Chemistry of Dithiolenes and Their Nickel and Molybdenum Complexes

Archana Nigam

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Abstract

A new class of dithiolene ligand containing a pyran ring that mimics a biologically important MPT (molybdopterin) have been proposed and the key reactions have been established to synthesize this ligand. Along with that, new dithiolene complexes of nickel $[\text{Ni(dt)}_2]^n$, where dt=dithiolene ligand, $n$=charge, have been synthesized and characterized by several spectroscopic techniques. A characteristic low energy charge transfer band in UV-visible spectra is found to be the good indicator of purity as well as the anionic states of the nickel complexes.

A ligand exchange reaction using neutral nickel complexes and molybdenum carbonyl complexes has been utilized to synthesize $(\text{LN}_2)$MoO(dt) type of complexes, where LN$_2$ = nitrogen based bis chelating ligand, to mimic the active site of mononuclear molybdoenzymes. We observed a ligand exchange reaction to generate a Mo(dt)$_3$ type species but no target complexes were observed under the conditions we employed. Another set of reactions involving complexes having higher oxidation state of Mo and LN$_2$ ligands showed promising results. $^1$H NMR, IR Spectroscopy and Mass spectrometry results showed that we have synthesized complexes of type $(\text{LN}_2)$MoO(dt) and $(\text{LN}_2)$Mo(CO)$_2$(dt), where LN$_2$ = 1,10-Phenanthroline.
Acknowledgement

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### Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>bdt$^{2-}$</td>
<td>benzene-1,2-dithiolate</td>
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<td>BEDT-TTF</td>
<td>Bis(ethylenedithio)tetrathiafulvalene</td>
</tr>
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<td>COSY</td>
<td>Correlated Spectroscopy</td>
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<td>dddt$^{2-}$</td>
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<td>DFT</td>
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<td>Dimethyl sulfoxide Reductase</td>
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Chapter 1

Chemistry of Dithiolene Ligands: Synthesis and Characterization of A New Dithiolene Ligand

1.1. Introduction

Over the past few decades, there has been an enormous upsurge in interest of the chemistry of transition metal complexes containing sulfur ligands. There are several reasons for this increase; the major one is the revitalization of the chemistry of the unsaturated sulfur donor ligands. The interests in the complexes of these ligand systems range from purely academic syntheses to large-scale industrial production. There have been several important and useful reviews of the different aspects of metal sulfur chemistry. Older reviews by Harris and Livingstone\(^1\), Jorgensen\(^2\) highlight sulfur ligands in general, whereas reviews by Gray\(^3\), McCleverty\(^4\), Schrauzer\(^5\), and Hoyer\(^6\), and recent review by Stiefel\(^7\) covered the chemistry of 1,2-dithiolene complexes in a great depth.

Another major reason for the expansion of the field of dithiolate chemistry includes the correlations of model dithiolate complexes with biological systems containing transition metal-to-sulfur bonds and the numerous commercial applications of the dithiolate complexes. The patent literatures abound with examples of the uses and applications of these compounds. The important applications of these complexes include polymerization catalysts, catalytic inhibitors, oxidation catalysts, semiconductors, mode locking additives in neodymium lasers, wear-inhibiting additives in lubricants, polarizers in sunglasses and fingerprint developers in criminal investigations. This list exemplifies the diversity of the applications of these complexes. The discovery of the unsaturated 1,2-dithiol ligands and their metal complexes were one of the main reasons for the increase of
interest in the chemistry of transitional metal sulfur complexes. These ligands form five-membered unsaturated chelate rings when complexed with the metal.

1.2. History of the discovery and advancement of dithiolene ligands:

Clark and co workers\(^8\) first reported the 1,2-dithiolene complexes in the mid 1930’s. They discovered that toluene-3, 4-dithiol (Figure 1 (a)) and chlorobenzene-3, 4-dithiol readily formed complexes when reacted with zinc, cadmium, mercury and tin. Later on, in 1957, Bahr and Schleitzer\(^9\) prepared a ligand, Na\(_2\)S\(_2\)C\(_2\)(CN)\(_2\) (Figure 1 (b)), which readily formed complexes with palladium, which they formulated as Pd(NH\(_3\))\(_2\)S\(_2\)C\(_2\)(CN)\(_2\) and Na\(_2\)[Pd(S\(_2\)C\(_2\)(CN)\(_2\))\(_2\)]. They further observed that the latter was apparently oxidized by iodine to an unidentifiable product. In 1959, Stevancevic and Drazic\(^10\) described the formation of square planar complexes of nickel, palladium and cobalt with quinoxaline-2,3-dithiol(QDTH\(_2\)) (Figure 1c). These were prepared in alkaline solution and appeared to be [M(QDT)\(_2\)]\(^2\). In 1960, Gilbert and Sandell\(^11\) reported that toluene 3,4-dithiol reacted with molybdate and formed a green colored complex, which they formulated as Mo\(^\text{VI}\) (S\(_2\)C\(_6\)H\(_3\)Me)\(_3\). They also isolated a red colored species, which they thought contained Mo\(^\text{IV}\), the first reported tris-substituted dithiolene complex. In 1962, G.N. Schrauzer and V.P. Mayweg\(^6\) reacted nickel sulfide and diphenylacetylene and prepared an unusual complex of nickel, NiS\(_4\)C\(_4\)Ph\(_4\). This intensely green colored complex was diamagnetic and volatile in nature. They further discovered that this green color is discharged in pyridine or piperidine solution and formed a red brown colored paramagnetic solution. In the same year H. B. Gray and his co-workers\(^12\) reported the synthesis of metal complexes of Na\(_2\)S\(_2\)C\(_2\)(CN)\(_2\) of the type [MS\(_4\)C\(_4\)(CN)\(_4\)]\(^2\) where M= Cu, Ni, Pd and Co. Later, King\(^13\)
reacted bis-perfluoromethylidithietene with molybdenum hexacarbonyl and synthesized the tris-substituted complex \([\text{MoS}_6\text{C}_6\text{(CF}_3)_6]\). In parallel, Davison, Edelstein, Maki and Holm\(^{14}\) discovered that there was only a two-electron difference between the neutral complex of Schrauzer, \(\text{NiS}_4\text{C}_4\text{Ph}_4\) and the dianionic species of Gray, \([\text{NiS}_4\text{C}_4\text{(CN)}_4]^2\). Owing to this difference, they proposed to affect the oxidation of dianion to neutral species and reduction of neutral species to dianionic complex via an intermediate monoanionic complex. They isolated several different monoanions, \([\text{Ni-S}_4]^1\), that were paramagnetic in nature. It was also discovered that these one-electron transfer reactions linking dianions, monoanions and neutral species could be detected polarographically or voltammetrically. In 1964, the majority of the work was done on planar dithiolene complexes but one of the most important developments were in the study of six coordinate complexes, which also underwent electron transfer reactions as the planar complexes. In 1965, Eisenberg and Ibers\(^{15}\) recognized that the geometry of \([\text{ReS}_6\text{C}_6\text{Ph}_6]^0\) is trigonal prismatic. Subsequently, two other trigonal prismatic complexes of \([\text{MoS}_6\text{C}_6\text{H}_6]^0\) and \([\text{VS}_6\text{C}_6\text{Ph}_6]^0\) were investigated by Smith, Schrauzer and coworkers\(^{16}\) and by Eisenberg, Gray and coworkers\(^{17}\) respectively. To date, many useful dithiolene ligands have been discovered, among which an important one is dimercaptodithiolene (dmit).

So, the interest in these complexes has sprung from the inability to assign formal oxidation states to the transition metal, the discovery of trigonal prismatic geometry in the tris complexes, and the facile one or two electron transfer reactions they undergo.

The difficulty in assigning formal oxidation states to the transition metal led to the conflicting nomenclature in these complexes. In planar \(\text{MS}_4\text{C}_4\text{R}_4\) complexes (Figure 2), three different limiting structures are possible in which metal could have formal oxidation
states of 0, 2+, 4+, while the ligands are either neutral ‘dithiodiketones’ or dinegative ‘dithiolates’. The bis-dithiodiketone (c) is unstable, as zerovalent metal complexes are not usually planar. Ligands in complexes of type (a), the dithiolato dianions, exist in complex anions as Ni[S₂C₂(CN)₂]²⁻. In neutral complexes, the ligands usually exist in the intermediate state between (a) and (c), having a delocalized ground state (b). So, according to Schrauzer, the complexes with delocalized ground states are termed as “dithienes” and the most reduced complexes are known as “dithiolates”. But, according to McCleverty, the term “1,2-dithiolene” or “dithiolene” denotes metal complexes of the general types [M–S₄]ⁿ⁺, [M–S₆]ⁿ⁻, and [M(L)ₓ–S₂,y⁻]ⁿ⁻ (where L may be any other ligand such as NO, PPh₃, or O). This terminology does not imply any particular formal oxidation state or structure.

In general, dithiolene represents a class of materials, which are unique in their ability to exist in several clearly defined oxidation states. They possess a high degree of electron delocalization and exhibit intense electronic transitions at unusually low energies. Dithiolenes are best considered to be a resonance hybrid of the limiting structures. In both bis- and tris- dithiolenes, the electron delocalization is not limited to the ligand but also includes the metals to give rise to cyclic delocalization (aromaticity). To symbolize this electron delocalization in dithiolenes, they can be represented in a manner similar to that used for benzene, by formulas containing a ring inside the framework given by the metal, sulfur and carbon atoms. So, dithiolene are termed as “non-innocent ligand”, but the term non-innocence is not a function of the ligand alone but it applies to particular combinations of metal and ligand where a strong mixing between ligand and metal frontier orbitals occur, such that assignment of oxidation states to individual metal and ligands component
is difficult. This behavior is more prominently seen in bis-dithiolene complexes of nickel, palladium and platinum.

1.3. General synthetic methods to synthesize dithiolene ligands:

Two main synthetic schemes have been proposed to synthesize dithiolenes. In the first and most frequently used method, either the free ethylenedithiol or an appropriate salt of the ethylene-dithiolato ligand dianion is reacted with a metal salt to produce anions of the dithiolenes, which may or may not be subsequently oxidized to the neutral species. The second one converts vicinal diketones into dithiodiketones and reacts these either with zerovalent metals to form dithiolenes directly or uses metal salt species.

1.3.1. Syntheses using ethylenedithiolates

Ethylene dithiols can be obtained from the cleavage of vicinal dithio-ethers, which can be prepared from cis-dichloro or dibromo alkenes through a stepwise synthesis (Figure 3, Route A). In the other method, ethylene dithiocarbonate is cleaved by alkali metal hydroxides or alkoxides to produce salts of ethylene dithiolates (Figure 3, Route B).

1.3.2 Syntheses using dithioketones

Several 1,2-dithiones can also be obtained from 1,2-diones by direct sulfurization with \( \text{P}_4\text{S}_{10} \) or \( \text{B}_2\text{S}_3 \). These dithiones can be converted to dithiolenes by reaction with a transition metal carbonyl or by reaction with metal salt. The alkyl and aryl substituted dithiolenes can be obtained by refluxing acyloins and benzoins with \( \text{P}_4\text{S}_{10} \) in dioxane or
xylene to produce a dithiophosphoric ester, which is reacted with a metal salt to produce the dithiolene complex.

1.4. Role of dithiolene in bioinorganic chemistry

As discussed above, dithiolenes have a long history of advancement within inorganic chemistry, but they also play an important role in biological systems. They are one of the oldest ligands designed by nature to perform biochemical transformations. Dithiolenes containing enzymes can be found in almost all living organisms. After the discovery of dithiolenes in enzymes, this particular bidentate sulfur ligand became an interesting field of research to the scientists studying biological systems. Dithiolene containing enzymes are metallo-enzymes in which metal chelated by dithiolene is either molybdenum or its analogue tungsten. In 1992 the structural unit of dithiolene in molybdenum enzymes was discovered and referred as molybdopterin,\textsuperscript{19} a cofactor that coordinates to molybdenum center. Later, in 1995 after its discovery and structural characterization in a tungsten enzyme,\textsuperscript{20} it is better known as the metal binding pyranopterin dithiolene (MPT). This cofactor is composed of a dithiolene group located on a pyran ring, which is further fused to the reduced pyrazine ring of the pterin core (Figure 4). In this pterin core, both pyran and pyrazine rings are distinctly nonplanar, where the pyran ring adopts a half chair conformation and the plane of the ring deviates $\sim 40^\circ$ from the plane of the pterin ring.\textsuperscript{21} It is significant that the pterin nucleus does not coordinate directly to the metal but it is the dithiolene group that is coordinated to metal center. It is believed that the role of this cofactor is to modulate the reduction potentials of the metal center and mediate the electron transfer processes to other redox active centers. It also
lowers the activation energy for oxygen atom transfer reactions by strong S→M σ and π donation and also provides basic sites for protons that are part of redox processes. Thus, MPT is a pyran substituted asymmetric dithiolene ligand, which possesses a pterin unit. Pterins are redox active centers due to the presence of nitrogen heterocyclic structure and can exist in various oxidation and reduction states.

After the discovery of the dithiolene in the biological systems, considerable amount of new dithiolene ligands and their metal (especially molybdenum and tungsten) complexes have been synthesized and characterized. Many of these systems provide significant calibration of information based upon spectroscopic and reactivity features of biological enzymes. Some important dithiolene ligands, which have been used to synthesize model complexes of MPT containing enzymes, are shown in Figure 5. Important reports on the syntheses, spectroscopic and reactivity properties of molybdenum and tungsten complexes using dithiolenes of type a, b, and c (Figure 5) have been published by several groups. For examples, the Holm group has synthesized several model analogues of molybdenum and tungsten compounds using a and c types of dithiolene ligands. These model molecules show interesting resemblance to the structural and spectroscopic features of the active site of the metallo-enzymes. It is important to note that these complexes only mimic the dithiolene moiety of the pterin molecule but not the whole. The Garner group has synthesized asymmetrical dithiolene complexes using the ligands given in the Figure 5b to study the properties of the complexes and correlate those with that of the MPT. These are the closest structural model complexes of MPT available to date. Recently the same group has successfully synthesized the protected form of pyranopterin-ene-dithiolate ligand but the complexation of this ligand with
molybdenum or tungsten has not yet been achieved. They have also demonstrated the acid-sensitive nature of the tricyclic pyranopterin ring (N, C, O system), which in the presence of acidic medium opens the pyran ring, so the complexation of metal ions can only be achieved using basic conditions to retain the pyran ring system.

There is no complete model complex available to date, which contains all the three-redox active centers, molybdenum or tungsten metal ion, ene-dithiolate moiety, and the hydrogenated pyranopterin. In order to understand the effect of a pyran ring we proposed a strategy to synthesize a new dithiolene ligand with the pyran moiety (Scheme 1). Though this ligand will lack the important pterin ring, we anticipate that this new dithiolene ligand will provide valuable information to bioinorganic chemistry. The chemistry of this new dithiolene ligand may also be useful in studying the physical properties of other metal-dithiolene complexes.

1.5. Experimental

Unless specified, all reactions were performed under an atmosphere of argon using Schlenck techniques. Reaction mixtures were stirred magnetically. The majority of the chemicals was purchased from Aldrich chemical company and Acros chemical company and was used as received without further purification. Chlorine gas was obtained from Aldrich chemical company in a lecture bottle and used in the reaction without purification. Commercial grade solvents were dried and distilled before use. Toluene, benzene and hexane were dried and distilled over Na-wire/ benzophenone; chloroform and pentane were dried and distilled over CaH₂.
Room temperature $^1$H spectra were recorded using a Bruker ACP-300 spectrometer at 300.133 MHz and a Varian Unity spectrometer at 499.83 MHz frequencies, respectively. Room temperature $^{13}$C spectra were recorded using a Bruker ACP-300 spectrometer and a Varian Unity spectrometer at 75.469 MHz and 125.68 frequencies, respectively. Mass spectra were recorded in a Waters LCQ ESI/APCI quadrupole mass spectrometer in ESI and/or APCI modes. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1760X spectrometer on NaCl plates or in KBr pellets. Melting points were determined by Mel-Temp II apparatus using a glass capillary. Chromatographic purifications were done on silica gel (63-200µm, 60 Å) purchased from Sorbent Technologies Company. Thin layer chromatography (TLC) was done on silica coated TLC plates (plastic backed) from EM Science.

**Synthesis of 2,3-dichlorotetrahydro-2H-pyran (1)**

A schlenk flask was charged with 3,4-dihydro-2H-pyran (20g, 238 mmol) and dry pentane (65 mL) was added to it under an argon atmosphere. The contents were cooled to –78 ºC using an acetone-dry ice bath and chlorine gas was slowly bubbled through a stirred solution while maintaining the temperature at –78 ºC until the yellow color persisted. Argon gas was then passed through the reaction solution to expel the excess of dissolved chlorine gas. The solvent was evaporated under reduced pressure to get colorless mobile liquid. The liquid was distilled at ~55 ºC in vacuum, which yielded a clear colorless liquid in 92.1% (219 mmol) yield.

