Werner complex where one can easily assign the oxidation state, because ligands here are indeed redox-inactive.[1]

In the process of oxidative addition in metal complexes of redox-inactive ligands, there will be change in oxidation state of metal keeping the oxidation state of ligand unaffected which is the property of traditional ligands as shown in Fig.1.

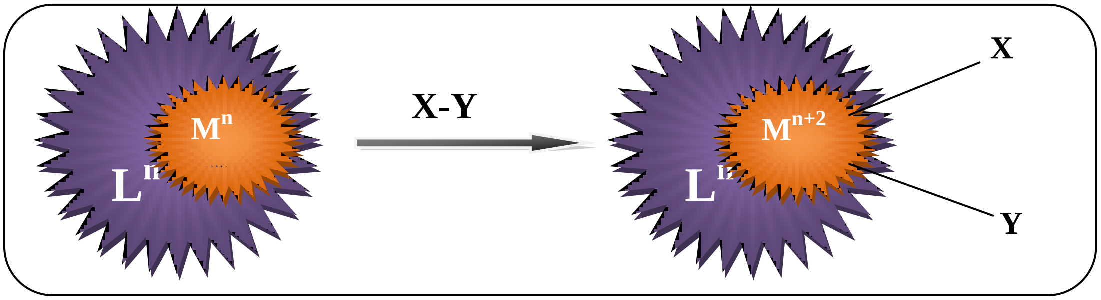


Fig.1 Oxidative addition in case of Traditional Ligands

1.3 Non-innocent Ligands

We know that the common behavior of transition metal complexes during redox processes involve oxidation or reduction at the metal center, leaving the ligand unaffected. Although in some cases ligands also participate in the redox process. In those cases, ligand is referred as redox-active (redox-noninnocent ligand).

The term "non-innocent" implies an uncertainty and refers to the ambivalence of oxidation state assignments in complexes bearing both redox active ligands and redox active metals[2].

Non-innocent ligands are those ligands which actively participate in redox activity. Due to charge transfer between metal and ligand, the oxidation state of metal remains ambiguous. Metal and the ligand can co-operate in a synergistic manner, and their interplay facilitates chemical processes. In the process of oxidative addition in metal complexes of redox-active ligands, there will be change in oxidation state of ligand keeping the oxidation state of metal unaffected which is the property of redox active ligands[3] as shown in Fig.2

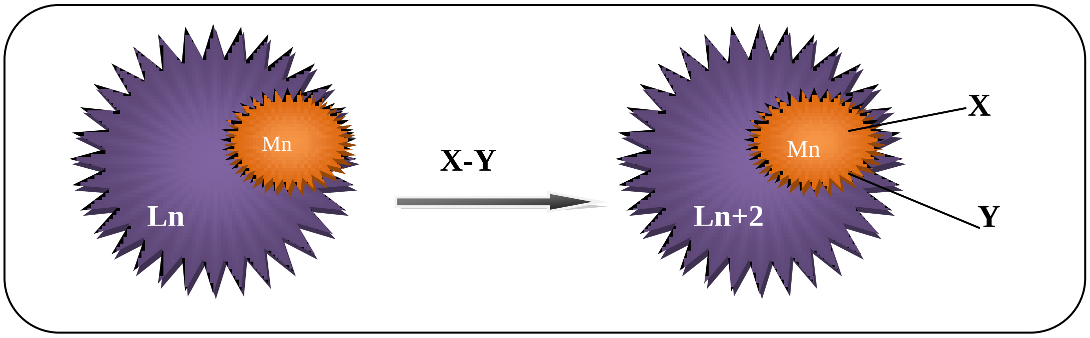


Fig.2 Oxidative addition in case of redox-active ligands

There are number of redox-active ligands known which engage with a metal in complexation reaction, for example porphyrins, phenolates, catecholates, aminophenolates, phenylenediamines, and diimines[4].

Redox-active or non-innocent behavior of ligands stems from frontier ligands orbitals that lie in both the energetic and special proximity to the d-orbitals of the coordinated metal ion, often leading to extensive mixing of the metal and ligand frontier orbitals[5]. This mixing results to the difficulty associates with assignment of formal oxidation states of metal as well as ligand. This problem is illustrated in the resonance structures of Fig.3 where there is a distribution of valence electrons of metal and ligand without changing the total number of valence electrons in the system. As we can clearly see that in one case it is metal based oxidation where oxidation state of metal is changed without changing the oxidation state of ligand and in other case it is ligand based oxidation, we cannot tell the oxidation state of metal as ligand is participating in the redox activity[6].

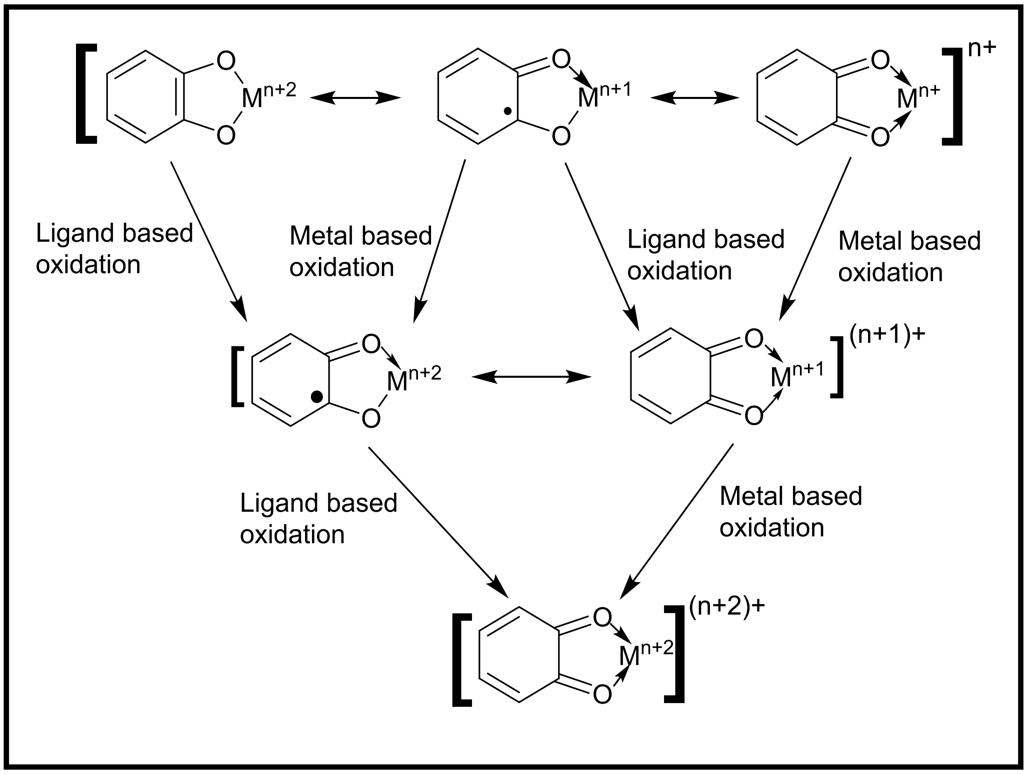


Fig 3 Metal–ligand non-innocence and cooperative redox behavior using catecholate as the prototypical redox-active ligand

1.4 Importance of Redox active ligands

In most cases, expensive noble metals are used in catalysis for Multi-electron reactions as they often tend to undergo two-electron oxidation state changes. There is an urgent need for an alternative to these expensive metals that is using easily accessible base metals. Base metals have the tendency to undergo one-electron oxidation changes, and in order to confer nobility to base metal we need to develop new approaches. In this aspect, "redox non-innocent" ligands are the key to overcome this problem. As base metals with redox active ligands enable new reaction pathways, this is not the case in other metal complexes[7]. Redox active ligands provide a strategy to realize the requisite multi-electron reactivity within a transition metal complex. One can tune the redox-potentials of the ligand and sterics around the metal center by focusing on ligand design[2].

Such species offer a unique opportunity to modify the reactivity of transition metal complexes[8]. Redox transformations of coordination compounds have drawn considerable amount of attention because of their (catalytic) reduction and oxidation reactions mediated by transition metal complexes. In case of metallo-enzyme active site in particular, the reactivity relies on the synergistic manner in which metal and ligand cooperate. The enzymes galactose oxidase, hydrogenases, and cytochrome P450 are the best described examples of such systems. In these cases, the ligand is referred to as being "redox non-innocent" or "redox active"[2]. Apart from the more obvious advantages from non-innocence, e.g. lowered reorganization energy for electron transfer through delocalization or spin crossover, the cooperation[9]between two different non-innocent ligands occurs in several bioinorganic configurations with the benefit of multifunctionality such as separated but communicating electron transfer and reaction centers. Functional modeling of such combinations is also possible, e.g. by assembling NO together with porphyrin or quinonoid ligands at ruthenium[10]. In particular, the thiocyanato complex $(NBu_4)_2[Ru\ (4, 4 - (COOH)\ (COO)\ bpy)_2(NCS)_2]$, also called N719 or "red dye", exhibited an extinction coefficient of $\sim$14,000 M^{-1} cm^{-1} at 534 nm and an incident photon-to-current conversion[11].

Apart from biological importance, these types of ligands can also act as photo-sensitizers. Grätzel and coworkers reported a series of ruthenium complexes of the form $[Ru\ (4,4 - (COOH)_2bpy)_2(X)_2]^{2+,}$ where X= Cl, Br, I, CN, or SCN^- , that proved to be excellent photo-sensitizers for TiO_2. In particular, the thiocyanato complex $(NBu_4)_2[Ru(4,4$ - (COOH efficiency (IPCE) exceeding 80% between 480 and 600 nm. It has been suggested that thiocyanate ligands improve visible-light absorption and facilitate charge transfer between the photoexcited chromophore such complexes are depicted in Fig.4. A number of heteroleptic ruthenium sensitizers of the form $[Ru(4,4 - (COOH)_2bpy)(4,4 -(R)_2bpy)(NCS)_2]$ where R = alkyl thiophene, alkyl furan , phenylene vinylene, or 2-thiophene-2-yl-vinyl exhibited high extinction coefficients. The iodide/triiodide redox mediator, leading to higher DSSC efficiencies. It has been suggested that both Both linkage isomers of the SCN^- complexes are probably involved. Attempts to extend absorbance to longer wavelengths resulted in the development of N749, or “black dye”, a ruthenium complex with three thiocyanato ligands and a terpyridine ligand with three carboxylate anchors. N749 has a red-shifted MLCT band and a broad IPCE spectrum extending into the near-IR region up to 920 nm. A ruthenium complex with two thiocyanato ligands and a quaterpyridine ligand with two carboxylate anchors and two tert-butyl substituents also exhibited a red-shifted absorption spectrum but had a lower IPCE, possibly due to aggregation of the sensitizer on TiO_2.

Ruthenium–polypyridyl sensitizers: Owing to their broad coverage and high molar absorptivity in the visible region and acceptable redox potentials, ruthenium–tris (bipyridyl) complexes are appealing photo-sensitizers for light-driven water-splitting photo-anodes. Ruthenium–polypyridyl complexes have broad absorption spectra, long-lived excited-state lifetimes, and good electrochemical stability. By substituting the ancillary ligands, typically bipyridines or terpyridines, we can tune the Spectroscopic and electrochemical properties[12].