$^1$H NMR (C$_6$D$_6$): δ = 5.91(s), 5.86 (d, J = 3Hz), 3.80 (s), 3.50-3.76 (m), 3.29-3.43 (m), 3.16-3.24 (m), 1.73-2.15 (m), 1.32-1.60 (m), 1.09-1.26 (m), 0.95-1.08 (m), 0.73-0.91(m);
**Synthesis of tetrahydro-3αH-[1,3]dithiolo[4,5-β]pyran-2-thione (2)**

In a round bottom flask, sodium hydrosulphide hydrate (1.10g, 19.69 mmol) was dissolved in DMF (15 mL) and carbon disulfide (1.49g, 19.69 mmol) was added to it at room temperature during a time span of 30 min. The reaction mixture was warmed to 40°C and 2,3-dichloropyran (2g, 13.00 mmol) in DMF (2 mL) was added to it and the reaction mixture was allowed to stir for an additional 2 hrs. Water (100 mL) was added to the reaction mixture followed by the addition of chloroform (75 mL). The chloroform layer was separated and washed with several aliquots of water to obtain a clear layer of chloroform, which was again separated from the aqueous layer and dried over anhydrous Na₂SO₄. Evaporation of the chloroform layer afforded a yellow colored mobile liquid, which was chromatographed on a silica gel column using a mixture of hexane and chloroform (2:1) as eluent. The first yellow band was collected and evaporated to yield a yellow color solid product. Yield 25% (3.21 mmol).

**1H NMR (C₆D₆):** $\delta = 0.71$ (dd, 1H, $J = 2$ Hz, 13.5 Hz), 0.84-1.04(m, 2H), 1.14-1.20(m, 1H), 2.75(dd, 1H, $J = 3$Hz, 12Hz), 3.42(dd, 1H, $J = 5$Hz, 12.6Hz), 3.50(dt, 1H, $J = 4$Hz, 12Hz), 4.71 (d, 1H, $J = 10$Hz); **13C NMR (C₆D₆):** $\delta = 220.27$, 94.60, 69.06, 60.35, 26.40, 24.75 ; IR (KBr): 1093 (C=S); mass spectra (m/z) (ESI⁺): 192.3 (100%, m/z) [C₆H₈S₃O (M⁺), 192]; mp: 73-74 °C.

**Synthesis of tetrahydro-3αH-[1,3]dithiolo[4,5-β]pyran-2-one (3)
A schlenk flask was charged with 2 (0.10g, 0.52 mmol) and dry dichloromethane (10 mL) was added to it at room temperature. Addition of acetic acid (1mL) and mercuric acetate (0.20g, 0.62 mmol) at room temperature changed the color of reaction mixture from yellow to white within an hour with a precipitation of a white solid. The reaction was stirred for 2 hrs and the solvent was evaporated in vacuo. The residue was dissolved in chloroform and passed through the silica gel column. The filtrates were combined and evaporated to get the pure off-white product. Yield 98% (0.50 mmol). $^1$H NMR (C$_6$D$_6$): $\delta = 0.72$-$0.78$ (m, 1H), $0.85$-$0.96$(m, 1H), $1.06$-$1.16$(m, 1H), $1.18$-$1.25$(m, 1H), 2.79-$2.87$ (m, 1H), 3.28-$3.36$(m, 1H), 3.42-$3.48$ (m, 1H), 4.66 (dd, 1H, J = 2Hz, 10Hz), $^{13}$C NMR (C$_6$D$_6$): $\delta = 188.95$, 91.27, 69.41, 55.36, 26.69, 25.79; IR (KBr): 1653 (C=O); mass spectra (m/z) (GC MS): 177 (25%, [M+H]) [C$_6$H$_8$S$_3$O (M$^+$), 176]. melting point 46-48 °C.

**Attempted synthesis of 6,7-dihyro-5H-[1,3]dithiolo[4,5-β]pyran-2-thione (4) using 3 and DDQ in toluene**

In a schlenk flask, solution of 2 (0.17g, 0.88 mmol) in dry toluene (10 mL) and DDQ (0.22g, 0.975 mmol) was refluxed for 48hrs. The solvent was evaporated in vacuo and the residue was chromatographed on a silica gel column using a mixture of hexane and chloroform (2:1) as eluent. The first fragment was pale yellow in color, which was analyzed by $^1$H, $^{13}$C NMR, IR, and GC-MS (yield: 10%). The second fragment was the starting material of the reaction (yield: ~65%). The third fragment was also dark yellow in color and analyzed by $^1$H, $^{13}$C NMR, and IR spectroscopies (yield 22%).
Attempted synthesis of 4 using 3 and DDQ in benzene

In a schlenk flask, a solution of 2 (0.170 g, 0.88 mmol) in dry benzene (10 mL) and DDQ (0.220 g, 0.975 mmol) was refluxed for 48 hrs. The solvent was evaporated in vacuo and the residue was chromatographed on a silica gel column using a mixture of hexane and chloroform (2:1) as eluent. The first fragment was the starting material (~15%). The second fragment was orange yellow in color, which was obtained using a mixture of hexane and chloroform (1:1) as eluent. This fraction showed closely separated multiple spots on TLC, therefore it was again run on preparatory TLC plate. The isolated bands still showed two merging spots.

1.6. Results and Discussions

The synthetic scheme of the pyran-dithiolene ligand is outlined in the Scheme 1. The precursor compound 3,4-dihydro-2H-pyran was reacted with Cl₂ gas in the pentane media to give pyran dichloride 1, which on the treatment with NaHS (or Na₂S) in CS₂ affords thione 2. To get the target ligand 5, 2 can be converted into 4 by reacting it with 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ), which will remove the reactive protons of C2 and C3 and generate a double bond. Later, 4 can be converted to 5 by reacting with Hg(AcO)₂ in acetic acid. In a different method, 2 will be converted to ketone 3, which can be converted to 5 by reacting it with DDQ or by NBS (N-bromosuccinimide) followed by treatment with Zn-dust.

Synthesis of 2,3-dichloropyran 1 follows the procedure described by Stone and Daves³⁰ and later by Crombie and Wyvill.³¹ In the reaction setup, chlorine gas was slowly passed using a thin Teflon tube through the cold solution of 3,4-dihydro-2H-pyran in dry
pentane. A vigorous reaction was observed with the change in the color of reaction mixture from clear to yellow. After 25 min of gas flow the reaction mixture settled down indicating the completion of the reaction, however, Cl₂ gas was allowed to flow through the reaction mixture for an additional 10 min to ensure the completion of the reaction. Argon was then bubbled through the reaction mixture to remove the dissolved Cl₂ gas and the solvent was removed under low pressure to yield a colorless liquid. The compound was purified using distillation under reduced pressure. ¹H and ¹³C NMR analyses showed that the compound (I) was obtained as a mixture of cis- and trans-isomers (Figure 6), which was consistent with the earlier analysis done by Lemieux and Fraser-Reid using NMR spectroscopy.³² They showed that the reaction product of such a reaction is always a mixture of cis and trans-isomers, which can be enriched with the thermodynamically favorable trans-isomer by equilibration with tetrabutylammonium chloride. Later, Stone and Daves identified that the use of different solvent systems can change the ratio of cis- and trans-isomers. In non-polar solvents like pentane, the cis-isomer is the major product (~80%), while polar solvents like tetrahydrofuran prefer trans-isomer as the major product (70%).

The generation of cis- and trans- mixture can be rationalized on the basis of simple mechanistic view,³¹ where the addition of a chloronium ion into 2,3 dihydropyran can generate intermediates of types A and B as shown in Scheme 2. Intermediate B can be stabilized due to the neighboring oxygen atom and therefore two resonating structure B1 and B2 can be drawn for the cation. In the case of cyclic chloronium cation A, entering of the second Cl⁻ ion will only be possible from the back side of the ring giving rise to a S₉N₂ type attack to yield the trans-products P1 and P2. This mechanism is
supported by the fact that the reaction with bromine and iodine afford only trans- product due to the major contribution of an intermediate of type A during the course of reaction. However, in the case of intermediate B1, the sp² hybridized planar cationic center could be attacked by the Cl⁻ from both sides of the plane and therefore give rise to the formation of cis- and trans- isomers. Based upon this analysis one may conclude that the chlorination of 2,3-dihydropyran always gives a mixture of cis- and trans-isomers. It is important to note that the trans-isomer P2 is thermodynamically more favorable than the P1 due to the sterically less hindered e,e (equatorial, equatorial) disposition of Cl groups. Similarly, P3 is the favorable cis-isomer due to the less 1, 3-dipolar-interaction between H and Cl atoms. It is interesting to note that the proton at the CHCl next to oxygen atom of pyran ring shows different coupling constants for the cis- and trans-isomers in the ¹H NMR spectrum. In the case of cis-isomer, it comes as a doublet with a coupling constant J = 3-4 Hz, while in trans-isomer the value of J <1 Hz, and therefore it appears as a singlet. On the basis of integration of these sets of peaks, we obtained 55: 45 mixtures of cis-(d, 5.86 ppm, J = 3Hz) vs trans-(s, 5.91 ppm) isomer in the reaction using pentane as solvent at –78 °C, which was less than that obtained by Stone and Daves using similar reaction conditions.³⁰ The probable reason may be the temperature fluctuations during the reaction period. We used the mixture of isomers of compound 1 in the synthesis of compound 2 without further purifications.

Compound 2 was synthesized by following the procedure reported by Hartke et al,³³ where they reacted cis-2,3-dichloro-1,4-dioxane with carbon disulfide and sodium sulfide in dimethylformamide to obtain cis-2,5-Dioxo-7,9-dithiabicyclo[4.3.0]nonan-8-thione (Figure 10). To obtain the cis- product of compound 2, the mixture of 2,3-dichloro
pyran (enriched with cis-isomer), was treated with the mixture of carbon disulfide and sodium hydrosulfide hydrate in dimethylformamide maintaining the temperature at 40 °C. After the completion of reaction (monitored by TLC analysis), it was quenched with water and extracted by chloroform. The chloroform layer was washed several times with water to remove the haziness of the layer and to obtain the clear transparent liquid. The layer was dried over anhydrous Na₂SO₄ and was evaporated under reduced pressure to obtain the clear yellow liquid. The yellow liquid was loaded on a silica gel column and eluted with the mixture of hexane and chloroform (2:1). The first yellow band was collected and evaporated to obtain a yellow crystalline compound in 25 % yield. We were expecting a low yield from the reaction as we started this reaction using a mixture of cis- and trans-isomers of 1. In the case of cis-2,3-dichloro-1,4-dioxane, a yield of (68%) has been reported because the pure cis-isomer was used in the reaction, which favors the 5-membered ring formation at the 2,3-position of the dioxane ring. Taking in to account that we had started with 55% of the cis-isomer, the calibrated yield of the final product can be assumed as 45%. The compound was analyzed by using ¹H and ¹³C NMR spectroscopy, mass spectrometry, and IR spectroscopy. ESI Mass spectrometry showed a peak for M⁺ at 192 (m/z) in the (+) ve mode and the isotope distribution pattern also matched with the theoretical isotope distribution of the molecular ion. A sharp melting point of the solid between 73-74 °C also showed the purity of the compound. ¹H NMR analysis was complicated due to the couplings (through bonds and through space) among protons of pyran ring. A doublet at 4.71 ppm can be assigned for the proton at C2 carbon on the basis of chemical shift and splitting pattern. The magnitude of the coupling
constant of C2 proton $J = 10\text{Hz}$, shows that the ring conformation of cis-isomer has been changed because of a new 5-member ring formation.

Proton single frequency decoupling experiments were conducted (in Bruker 300MHz spectrometer) to study the coupling among the protons and the results are shown in Figure 14. In addition to decoupling experiment, a two dimension $^1\text{H}-^1\text{H}$ COSY experiments were also performed and the assignments of the peaks were made on the results obtained. (Figure 13). An array of different pulse widths (pw) was used to find the $180^\circ$ pulse width with zero intensity of the proton at 4.71 ppm. Thus determined, pw = 11$\mu$s was used as the $180^\circ$ pulse (pw = 5.5$\mu$s for $90^\circ$ pulse) for the experiment. Analysis of the cross-peaks on COSY spectrum (Figure 13) shows that the doublet at 4.71 ppm is correlated with the multiplet at 3.5 ppm. Since proton at C2 is coupled with the proton at C3, we may assign the multiplet at 3.5 ppm for the proton at C3. The pattern shows that the multiplet is of dt (doublet of a triplet) type, which signifies the presence of three neighboring protons, which involves one proton from C2 and two protons from C4. Based on the chemical shifts, peaks at 2.75 ppm and 3.42 ppm can be assigned to the two protons of C6. Peak at 2.75 has a dt pattern, peak at 3.42 ppm has a dd (doublet of a doublet) pattern. Remaining four sets of multiplets in the up field region can be referred to the four protons of C4 and C5, which is supported by correlation and decoupling experiments. $^{13}$C NMR of compound 2 was easier to interpret because of only six-carbons in the molecule and the assignment of each carbon can be made on the basis of its chemical environment. A distinct peak at 220.3 ppm can be assigned to the thione group. A peak at 94.6 ppm can be assigned to the C2 due to the attachment with the two electron-withdrawing groups. Peaks at 69.06 and 60.35 can be assigned to the other peaks.
can be assigned to the C3 and C6 carbons, and peaks at 26.40 and 24.75 can be assigned to C4 and C5 respectively. Infrared spectrum of the compound has a signal at 1093 cm\(^{-1}\) for C=S stretch completing the full spectroscopic characterization of compound 2. It should be noted that the compound 2 has two chiral centers at C2 and C3 respectively; therefore this compound should be optically active. However, we have not attempted to find the optical rotation of 2. It is important to note that we wanted to dehydrogenate this compound and generate a double bond between C2 and C3 carbons, which will remove the optical activity of this complex by converting sp\(^3\) hybridized carbons to sp\(^2\) hybridized ones.

Compound 3 was synthesized by reacting 2 with mercuric acetate in the acetic acid.\(^{33}\) The color of the reaction mixture changed from pale yellow to white in one hour indicating the completion of the reaction. The progress of reaction was also monitored by TLC analysis, where only one spot was observed for the product. The purification of the product was done by dissolving the reaction mixture in chloroform and passing it through a silica pad. Evaporation of organic filtrate under reduced pressure gave a liquid compound, which turned into a white solid after some time. The sharp melting point between 46-48 °C shows that the compound was pure. Characterization of this compound was done by \(^1\)H and \(^{13}\)C NMR, IR spectroscopies, and GC MS. Comparison of \(^1\)H NMR spectra of compound 3 (Figure 15) and compound 2 shows similarities in the peak pattern; however, some shifts were observed in the chemical shift values. Also in the case 3, peaks of all eight protons are well resolved and distinct. Peak assignments of 3 were done with the help of COSY spectrum that is shown in Figure 16. It is interesting to note that the doublet of C2 proton has no prominent shift in the \(\delta\)-value, however, it is now
coupled with the peak (multiplet) at 3.35 ppm. It shows that the proton on C3 and one of the proton of C6 have switched their positions in 3, however, the second proton of C6 has shifted and come at 2.83 ppm. Four multiplets between 0.6-1.3ppm range can be assigned to the four protons of C4 and C5. $^{13}$C NMR shows a C=O peak at 189.2 ppm (Figure 15), which is about 30 ppm shifted then the thione 2. All other carbon peaks show no significant shift and can be directly compared with the $^{13}$C NMR of thione 2. In the IR spectra, the C=S stretch of 2 disappeared and new peaks between 1620-1730 cm$^{-1}$ appeared containing one carbonyl group most likely at 1723 cm$^{-1}$. Finally, GC-MS analysis showed a [M+H]$^+$ peak at 177 m/z with the identical isotope distribution.

A clean reaction of compound 3 shows that there was no ring opening in the pyran ring under strong acidic media. In other pyran related compounds like Garner’s organic ligand shows ring opening even weak silica media. This was an interesting result in terms of chemical stability of the ligand, which opens an alternative route ($3 \rightarrow 5$, Scheme 1) to synthesize the target compound. Once again we did not attempt to find the optical rotation of the molecule.

Insertion of a double bond between C2 and C3 carbon by DDQ is reported to be a facile reaction, however, the poor yields were reported.$^{33}$ When compound 2 was reacted with DDQ in toluene to get 4, the first fraction of the silica column was identified as an unusual product, characterized as an open ring alcohol (shown in Figure 18). This compound was identified on the basis of, $^{13}$C NMR, and IR spectroscopies (Figure 19). A simplified splitting pattern of methylene protons was observed in $^1$H NMR spectrum, which indicated that it was not a cyclic pyran type compound. The presence of aromatic protons showed that the solvent had reacted with the parent compound 2 and opened the
pyran ring. Signal at 4.8 ppm can be assigned to the methylene protons of the benzyl group attached to the compound. In the $^{13}$C NMR spectrum, there were signals for a double bond in addition to the aromatic carbons. Other important signal like C=S peak at 227 ppm was also there which showed that the five membered thione ring is probably intact. IR spectrum also supported the proposed structure (Figure 20). The second yellow spot was recovered as the unreacted compound. The third yellow fraction had signals for eight protons in the $^1$H NMR spectrum and its $^{13}$C NMR spectrum was very similar to the $^{13}$C NMR of 2 (Figure 21), which showed that there might be some ring rearrangement took place in the molecule. In any case it was not the target compound that we were looking for. Because toluene was reacting with the desired product, we tried benzene as a solvent under similar conditions. The first compound was absent but there were several closely separated spots shown on TLC analysis. A silica gel column was tried for the purification of the compounds but mixture of different spots was coming together. Even a preparatory TLC purification could also not give us the pure compound.

The other alternative routes to obtain target compound 5 are shown in Scheme 1. Compound 3 can be reacted with NBS (N-bromosuccinimide) in CCl$_4$ to brominate the C2 and C3 carbons selectively, which can be reacted further to Zn-dust to debrominate the molecule to get 5. In addition to that a DDQ reaction may also be tried with 3 to see the outcome.

1.7. Conclusion
Chemistry of biologically and commercially relevant dithiolene ligands has been discussed and a new synthetic route has been developed to synthesize a new dithiolene ligand containing a pyran ring. However, the final dithiolene compound 5 could not be achieved but initial compounds 1, 2, and 3 have been synthesized and characterized using several spectroscopic and spectrometric techniques. New synthetic schemes have been proposed to synthesize compound 5 using the same starting compounds.
1.8 Figures and Schemes

Figure 1: Some important dithiolene ligands used in earlier studies.

Figure 2: Different oxidation states of a dithiolene ligand in a nickel complex.
Figure 3: General routes to synthesize dithiolene ligands (adapted from reference 18).

Figure 4: The structure of MPT
Figure 5: The structures of few dithiolene ligands, which are used to synthesize the model complexes of MPT.
Scheme 1

3,4-dihydro-2H-pyran

Cl₂
Pentane, -78°C

Cl

NaHS·xH₂O

CS₂

Hg(CH₃COO)₂
AcOH

DDQ, Toluene

Hg(CH₃COO)₂
AcOH

1

2

3

4

5

(1)NBS, (2)Zn
or DDQ, toluene
Figure 6: $^1$H NMR of compound 1 in benzene-$d_6$.

Figure 7: $^{13}$C NMR of 1 in benzene-$d_6$, which shows 10 peaks indicating a mixture of cis- and trans-isomers.
Figure 8: ESI MS of 1 (2,3-dichloropyran) recorded in the positive mode. Only the [M-Cl]$^+$ ion is matched, which is consistent with the earlier reports.

Figure 9: Favored cis-and trans-isomers and their coupling constant values between proton on C2 and C3.
Scheme 2:

Figure 10: cis-2,5-Dioxo-7,9-dithiabicyclo[4.3.0]nonan-8-thione.
Figure 11: ESI MS of 2 in the positive mode.

Figure 12: $^1$H and $^{13}$C NMR of 2 in benzene-d$_6$ recorded at 500 MHz frequency.
Figure 13: $^1$H-$^1$H COSY spectrum of 2 done at 500 MHz frequency. Solvent: benzene-d$_6$ at room temperature.
Figure 14: Single frequency proton NMR decoupling experiments of 2 done at 300 MHz frequency (solvent: benzene-d$_6$). Solid bar shows the location of decoupler.

Figure 15: $^1$H and $^{13}$C NMR of compound 3 in benzene-d$_6$. 
Figure 16: $^1$H-$^1$H COSY experiment of compound 3 in benzene-d$_6$. 
Figure 17: Infrared spectra of 2 and 3.
Figure 18: 4-benzyl-5-(3-hydroxypropyl)-1,3-dithiole-2-thione. An unusual side product from the reaction between 2 and DDQ in refluxing toluene.

Figure 19: $^1$H and $^{13}$C NMR of 6 in benzene-$d_6$ and chloroform-$d$ respectively.
Figure 20: Infrared and GC MS spectra of 6.
Figure 21: $^1$H and $^{13}$C NMR of third spot from the reaction between 2 and DDQ in toluene media. Spectra recorded in benzene-d$_6$. $^{13}$C NMR shows similar peaks as 2. $^1$H NMR has eight proton signals.
1.9 References


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Chapter 2

Dithiolene Complexes of Nickel

2.1. Introduction

Nickel complexes with sulfur coordination spheres have been known to act as model complexes for the active sites of nickel enzymes. However, the interest in nickel complexes with sulfur containing ligands is not only limited to bioinorganic chemistry but also in materials chemistry. Nickel complexes with sulfur donors are known to possess properties such as metallic-conductivity\(^1\), optical nonlinearity\(^2\), ability to reversibly react with olefins through a redox couple leading to olefin purification\(^3\), near IR absorbers in laser Q-switch dyes\(^4\) and others. These applications arise due to a combination of functional properties, specific geometries and intermolecular interactions.

Nickel-dithiolenes represent a class of bis-dithiolene complexes, which show important, and unusual properties such as the very intense electronic transition in the near IR, the capability to exist in different well-defined oxidation states connected through reversible processes and electrical conductivity. These square planar complexes exhibit a high degree of electron delocalization in the ring, including the metal ("aromaticity"), which is responsible for the low energy electronic absorption assigned to a \(\pi \rightarrow \pi^*\) transition between the HOMO and the LUMO, which occurs at unusually low energy. This extensive electron delocalization, while making these complexes useful as near-infrared (NIR) dyes, is irrelevant to intramolecular charge transfer, a crucial factor in generating second order nonlinear optical (NLO) properties. Nickel dithiolene complexes can exist in three member electron transfer series.
This series also shows that nickel dithiolene complex can exist in three forms: dianionic, monoanionic, and neutral which can be differentiated by spectroscopy and magnetic moment calculations.

2.1.1. Types of dithiolene complexes

There are two classes of dithiolenes: bis dithiolene and tris dithiolene. In bis dithiolenes, the ligands are arranged in square planar fashion with all S-M-S bond angles very close to 90°. Depending on the central metal, the neutral bis dithiolene may exist as planar monomers or dimers with either metal-metal bonds or with metal sulfur bonds (Figure 1). Examples of this class are the diamagnetic d⁸ complexes of Ni, Pd and Pt. In tris-dithiolenes, the ligands are arranged in trigonal prismatic geometry rather than octahedral coordination geometries. Examples of this class are the ditholenes of Cr, Mo, W. The neutral tris-dithiolenes exhibit trigonal prismatic arrangement but anionic tris dithiolenes exhibit distorted octahedral geometry because the increased charge density on the sulfur atoms leads to the repulsive interactions for which the octahedral coordination geometries is preferred. In this chapter, we will discuss the synthesis and characterization of bis-dithiolene complexes of nickel.

2.1.2. Syntheses of nickel-dithiolene complexes

2.1.2.1 Complexes derived from dianionic dithiolates

The ligands that are most readily available as dianion dithiolates are Na₂S₂C₂(CN)₂ (Na-mnt) and Na₂S₂C₂H₂. Treatment of these ligands with nickel salts in aqueous or
alcoholic solutions resulted in the formation of dianionic species, \([\text{NiS}_4\text{C}_4(\text{CN})_4]^{2-}\) or \([\text{NiS}_4\text{C}_4\text{H}_4]^{2-}\). Bahr and Schleitzer\(^9\) synthesized the ligand, maleonitrile dithiolate (mnt) by dimerization of sodium dicyanodithioformate in water for 24 hours via a spontaneous desulfurization; improved yields were reported for the same reaction in refluxing chloroform for 8 hours. Similarly, Schroth and Peschel prepared the parent unsubstituted ligand sodium salt of cis-1,2-ethylenedithiol (Na\(_2\text{S}_2\text{C}_2\text{H}_2\))\(^5\). They reacted cis-1,2-dichloroethylene, benzyl chloride and thiourea in refluxing ethanol to obtain dibenzylidithioether which was further reacted with sodium in liquid ammonia, the benzyl groups were cleaved, forming the disodium salt of the dianion.

2.1.2.2. Complexes derived from dithietenes

The neutral nickel complex of bis-perfluoromethylidithiolenes was obtained from the direct reaction between the nickel carbonyl and the dithietene, \(\text{S}_2\text{C}_2(\text{CF}_3)_2\).\(^6\)

\[
\text{Ni}(\text{CO})_4 + 2(\text{CF}_3)_2\text{C}_2\text{S}_2 \rightarrow [\text{NiS}_4\text{C}_4(\text{CF}_3)_4]^+ + 4\text{CO} \quad \text{(1)}
\]

2.1.2.3. Complexes derived from Arene-1,2-dithiols

The dianionic and monoanionic complexes of nickel were obtained by treatment of the divalent nickel salts with the disodium salts of benzene-1,2-dithiol, and its derivatives. Similarly, the dianionic nickel complex\(^7\) of quinoxaline-2,3-dithiol was synthesized by treating the nickel salts with the ligand in the presence of base.

2.1.2.4. Complexes derived from disubstituted ethylene dithiophosphoric esters

The neutral complexes of nickel\(^8\) were synthesized by the reaction of thiophosphoric ester in hot dioxane or xylene with the suitable nickel salts e.g. halides, acetates, acetylacetonate, or carbonyl solubilized in water, ethanol or benzene. The metal salts employed in this reaction was in its lowest oxidation state, since the use of metal ions in high
oxidation states necessitated the use of larger amounts of thio-ester, which functioned as the reducing as well as the complexing agent. Neutral complexes of the nickel group containing many different alkyl or aryl groups have been synthesized using this methodology.

2.1.2.5. Complexes derived from oxidation of dianionic dithiolene complexes

The oxidation of anionic dithiolene complexes may be achieved by using a number of different oxidizing agents. The actual choice of reagents depends on the values of the half-wave potentials for the one or two-electron transfer reactions. The most common oxidizing agents are air, iodine, oxygen, and in special cases, the powerful one-electron oxidizing agents $[\text{Ni(tfd)}_2]$.

2.1.2.6. Complexes derived from reduction of neutral dithiolene complexes

Similarly, the reduction of neutral dithiolene complexes may be achieved by using a number of different reducing agents. The choice of reducing agents depends on the half-wave potentials for the desired reaction. Common reducing agents include $o$- and $p$-phenylenediamine, hydrazine, borohydride ion, zinc in pyridine, amalgams, and alkali metal alkoxides. In some cases, weakly basic solvents such as ketones or alcohols affect one-electron reductions. Among these reducing agents, hydrazine was found to have disadvantages because of its reaction with the complex. In the reduction of $[\text{NiS}_x\text{C}_4\text{Ph}_4]^9$, hydrazine was retained in the reduced complex after it had been isolated.

2.1.2.7. Complexes derived from ligand-exchange reactions

The dithiolene complex act as oxidizing agents and this raised an interesting problem that in reactions incorporating these complexes, whether ligand-exchange reaction or scrambling took place, i.e.

$$\text{NiS}_x\text{C}_4(\text{CF}_3)_4 + [(\text{C}_6\text{H}_4)_x\text{N}]_2[\text{PdS}_x\text{C}_4(\text{CN})_4] \rightarrow [(\text{C}_6\text{H}_4)_x\text{N}]_2[\text{PdS}_x\text{C}_4(\text{CN})_4] + [(\text{C}_6\text{H}_4)_x\text{N}]_2[\text{NiS}_x\text{C}_4(\text{CF}_3)_4]$$ \quad (2)
These reactions were studied by the polarographic method. It was discovered that when neutral complex and dianionic complex or two monoanionic complexes were refluxed together, the products were mainly monoanionic complexes, as illustrated in the above example.

### 2.1.3. General Characteristics of nickel-dithiolene complexes

#### 2.1.3.1. Electronic spectra of nickel dithiolene complexes

Earlier attempts have been made to assign the electronic transitions of the Ni-dithiolene complexes and have been reviewed by McCleverty.\(^{10}\) The most characteristic feature of the neutral, monoanionic and some dianionic complexes are the intense absorptions occurring at low lying energy levels in the visible and near infra red regions. The high extinction coefficient in the neutral complexes shows that the nature of these bands is of charge transfer type rather than of d-d transitions. In an earlier work Schrauzer and Mayweg\(^{11}\) assigned the strong low energy absorptions in \(\text{[NiS}_4\text{C}_4\text{R}_4]^{0,1^-}\) as \(\pi \rightarrow \pi\) charge transfer transitions, which was sensitive to the inductive effect of \(R\) groups in oxidized dithiolenes and hence, involved molecular orbitals extending over the whole molecule. In the monoanionic complexes, this inter \(\pi\) transition was shifted to longer wavelength and with diminished intensity. The reason for this hypsochromic shift was the \(2b_1\text{u}\) orbital, which derived most of its character from ligand \(\pi\) orbitals just like the \(3b_2\text{g}\) orbital and its absolute energy was dependent on a substituent effect.

In the dianions, however, the low energy transitions were absent but d-d transitions were observed which were assigned as \(d_x^2 - 2y^2 \rightarrow d_{xy}\). Similarly, in case of \(\text{[NiS}_4\text{C}_4(\text{CN})_4]^{2^-}\), Gray and his colleagues\(^{12}\) assigned the spectral transitions, which were similar to those of
Schrauzer and Mayweg\textsuperscript{11}, but differences occurred in the description of the low-energy charge transfer bands. The observed electronic spectrum of $[\text{NiS}_4\text{C}_4(\text{CN})_4]^{-2}$ consists of two $L \rightarrow M$ charge transfer bands shown by square planar halides, the $M \rightarrow L$ band system shown by square planar cyanides. In case of the monoanions, the low energy intense band was assigned to a $L(\pi) \rightarrow M$ transition.

2.1.3.2. Electronic structures of nickel dithiolene complexes

Extensive studies have been undertaken to describe the electronic structure and the spectroscopic features of metallo dithiolene complexes. The MO calculations have been done on the Ni-dithiolene complexes, where the results show the dependency on the relative ordering of the valence molecular orbitals as well as the degree of covalence between metal-sulfur bonds. In the earlier studies Schrauzer and Mayweg formulated a resonance structure of $[\text{MS}_4\text{C}_4(\text{R}_4)]^0$, where $M=\text{Ni}$ and $R=\text{H}$ (see Figure 2, Chapter 1), where a divalent Ni-ion is complexed by two spin paired monoanions. The essential feature of the electronic structure of the neutral molecule was the behavior of the lowest unoccupied ligand $\pi$ molecular orbitals and their interaction with the central metal ion orbitals. Hoffman et al have presented a MO diagram for simple $[\text{Ni(edt)}_2]$ complex,\textsuperscript{13} where edt = ethylene dithiolate. The electronic structure description is quite complex, however, a simple picture can be drawn from their results. The energy of the five $d$-orbitals of Ni follows the typical behavior of a square planar complex. The presence of low-lying filled ligand orbitals shows their $\pi$ or $\sigma$ donor behavior. The metal $d_{xy}$ orbital is raised considerably in energy due to a mixing of a $\sigma$-type dithiolene orbital of the same symmetry. This severe destabilization of the $d_{xy}$ orbital
disfavors the electron occupation and therefore neither Ni(I) nor Ni(0) state electronic configuration is anticipated for these complexes.

Figure 2 in chapter 1 shows that depending upon the type of dithiolene ligand; it may exist as radial anionic or neutral forms. It is interesting to note that when the valence ionization energy of the dithiolene ligand is similar to that of metal, a highly covalent situation emerges and a description of formal oxidation states for Ni and the dithiolene becomes somewhat ambiguous. This similarity of valence ionization energy of metal and ligand give rise to the non-innocent behavior of these ligands. An extreme case of non-innocence of these ligands in the [M(dithiolene)₂]₀, 1⁻, 2⁻ is described by Holm et al (Figure 2)¹⁴. Different oxidation states of Ni are assumed due to the large destabilization of the metal dₓᵧ orbital. However, ground state spectroscopic results support the Ni(II) state of these complexes.

In a recent work, Holm et al have synthesized and structurally characterized all three forms of [Ni(C₂S₂Me₂)₂]z complex, where z = 0, -1, and -2.¹⁴ All complexes have similar features in their electronic spectra as other dithiolene complexes discussed above. To describe the electronic transitions, density functional theory (DFT) calculations on the crystallographically defined and optimized structures of [NiS₄C₄Me₄]ⁿ were performed. As shown in Figure 3, the ground state for [NiS₄C₄Me₄]₀ was calculated as ….(18a₁g)²(4b₃g)²(6b₁u)²(5b₂g)⁰(13b₁g)⁰… The orbital composition, shown in Table 1, shows that the highest occupied molecular orbital (HOMO) of the neutral complex (6b₁u) is primarily ligand based with a very small contribution from the metal 4pₓ orbital. The lowest unoccupied molecular orbital (LUMO) of the neutral complex (5b₂g) becomes the singly occupied molecular orbital (SOMO) in the case of monoanionic complex and a HOMO in
the case of dianionic complex. According to Schrauzer and Mayweg the intense transition at the low-lying energy regions can be assigned as $6b_{1u} \rightarrow 5b_{2g}$. Because of the ligand-based character of the HOMO, the effects of substituents on the dithiolene complexes are very prominent in the electronic spectra of neutral as well as monoanionic complexes. In the case of monoanionic complex the $3b_{2g}$ orbital became half-filled and in dianionic complex it is totally filled. The half filling of the $5b_{2g}$ orbital in monoanion complex alters the separation $6b_{1u} \rightarrow 5b_{2g}$ through secondary interaction thus resulting a less intense band in low energy region. However, in the case of dianionic complex the occupation of $5b_{2g}$ by two electrons would cause low energy transition to vanish.