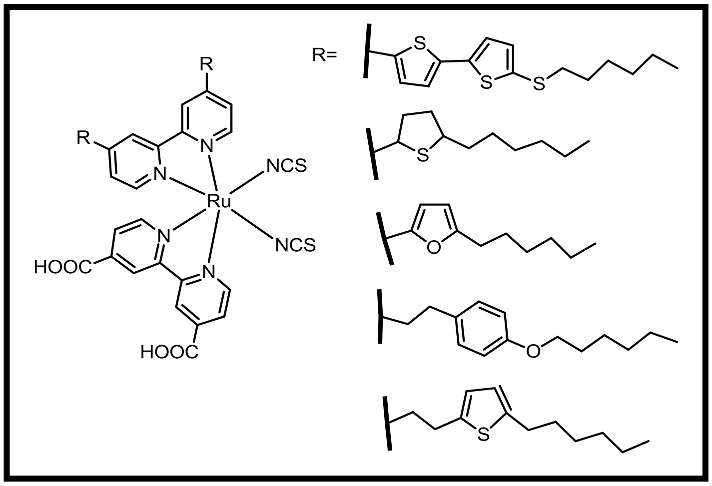


Fig.4. A number of heteroleptic ruthenium sensitizers

1.5 Strategies of using Redox-active Ligands in Catalysis

In usual approaches, the performance of the catalyst in which the ligands play a “Spectator” role can be controlled by the steric and electronic properties of the ligands. Recent approaches make use of ligands, which are electronically more involved to dictate the elementary bond activation steps in a catalytic cycle and thus play a much more prominent role [13]. This class of ligands has a unique ability to impart novel reactivity to the adjacent metal complexes by controlling the loss or gain of protons and electrons, thus permitting the overall framework to adopt a different electronic structure which is the key to achieve new types of reactivity with high selectivity.

Redox active ligands, both in “**spectator**” or “**actor**” mode, can influence the overall reactivity and the selectivity of the catalyst. Four main strategies can be distinguished in this context (Figure5):

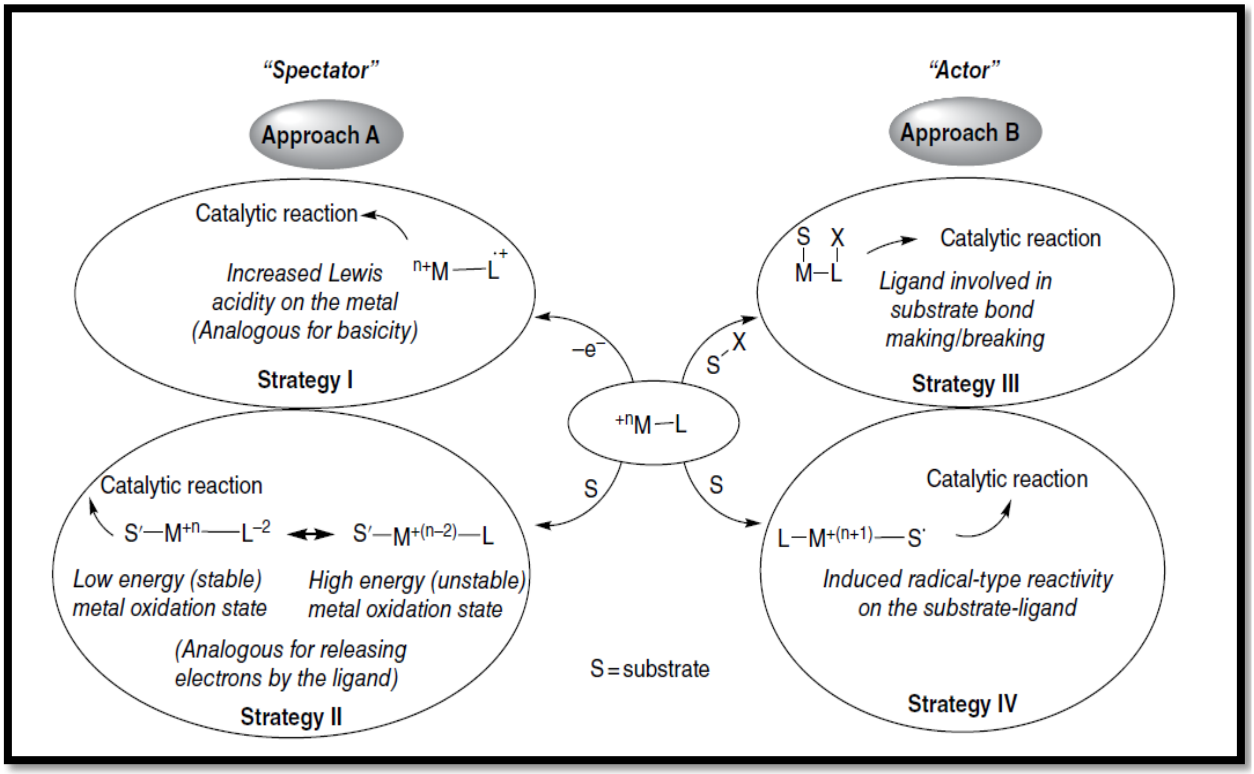


Figure 5 Strategies of using redox non-innocent ligands in catalysis.[13]

1.5.1 Strategy I. Redox non-innocent ligands used to modify the Lewis acid–base properties of the metal

As an electronic mediator, the redox active “spectator” ligand can modify and control the Lewis acidity of the metal ions by selective ligand reduction/oxidation, thereby influencing the substrate affinity of the metal as well as the energy profile of subsequent follow-up reactions. Lewis acidity or basicity of metal ion plays an important role in catalysis. Metal ion forms adduct with the lone pair bearing an electronegative atom in the substrate (such as oxygen {both sp^2 and sp^3}, nitrogen, sulfur and halogens) which is influenced by enhanced Lewis acidity of a transition metal catalyst. Substrate gets activated towards nucleophilic attack, heterolytic bond cleavage or cycloaddition with 1,3 dienes and 1,3 dipoles due to partial charge transfer. Similarly, enhancement in Lewis basicity of a catalytically active metal complex can be beneficial in controlling its catalytic reactivity. We can tune the Lewis acidic properties of a metal by controlling the redox events of the coordinated redox-noninnocent ligands without changing the steric environment of the complex. This concept has been recently applied in the oxidation of $H_{2,}$ Ir (III) catalyst containing a redox non-innocent ligand[14].

1.5.2 Strategy II. Redox non-innocent ligands as electron reservoirs

As a discrete “electron reservoir”, the redox active ligands can store electrons from the metal on the ligand in elementary steps generating excessive electron density, and releasing electrons to the metal in elementary steps generating deficiencies, in all cases avoiding uncommon oxidation states of the metal. This is the most important application of redox-noninnocent ligands in catalysis. Mostly precious metals are used in homogeneous catalysis which involves multi-electron transfer between the metal and activated substrate. It is difficult to achieve those using cheaper and more abundant first row transition metals which often prefer one electron redox events. . Incorporation of redox active ligands provides us a way to use the cheap first row transition metals for multi-electron transfer. There are several chemical transformations which were successful with the use of concept of a spectator redox active ligand as an electron sink or reservoir. For example oxidation process of water is a thermodynamically unfavorable process which involves transfer of four electrons. Binuclear Ruthenium complexes have been used for water oxidation. The counterpart of catalytic water oxidation to O_2, catalytic H_2 evolution via water reduction, is of equal importance in the context of water splitting (artificial photosynthesis).

1.5.3 Strategy III. Cooperative ligand-centered reactivity based on redox active ligands

As a cooperative “actor”, Redox active ligands generate reactive ligand radicals during catalytic turnover which actively participates in bond making/ breaking. Cooperative substrate activation by the redox non-innocent ligand and the metal allows reactions that are difficult to achieve otherwise. In these approaches (Strategies I and II) the reactivity is metal centered, however other cases are possible in which the redox active ligand plays direct role, participating in bond making/breaking. Several reported catalytic processes are inspired by this nature of redox active ligands. As a mimic of the well-studied galactose oxidase, a copper (II) thiophenol complex catalyzes the oxidation of primary alcohols to aldehydes in the presence of O_2[15].

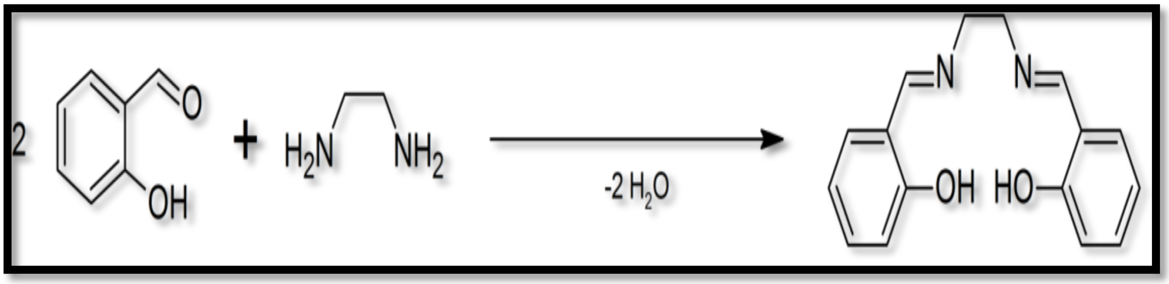
1.5.4 Strategy IV. Cooperative substrate-centered radical-type reactivity based on redox non-innocent substrates

The last strategy involves (radical-type) activation of the substrates or modification of the substrate reactivity in cases where the substrate itself acts as a redox non-innocent ligand. In this class, intrinsic redox feature of the substrate helps to achieve higher catalytic turnover. During coordination to redox active metal, redox active substrate can get reduced or oxidized by the metal center leading to an organic ligand centered radical. In variety of organometallic catalytic transformations this behavior has been applied. In this category of catalytic reactions metal-activated substrates bear radical-type spin density, thus leading to an open-shell intermediate with new type of substrate–ligand–radical reactivity.

1.6 Redox-Active Ligand: SALEN

The term Salen stands for a combination of **Salicylaldehyde** and **ethylenediamine**. Condensation reaction of a salicylaldehyde with an amine leads to the preparation of Salen [N,N'-bis (salicylidene)ethylenediamine)] .

It is an important chelating ligand. It has a lot application in coordination chemistry as well as homogeneous catalysis.



Scheme 1. Synthesis of Salen

Most of the Salen ligands mimic the activity of various enzymes. Co(Salen) are widely used in transport of oxygen. Salen metal complexes reversibly bind to the oxygen which leads to

Tsumaki described the first metal-salen complexes. He found that the cobalt (II) complex Co(salen) reversibly binds O_2, which led to intensive research on cobalt complexes of salen and related ligand for their capacity for oxygen storage and transport, looking for potential synthetic oxygen carriers[16] Cobalt salen complexes also replicate certain aspects of vitamin B_{12}.

The manganese-containing catalyst is used for the asymmetric epoxidation of olefins. In the hydrolytic kinetic resolution technique, racemic mixture of epoxides may be separated by selectively hydrolyzing one enantiomer, catalyzed by the analogous cobalt(III) complex[17]. In subsequent work, chromium (III) and cobalt (III) salen complexes were found to be good catalysts for preparing poly (carbonates) from carbon dioxide and epoxides[18].

Nickel-Salen Type Polymers are used as Cathode Materials for Rechargeable Lithium Batteries Salen-type redox polymers were shown to be applicable as electrode material in Li-ion battery[19].

1.7 Thio-Salen (Sulfur based Salen)

Thiosalen derivatives are Schiff base ligands where the sulfur atoms are substituted with oxygen atoms in Salen ligands. The replacement of two phenoxide oxygen atoms in salen by two thiolate sulfur atoms lead to changes in redox properties of the corresponding complexes. Since sulfur is medium strength soft base it is often expected that co-ordination by sulfur will stabilize metals in low oxidation states. High polarizability, less electronegativity of sulfur will completely change the properties of these ligands. Complexes of thiolate ligands have attracted increased attention in recent years because of the recognition of the biological significance of metal-cysteine sulfur interactions[20].

Metallosalens have great importance in catalytic reactions because of their redox-active behavior. Despite the significant amount of research on redox non-innocence of salens, thiosalens have not been investigated thoroughly. Only few MN_2S_2 complexes have been synthesized as structural and spectroscopic models for the active site co-ordination environment of a number of metalloproteins. For example, Copper metal interacts with cytochrome c oxidase and Zinc with LADH case studies. Copper (I)-N_2S_2-salen type complex covalently anchored onto MCM-41 silica: an efficient and reusable catalyst for the A3-coupling reaction toward propargylamines [21]. Furthermore, the electronic tuning of the coordination environment will be regulated by making appropriate changes on the ligand backbone.

Fabrice Thomas and Xavier Ottenwaelder have investigated the oxidative chemistry of the nickel(II) complex 1 of the novel Salophen ligand 4,5-bis (dimethylamino)benzene-1,2-bis(3,5-di-tert-butylsalicylimine)[22] where $(NMe_2)_2$-substitutions were incorporated in the aromatic backbone as shown in Fig.6. In complexes with a non-innocent ligand, the locus of oxidation (or reduction) is dictated by the respective symmetry and energy of the frontier orbitals of the metal ion and those of the organic framework[23]. Thus, redox locus can be shifted from metal to the ligand by tuning the electronics of the ligand. The strongly electron-donating dimethylamino (NMe_2) substituents direct the oxidation site towards the aromatic part of the ligand, whereas a metal-centered oxidation process is observed for the parent, unsubstituted complex. They shifted the redox locus by introducing two electron rich groups in the ligand backbone.

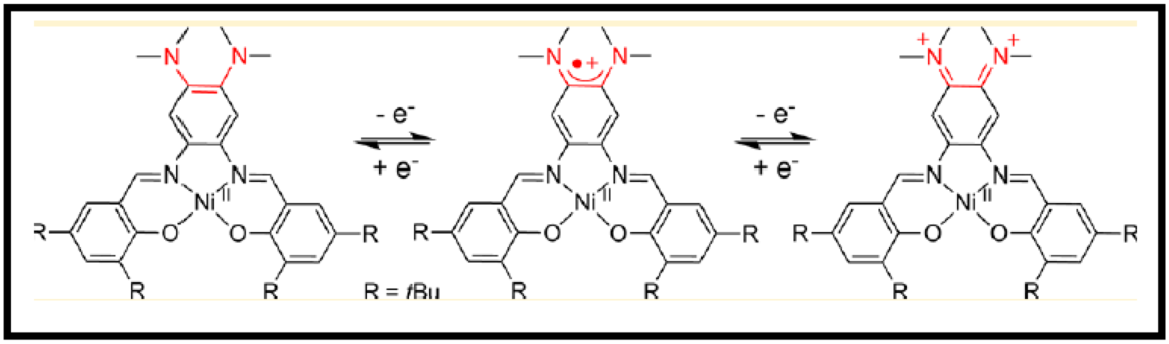


Fig 6. Nickel Salophen Complex

We plan to investigate the redox properties of 3d transition metals on the platform of thiosalen ligands. On the Other hand, it is anticipated that with the introduction of NMe_2 groups, the redox properties will be completely different.

Herein, we attempt to synthesize multiple 3d-metal complexes of thiosalen and understand their redox behavior to bring a straight comparison with salens.

Chapter 2

EXPERIMENTAL WORK

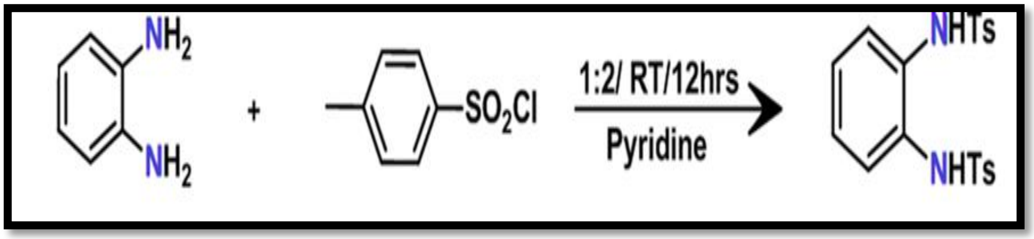
2.1 Research Plan

Our main focus is on synthesizing metal complexes of 3d-transition metals on the platform of thio-salen ligands. Redox properties of sulfur containing ligands will be entirely different. Moreover metal-sulfur interactions are known in many biological enzymes. Magnetic and electrochemical studies of such metal complexes will be interesting.

2.2 Experimental Section

2.2.1 Synthesis of N, N'-ditoluene-sulphonyl-o-phenylenediamine

To a solution of o-phenylenediamine (1.08gm, 10mM) in pyridine (15mL) was added a drop-wise the p-toluene sulfonyl chloride (3.813gm, 1:2M) taking care to see that the temperature of the reaction does not rise above the RT. The progress of the reaction was monitored by TLC. Once the reaction is completed after 12hrs, the mixture was poured into ice-water (50mL).The separated product was filtered, then washed 5 times with water and dried properly under vacuum. Yield for this reaction was 82%[24]. IR data analysis of peaks as shown in Fig . 3319, 3223(s,-NH-), 1622(w), 1595(s), 1498(s), 1413(m), 1325(s),1147(s).



Scheme 2. Synthesis scheme of N, N'-ditoluene-sulphonyl-o-phenylenediamine

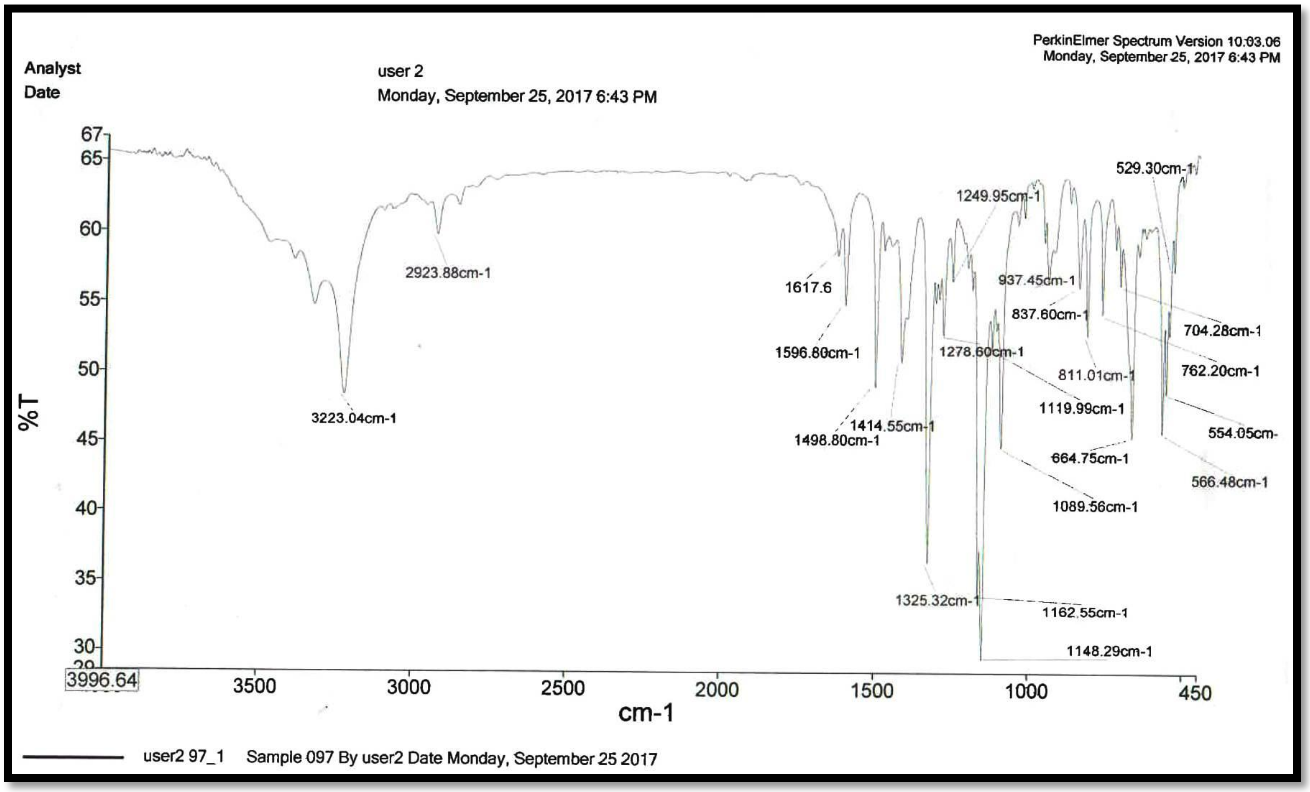


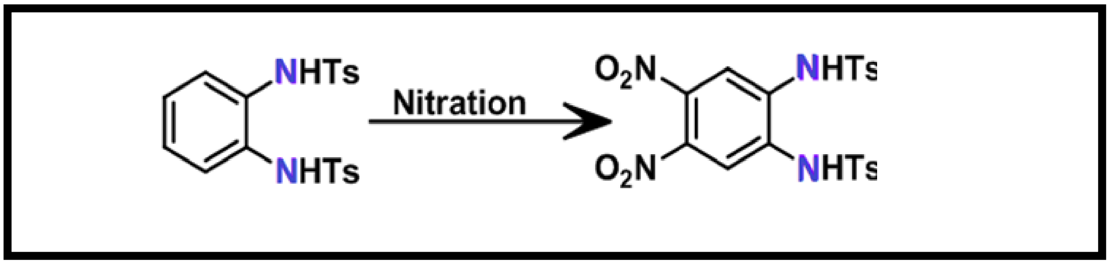
Fig.7. IR data analysis of N'-ditoluene-sulphonyl-o-phenylenediamine

2.2.2 Synthesis of 4,5-dinitro-NN'-ditoluene-p-sulphonyl-o-phenylenediamine

First trial of the synthesis was done by following the procedure mentioned below. About one-third of a solution of fuming nitric acid (4.2 mmol) in glacial acetic acid (15 ml.) was added to a stirred suspension of N,N'-ditoluene-sulphonyl-o-phenylenediamine (2.4mmol) in acetic acid (7 ml.) at 60°C. After complete addition the temperature was kept below 70°C. The mixture was heated further to 70°C and stirred for 30 min., then cooled and filtered. Multiple attempts to crystallization from a mixture of ethanol and glacial acetic acid were failed[25].

The synthetic process which was found out from many trials and optimization is the following.

Taking 0.5gm of N,N’-ditoluene-sulphonyl-o-phenylenediamine in an RB with an addition of 1mL of glacial acetic acid. The solution was warmed until precipitate starts coming. 2mL of conc. H_2SO_4 was added into it. Maintaining the temperature at 0°C, addition of nitrating mixture was done drop-wise. After stirring at 0°C for 10 mins, it was stirred for 2 hrs at RT. After the completion of reaction of reaction (monitored by TLC), ice-water was poured into it. The reaction mixture was filtered and yellow colored compound was collected. The nature of the product was confirmed by NMR.