Aragoni et al\textsuperscript{40} has performed a hybrid-DFT calculation to get an insight on the properties of the Ni-dithiolene complexes. They have also found a ligand based HOMO for complexes having variety of substituents on dithiolene complexes of Ni. A pictorial representation of the HOMO and LUMO of $[\text{Ni(C}_2\text{S}_2\text{Me}_2)_2]$ is given in the (Figure 4A), which shows that the LUMO has a small contribution from the Ni atomic orbitals. Similar results were also obtained by Hoffman et al,\textsuperscript{15} who calculated the spin densities localized on the individual atoms of a well known complex $\text{Ni(mnt)}_2^-$ using ENDOR and ESEEM spectroscopies (Figure 4B). Their Extended Hückel and DFT calculations show that the SOMO orbital of $\text{Ni(mnt)}_2^-$ is $b_{2g}$ and primarily a ligand based orbital.

2.1.3.3. Electrochemical studies of nickel dithiolene complexes

The growth of the chemistry of 1,2-dithiolene complexes was partly due to the discovery of facile one- and two-electron transfer reactions exhibited by these species. McCleverty\textsuperscript{10} and Wang\textsuperscript{16} have considered the electrochemistry of the 1,2-dithiolene complexes in great
The following aspects of the electro-chemical behavior of planar bis dithiolene nickel complexes were noted:

(a) Reduced species with a redox potential < 0.00 V can be oxidized by air in solution, whereas reduced species with redox potential > 0.00 V are air-stable.

(b) Oxidized species with a redox potential > 0.20 V can be reduced by weakly basic solvents such as ketones or alcohols.

(c) Oxidized species with redox potential lying between +0.20 V and -0.12 V can be reduced by stronger bases such as aromatic amines (e.g. α- or p- phenylenediamines).

(d) Oxidized species with redox potential < (-0.10 V) are readily reduced by strong reducing agents such as hydrazine, sodium amalgam, zinc in pyridine or alkali metals in ethanol.

(e) Reduced species with redox potential > (+0.40 V) can be oxidized by iodine, or by oxidizing agents like [NiS₄C₄(CF₃)₄] which can undergo one-electron transfer reaction.

Therefore, it was emphasized that care should be taken while choosing the oxidizing and reducing agents because certain agents like hydrazine can act as coordinating ligands. It was also realized that reductions of oxidized species in couples that have a value more negative than -0.95 V or the oxidation of the reduced species that have a value more positive than +0.95 V are not possible by chemical means as reagents capable of this action destroy the complexes.

2.1.3.4. Infrared studies of nickel dithiolene complexes
Three characteristic absorption bands $\nu_1$, $\nu_2$, $\nu_3$ are usually observed in the infrared spectra of nickel dithiolene complexes in the region between 3000 and 600 cm$^{-1}$. $\nu_1$ and $\nu_2$ are described as the perturbed “C=C” and “C=S” stretching frequencies, respectively, whereas $\nu_3$ can be assigned as the stretching vibration of the group, which is strongly substituent dependent. Metal sulfur stretching frequencies occurs in the region between 490 and 300 cm$^{-1}$. These frequencies also depend on the nature of the ligand substituent R, and vary with the overall charge, z, on the complexes. Thus, when the overall charge decreased i.e. when the complexes are oxidized, the electrons are being withdrawn from ligand molecular orbitals and thus ligand gets oxidized from dithiolates to dithioketones. This causes the shortening of the C-S bond and lengthening of the C=C or ethylenic bond. In case of dianions, the lengthening of C-S bond occurs which suggests the reduction of ligand to dithiolato dianions.

2.1.3.5. X-Ray Photoelectron Spectral (XPS) studies of nickel dithiolene complexes

The ionization energies of electrons can be determined by using Einstein relationship:

$$E_i = h\nu - E_e$$

Where, $E_i$ is the ionization energy, $h\nu$ is the X-ray energy, and $E_e$ is the kinetic energy of the ejected photoelectron. The binding energy of the electron, which is closely related to the ionization energy, is influenced by the electron density surrounding the atom and by the structural arrangement of other atoms within the solid. The core binding energies of electron of the central atom varies as the valence electron density of the atom is charged through a series of bonding conditions. The binding energy can be determined by X-ray photoelectron spectroscopy. XPS has been used to understand the bonding in transition metal dithiolenes,
as the metal and sulfur binding energies can be related to the charges on the atoms. Grim and colleagues have determined the binding energies for the metal and sulfur atoms in $[M(mnt)_{2}]^{1-2-}$ and $[M(S_{2}C_{2}Ph_{2})_{2}]^{0-2-}$ (M = Ni, Pd, Pt). Initially, the data were interpreted in terms of Ni being assigned a formal oxidation state of ‘0’ with the additional charge residing on the ligands. It was discovered that the binding energies of Ni(II) overlap with those of Ni(0) compounds, and that was the electronegativity of the ligands affect the binding energies significantly. Thus in the series $[Ni(S_{2}C_{2}Ph_{2})_{2}]^{z}$ (z = 0, 1-, 2-), the binding energies of the sulfur decreases as z decreases from 0 to 2-, which indicates that charge resides largely on the sulfur atoms. However, in case of mnt complexes, metal and sulfur binding energies are constant, which indicates that in gaining an electron the extra negative charge is delocalized over the electronegative cyanide group. Further, in case of paramagnetic monoanions, the unpaired electron primarily resides on the ligand, which is proved by the absence of fine structure in the XPS. This also proves that metal exists in +2 oxidation state with the extra negative charge residing primarily on the ligands and also demonstrates the valence electron delocalization in the complexes. Hoyer and coworkers determined the XPS of $[M(S_{2}C_{2}H_{2})_{2}]^{n}$ (M = Ni or Cu; n = 0 or 1-) and found the charge at the sulfur atoms dependent on the total charge on the complexes.

2.1.3.6. EPR and ENDOR-ESEEM studies of nickel dithiolene complexes

Nickel dithiolene complexes display a redox activity over all three oxidation states without perturbing their square planar geometry. Extensive studies have been done on the electronic structure of square planar metallo-bis (dithiolenes) to understand the changes, which occur in their oxidation states, and to understand whether the observed redox activity is ligand or metal based. The paramagnetic nickel dithiolenes are the best systems to study...
the above properties as they contain the unpaired electron. These complexes are studied by techniques such as EPR, electron-nuclear double resonance (ENDOR), and electron spin echo envelope modulation (ESEEM) spectroscopies.

In earlier work of EPR studies, Holm, Maki, and coworkers\textsuperscript{22,23} conducted their studies on paramagnetic $[\text{Ni}(\text{mnt})_2]^{1-}$ complex and revealed that 50-80\% of the spin density localized on the four sulfur atoms of the dithiolene ligand. Similarly, Hoffman and coworkers determined the spin density localized on the cyano-carbon, cyano-nitrogen and ethylene-carbons on $[\text{Ni}(\text{mnt})_2]^{1-}$ by using a ENDOR-ESEEM spectroscopies.\textsuperscript{13} They interpreted that 10\% of the unpaired spin density resides on the olefinic carbon atoms, 4\% on the cyano nitrogen indicating that the bulk of the unpaired spin density resides on the NiS\textsubscript{4} core. Extended Huckel and DFT calculations support these results.\textsuperscript{24}

\textbf{2.1.4. Applications of nickel-dithiolene complexes}

Nickel dithiolene complexes possess a wide variety of applications owing to their planar structure, one-electron transfer reactions, low energy absorption in the visible or NIR region. Here, we discuss some of the important applications of nickel dithiolene complexes.

\textit{2.1.4.1. Separation and purification of olefins using nickel dithiolene complex:}

In the chemical and petrochemical industry, olefins are the largest volume feedstock and are used in the production of polymers, acids, alcohols, esters, and ethers\textsuperscript{25}. Generally, olefins are produced by steam or catalytic cracking and separated by cryogenic distillation\textsuperscript{26}. The latter is an energy intensive process that contributes roughly 75 \% of the overall olefin production cost\textsuperscript{27}. It was found that the use of chemically specific separation reagents driven by electrical energy is a potentially inexpensive and efficient approach for separation of olefins. It has been reported that redox active copper salts reacts with olefins reversibly but
the only drawback was that carbon monoxide, acetylenes, and hydrogen sulfide poison these metal systems.

In 1965, Schrauzer et al. first reported that \([\text{M(S}_2\text{C}_2\text{Ph}_2)_2]\) (\(\text{M} = \text{Ni, Pd, Pt}\)) reacts with unsaturated hydrocarbons like substituted but-1,3-dienes, cyclic 1,3-dienes, 1,3,5-cyclooctatriene, cyclooctatetraene, and norbornadiene forming 1:1 adducts. These adducts were generally insoluble in organic solvents, thermally unstable, and often decomposed on exposure to light. Further, the electronic spectra of these adducts showed that the intense absorptions in the visible region associated with the oxidized dithiolenes were absent and also the infrared frequencies associated with the oxidized dithiolenes were absent. Thus, it was suggested that these complexes contain dithiolate ligands. However, the spectral data and the lability of these complexes also indicated that they were not simple transition metal \(\pi\)-complexes. It was further indicated that there was an interaction with the sulfur atoms of one dithiolene had occurred thus forming labile C-S bonds. Later, Wing et. al. reported that \(\text{Ni[S}_2\text{C}_2(\text{CF}_3)_2]\) reacts with norbornadiene and 2,3-di-methyl-1,3-butadiene to form 1:1 olefin adducts, where the olefin binds to ligand S atoms rather than the metal. But the major contribution came from Wang and Stiefel, where they applied these dithiolene complexes in the purification of olefins. They reacted simple aliphatic olefins with \(\text{Ni[S}_2\text{C}_2(\text{CF}_3)_2]\) and found that these complexes are capable of binding olefins when they are in their oxidized state and form 1:1 adduct with the olefins. Further, by the electrochemical studies on \([\text{Ni(mnt)}_2]\), they found out that the nickel dithiolene complexes are capable of binding olefins reversibly by a redox switch. By adding or removing an electron changes the oxidation states of the complexes, the oxidized state binds the olefin and the reduced state releases it. On the basis of their results, they proposed the electrochemically driven olefin
separation and purification (Figure 5), where the electrochemically generated neutral dithiolene binds the olefin and further releases it on the electrochemical reduction of the adduct. Further, they found that the nickel dithiolenes are tolerant to catalytic poisoning due to the materials present in the olefin stream because the olefin binding occurs through the sulfur ligand rather than the metal center. Thus, the olefin can be separated and purified by the other components present in the olefin stream.

2.1.4.2. Nickel dithiolenes as near Infra Red dyes

The intense electronic transition in the near IR region, ability to exist in well defined oxidation states, high thermal stability and photo stability towards long wavelength radiation, makes nickel dithiolene complexes useful substrates in Q-switches and mode-locking applications for different IR lasers. The dye molecule serve as bleachable absorbers to allow bleaching of dye solution at a desirable level of photon flux and placing such a dye solution into the laser cavity affects the conversion of low power CW radiation into very short and extremely intense pulses. Drexhage and Mueller-Westerhoff were the first ones to apply this technique to the Q-switching of the Nd glass and Nd-YAG lasers, using nickel dithiolene.\textsuperscript{30} It was observed that dithiolenes withstand long term exposure to IR radiation while most of the organic dyes, which absorb in this region, show low photo stability and decompose instantly. Higher delocalization within the nickel dithiolene complexes make them more useful applicants in these systems than that of Pd and Pt analogues.\textsuperscript{31,32,33} Most of them absorb at wavelength higher than 700nm\textsuperscript{34,35,36,37} with extinction coefficients of at least 20,000dm\textsuperscript{3} mol\textsuperscript{-1} cm\textsuperscript{-1}. Many investigations focused on the influence of the ligand on the properties of the complexes and to increase the intensity of the absorption to the maximum at lower energy. It was further concluded that dithiolene complexes should
contain an extended π architecture with electron donating substituents, which are coplanar with the nickel dithiolene unit, and sterically bulky substituents in order to increase the solubility. Several symmetrical and unsymmetrical nickel complexes were synthesized with these concepts. Some of the ligands used in these complexes are shown in Figure 6. Most of these complexes are neutral with large λ values and high extinction coefficients. Few of these complexes absorbs at ~ 1000nm with a molar extinction coefficient of 80,000 dm$^3$ mol$^{-1}$ cm$^{-1}$, one of the largest values reported in the literature.

2.1.4.3. Nickel dithiolenes as conducting materials

Bis nickel dithiolene complexes possess an extended delocalized core with central metal, four sulfurs and the C=C units. In a few cases, this delocalization can be further extended by choice of appropriate groups, which lead to a number of important properties:

(a) Low energy absorption in the visible or NIR region.
(b) Distribution of frontier orbitals over much or the entire molecule.
(c) Electrochemical behavior with one or more reversible redox processes.
(d) Large sulfur atoms compose part of the delocalized core and can mediate intermolecular interactions.

The above-mentioned properties allow the design and assembly of electronic materials such as conducting and magnetic solids. Although the first dithiolene ligands were synthesized as early as 1957, it was only in 1969 that electrical properties of some bis- and tris- dithiolenes were studied and reported. Since then, intensive research has been done for electrical conductors and superconductors using dithiolene complexes, mainly, bis-dithiolene square planar d$^8$ metal complexes. In 1980, the first dithiolene complex was synthesized and characterized which exhibited metal like conductivity, $(\text{Perylene})_2[\text{Pt(mnt)}_2]$ (Per=C$_{20}$H$_{12}$).
but in this compound perylene organic molecule was responsible for the conductivity instead of dithiolene moiety. Hence, the first reported dithiolene complex which exhibited metal like conductivity was (H$_3$O) Li[Pt(mnt)$_2$]·1.67H$_2$O.$^{44}$ Later on, in 1975, Steimecke et.al reported the dmit$^2^-$ ligand,$^{45}$ which proved to be precursors to conducting and magnetic molecular systems. There are nearly 380 complexes of dmit$^2^-$ that were used as conducting and magnetic materials. Another good candidate for preparation of conducting materials was dddt$^2^-$ (Figure 7); Vance et.al$^{46}$ first reported its complex in 1985. It has been known that metal-bis-1,2-dithiolenes possess similarity to organic electron donors of the tetrathiafulvalene (TTF) family with the central metal in place of the C=C bond, so [M(dddt)$_2$] are nearly similar to BEDT-TTF (Figure 7) donor molecule and thus, has been extensively used in the preparation of molecular organic superconductors. Several other ligands and their metal complexes have been synthesized and characterized which are used as conducting and magnetic materials. Reviews by Faulmann et. al,$^{47}$ Robertson et. al,$^{48}$ and Ouahab$^{49}$ describe the conducting and magnetic assemblies of the dithiolene complexes in detail.

Besides the above applications, nickel dithiolene complexes also possess second and third –order nonlinear optical properties and considered as promising candidates for all optical signal processing devices.$^{50,51,52,53}$

2.1.4.4. Use of neutral nickel dithiolene complex as ligand exchange reaction with molybdenum hexacarbonyl

Holm et.al have developed and modified a route, originally reported by Schrauzer et. al,$^{54}$ to synthesize bis(dithiolene) monooxo molybdenum complexes.$^{55}$ They used neutral nickel bisdithiolene complex of the dithiolene ligand, which cannot be isolated in free form.
The nickel complex undergoes ligand exchange reaction with tricarbonyl precursor of molybdenum to give dicarbonyl complex of bis(dithiolene) molybdenum complex as shown in reaction (3)

\[
[\text{Mo}(\text{CO})_4(\text{MeCN})_2] + 2[\text{Ni}(S_2C_2R_2)_2] \rightarrow [\text{Mo}(\text{CO})_2(S_2C_2R_2)_2] + [\text{Ni}^{II}_2(S_2C_2R_2)_2] + 3\text{MeCN} + \text{CO}
\]

In the above reaction, by transferring a dithiolene moiety from nickel to the molybdenum center, the oxidation state of molybdenum was changed from zero to four. The dicarbonyl precursor of molybdenum was further reacted with Et₄NOH to give the monooxo bis(dithiolene) molybdenum complex. This route was helpful to synthesize bisdithiolene complex of the ligands, which cannot be isolated in the free dithiol form.

In our project we planned to synthesize the monooxo(dithiolene)molybdenum complex to mimic the active site of molybdoenzymes (discussed in chapter 3). To initiate the project, we chose the dithiolene ligand with meta-substituted phenyl moiety (scheme1), which cannot be obtained in the free dithiol form. This ligand can be easily reacted with a nickel salt to produce the nickel dithiolene complex by adopting the method of Schrauzer et.al.⁸,⁹ The neutral form of this nickel dithiolene complex can be reacted with carbonyl complexes of molybdenum by following the methodology of Holm et.al.⁵⁵ to give the target molybdenum dithiolene complex.

2.2. Experimental

All the experiments were performed in oven-dried glasswares. Unless specified, all reactions were performed under an atmosphere of argon using Schlenk and dry box techniques. Reaction mixtures were stirred magnetically. The majority of the chemicals was purchased from Aldrich and Acros chemicals and was used as received without further
purification. Commercial grade solvents were dried and distilled before use. Dioxane, hexane, tetrahydrofuran, toluene and diethyl ether were dried and distilled over Na-wire/benzophenone; methanol and ethanol were refluxed over Mg-turnings/iodine; methylene chloride were dried and distilled over CaH₂; acetonitrile was distilled over P₂O₅. Dry dimethylsulfoxide and dry dimethylformamide were obtained from Acros chemicals.