Scheme 3.Synthesis of 4,5-dinitro-N,N'-ditoluene-p-sulphonyl-o- phenylenediamine

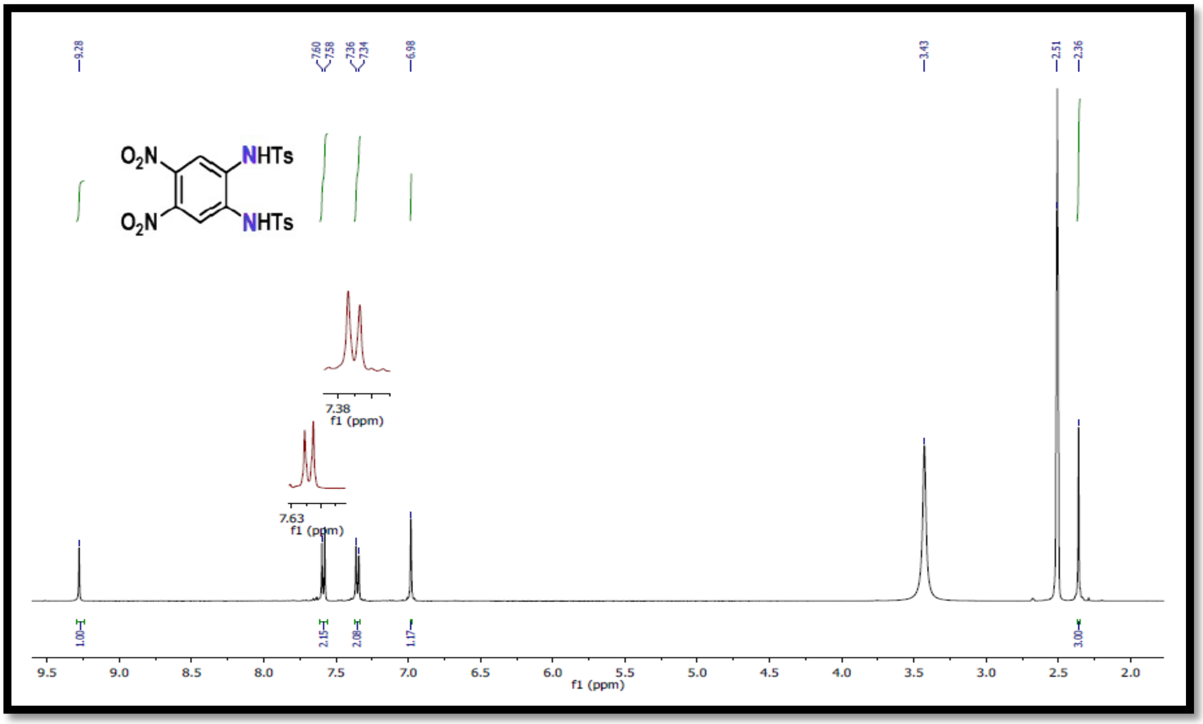
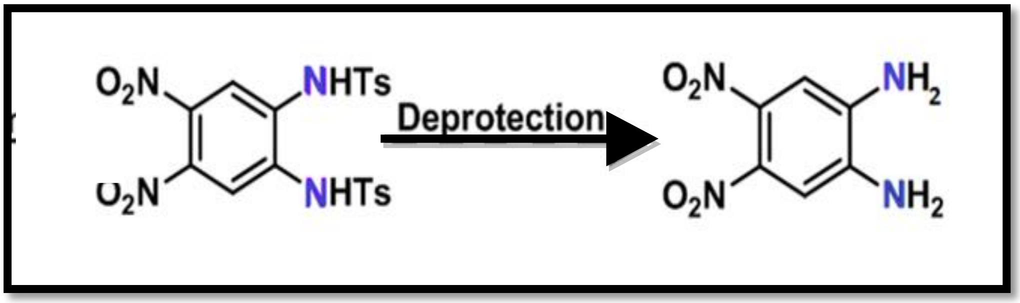


Fig 8 NMR of 4,5-dinitro-N,N'-ditoluene-p-sulphonyl-o- phenylenediamine

2.2.3 Detosylation of 4,5-dinitro-N,N'-ditoluene-p-sulphonyl-o-phenylenediamine to synthesize 4,5-dinitro-o-phenylenediamine

Taking 1 gm of crude 4,5-dinitro-NN'-ditoluene-p-sulphonyl-o- phenylenediamine) into an RB, concentrated sulphuric acid (1.5 mL) and water(0.5 mL) was added and heated on the oil bath at 100°C for 5 hrs. Then the mixture was poured into ice-water, warmed it for some time and stirred for 30mins. Mixture was neutralized with addition of solid sodium carbonate. The product was extracted from diethyl ether. The crude red colored product was obtained after rotary evaporation as shown in the Fig.9 and confirmed by NMR.



Scheme 4. Synthesis of 4,5-dinitro-o-phenylenediamine

Fig.9 .Tosylated Product

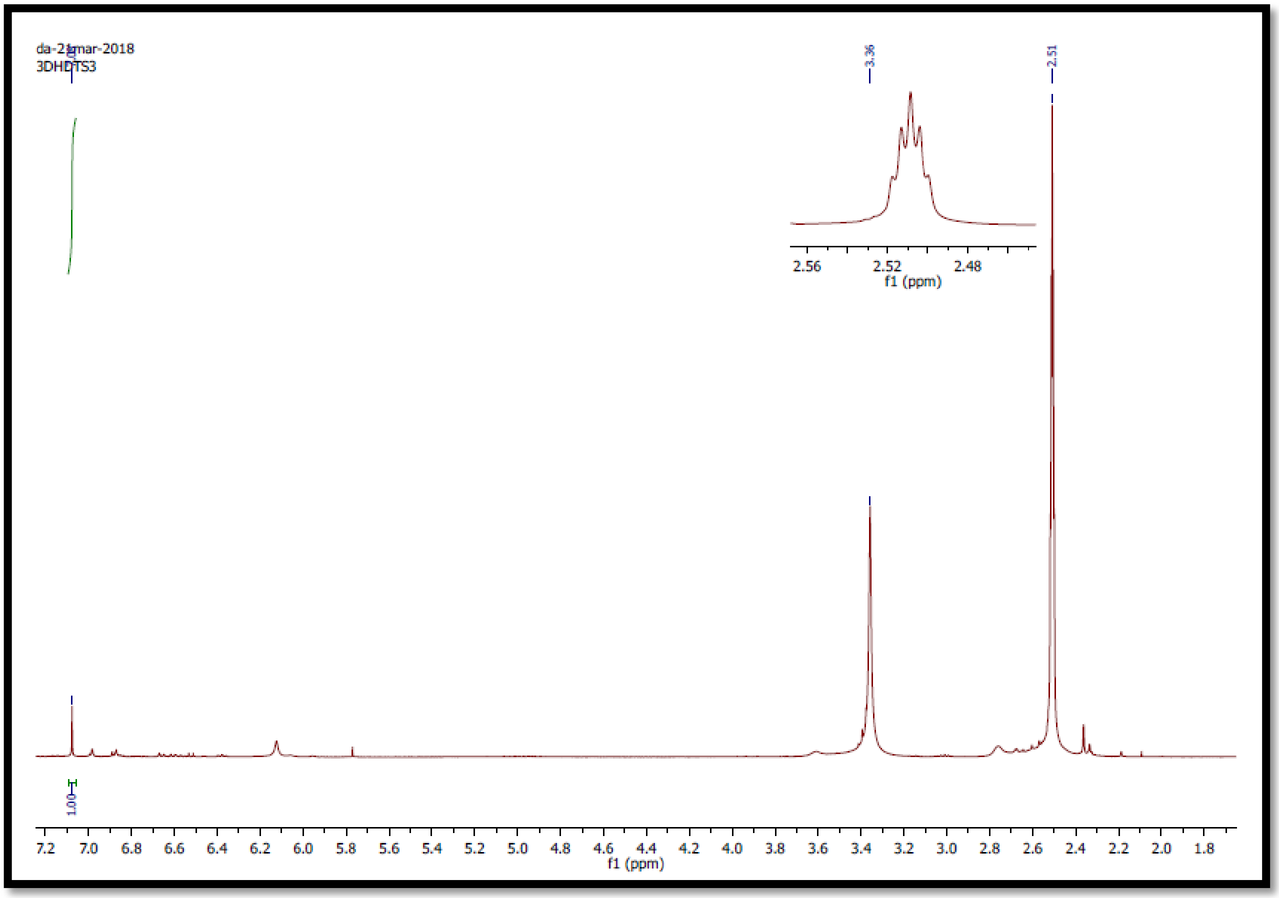
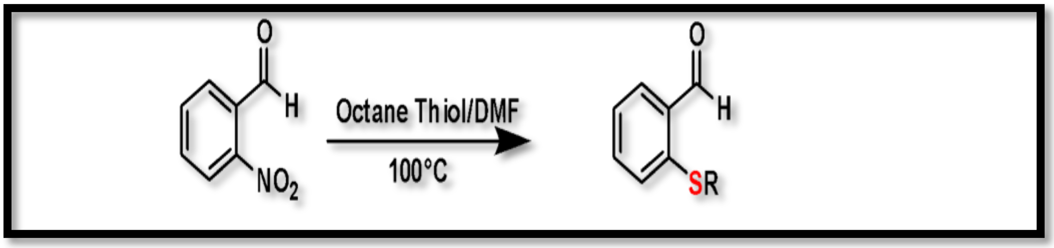


Fig. 10 NMR data of 5-dinitro-o-phenylenediamine

2.2.4 Synthesis of 2-octylthiobenzaldehyde



Scheme 5. Synthesis of 2-octylthiobenzaldehyde

Firstly we tried to synthesize 2-mercaptobenzaldehyde; we found that does not our use for the purpose of synthesizing these ligands. There are two main problems to overcome in the preparation of complexes of thiolate ligands: oxidation of the ligands to disulfides with concomitant metal reduction and the uncontrolled formation of multinuclear complexes due to the propensity of thiolate sulfur atoms to bridge between metal atoms [26].

A modified literature[27] was used. A mixture of 2-nitrobenzaldehyde (Aldrich) (1.51 g, 10mmol), 1-octane thiol (1.46g, 10mmol) (Aldrich), K_2CO_3 (1.38 g,), and DMF 10mL) was held at 110 °C for 22 h, and then cooled to room temperature. Then reaction mixture was diluted with Et_2O (75mL), and the resulting mixture was filtered. Rotary evaporation left yellowish brown oil, which was dried for 15h and purified with column chromatography (packed with silica gel in hexane and eluted with hexane to give us 2-octylthiobenzaldehyde) (1.18g, 54%). The nature of the product was confirmed by NMR (400MHz).

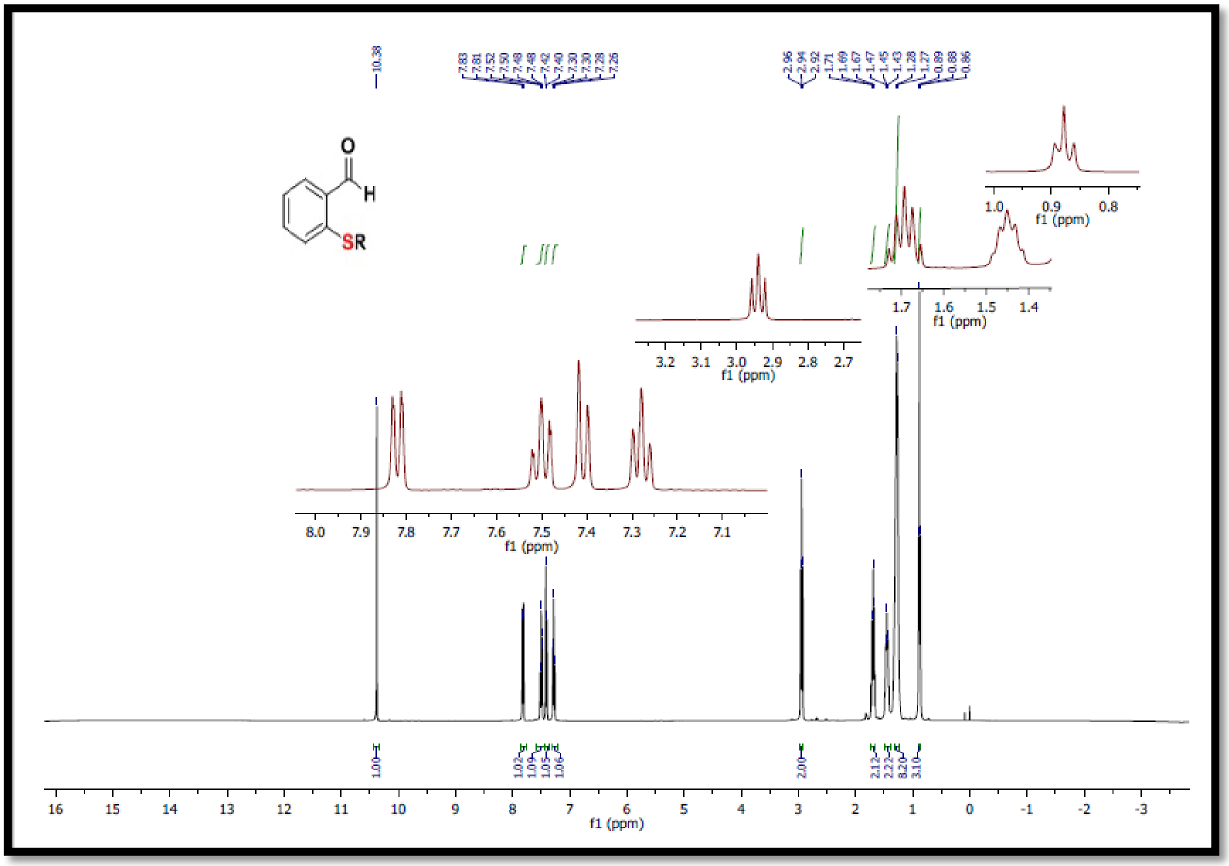
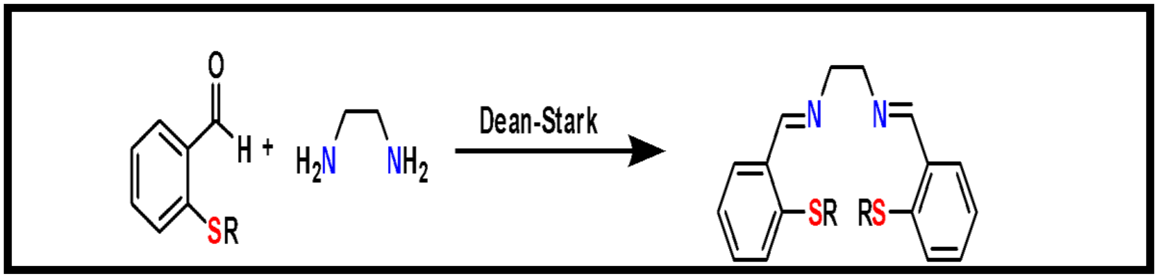


Fig.11. NMR data of 2-octylthiobenzaldehyde

We have synthesized 2-t-butylthiobenzaldehyde using t-butylthiol and o-nitrobenzaldehyde by the same procedure as mentioned in case of octylthiol. We purified the product using partition coefficient experiment then column chromatography. The product was light brown in color and confirmation was done by NMR (400MHz).

2.2.5 Synthesis of N,N’-Bis[(2-alkylthio)phenyl)methylene]-1,2-ethanediamine(L1)

There are reports where it has been claimed that the ^{t}Bu protection of the thiol cleaves during metalation. Keeping that in mind we attempted to synthesize 2-alkylthiobenzaldehyde. We have synthesized 2-t-butylthiobenzaldehyde using t-butylthiol and o-nitrobenzaldehyde by the same procedure as mentioned in case of octylthiol. We isolated the product by separatory funnel and purified further by column chromatography. The product was light brown in color whose identity was confirmed by NMR.



Scheme 6. Synthesis of N, N-Bis[(2-alkylthio)phenyl)methylene]-1,2- ethanediamine

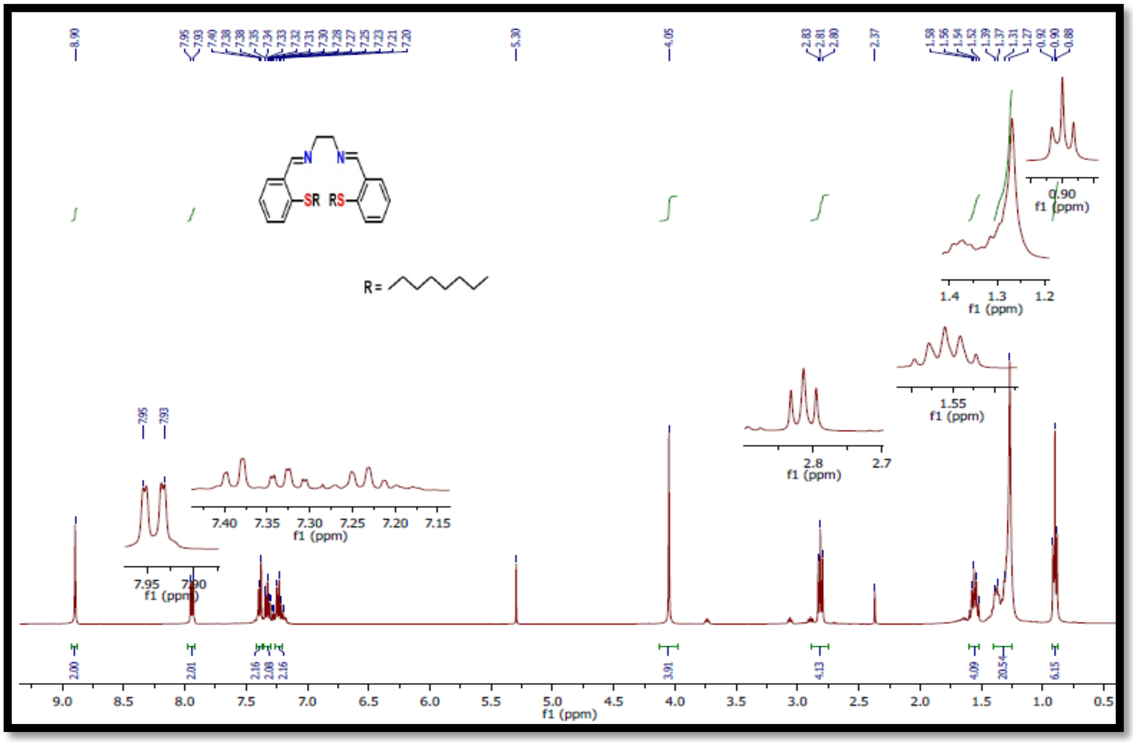


Fig.12 NMR of N, N-Bis[(2-alkylthio)phenyl)methylene]-1,2- ethanediamine

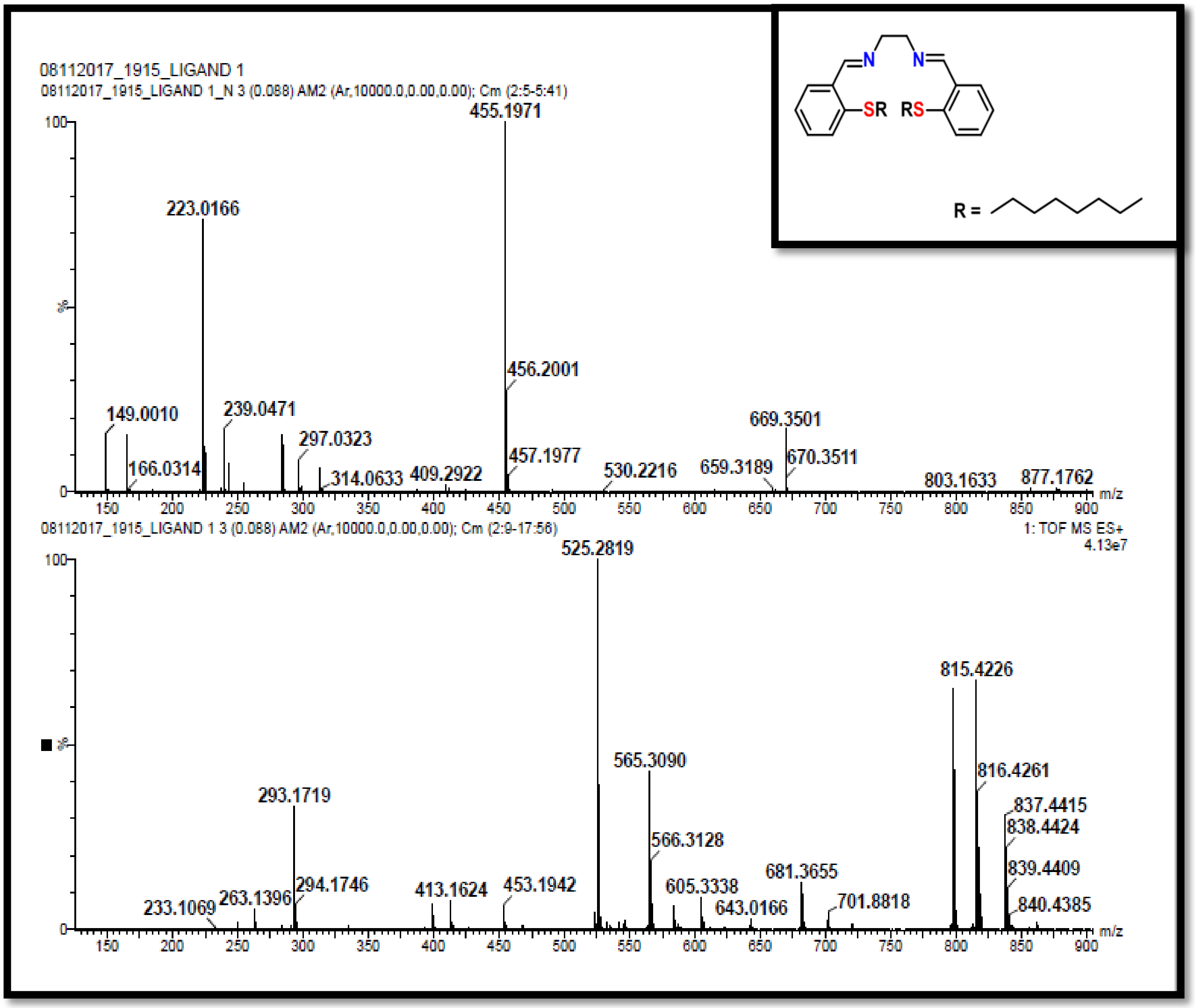
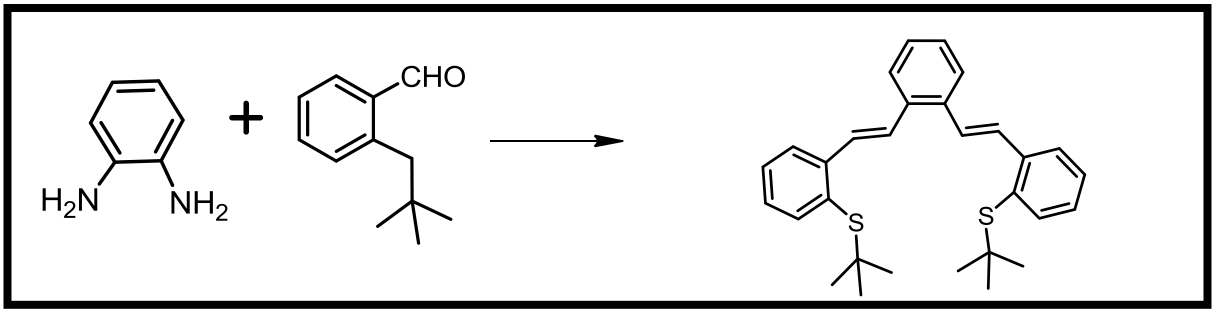


Fig.13 Mass spectrum of N, N-Bis[(2-alkylthio)phenyl)methylene]-1,2-ethanediamine

2.2.6 Synthesis of ligand N, N’-Bis [(2-alkylthio) phenyl) methylene]--o-phenylenediamine (L2)

A solution of 2-alkylthiobenzaldehyde (6.4mmol) and o-phenylenediamine (3.2mmol) in toluene (25mL) was heated to reflux under a dean-stark trap for 24 h and allowed to stand at 25 °C for 6 hrs over $MgSO_4$. Thereafter the product was filtered and collected as yellow colored oil. IR data of the ligand is shown in Fig.14.