Room temperature ¹H and ¹³C NMR spectra were recorded using a Bruker ACP-300 spectrometer at 300.133 MHz and 75.469 MHz frequencies, respectively. Mass spectra were recorded in a Waters LCQ ESI/APCI Quadropole Mass spectrometer in ESI and/or APCI modes. Gas Chromatography mass spectrometry was performed at Varian 3410 high temperature gas chromatograph coupled to a Varian Saturn II ion trap mass spectrometer. Electronic spectra were recorded in Cary 3 and Cary 18 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1760X spectrometer on NaCl plates or in KBr pellets. Electrochemical investigations were performed at room temperature using CV-50W voltammetric analyzer with a typical three-electrode system: platinum or graphite-working electrode, Ag/AgNO₃-reference electrode, and Pt wire-auxiliary electrode. 0.1M TBAP (tetrabutyl ammonium perchlorate) was used as a supporting electrolyte solution. Redox potentials are referenced internally with respect to a ferrocene/ferrocenium (Fc/Fc⁺) redox couple by adding Fc into the electrolytic mixture. Magnetic susceptibility measurements were done on a Johnson-Matthey Evans Balance. Conductivity measurements were recorded on a VWR conductivity meter.

Synthesis of 3,5-dibromobenzaldehyde
In a round bottom flask 1, 3, 5 tri-bromobenzene (1g, 3 mmol) and anhydrous diethyl ether (10 mL) was placed under an argon atmosphere. The contents were cooled to −78°C (acetone-dry ice) and n-butyllithium (2 mL of 2.5 M in hexane solution, 3 mmol) was added at an even rate over 30 min while maintaining the internal temperature at −78°C. The solution was stirred for an additional 30 min. After 30 min, to the same solution dry DMF (1.06 mL, 8.4 mmol) was added at −78°C. The solution was further stirred for 1 hr. After stirring, the reaction mixture was hydrolyzed with 2 N HCl (100mL) and the contents were extracted with ether. The ether layer was dried over MgSO$_4$ and the solvent was evaporated to get 630 mg of a white solid. Yield : 80% (2.39 mmol).

$^1$H NMR (CDCl$_3$): δ = 9.99(s, 1H), 7.95(s, 3H); $^{13}$C NMR (CDCl$_3$): δ = 189 (C=O), 139, 138, 131, 124 (aromatic); IR (KBr): 1693 (C=O); GC-MS: 263 (100%, m/z) [C$_7$H$_4$Br$_2$O (M$^+$), 263.8].

**Syntheses of 3,5-dibromobenzoin and 3,5-dibromobenzil.**

1$^{st}$ Method:

A mixture of 3,5-dibromobenzaldehyde (300mg, 1.136 mmol) dissolved in ethanol (7mL) and KCN (36mg, 0.568 mmol) dissolved in water (4mL), stirred for 10 min. Then, the contents were heated at 80°C in a water bath for overnight. The reaction mixture was shook with saturated aqueous NaHCO$_3$ solution and extracted with chloroform followed by diethyl ether. Both organic layers were washed with saturated aqueous NaHSO$_3$ solution and dried over Na$_2$SO$_4$. After evaporation chloroform layer yielded a pale yellow solid (benzil, 113 mg, 0.21 mmol) and etheral layer yielded a yellow solid (benzoin, 50 mg, 0.094 mmol).
Benzil: $^1$H NMR (CDCl$_3$): $\delta = 8.05$ (s, 2H, aromatic), 7.8 (s, 1H, aromatic); $^{13}$C NMR (CDCl$_3$): $\delta = 164$ (C=O), 138, 134, 131, 123 (aromatic); IR (KBr): 1642 (C=O). Yield = 38%.

Benzoin (cis and trans mixture): $^1$H NMR (CDCl$_3$): $\delta = 8.0$ (s, aromatic), 7.8 (s, aromatic); 7.5 (s, aromatic), 6.4 (br, s, CHOH), 5.9 (br, s, CHOH); $^{13}$C NMR (CDCl$_3$): $\delta = 164$ (C=O), 142, 138, 134, 133, 131, 128, 122 (aromatic), 72 (CHOH); IR (KBr): 1727 (C=O). Yield = 17%.

2nd Method:

3,5-dibromobenzaldehyde (3.14g, 11.89 mmol) was taken in schlenck flask and dissolved in DMF (12mL) at room temperature under argon atmosphere. Tetra butyl ammonium bromide (0.32g, 1.0 mmol) followed by KCN (0.015g, 0.211 mmol) was added into the above reaction mixture under argon atmosphere and the resulting solution was stirred at room temperature under argon atmosphere for 18-20 hours. The solvent was distilled and the resulting residue was poured in water and extracted with DCM. The organic extracts were washed with brine and dried over MgSO$_4$. The gummy material obtained after evaporation of solvent was crystallized at a low temperature by keeping the material in a refrigerator. The product was recrystallized using DCM/EtOH to obtain a solid. The colored solid material was yellow. Yield: 30%, (3.56 mmol)

Synthesis of $\text{(Bu}_4\text{N})[\text{Ni(S}_2\text{C}_2(\text{C}_6\text{H}_3\text{Br}_2)_2)_2]$

In a 250ml Schlenk flask, 3,3',5,5'-tetrabromobenzil or benzoin (0.940g, 1.787 mmol), P$_4$S$_{10}$ (1.58g, 3.574 mmol) and dry dioxane (7mL) were added under argon atmosphere and the mixture was refluxed at 110ºC for 5-6 hrs. After refluxing, the reaction
was filtered to remove unreacted P₄S₁₀ and washed with a minimal quantity of dioxane. To the filtrate, NiCl₂·6H₂O (0.472g, 1.988 mmol) dissolved in 1mL. of distilled water was added. The mixture was refluxed at 90°C for 2hrs. After 90 minutes tetrabutylammonium bromide was added to the reaction mixture and stirred overnight without refluxing. The solvent was evaporated, and the oily residue was washed with petroleum-ether several times. Recrystallization was done by dissolving the residue in warm DCM and adding isopropanol (dropwise) while keeping the mixture over water-bath. After addition, the contents were left overnight for crystallization. A deep reddish violet colored crystalline compound was formed. Yield: (47.6%, 0.426 mmol.). Absorption spectrum (dichloromethane) λ max, nm (εM, mol⁻¹cm⁻¹): 280 (23000), 320 (25000), 380 (sh, 13000), 518 (2000), 680 (500), 934 (5000). Mass spectra (m/z) (ESI-): 1173 (100%, m/z) [C₂₈H₁₂S₄Br₈Ni (M⁻), 1173].

Synthesis of [Ni(S₂C₂(C₆H₃Br₂)₂)₂]

In a 250ml Schlenk flask, 3,3',5,5'- tetrabromobenzil or benzoin (0.32g, 0.61 mmol), P₄S₁₀ (0.53g, 1.2 mmol) and dry dioxane (7 mL) were added under argon atmosphere and the mixture was refluxed at 110 °C for 5-6 hrs. After refluxing, the reaction was filtered to remove unreacted P₄S₁₀ and washed with minimal quantity of dioxane. To the filtrate, NiCl₂·6H₂O (0.16g, 0.68 mmol.) in distilled EtOH (5mL) was added. After addition, the color of reaction mixture changed to reddish brown. The whole mixture was refluxed and stirred at 90°C for 2hrs, and the reaction flask was capped and kept in refrigerator for 20 hrs. Excess P₄S₁₀ precipitated out and was centrifuged and a clear reddish brown solution was evaporated. The residue was dissolved in a minimal quantity of
dichloromethane, and MeOH was added as a precipitant to give crystalline green colored compound. Yield: (12%, 0.07 mmol.). Absorption spectrum (dichloromethane) $\lambda_{\text{max}}$, nm ($\varepsilon_m$, mol$^{-1}$cm$^{-1}$): 270 (43000), 316 (60000), 383 (sh, 11803) 582 (2200), 834 (30,662). mass spectra (m/z) (ESI-): 1173 (100%, m/z) [C$_{28}$H$_{12}$S$_4$Br$_8$Ni (M$^-$), 1173].

**Attempted synthesis of (Et$_4$N)$_2$[Ni(S$_2$C$_2$(C$_6$H$_5$)$_2$)$_2$]$m_2$**

In a Schlenk flask, sodium was added to a solution of anthracene in 2 mL of THF in anaerobic condition. The dark blue solution was stirred for 6 ~ 7hrs and then filtered. The filtrate was added dropwise by a cannula to a solution of neutral Ni–complex in 2mL of THF. As the reaction proceeded, the mixture became reddish violet. The solution was stirred overnight and then a solution of Et$_4$NBr in acetonitrile was added. The solvent was evaporated and the residue was washed with ether. The residue was dissolved in a minimal quantity of acetonitrile, filtered and layered with ether. The reddish violet crystalline compound was obtained. The data of this compound matched with the monoanionic nickel complex.

**Synthesis of [Ni(S$_2$C$_2$(C$_6$H$_5$)$_2$)$_2$]**

In a 500mL Schlenk flask, benzil or benzoin (5g, 23.8 mmol), P$_4$S$_{10}$ (21.1g, 47.6 mmol) and dry dioxane (7mL) were added under argon atmosphere and the mixture was refluxed at 110ºC for 5-6h. After refluxing, the reaction was filtered to remove unreacted P$_4$S$_{10}$ and washed with minimal quantity of dioxane. To the filtrate, NiCl$_2$·6H$_2$O (6.27g, 26.4 mmol) in distilled water (1mL) was added. The mixture was refluxed at 90ºC for 2hrs. A green colored compound was isolated, which was filtered and washed with methanol,
water. The crude product was recrystallized using dichloromethane/MeOH. Yield: (30%, 7.19 mmol). Absorption spectrum (dichloromethane) $\lambda_{\text{max}}$, nm ($\varepsilon_{\text{M}}$, mol$^{-1}$cm$^{-1}$): 312 (44074), 371 (sh, 10785), 437 (sh, 2643), 596 (1920), 852 (27475). mass spectra (m/z) (ESI-): 542 (100%, m/z) [C$_{28}$H$_{20}$S$_4$Ni (M$^-$), 542].

**Synthesis of $[$Et$_4$N$] $[\text{Ni(S}_2\text{C}_2\text{(C}_6\text{H}_5)_2\text{)}_2]$**

**1$^{\text{st}}$ Method:**

In a schlenk flask, the neutral Ni-complex (0.1g, 0.18 mmol) was dissolved in THF and stirred. In another schlenck flask, (Et$_4$N)(BH$_4$) (0.03g, 0.18 mmol) was dissolved in acetonitrile. The (Et$_4$N)(BH$_4$) solution was transferred into the solution of neutral Ni-complex by using cannula. The color of mixture changed from bluish green to reddish – violet. The mixture was stirred for nearly 21 hrs. The solvent was evaporated off and the residue was redissolved in acetonitrile and filtered to get reddish- violet filtrate and orange colored compound as a residue. The filtrate was concentrated and layered with ether to get reddish violet compound with some white color impurity, which was redissolved in THF and filtered to get clear reddish violet solution. The solvent was evaporated to give reddish violet compound. Recrystallization was done by dissolving the crude product in hot acetone and adding methanol as a precipitant. The reddish purple colored compound was obtained which was washed with methanol and dried in vacuo. Yield: (12.1%, 0.02 mmol.). Absorption Spectrum (dichloromethane) $\lambda_{\text{max}}$, nm ($\varepsilon_{\text{M}}$, mol$^{-1}$cm$^{-1}$): 264 (38320), 313 (43639), 367 (sh, 12637), 528 (1624), 680 (500), 935 (15217). mass spectra (m/z) (ESI-): 542 (100%, m/z) [C$_{28}$H$_{20}$S$_4$Ni (M$^-$), 542].

**2$^{\text{nd}}$ Method:**
In a Schlenk flask, neutral Ni-complex (0.500g, 0.92 mmol) and p-phenylene diamine (0.25g, 2.3 mmol) were dissolved in dry methyl sulfoxide (10mL). The reaction mixture was stirred and color of mixture changed from dark green to reddish brown. After 2hrs of stirring, the mixture was poured into a solution of Et₄NBr (0.42g, 2.01 mmol) in EtOH (15mL). Red crystalline compound was recrystallized using hot acetone/MeOH to give dark purple red compound, which was washed with cold methanol and dried under reduced pressure. Yield: (55%, 0.51 mmol).

**Attempted synthesis of (Et₄N)₂[Ni(S₂C₂(C₆H₅)₂)₂]**

In a Schlenk flask, fresh sodium (0.01g, 0.37 mmol) was added to a solution of anthracene (0.065g, 0.37 mmol) in 2 mL of THF in anaerobic condition. The dark blue solution was stirred for 6-7 hrs and then filtered. The filtrate was added dropwise by a cannula to a solution of neutral Ni–complex (0.1g, 0.18 mmol) in THF (2mL). As the reaction proceeded, the reaction mixture became reddish violet. The solution was stirred overnight and then solution of Et₄NBr (0.08g, 0.37 mmol) in acetonitrile was added. The solvent was evaporated and the residue was washed with diethyl ether. The residue was dissolved in minimal quantity of acetonitrile, filtered and layered with ether. The dark purple colored compound was obtained that matched well with the monoanionic form of nickel complexes.

**Synthesis of [Bu₄N]₂[Ni(S₂C₂(CN)₂]**

In a flask, Na₂mnt (1.71g, 9.24 mmol) was dissolved in 30 mL of ethanol/water (1:1) and stirred. In another flask, dissolve NiCl₂·6H₂O (1g, 4.2 mmol) in 7.5 mL of H₂O
and add in Na₂mnt solution slowly with stirring. The dark red solution was formed which was further stirred for 5 minutes after the addition was complete and then the solution was filtered. To the filtrate, tetrabutylammonium bromide dissolved in ethanol was added slowly with agitation, which separated orange red crystals immediately. The crystals were separated by filtration, washed with H₂O (10 mL) followed by ethanol/water (10 mL, 1:1) and dried. Recrystallization was done by dissolving the crystals in hot boiling acetone (80 mL), filtered, then adding isobutylalcohol (35 mL) slowly to the filtrate. The mixture was sat at room temperature overnight. The next day, deep red crystals of the complex formed, which were collected and washed with isobutylalcohol followed by hexane. Yield: (45.2%, 1.89 mmol.). Absorption Spectrum (acetonitrile) \( \lambda_{\text{max}} \), nm (\( \epsilon_M \), mol⁻¹ cm⁻¹): 377 (8258), 468 (4474), 514 (1736), 855 (80). mass spectra (m/z) (ESI-): 338 (100%, m/z) [C₈S₄N₄Ni (M⁻), 338].

**Synthesis of [Bu₄N][Ni(S₂C₂(CN)₂]**

An iodine solution (0.3g, 1.2 mmol) in methylsulfoxide (1mL) was added in one portion to the solution of dianionic complex of Ni (mnt)₂ (0.5g, 0.75 mmol) in methylsulfoxide (4 mL). The mixture was immediately added to ethanol (12.7mL) and stirred for 20-30 min at room temperature. The black crystalline compound was isolated, filtered and washed with ethanol (5-6 times) followed by ether. Recrystallization was done by dissolving the compound in hot acetone and adding ether. Keeping the mixture overnight at room temperature gives black crystalline compound. Yield: (65.3%, 0.4 mmol.). Absorption spectrum (acetonitrile) \( \lambda_{\text{max}} \), nm (\( \epsilon_M \), mol⁻¹ cm⁻¹): 346 (sh, 11372), 475
(2510), 538 (670), 602 (461), 863 (9700). mass spectra (m/z) (ESI-): 338 (100%, m/z) 
\[C_8S_4N_4Ni (M^{-}), 338]\.

Attempted synthesis of \([\text{Ni}(S_2C_2\text{CN})_2]\)

The dianionic complex of Ni \((\text{mnt})_2\) (0.05g, 0.075 mmol) was dissolved in acetonitrile and ceric ammonium nitrate (0.05g, 0.075 mmol) dissolved in acetonitrile was added into the above reaction mixture. The reaction mixture was stirred for 2-3 days to give dark brown color mixture. The solvent was evaporated producing a black colored compound, which on characterization showed the features of monoanionic Ni(mnt)_2 complex.

2.3. Results and Discussions
2.3.1. Synthesis and Characterization of Ligand

Scheme 1 presents a synthetic route for a new 3,5-dibromophenyl dithiolene ligand and its nickel complex \([\text{Ni}\{C_2S_2(C_6H_3Br_2)_2\}_2]\) (1). The synthetically available 1,3,5-tribromo benzene was reacted with n-butyl lithium to form 3,5-dibromophenyllithium, which was not isolated and further reacted with DMF to form 3,5-dibromobenzaldehyde (1a). The standard workup procedure yields a good yield of the product, which was not purified further. The product was analyzed by using \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR spectroscopy, GC-MS and IR spectroscopy. A singlet at 9.9 ppm was the characteristic peak of aldehyde proton in the \(^1\text{H}\) NMR spectrum (Figure 8). A peak at 189 ppm was the characteristic peak of carbonyl followed by 4 aromatic peaks in the \(^{13}\text{C}\) NMR spectrum (Figure 8). In GC-MS, the molecular ion peak was at 263 m/z. IR spectrum had a characteristic carbonyl stretch of
substituted benzaldehyde at 1693 cm$^{-1}$. 1a was further reacted with an ethanolic solution of potassium cyanide to undergo benzoin condensation to form its benzoin. Here we obtained a mixture of benzoin (1b) and benzil (1c) (oxidized product of benzoin), which was analyzed by TLC and purified by extraction with two different solvents. The products were analyzed by $^1$H, $^{13}$C NMR and IR spectroscopy. The spectroscopic results for 1c reveal a symmetric structure (Figure 9), however the characteristic peaks at 6.4 and 5.9 ppm in proton spectrum showed the presence of isomers in benzoin. The yields of both compounds were low, which might be due to the deactivating nature of the Br-group at the both meta positions of the phenyl ring. In a different procedure, we have obtained a better yield to synthesize pure 1b by reacting 1a with KCN and Bu$_4$NBr in DMF solution under inert atmosphere.$^{56}$ 1b and 1c were reacted with P$_2$S$_5$ under inert atmosphere to make the thiophosphoric ester (1d). It is interesting to note that both benzil and benzoin are reported to form the same thiophosphoric ester; $^{57}$ therefore the isolation of benzil and benzoin in the previous step was not necessary. Schrauzer et al have isolated the first thiophosphoric ester (I) from benzoin (shown in Figure 10) and showed the applicability in the syntheses of transition metal complexes and organic compounds. $^8$ In our case, we have not checked the stability of 1d and it was used for Ni-complex formation without isolation and purification as described in literature.