Scheme 7. Synthesis of ligand N, N'-Bis [(2-alkylthio) phenyl) methylene]--o-phenylenediamine

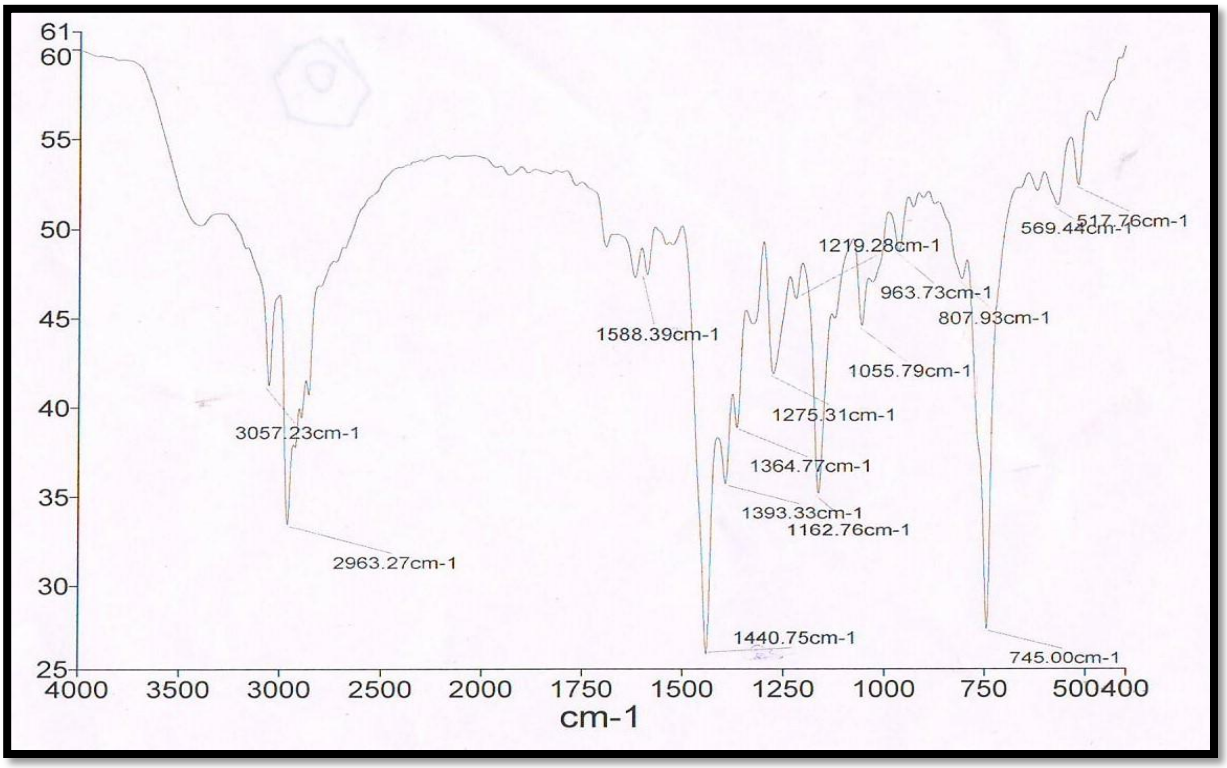
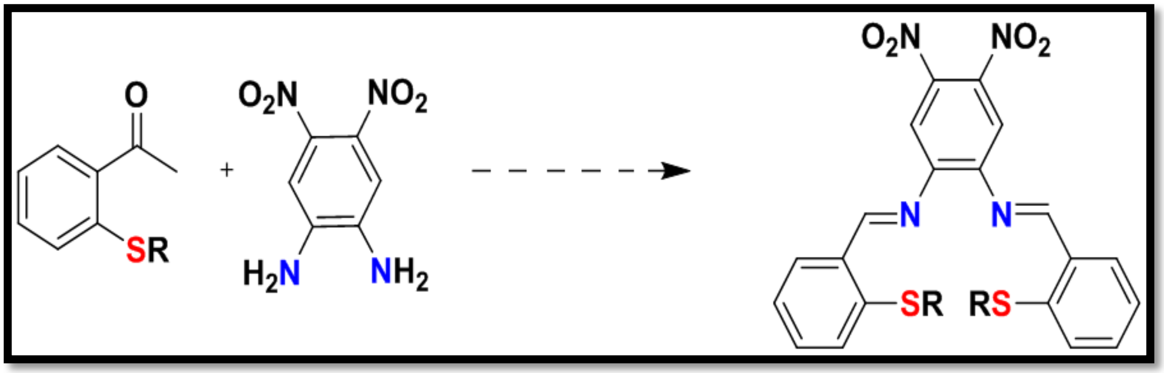


Fig14. N, N'-Bis [(2-alkylthio) phenyl) methylene]-o-phenylenediamine

2.2.7 Synthesis of N, N'-Bis [(2-alkylthio) phenyl) methylene]-4, 5 -dinitro-o-phenylenediamine

A solution of 2-alkylthiobenzaldehyde (5.2mmol) and 4,5-dinitro-o-benylenediamine (2.6mmol) in toluene (25mL) was heated to reflux under a Dean-Stark trap for 24 h and allowed to stand at 25 °C for 12hrs over $MgSO_4$. Thereafter the product was filtered and collected as yellowish brown colored oil. The formation of the ligand was confirmed by

NMR as shown in Fig.15. IR data of the ligand in Fig.16. shows a sharp peak at 1693 which confirms the immine formation.



Scheme 8 Synthesis of N, N'-Bis [(2-alkylthio) phenyl) methylene]-4, 5 -dinitro-o-phenylenediamine

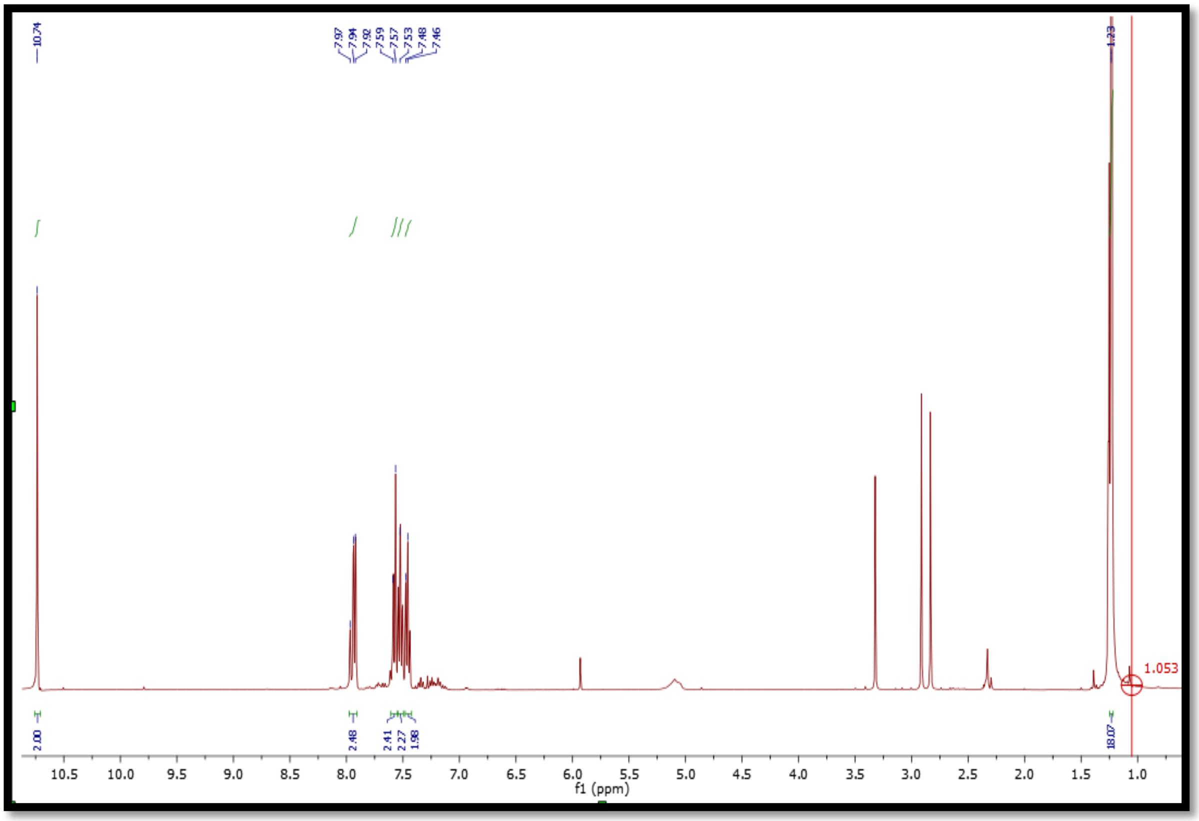


Fig15. NMR of N, N'-Bis [(2-alkylthio) phenyl) methylene]-4,5-dinitro-o-phenylenediamine

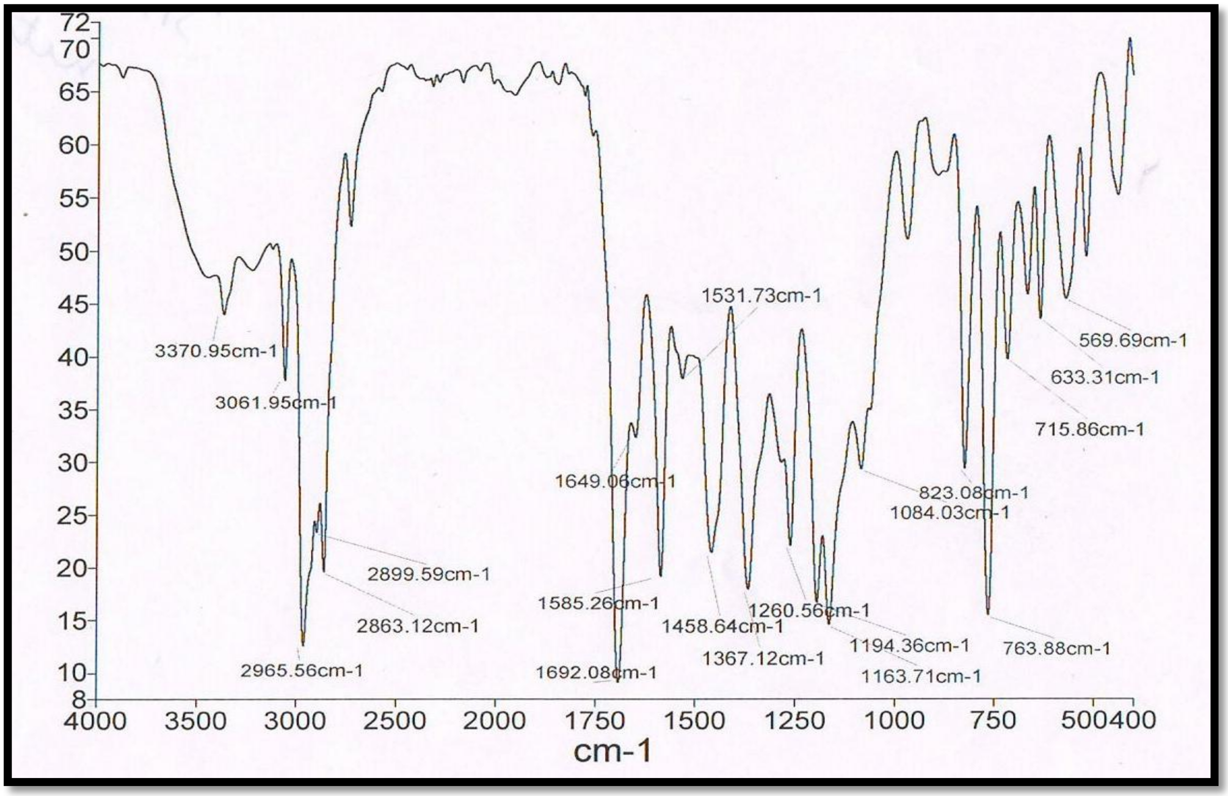


Fig16. IR of N, N'-Bis [(2-alkylthio) phenyl) methylene]-4,5-dinitro-o-phenylenediamine

2.2.8 Synthesis of 2-[2-(t-butyl)phenyl]-1H-benzimidazole]

o-phenylene diamine was dissolved in ethanol, once it is completely dissolved t-butyl thiol was added to the ethanolic solution in RB. The mixture was stirred for 24 hrs at reflux.
New type of crystals were obtained after crystallization of the crude product from ethanol.
XRD data of the synthesized product is given below in Fig.17.

The X-ray crystal structure analysis of ligand structure reveals that it crystallizes in orthorhombic crystal system with *Pbca* space group. Single crystal X-ray diffraction data of the ligand structure were collected using a Rigaku XtaL ABmini diffractometer equipped with Mercury CCD detector. The data were collected with graphite monochromated Mo-Kα radiation (λ=0.71073 Å) at RT using ω scans. The data were reduced using Crystal Clear suite 2.0. and the space group determination was done using Olex. The structure was resolved by direct method and refined by full-matrix least-squares procedures using the SHELXL 2014/7 software package using OLEX2 suite.

There are numerous compounds known in nature, where benzimidazole system plays an important role of biological interest as well as in medicinal chemistry research. Iron−sulfur clusters have lot of applications which includes their use in redox reactions, sensing and most important electron transport. These clusters play an important role during electron transfer as structural gates and as a mediating proton coupled electron transfer (PCET) in the Q-cycle[28].

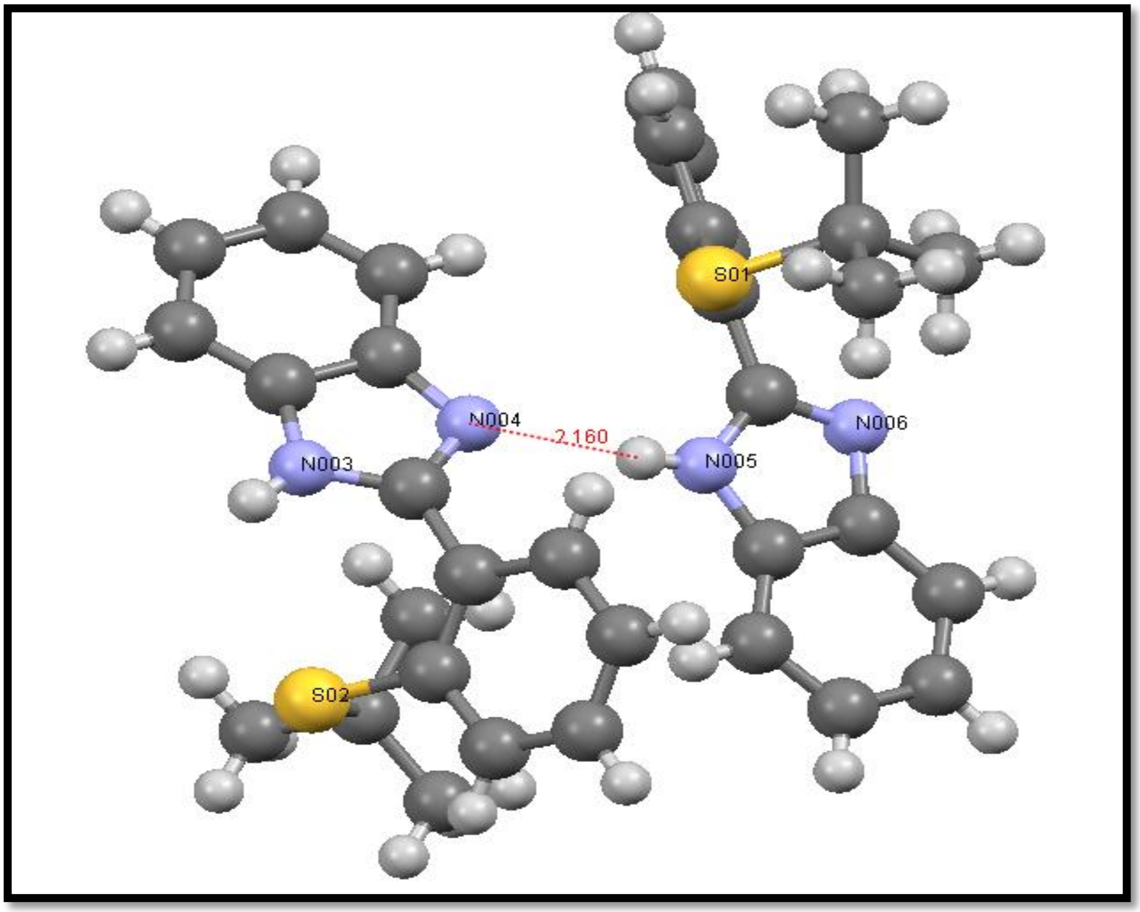


Fig. 17 Crystal structure of 2-[2-(t-butyl)phenyl]-1H-benzimidazole]

2.2.9 Synthesis of 2-[2-(t-butylthio)phenyl]-1H-phenanthro[9,10-d]imidazole

Phenanthrenediamine was dissolved in ethanol; once it is completely dissolved t-butyl thiol was added to the ethanolic solution in RB. The mixture was stirred for 24 hrs at reflux.

New type of crystals was obtained after crystallization of the crude product from ethanol. The X-ray crystal structure analysis of ligand structure reveals that it crystallizes in monoclinic' crystal system with $P\text{-}1_{21}$ space group.. An ORTEP of the ligand structure is shown in the **Fig.18**

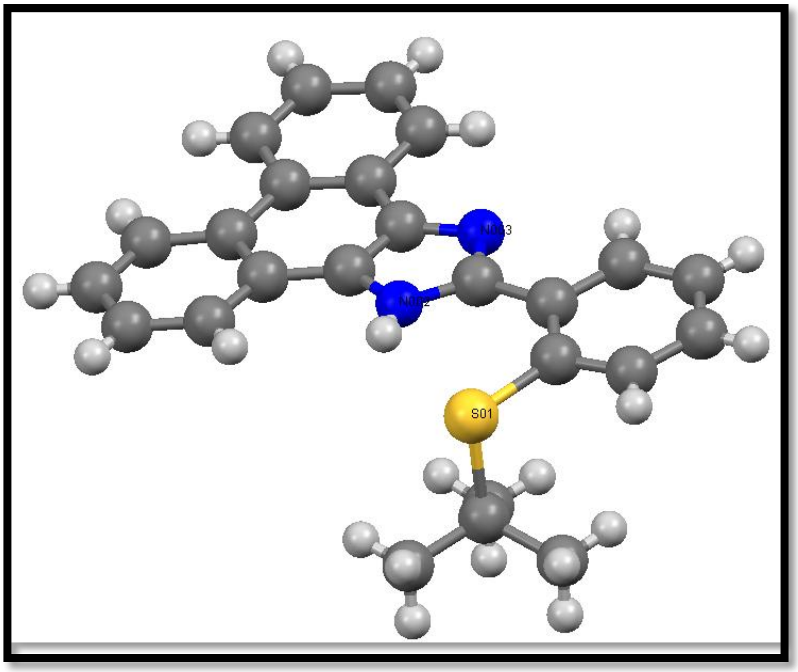


Fig 18. Crystal Structure of 2-[2-(t-butylthio)phenyl] -1H-phenanthro[9,10-d]imidazole

2.3 Synthesis of Metal complexes of 2-[2-(t-butyl) phenyl]-1H-benzimidazole]

We have synthesized Cu-complexes of 2-[2-(t-butyl) phenyl]-1H-benzimidazole]. Ligand (10mmol) was dissolved in a hot ethanol and metal acetate salt (10mmol) in cold ethanol. Solution was stirred and refluxed for 4hrs. On addition of Copper metal salt color of the mixture immediately changed from blue to brown color. The X-ray crystal structure analysis of Cu(II) complex reveals that it crystallizes in triclinic' crystal system with *P-1* space group. Molecular formula of the complex is $C_{34}H_{36}C_{l4}Cu_{2}N_{4}S_{2}$ with molecular weight 833.67. An ORTEP of the Cu(II) complex is shown in the **Fig.19**

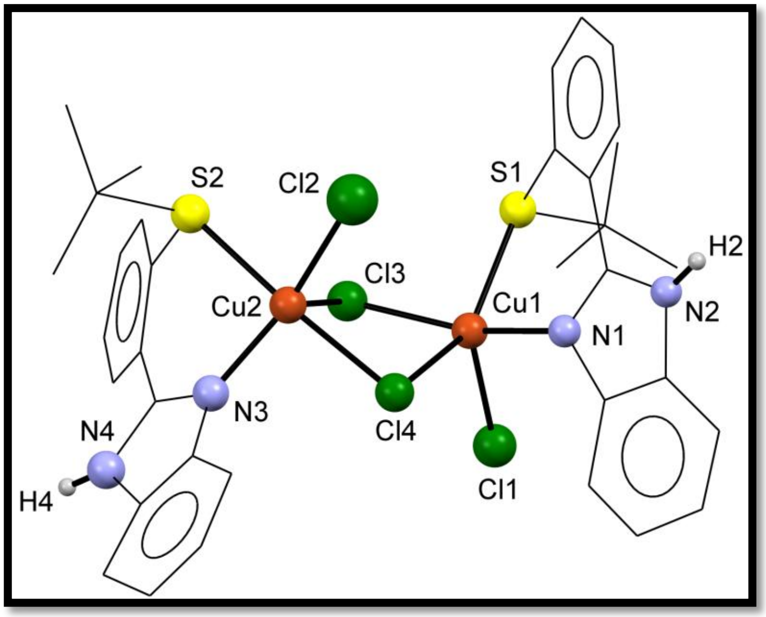


Fig. 19 Crystal structure of metal complex of 2-[2-(t-butyl)phenyl]-1H-benzimidazole]

2.4 Metalation of N,N’-Bis[(2-alkylthio)phenyl)methylene]-1,2-ethanediamine

Dry ethanol was used for metalation in a schlenk. Ligand (5mmol) was dissolved in a hot ethanol and metal acetate salt (5mmol) in cold ethanol. The solution was stirred for 4 hrs on a hot plate at 80°C maintaining the reaction mixture under inert atmosphere. On addition of copper metal salt color of the mixture immediately changed from blue to dark green as shown in the Fig.20.