### 2.3.2. Synthesis of Nickel dithiolene Complexes

The neutral and anionic nickel complexes of 1 were obtained from the method initially developed by Schrauzer et al $^9$ and later modified by Holm et al. $^{57}$ Reaction of thiophosphoric ester (1d) with the Ni (II) salts, generally hydrated NiCl$_2$, gave a reddish-
brown solution (Scheme 1). The green colored neutral \( [\text{Ni}\{\text{C}_2\text{S}_2(\text{C}_6\text{H}_3\text{Br}_2)\}_2] \) 1 was obtained by evaporating the solvent followed by redissolving the residue in minimal amount of methylenechloride and precipitating it by adding excess of methanol and leaving the mixture at low temperature for overnight. The monoanionic \( [\text{Ni}\{\text{C}_2\text{S}_2(\text{C}_6\text{H}_3\text{Br}_2)\}_2]^- \) was synthesized by using the similar procedure for neutral complex, but after 90 min of stirring of \( 1d \) and \( \text{NiCl}_2 \), a stoichiometric amount of \((\text{Bu}_4\text{N})\text{Br}\) was added to the reaction mixture. The compound was initially obtained as a red violet colored oil, which was washed with petroleum ether/hexane and recrystallized by a mixture of methylene chloride and 2-propanol to get a reddish violet needle shaped crystalline compound. The reduction of neutral \( [\text{Ni}(\text{C}_2\text{S}_2\text{Me}_2)_2] \) could be reduced to dianionic \( [\text{Ni}(\text{C}_2\text{S}_2\text{Me}_2)_2]^{2-} \) with sodium anthracenide.\(^{14}\) Therefore, the synthesis of dianionic \( [\text{Ni}\{\text{C}_2\text{S}_2(\text{C}_6\text{H}_3\text{Br}_2)\}_2]^{2-} \) was attempted by reducing the neutral complex of 1 with sodium anthracenide but only the monoanionic complex was obtained.

Several other nickel dithiolene complexes have also been synthesized in neutral and anionic forms (Figure 11). The dianionic and monoanionic forms of \( \text{Ni}(\text{mnt})_2 \) (2) were synthesized using the published procedures.\(^6\) The two forms differ in color and are stable in air. Attempts to make the neutral form of 2 by using strong oxidizing agent e.g.; \((\text{NH}_4)_2\text{Ce(NO}_3)_6\) were failed, which yielded mono anionic form of 2. Earlier studies have also reported unsuccessful results for the synthesis of neutral complex of 2. Complex \( [\text{Ni}(\text{C}_2\text{S}_2\text{Ph}_2)_2] \) (3) was also synthesized by using the reported procedures.\(^9\) Here we were able to synthesize the neutral and monoanionic forms for complex 3. Attempts for synthesizing dianionic complex of 3 by using sodium anthracenide yielded the monoanionic complex. It is interesting to note that the chemical oxidation (or reduction) of
these complexes strongly depends on the nature of substituents on the dithiolene ligand. However, formation of all forms of Ni dithiolene can be seen in the electrochemical studies.

2.3.3. Characterization of Complexes

2.3.3.1. Mass Spectrum

The syntheses of [Ni\{C_2S_2(C_6H_3Br_2)\}_2] and other complexes were confirmed by electrospray ionization mass spectrometry (ESIMS) in the negative ion mode. The characteristic molecular ion peaks for Ni-complexes were detected with the 100% intensity. Neutral and monoanionic complex of 1 gave a base peak at 1173 m/z for M^-, which matches with the theoretical mass spectrum of the complexes (Figure 12). Similarly other complexes were also analyzed (Figures 13 and 14) and the molecular ion peak was detected in the negative mode. The dianionic complex of 3 was not detected in the m/z range; however M^- peak was detected as the base peak like in the case of monoanionic form.

2.3.3.2. Electronic Spectroscopy of Complexes

As discussed in section 2.1.3.1, electronic absorption spectroscopy is an excellent tool to define the neutral or anionic nature of the Ni-dithiolene complexes. A strong absorption band at the low energy region (near IR region) is a characteristic of neutral complex, which shifts to the low energy with diminished intensity in the monoanionic complex and vanishes in the dianionic complex.

Electronic spectra of the neutral and monoanionic complexes of 1 were recorded in methylene chloride at the room temperature and given in (Figure 15). The near IR features of
complexes were compared with the features of neutral and anionic complexes of 2 and 3 (Figure 16), which shows a direct similarity in the electronic transitions. The position of the maxima in the low energy region is strongly dependent on the electronic nature of the substituent on the dithiolene ligand. In the case of monoanionic complexes consisting different groups on the dithiolene ligand, the low energy band shifts to the lower energy (or higher wavelength) side with the increase of the electron releasing character of the substituent. For example, among the given complexes 2 has a strong EWG ‘CN’ then complex 1, which has 3,5-dibromo group, and then 3 with phenyl group on the dithiolene ligand, therefore, the low energy \( \lambda_{\text{max}} \) follows the following trend: \( 2 > 3 > 1 \). Similar results can also be seen in the neutral Ni-dithiolene complexes \([\text{Ni}\{(\text{S}_2\text{C}_2\text{(p-C}_6\text{H}_4\text{X)}_2\})_2\}\] reported by Holm et al.\(^{57}\) A consistent change in the band maxima can be seen in the \([\text{Ni}\{(\text{S}_2\text{C}_2\text{(p-C}_6\text{H}_4\text{X)}_2\})_2\}\] complexes, where a shift towards the lower energy with the EWG at the \textit{para} position on the phenyl group has been observed.\(^{57}\)

2.3.3.3. \textit{Infra Red Spectroscopy of Complexes}

As described in the section 2.1.2.4., three characteristic absorption bands are usually observed in the IR spectra of nickel dithiolene complexes. In the monoanionic complex of 1, the band at 1356-1361 cm\(^{-1}\) may be assigned to the perturbed C=C stretch and the band at 1200 cm\(^{-1}\) corresponds to the perturbed C=S bond. Further the band at 900 cm\(^{-1}\) is tentatively assigned to the stretching vibration of the group as shown in Figure 17.

2.3.3.4. \textit{Electrochemical Studies of Complexes}

Electrochemical properties of all Ni-complexes were studied by using cyclic voltammetry in methylene chloride and acetonitrile. A standard three-electrode system (Pt-
disk: working electrode; Pt wire: auxiliary electrode; Ag\(^+\)/Ag: reference electrode) was used for the measurements. (Figure 18) shows a cyclic voltammogram for complex 1. There are two 1-electron waves for complex 1 were observed, which can be assigned as \([\text{Ni}\{\text{C}_2\text{S}_2(\text{C}_6\text{H}_3\text{Br}_2)_2\}_2]/[\text{Ni}\{\text{C}_2\text{S}_2(\text{C}_6\text{H}_3\text{Br}_2)_2\}_2]^2^-\) (a) and \([\text{Ni}\{\text{C}_2\text{S}_2(\text{C}_6\text{H}_3\text{Br}_2)_2\}_2]/[\text{Ni}\{\text{C}_2\text{S}_2(\text{C}_6\text{H}_3\text{Br}_2)_2\}_2]^2^-\) (b) redox couples. The peak assignments were based upon the potential range of the redox signal. The reversibility of redox waves was determined by plotting the current of the peak (oxidation or reduction) maxima with the square root of the scan rate. The linear relation shows the reversible behavior of the redox couples.

Redox properties of these complexes are strongly influenced by the substituents on the dithiolene ligands because of the ligand-based nature of the HOMO. Holm et al\(^{57}\) have shown a Hammett type linear relationship between reduction potential of \([\text{Ni}\{(\text{S}_2\text{C}_2(\rho-\text{C}_6\text{H}_4\text{X})_2\}_2]\) complexes. Again, like electronic transitions, there is no general linear relation is observed for the reduction potential with Hammett parameters.

### 2.3.3.5. Conductivity measurements of Complexes

Conductivities were measured in the solution phase in nitromethane (spectrograde) at room temperature. Calculations were done using the formula:

\[
\Lambda_M = \frac{\kappa}{[C]}
\]

where \(\Lambda_M\) = molar conductance and its unit is ohm\(^{-1}\)cm\(^2\)mol\(^{-1}\), \(\kappa\) = specific conductance, and \([C]\) is the molar concentration of the complex. Table 2 shows the \(\Lambda_M\) values for the electrolytic nature of different complexes. The anion vs. cation ratio of the electrolytes was determined by comparing the \(\Lambda_M\) values with the general range for different electrolytes in nitromethane solution.\(^{58}\) For example the \(\Lambda_M\) values 63-69 for complex 1-3 show the 1:1...
electrolytic composition of the complexes and because the general range for 1:1 electrolyte in nitromethane is 60 to 115 ohm⁻¹cm²mole⁻¹. Similarly the 1:2 electrolyte has a ΛM range of 115-250 ohm⁻¹cm²mole⁻¹, which includes one of the dianionic complexes of 3. The molar conductance of neutral complexes is zero because of their non-electrolytic nature.

2.3.3.6. Magnetic measurements of Complexes

Magnetic susceptibilities were measured at 293K. The instrument was calibrated using CoCl₂.6H₂O and CuSO₄.5H₂O as standards. Mass susceptibility was calculated using the below given formula:

\[
\chi_g = \frac{C_{Bal}l(R-R_0)}{m} \times 10^{-9}
\]

where, l = sample length (cm), m = sample mass (gm), R₀ = voltage deflection (instrument reading) due to the empty tube, R = voltage deflection due to the sample in the tube, , and C_{Bal} = balance calibration constant (1.042).

The molar susceptibility was calculated using the formula,

\[
\chi_m = \chi_g \times \text{molecular weight}
\]

In order to accurately determine the magnetic response from the unpaired electrons of the sample, the magnetic response from all filled electron shells (which are diamagnetic) in all atoms of the sample was subtracted out from the value of molar susceptibility. Thus, the corrected molar susceptibility was calculated by:

\[
\chi_A = \chi_m - (\text{sum of all diamagnetic correction factors})
\]

The effective magnetic moment was calculated using the below given formula:

\[
\mu_{eff} = 2.828 \sqrt{\chi_A T}
\]
The effective magnetic moment, which has units of Bohr Magnetons, reflects the number of unpaired electrons \((n)\) in a molecule. The values for \(\mu_{\text{eff}}\) as a function of \(n\) can be calculated from the following formula:

\[
\mu_{\text{eff}} = \sqrt{n(n + 2)}
\]

The results of the magnetic moment of the complexes are tabulated in the Table 2. Complexes having \(\mu_{\text{eff}}\) around 1.77 have one unpaired electron in the complex and therefore have paramagnetic nature. Complexes having \(\mu_{\text{eff}} = 0\), have no unpaired electrons and therefore they are diamagnetic in nature.

### 2.4. Conclusion

(1) The new neutral and monoanionic forms of nickel dithiolene complexes with meta-substituted phenyl moiety (1) were synthesized and characterized by various spectroscopic techniques.

(2) The nickel dithiolene complexes with “phenyl” (2) and “CN”(3) groups were also synthesized and characterized.
2.5 Figures and Schemes

Figure 1: Dithiolenes exist as monomer and dimer forms.

Figure 2: Non-innocent behavior of dithiolene complexes. (adapted from Reference 14.)
Figure 3: Energy level diagrams for members of the series $[\text{Ni(S}_2\text{C}_2\text{Me}_2)]^{0, 1, 2-}$ obtained by the DFT calculation. (Figure adapted from reference 14.)

Figure 4: HOMO and LUMO of $[\text{Ni(C}_2\text{S}_2\text{Me}_2)]_2$ complex (adapted from reference 40.); (B) SOMO of $[\text{Ni(mnt)}_2]^{1-}$ (adapted from reference 15)
Figure 5: Electrochemically driven olefin separation. (adapted from Reference 3.)

Figure 6: Ligands for near IR dyes
Figure 7: Electrical conductors.

Figure 8: NMR Spectra of 3,5-dibromobenzaldehyde.
Figure 9: NMR Spectra of 3,5-dibromobenzil

Figure 10: Adapted from reference 8.
Figure 11: Other Ni complexes

Calculated isotopic distribution

Experimental result

Figure 12. Mass spectrum of 1 in ESI- mode.

Figure 13: Mass spectrum of 2 in ESI- mode.
Figure 14: Mass spectrum of 3 in ESI- mode.

Figure 15: Electronic Spectra of 1 in methylene chloride.
Figure 16: Electronic spectra of 2 and 3.

Figure 17. IR spectrum of 1 in KBr pellet.
Figure 18: (A) Redox couples for complex 1 in methylene chloride, Pt: working electrode, Pt-wire: auxiliary electrode, Ag/AgNO₃: reference electrode, TBAP: supporting electrolyte. (B) Plot of current vs. square root of scan rate.
Scheme 1

\[
\text{Br-Br-Br} \xrightarrow{n-\text{BuLi}, (\text{CH}_3)_2\text{NC(O)H}} \text{Br-Br-Br} \xrightarrow{\text{KCN}} \text{Br-Br-Br} + \text{Br-Br-Br}
\]

\[
\text{S-S-S-Ni} \xrightarrow{0/1-} \text{S-S-S-Ni} \xleftarrow{\text{Ni}^{2+}} \text{S-S-S-P}_{\text{S-S}}\]

2.6 Tables

Table 1. Composition of the selected orbitals of $[\text{Ni(S}_2\text{C}_2\text{Me}_2)_2]^z$ (adapted from 14)

<table>
<thead>
<tr>
<th>MO</th>
<th>$z$</th>
<th>Ni(3d$_{xz}$)</th>
<th>Ni(3d$_{yz}$)</th>
<th>Ni(4p$_z$)</th>
<th>S(3p$_z$)</th>
<th>C(2p$_z$)</th>
<th>H(1s)</th>
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<tr>
<td>5b$_{2g}$</td>
<td>0</td>
<td>13.31</td>
<td></td>
<td>59.20</td>
<td>24.97</td>
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<td></td>
<td>1-</td>
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<td>1.64</td>
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<td></td>
<td>49.48</td>
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<td>5.61</td>
<td>43.37</td>
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<td>1-</td>
<td>5.17</td>
<td>50.32</td>
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<tr>
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<td>2-</td>
<td>77.32</td>
<td>12.12</td>
<td>7.83</td>
<td>1.45</td>
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</table>

Table 1: Characteristic table of six nickel dithiolene complexes.

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<tr>
<th>Complex$^z$</th>
<th>Base Peak</th>
<th>Electronic Spectra $\varepsilon$ ($\lambda$)</th>
<th>Electrochemistry $E_{1/2}$ ($\Delta E$) mV Vs. $F_{C^+}$ / $F_C$</th>
<th>$\mu_{eff}$ B.M.</th>
<th>$\Lambda_M$ Ohm$^{-1}$ cm$^2$ mol$^{-1}$ in nitromethane</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>1173</td>
<td>30,662 (834)</td>
<td>-288 (114)</td>
<td>~0</td>
<td>Non-conducting</td>
</tr>
<tr>
<td>1$^{1-}$</td>
<td>1173</td>
<td>6500 (927)</td>
<td>-1065 (130)</td>
<td>1.77</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>542</td>
<td>27,500 (852)</td>
<td>-258 (94)</td>
<td>~0</td>
<td>Non-conducting</td>
</tr>
<tr>
<td>2$^{1-}$</td>
<td>542</td>
<td>15,200 (935)</td>
<td>-1275 (133)</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>3$^2$</td>
<td>338</td>
<td>80 (855)</td>
<td>-262 (68.5)</td>
<td>~ 0</td>
<td>187</td>
</tr>
<tr>
<td>3$^{1-}$</td>
<td>338</td>
<td>9700 (863)</td>
<td></td>
<td>1.54</td>
<td>69</td>
</tr>
</tbody>
</table>

$z$ = Charge
2.7 References


Chapter 3

Dithiolene Complexes of Molybdenum: Models for Mononuclear Molybdenum Oxotransferases

3.1. Introduction

Molybdenum is the only second-row transition metal, which is known for the biological functions. Its importance in biological systems has been known for 80 years. It is required by bacteria, fungi, archaea, plants, animals and even humans for their metabolic activities. The requirement for molybdenum by these organisms is due to its presence at the active sites of metalloenzymes. These metalloenzymes play a key role in the metabolism of nitrogen, sulfur, carbon, arsenic, selenium and chlorine compounds. Molybdenum also plays a vital role in the biogeochemistry of nitrogen, sulfur, carbon, arsenic, selenium and chlorine compounds. Molybdenum is one of the minor components found in the earth’s crust but it is widely used for the biological processes. Molybdenum is the most abundant transition metal in the sea at a concentration of about 110 nM, but it is present at about 50 nM in case of terrestrial environments. It is not surprising, thus, that molybdenum has been widely incorporated into biological systems.

Molybdenum enzymes can be broadly divided into two classes of families based upon the number of metal atoms involved in the catalytic active site of enzymes. The first class is so called iron-molybdenum cofactor, or FeMoco, that is present in the enzyme called nitrogenase, one of the multinuclear molybdoenzymes. The crystal structure of nitrogenase at 2.2 Å resolution shows that the cofactor consists of two sulfur bridged
cuboidal fragments, one containing four iron-four sulfur atoms, and the other three iron-three sulfur and the molybdenum atom (Figure 1). The second class is known as mononuclear molybdoenzymes, which require only one metal center to perform the catalytic reactions. It is interesting to note that in all mononuclear molybdenum enzymes, one or two organic cofactor(s) is necessary for the catalytic activity of the enzymes and is termed the pyranopterin cofactor. This cofactor, in the case of molybdenum, is termed as molybdenum cofactor or Moco (Figure 2). The properties of this cofactor have already been discussed in chapter 1. The term Moco refers to the metal center and its inner coordination sphere, which means it is not a single, unique moiety, but rather a diverse collection of protein bound sites that have certain common features like coordination of one or two MPTs (see chapter 1) via the dithiolene group and the remainder of the metal’s coordination sphere. The metal coordination sphere is taken up by non-protein ligands like oxo, hydroxo, water, or sulfido groups, and in some cases, an amino acid side chain is coordinated. In this chapter, we will focus on the study of mononuclear molybdoenzymes.

3.2. Classification of the mononuclear molybdenum enzymes

Hille has subdivided the mononuclear molybdenum enzymes into three families: sulfite oxidase, DMSO reductase, and xanthine oxidase based on the number of oxo-ligands and dithiolene ligands associated with the molybdenum center (Figure 3). The representative members of each family have now been crystallographically characterized. The common features exist among the three families are the dithiolene ligand, the existence of molybdenum between IV, V, and VI oxidation states, the presence of at least
one oxo ligand coordinated to molybdenum. These mononuclear molybdoenzymes are often referred to as oxo-molybdenum enzymes because of the presence of oxo ligand. The three families are differentiated on the basis of terminal oxo versus sulfido ligation at molybdenum, number of dithiolene ligands coordinated to molybdenum center, and the presence of prosthetic groups.

3.2.1. The Eukaryotic oxotransferases or Sulfite Oxidase (SO) family

The sulfite oxidase family is characterized by the presence of a single dithiolene unit, dioxo group coordinated to molybdenum center, and a monodentate thiolate ligand (Figure 3). The enzymes of this family catalyze the oxygen atom transfer reactions and thus known as oxotransferases. The sulfite oxidase family consists of sulfite oxidase (isolated from chicken or rat liver) and assimilatory nitrate reductase (obtained from algae and higher plants) family of enzymes. The crystal structure of chicken sulfite oxidase shows the presence of one cis-MoO$_2$ unit in the active site of oxidized species along with the single pyranopterin cofactor. In this enzyme, the molybdenum is coordinated by five ligands with square pyramidal coordination geometry. The equatorial plane is occupied by three sulfur ligands, one water/ hydroxo ligand with oxo ligand in the axial position. Both sulfite oxidase and nitrate reductase possess another redox-active center along with the molybdenum center, a $b$-type cytochrome in sulfite oxidase and $b$-type cytochrome and FAD in nitrate reductase. Sulfite oxidase catalyzes the physiological oxidation of sulfite to sulfate whereas nitrate reductase catalyzes the reduction of nitrate to nitrite.

3.2.2. The Prokaryotic oxotransferases or DMSO reductase family
The DMSO reductase family consists of a number of molybdenum enzymes, which are obtained from bacterial and archaeal sources. The DMSO reductase family is characterized by the presence of single oxo ligand coordinated to the molybdenum (VI) center, two dithiolene moiety and attachment to the proton by serine, cysteine, or selenocysteine protein residue (Figure 3). The enzymes of this family catalyze the reductive deoxygenation of dimethyl sulfoxide to dimethyl sulfide as shown in reaction 1:

\[
(CH_3)_2SO + 2H^+ + 2e^- \rightarrow (CH_3)_2S + H_2O \quad \text{(1)}
\]

Thus, these enzymes participate in oxygen atom transfer processes and therefore known as oxo transferases. The crystal structure of DMSO reductase obtained from \textit{Rhodobacter sphaeroides}\textsuperscript{15, 16} was the first one to be determined, thereby crystal structures of several other enzymes were also determined. The crystal structures of these enzymes reveal that the active sites of these enzymes include the two-pyranopterin cofactor with two other ligands in a trigonal prismatic coordination geometry. In DMSO reductase from \textit{Rhodobacter sphaeroides}, the molybdenum center is coordinated by a terminal oxo ligand as the fifth ligand and serinate from the polypeptide as the sixth ligand. In dissimilatory nitrate reductase (Nap) from \textit{Desulfovibrio desulfuricans}\textsuperscript{17} and in the \textit{E.Coli} formate dehydrogenase\textsuperscript{18}, the sixth serine ligand is replaced by a cysteine and selenocysteine, respectively. Arsenite oxidoreductase from \textit{Alcaligenes faecalis} has no protein ligand coordinated to the metal but an OH group occupies the position as the sixth ligand coordinated to the metal center\textsuperscript{19}. There also few enzymes which possess a Mo=S group rather than a Mo=O group\textsuperscript{20}. Some of the enzymes of this family possess molybdenum center as their only redox active center\textsuperscript{16} Examples of this class of enzymes are, Rhodobacter DMSO reductase, TMAO reductase, and biotin- S- oxide reductase. All
dissimilatory nitrate reductases, formate dehydrogenase H and N and arsenite oxidoreductase possess additional redox active centers, generally iron sulfur clusters.

3.2.3. The Molybdenum Hydroxylases or Xanthine oxidase family

Xanthine oxidases occur in the liver and kidneys of humans and animals. Members of this family catalyze hydroxylation reactions as shown in reaction 2; thus known as hydroxylases.

\[
RH + H_2O \rightarrow ROH + 2H^+ + 2e^- \quad (2)
\]

This family is characterized by the presence of oxo and sulfido ligand coordinated to Mo(VI) state, a single dithiolene moiety, an oxygen donor ligand such as water or hydroxide (Figure 3). This family also constitutes the largest group of mononuclear molybdenum enzymes. Nearly 20 enzymes have been characterized, so far, ranging from higher organisms to bacteria that are responsible for the hydroxylation of aromatic heterocycles.\(^\text{10}\) The aldehyde oxidoreductase from *Desulfovibrio gigas* was the first mononuclear enzyme in Xanthine oxidase family whose X-ray crystal structure has been reported.\(^\text{21,22}\) The crystal structures of CO dehydrogenase\(^\text{23}\) and bovine xanthine oxidoreductase\(^\text{24}\) have also been reported. As shown in Figure 3, the active site of this group of enzymes consists of the pyranopterin cofactor ligated to an MoOS(OH) unit with a square pyramidal coordination geometry. The crystal structure of *D. gigas* aldehyde oxidoreductase reveals the presence of apical Mo=S group with the Mo=O group trans to the ene-dithiolate moiety and the Mo-OH group pointing towards the solvent access channel to the active site of enzyme. It was also determined by the X-ray crystallography that enzymes of the hydroxylase family possess multiple redox-active centers with the
presence of iron-sulfur clusters in addition to the molybdenum. A majority of these enzymes also possess FAD as redox active prosthetic groups.

Stolz and Basu\textsuperscript{25} have classified nitrate reductase family of enzymes into three classes: eukaryotic assimilatory NR (Euk-NR), the membrane-associated prokaryotic NR (Nar), and a clade that includes both the periplasmic NR (Nap) and prokaryotic assimilatory NR (Nas) based upon the phylogenic relationship and similarities in the structure and function.

3.3. Modeling of the enzymes

In order to understand the complex function and bioinorganic chemistry of mononuclear molybdoenzymes, several synthetic molybdenum complexes have been synthesized using abiological and biologically relevant ligand systems. By studying the characteristics and properties of these small molecules, one can learn the functions and mechanisms of particular enzymes. These synthetic models may serve as: (i) structural analogues, which highlight the coordination pattern of the metalloenzymes, (ii) spectroscopic analogues to understand the spectroscopic features of the particular enzyme, and (iii) functional analogues, which mimic the functional features of the enzymes.

3.3.1 Model complexes using abiological ligands

These model systems are usually functional and spectroscopic models for molybdoenzymes. List of such complexes are very long which usually utilize O, N, S, Se, and P based ligands. Figure 4 shows some important members of model complexes containing abiological ligand systems. Considered here the relationship between these
complexes and active site of ligand system is primarily because of the presence of the MoO or MoO$_2$ unit. One of the earlier model complexes for SO family of enzymes were developed by the Holm group, where they synthesized complex of type A1 and A2 using sterically bulky ligand systems. The use of steric bulk in the ligand architecture prevented the thermodynamically favored comproportionation reaction during the oxygen atom transfer reactions of these complexes using oxygen abstractors like tertiary phosphines. Similarly Cervilla et al have synthesized complex A3$^{26}$ and Young et al have synthesized complex A4.$^{27}$ All of these complexes are crystallographically characterized and known to show an oxygen atom transfer (OAT) reaction similar to SO enzymes, where Mo center shuttles between Mo$^{VI}$ and Mo$^{IV}$ states during OAT reaction.

Recently the Basu group has shown a complete catalytic cycle for an OAT reaction between monooxo to desoxo center using complex B1.$^{28}$ It is a Mo$^V$ complex, which can be oxidized to Mo$^{VI}$ by one electron oxidation using (NH$_4$)$_2$Ce(NO$_3$)$_6$. This Mo$^{VI}$ complex can then react with an oxygen abstracter like a tertiary phosphine to transfer an oxygen atom Mo$^{VI}$O to PR$_3$ and generate OPR$_3$ and a Mo$^{IV}$ complex, which can abstract one oxygen from water to regenerate Mo$^{VI}$O complex. This complex shows all three oxidation states involved during the biological OAT reaction. Using another model system B2, Basu et al have highlighted the role of encapsulation of molybdenum center by using large dendritic building blocks around the Mo center and comparing them with the smaller homologues.$^{29,30}$ Enemark group has reported the synthesis of [LMoO(dt)] type of complexes (B3),$^{31}$ where they claimed that the fold angle of the dithiolene metallo-cycle along the S–S vector may play an important role in the catalytic reaction of enzymes.$^{32,33}$ Series C shows another important members of biologically relevant Mo(IV) complexes.
Complex C1 was isolated after a complete OAT reaction from A4 using PPh₃ in pyridine.³⁴ Smith et al have isolated an important intermediate complex C2 during the OAT reaction between a dioxo complex and PEt₃,³⁵ which serve a very important role in establishing the theoretical observations for an OAT reaction between cis-Mo⁶⁺O₂ center and tertiary phosphine.

3.3.2 Model dithiolene complexes of the molybdenum enzymes

As we have already discussed in the chapter 1, the discovery of pyranopterin dithiolate in metalloenzymes led the scientists to synthesize the model complexes of dithiolene ligands to mimic the active sites of these metalloenzymes. These model complexes were the structural, functional analogues of sulfite oxidase and DMSO reductase families. To our knowledge, to date no model complex with dithiolene ligand has been synthesized for the xanthine oxidase family. As mononuclear molybdenum enzymes can be differentiated on the basis of number of dithiolene ligands coordinated to molybdenum center, model systems of dithiolene can also be differentiated on the basis of number of dithiolene ligands attached to the metal center. In this section we will discuss about the molybdenum dithiolene complexes, some of them are biologically relevant and others are non-biological complexes.

3.3.2.1. Tris- dithiolene complexes of molybdenum

The tris-dithiolene complexes of molybdenum are not biologically relevant complexes but these complexes are important in dithiolene chemistry because of their trigonal prismatic geometry and reversible redox activity. These complexes can be
synthesized in a similar way as nickel dithiolene complexes (discussed in Chapter 2, Section: 2.1.2.). These complexes were synthesized using dianionic dithiolene ligands like \((\text{CN})_2\text{C}_2\text{S}_2^2\) and dithielenes \([(\text{CF}_3)_2\text{C}_2\text{S}_2^2]\).\(^{37,38}\) The complexes derived from arene 1,2-dithiols were also synthesized and characterized.\(^{39}\) All of these tris- dithiolene complexes are thermodynamically stable in one or more oxidation states. These complexes also exhibit intense transitions in the visible region of the electronic spectra.

### 3.3.2.2. Bis-dithiolene complexes of molybdenum

The bis-dithiolene complexes of molybdenum are important as they can serve as model complexes for DMSO reductase and sulfite oxidase families of enzymes. In 1969-1970, the bis-dithiolene molybdenum complex of mnt\(^2-\), \([\text{MoO(mnt)}_2]^2-\)\(^{40,38}\) was reported as a side product in the synthesis of tris-dithiolene complex of molybdenum. Subsequently, the other complexes of the composition \([\text{Mo}^{VI}_2\text{O}_2\text{L}_2]^{2-}\) or \([\text{Mo}^{IV}_2\text{OL}_2]\), where L is a dianionic or arene dithiolate ligand, mostly mnt\(^2-\) or bdt\(^2-\) were synthesized and characterized. The most important initial work on these molybdenum complexes came from the research groups of Nakamura\(^{41,42,43,44,45,46,47,48,49,50,51,52}\) and Sarkar.\(^{53,54,55,56,57,58}\) In recent years, Holm’s group has synthesized and characterized a large number of structural, functional and spectroscopic analogues of molybdenum enzymes.\(^{59,60,61,62,63,64,65,66,67,68,69,70,71}\) They have developed one of the promising routes to synthesize the molybdenum dithiolene complexes by simple ligand exchange reaction of \(\text{Mo(CO)}_3(\text{MeCN})_3\) and \(\text{Ni(S}_2\text{C}_2\text{R}_2)_2\) to obtain bis-dithiolene dicarbonyl complexes of molybdenum, \(\text{Mo(CO)}_2(S_2\text{C}_2\text{R}_2)_2\) (discussed in Chapter 2, Section 2.1.4.4.). These bis-dithiolene dicarbonyl molybdenum complexes are prominent precursors to synthesize the model complexes of mononuclear molybdenum...
enzymes. The other important work came from the Garner’s group, who synthesized the variety of heterocyclic ene-dithiolate ligands masked as 1,3-dithiole-2-thiones or -2-ones,\textsuperscript{72,73,74,75,76,77,78} which were subsequently reacted with [MoO\textsubscript{2}(CN)\textsubscript{4}]\textsuperscript{4-} to obtain the monooxobis-dithiolene complexes of molybdenum.\textsuperscript{75,76}

### 3.3.3.3. Mono-dithiolene complexes of molybdenum

This group of complexes is somewhat difficult to obtain. They can only be synthesized by the use of bulky ligands coordinated to the metal center to limit the number of ene-dithiolate ligands. In few cases, mono dithiolene complexes have been synthesized by the use of cyclopentadienylato ligands to occupy the residual coordination sites of the molybdenum center.\textsuperscript{79,80} Nicholas group had synthesized and characterized the monodithiolene complex of molybdenum by reacting MoO\textsubscript{2}Cl\textsubscript{2} with mnt\textsuperscript{2-} in tetrahydrofuran to obtain an orange colored species, which was stable below \(-45^\circ\text{C}\). This orange colored species further reacted with phosphines to give the monodithiolene derivative.\textsuperscript{81} This was the first example of structurally characterized monodithiolene molybdenum\textsuperscript{IV} complex. Similarly another route to synthesize monodithiolene complexes of molybdenum came from Enemark’s group, where they used the bulky heteroscorpionate ligand, trispyrazolylborate to synthesize the complex like (L-N\textsubscript{3})MoO(tdt),\textsuperscript{82, 83, 84} where tdt is toluene-3,4-dithiolate and L-N\textsubscript{3} is tris-pyrazolylborate. In these complexes, the molybdenum center was hexacoordinated with the oxidation state of +5. In order to synthesize the structural and functional analogues of sulfite oxidase family, Holm’s group proposed two synthetic routes to synthesize the monodithiolene complexes. In the first
route, they reacted \([\text{MoO(bdt)}_2]^-\) with PhSeCl, which resulted in the removal of one
dithiolene moiety and the formation of \([\text{MoOCl}_2(bdt)_2]\) (Reaction 2)

\[
[\text{MoO(bdt)}_2]^- + 2\text{PhSeCl} \rightarrow [\text{MoOCl}_2(bdt)]^- + C_6H_4(SSH)\cdot 2
\]

The chlorides of the complexes was substituted by other ligands to obtain mono-dithiolene
complexes of \([\text{MoO(SR)}_2(bdt)_2]^-\) (R = 2,4,6-\text{-i-Pr}_3C_6H_2) or \([\text{MoOCl(SR)(bdt)}_2]\). These
complexes and their derivatives were the first examples of five coordinate mono-dithiolene
\(\text{MV}O\) complexes, which have a square pyramidal geometry with an oxo group at an apical
position. Similarly in the second route, they also synthesized the \(\text{MoVI}\) monodithiolene
complexes where they reacted \([\text{MoO}_2(\text{OSiPh}_3)_2]\) with \(\text{Li}_2(bdt)\) in tetrahydrofuran to obtain
\([\text{MoO}_2(\text{OSiPh}_3)(bdt)]^+\) which was further reacted with 2,4,6-\text{-i-Pr}_3C_6H_2SH to form
\([\text{MoO}_2(S\text{C}_6\text{H}_2-2,4,6-\text{-i-Pr}_3)(bdt)]^+\). These complexes possess the square pyramidal
geometry with apical and basal positions occupied by oxo ligands. These complexes
closely resemble the active site of chicken liver sulfite oxidase. Recently, Sugimoto et al. synthesized and characterized the new structural models for the active sites of sulfite
oxidase and xanthine oxidase families. They synthesized the monodithiolene complexes of
\(\text{MoIV}\) by the reaction of \([\text{MoO}_2\text{Cl}_2(\text{Bu}_2\text{bpy})]\) with \(\text{Na}_2\text{mnt}\) and insitu reaction of \(\text{MoO}_2\text{Cl}_2\) with \(\text{Et}_4\text{en}, \text{Na}_2\text{mnt}\).