Fig20 Cu- complex

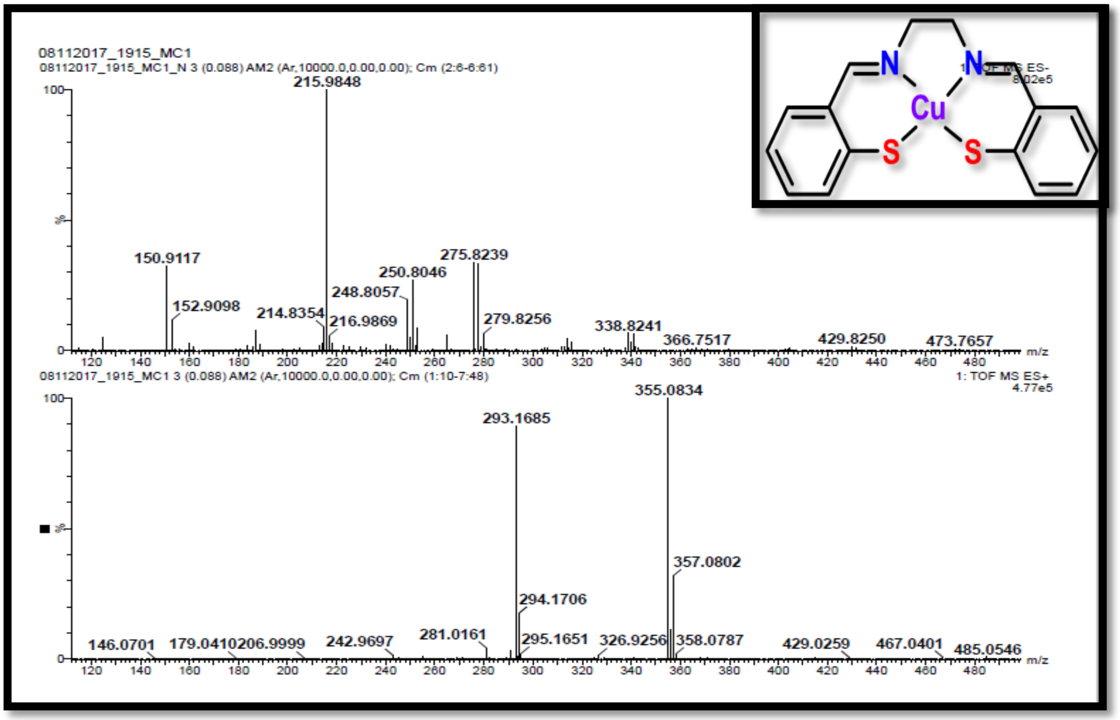


Fig21 Mass spectrum of the Cu-metal complex.

2.5 Magnetic susceptibility Vs Temp Plot

To evaluate the magnetic property of the synthesized complex we carried out the susceptibility measurement using SQUID. The plot of magnetic susceptibly Vs temp in Fig.21 shows a curve which implies the paramagnetic nature of the complex as with decreasing temperature , magnetic susceptibility value increases.

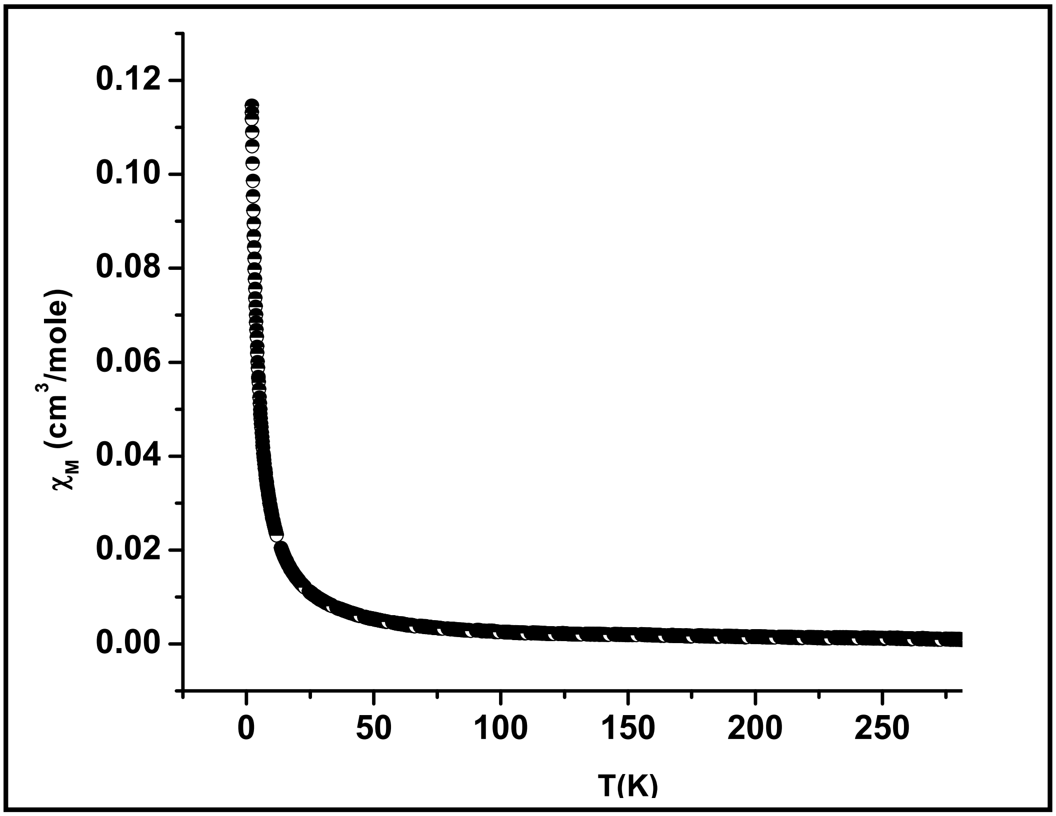


Fig.22 Magnetic susceptibility Vs Temp Plot

2.6 UV-Vis Analysis of metal complexes and ligands

Absorption bands of the Schiff base and its copper complex in acetonitrile solution in the 200-900 nm range are given in Fig. 24 -27**.** Schiff base ligand and Cu(II) complex is soluble in common organic solvents like methanol, acetonitrile, dichloromethane etc. The complex is stable in the solid state as well as in the solution phase. The UV-Vis spectra for ligands show high intensity transitions in the range of 200 to 400 nm. The Schiff base ligands shows the characteristic absorption bands at 275 nm because of π-π* and 336 nm is due to n-π* transition **.** On complexation, these bands were shifted to lower wavelength (bathochromic shift) region, suggesting the coordination of imine nitrogen and sulphur Cu(II) ion and new band generated at 600 nm for metal complex due to ligand to metal charge transfer transition**.**

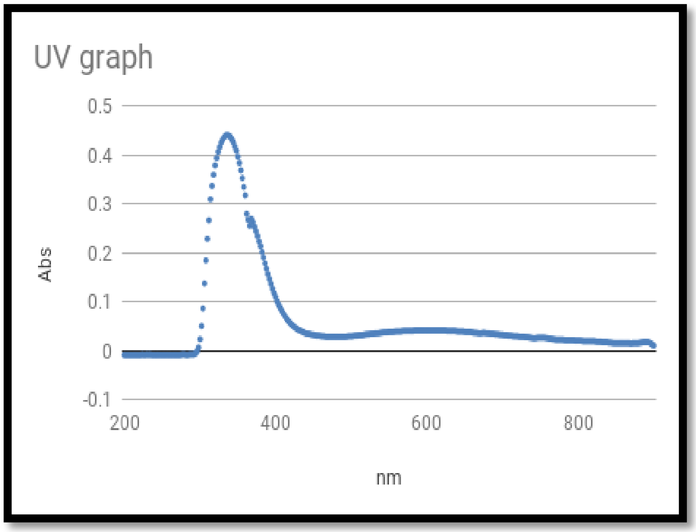


Fig.24 UV-Vis spectra of Cu- complex of L1

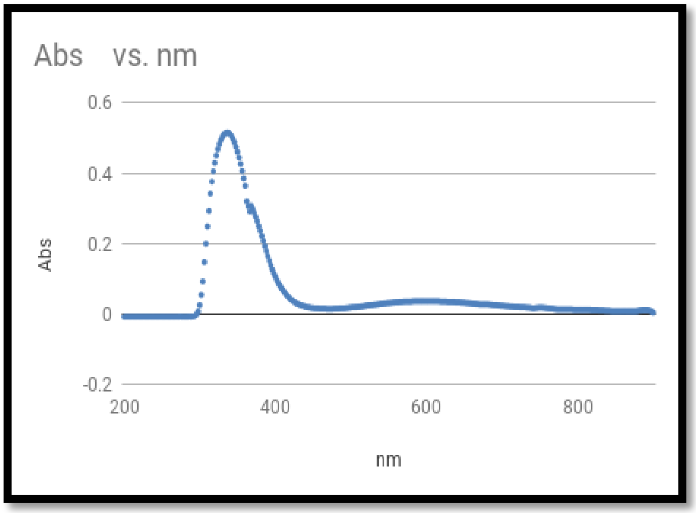


Fig.25 UV-Vis spectra of Cu- complex of L2

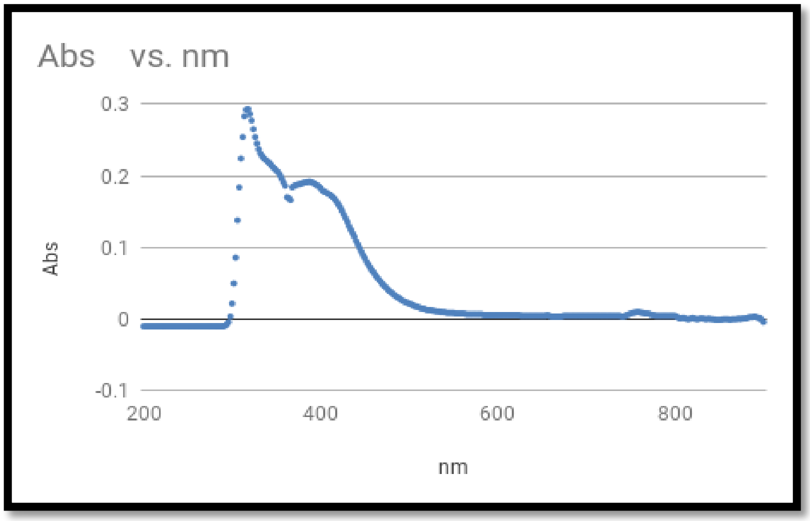


Fig. 26 UV-Vis spectra of L1

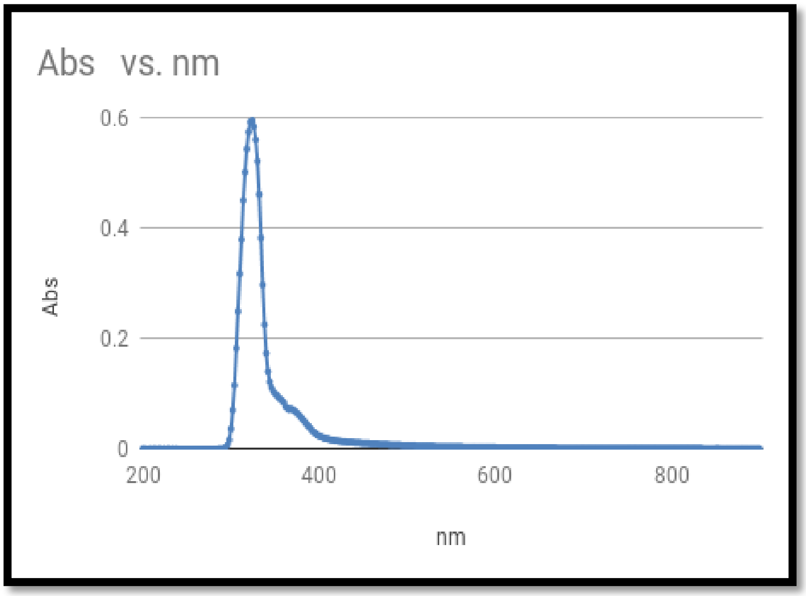


Fig.27 UV-Vis spectra of L2

Conclusion and Future Directions

To conclude I would like to start from the famous lines …

> Two roads diverged in a wood, and I—
> I took the one less travelled by,
> And that has made all the difference….
> -Robert Frost

In this Project we are exploring thiosalen ligands, which are almost like the road not taken and which has made all the difference. We attempted to synthesize the ligands having different groups on the backbone to create a difference in their redox properties. Formation of metal complexes of copper metal and redox active ligand were investigated by spectroscopic methods like UV-Vis, IR, mass Spectrometry. After a thorough characterization, we will do the electrochemical studies to find out the redox potential of the ligands and their metal complexes. We will be doing magnetic measurements to study the magnetic interactions between redox-active ligand and the metal center. We will be doing some computational studies. These metal-sulfur interactions are of great importance in biology. The imidazole type of ligands we have synthesized might have potential use in the field of drug delivery.

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