In our project, we plan to follow the methodology of Holm et al as discussed in
(Chapter 2, Section 2.1.4.4) to synthesize the molybdenum complex containing one
dithiolene unit, which will act as the model of sulfite oxidase family of molybdoenzymes.
Here, we chose the bis(3-tert butyl) pyrazolyl borate as the nitrogen donor ligand which
will coordinate as the non-dithiolene ligand as one moiety and impart the stability to the
molybdenum complex. As shown in Scheme 3, we decided to use nickel dithiolene
complexes (discussed in Chapter 2) to undergo ligand exchange reactions with molybdenum complex.

3.4. Experimental

All the experiments were performed in oven-dried glasswares. Unless specified, all reactions were performed under an atmosphere of argon using Schlenk and dry box techniques. Reaction mixtures were stirred magnetically. The majority of the chemicals was purchased from Aldrich and Acros chemicals and were used as received. Commercial grade solvents were dried and distilled before use. Hexane, tetrahydrofuran, and ether were dried and distilled over Na-wire/ benzophenone; methanol and ethanol was refluxed over Mg-turnings/iodine; toluene and methylene chloride were dried and distilled over CaH2; acetonitrile was distilled over P4O10. Dry dimethylsulfoxide and dry dimethylformamide were obtained from Acros chemicals.

Room temperature \(^1^H\) and \(^{13}\)C NMR spectra were recorded using a Bruker ACP-300 spectrometer at 300.133 MHz and 75.469 MHz frequencies, respectively. Mass spectra were recorded in a Waters LCQ ESI/APCI Quadropole Mass spectrometer in ESI and/or APCI modes. Electronic spectra were recorded in Cary 3 and Cary 14 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1760X spectrometer on NaCl plates or in KBr pellets. Chromatographic purifications were done on silica gel (63-200µm) purchased from Sorbent Technologies Company. Thin layer chromatography (TLC) was done on alumina coated and silica coated TLC plates (20x20 cm) from EM Science.
Synthesis of 3-tertbutyl pyrazole

In a round bottom flask, dry sodium methoxide (28.1g, 520 mmol) was dissolved in 160 mL of dry toluene and a mixture of pinacolone (54.1g, 540 mmol) and ethyl formate (44.4g, 599 mmol) was added to the above reaction mixture with rapid stirring. An exothermic reaction took place. After 30 minutes, the low boiling materials were distilled off under vacuum. Ice-cold water was added into the reaction mixture and the contents were stirred until the color of reaction mixture passed into the aqueous phase. The aqueous layer was separated and added to a solution of hydrazine monohydrochloride (35.6g, 520 mmol) in 160 mL of water. Oil was separated which was extracted with methylene chloride. The solvent was evaporated and the residue was distilled to get a gummy material, which solidified when kept at low temperature. Yield: 55.0% (286.0 mmol.) ¹H NMR (CDCl₃): δ = 12.30(s, 1H), 7.44(d, 1H), 6.03 (d, 1H), 1.32(s, 9H) ¹³C NMR (CDCl₃): δ = 30.5, 31.2, 102.4, 136.8, 158.2.

Synthesis of Bis (3-tertbutyl pyrazolyl) borate

In a schlenk flask, 3-tertbutyl pyrazole (2g, 2.2 mmol) and KBH₄ (0.395g, 7.32 mmol) were dissolved in anhydrous N,N-dimethyl acetamide (DMAC) (20 mL), stirred and heated at 120°C for 22hrs. Hydrogen gas is evolved during the reaction. After heating, the whole contents were distilled under vacuum at 130-135°C to remove all volatile impurities. The residue obtained was dissolved in tetrahydrofuran, stirred with celite and filtered to yield a clear white solution. The solvent was evaporated to get a thick white mass. Yield: 55.2% (8.89 mmol.) ¹H NMR (CDCl₃): δ = 1.21(s, 9H), 1.30(s,
9H), 6.01 (d, 2H, J = 14Hz), 7.45 (d, 2H, J= 10Hz); IR (KBr, cm⁻¹): 2261-2352 cm⁻¹ (B-H), Mass spectra (m/z) (ESI-): 259 (100%, m/z) [C₁₄H₂₄N₄B (M⁻), 259].

Synthesis of [Et₄N][L⁻⁻⁻⁴Mo(CO)₄]⁸⁷

In a schlenk flask, bis(3-tertbutyl pyrazolyl)borate (2.24g, 7.51 mmol) and Mo(CO)₆ (1.98g, 7.51 mmol) were dissolved in dry N,N-dimethylacetamide (20 mL), stirred and heated at 120 °C for 22 hrs. Carbonyl gas is evolved during the reaction. The color of reaction mixture changed from yellow to yellow-brown after 22 hrs. The solution was concentrated by distillation, cooled and a solution of Et₄NBr (1.54g, 7.51 mmol) in H₂O was added into the reaction mixture under inert atmosphere inside the wet-box. The contents were stirred for 15min and then the pale yellow compound was filtered and washed with water. Recrystallization was done by acetonitrile/ water (2:1) Yield: 16.0% (1.18 mmol.) ¹H NMR (CD₃CN): δ = 1.52(s, 9H), 1.64(s, 9H), 6.29 (m, 2H), 7.55 (m, 2H); IR (KBr, cm⁻¹): 1938, 1892, 1757 (CO) 2517 (B-H).

Synthesis of Mo(CO)₃(CH₃CN)₃⁸⁸

In a 250ml schlenk flask, Mo(CO)₆ (0.50g) was added in the excess of dry acetonitrile (50mL). The contents were refluxed for 4hrs under argon atmosphere. The reflux condenser was connected to an oil trap to see the evolution of CO gas and the separate the reaction mixture from any contact with air. After 5 min., the color of reaction mixture changes to yellow. The radiation from a light source was avoided. The solvent was evaporated under reduced pressure. A yellowish colored compound was obtained.
which was light and air sensitive. IR (KBr, cm\(^{-1}\)): 1778, 1826, 1908 (CO) 2279, 2311, 2363 (CN).

Synthesis of (Phen)Mo(CO)\(_4\)^\(^{89}\)

In a schlenk flask, 1,10-phenanthroline (1.80g, 10.00 mmol) and Mo(CO)\(_6\) (2.64, 10.0 mmol) were dissolved in dry toluene (20 mL), stirred and refluxed for 2.5 hrs under argon atmosphere. Carbonyl gas is evolved during the reaction. The color of reaction mixture turned red after 1 hr. After 2.5 hrs, deep red colored crystals were deposited on the walls of the flask. The solution was cooled, filtered and washed with toluene. The red colored crystals were dried in vacuo. Yield: 89.4% (8.94 mmol.) \(^1\)H NMR (CDCl\(_3\)): \(\delta =\) 9.49 (d, 2H), 8.45 (d, 2H), 7.97 (s, 2H), 7.77-7.73 (m, 2H), IR (KBr, cm\(^{-1}\)): 2007, 1866, 1827 (C=O)

Synthesis of (Phen)MoO\(_2\)Cl\(_2\)^\(^{90}\)

In a schlenk flask, MoO\(_2\)Cl\(_2\) (1.10g, 5.55 mmol) was dissolved in dry acetonitrile (15 mL) and 1,10-Phenanthroline (1.00g, 5.55 mmol) dissolved in acetonitrile (5 mL) was added to the reaction mixture. The white precipitate was formed which was stirred for 1 hr and after keeping it at low temperature for 30 minutes, it was filtered out. The white colored compound was dried in vacuo. Yield: 96.0% (5.29 mmol.) \(^1\)H NMR (CDCl\(_3\)): \(\delta =\) 9.9 (d, 2H), 8.45 (d, 2H), 8.10 (s, 2H), 8.05-8.09 (m, 2H); IR (KBr, cm\(^{-1}\)): 901, 934 (MoO\(_2\)).

Synthesis of (Phen)MoO(tdt)
In a schlenk flask, (Phen)MoO$_2$Cl$_2$ (0.50g, 1.31 mmol) was suspended in dry dichloromethane at -78°C. Now toluene 3,4-dithiolate (tdt) (0.20g, 1.31 mmol) and Et$_3$N dissolved in dichloromethane (15 mL) was added through cannula into the suspended solution of MoO$_2$Cl$_2$ at -78°C. The color of reaction mixture changed to reddish brown after addition of dithiolate ligand. The reaction mixture was stirred only for 15 min and the solvent was evaporated in vacuum. The residue was redissolved in dry DCM and the compound was precipitated as a reddish violet solid by the addition of dry hexane. The precipitate was filtered and washed with dry dimethoxyethane and dry toluene several times. Yield: 51.0% (0.67 mmol.) $^1$H NMR (CD$_3$CN): $\delta = 11.5$ (s, 1H), 9.8 (d, 2H), 9.12 (d, 2H), 8.5 (s, 2H), 8.20-8.35 (m, 2H), 7.8-8.0 (m, 3H), 3.86-3.60 (m, 2H), 2.52 (s, 3H), 1.88-1.65 (t, 3H). IR (KBr, cm$^{-1}$): 927 (MoO). mass spectra (m/z) (ESI+): 550.2 (100%, m/z) [C$_{25}$H$_{30}$O$_1$N$_2$S$_2$Mo$_1$ (M+Et$_3$NH)$^+$, 550.1], 487.1 (50%, m/z) [C$_{19}$H$_{14}$O$_1$N$_2$S$_2$Mo$_1$K$_1$, (M+K)$^+$, 486.9].

**Synthesis of (Phen)Mo(CO)$_2$(mnt)**

A schlenk flask was charged with solid Mo(CO)$_6$ (1.0g, 3.78 mmol) and immersed in a dry ice-acetone bath. A chlorine gas was condensed onto the solid and the mixture was stirred. The condensation was completed when the color of mixture turned yellow. The gas flow was stopped and the mixture was stirred at -78°C for 30 minutes. After 30 minutes, dry ice-acetone bath was removed and excess of chlorine gas was allowed to evaporate at room temperature under a stream of argon followed by pumping for 10 minutes. The residue was dissolved in dry methanol within 5 minutes and the solution of Na$_2$mnt (0.70g, 3.78 mmol) in methanol was added in it at -78°C. The color
of the reaction mixture changed from yellow to red. At the same time another solution of 1,10-phenanthroline (0.68g, 3.78 mmol) in dry methanol was added into it, which immediately yielded a reddish violet precipitate. The precipitate was filtered anaerobically and washed with dry methanol to yield a reddish violet colored compound. Yield: 84.2% (3.17 mmol.) \(^1\)H NMR (CD\(_3\)CN): \(\delta = 9.2\) (d, 2H), 9.0 (d, 2H), 8.4 (s, 2H), 8.0-8.2 (m, 2H); IR (KBr, cm\(^{-1}\)): 1889, 1963, 2206 (CN). mass spectra (m/z) (ESI\(^+\)): 528 (100%, m/z) \([C_{21}H_{14}O_{11}N_{6}S_{2}Mo_{1}, (M-CO+2CH_{3}CN)]^+, 528\], 509 (80%, m/z) \([C_{18}H_{6}O_{2}N_{4}S_{2}Mo_{1}Cl_{1}, (M+Cl)]^+, 509\].

**Synthesis of MoO\(_2\)Cl\(_2\)(OPPh\(_3\))\(_2\)**

Molybdic acid (4.0g) was dissolved in HCl (30 mL) and a solution of OPPh\(_3\) (2.3g in 10 mL of ethanol) was added to it. An off-white precipitate appeared, which was filtered and washed with ether several times. The solid was then recrystallized from dichloromethane and the yield was 2.89g (92.5%). IR Spectrum IR (KBr, cm\(^{-1}\)): 946 and 905 cm\(^{-1}\) (MoO\(_2\)),

**Attempted Reactions:**

**Ligand exchange reaction using \(L^{1Bu}\)Mo(CO)\(_4\) and [Ni(S\(_2\)C\(_2\)(C\(_6\)H\(_5\))\(_2\)]**

In a schlenk flask, \(L^{1Bu}\)Mo(CO)\(_4\) (0.04g, 0.09 mmol) was dissolved in tetrahydrofuran and added to the solution of neutral [Ni(S\(_2\)C\(_2\)(C\(_6\)H\(_5\))\(_2\)] (0.05g, 0.09 mmol) in tetrahydrofuran under strict anaerobic conditions. The dark green colored solution of [Ni(S\(_2\)C\(_2\)(C\(_6\)H\(_5\))\(_2\)] immediately changed into red-violet after the addition of yellow brown solution of \(L^{1Bu}\)Mo(CO)\(_4\). The reaction mixture was stirred and monitored...
by TLC analysis. The stirring was continued for 2 days and after 2 days the reaction was stopped. The solvent was evaporated and the residue was dissolved in acetonitrile in which ether was added as a precipitant to give a green colored compound and a brown colored filtrate. Further TLC analysis of precipitate and filtrate showed spots of unreacted Ni-complex along with two different spots. Purification was then done with prep TLC to isolate these spots.

**Reaction using Mo(CO)$_3$(CH$_3$CN)$_3$, [Ni(S$_2$C$_2$(C$_6$H$_5$)$_2$)$_2$], and K L$^{l-Bu}$**

In a schlenk flask, Mo(CO)$_3$(CH$_3$CN)$_3$ (0.10g, 0.34 mmol) was dissolved in tetrahydrofuran (5 mL) and to this solution was added the solution of KL$^{l-Bu}$ (0.10g, 0.34 mmol) in tetrahydrofuran (5 mL), which changed the color of reaction mixture to amber. The reaction mixture was stirred for two days and the solvent was evaporated to get a yellow brown solid product, which was found to be air and light sensitive. An IR was recorded for this product and then the solid product was redissolved in tetrahydrofuran. A neutral [Ni(S$_2$C$_2$(C$_6$H$_5$)$_2$)$_2$] (0.18g, 0.34 mmol) dissolved in dry tetrahydrofuran was added to the above solution under strict anaerobic conditions. The brownish-yellow solution changed into red-violet. The reaction was monitored by TLC analysis and was stirred for 2 days at room temperature where similar spot pattern was seen as described above. Purification was attempted using precipitation of a solid by using a mixture of DCM and hexane but the target compound was not obtained.
Reaction between L\textsuperscript{t-bu}Mo (CO)\textsubscript{4} and bdt\textsuperscript{2−} at 50 °C

In a schlenk flask, Bis(3-tertbutyl pyrazolyl)borate (0.10g, 0.35 mmol) and Mo(CO)\textsubscript{6} (0.09g, 0.35 mmol) were dissolved in dry N,N-dimethylacetamide (20 mL), stirred and heated at 120 °C for 22 hrs. Carbonyl gas was evolved during the reaction. The color of reaction mixture changed from yellow to yellow-brown after 22 hrs. The solution was evaporated and the residue was redissolved in dry tetrahydrofuran (10 mL). In another schlenk flask, H\textsubscript{2}bdt (0.50 g, 0.35 mmol) was dissolved in dry tetrahydrofuran and triethylamine (0.10 g, 0.98 mmol) was added to it. The whole mixture was then transferred to the mixture of L\textsuperscript{t-bu}Mo(CO)\textsubscript{4} by using cannula. The color of reaction mixture was changed from yellow-brown to burgundy after addition of H\textsubscript{2}bdt+Et\textsubscript{3}N. The reaction mixture was then stirred for 3.5 hrs at 50 °C and then solvent was evaporated to get a burgundy colored residue. The purification was done using silica gel column inside the dry box. The first band was dark green in color, which was eluted using toluene/acetonitrile (2:1). The second band was orange in color, which was eluted using toluene/acetonitrile (1:1). The two compounds were analyzed by IR and Mass spectrometry. Orange compound: yield: 11.76 % (0.04 mmol); mass spectra (m/z) (ESI-): 394 (100%, m/z) [C\textsubscript{12}H\textsubscript{8}OS\textsubscript{4}Mo, (M)\textsuperscript{−}, 394]. Green compound: yield: 2.51 % (8.72 mmol). mass spectra (m/z) (ESI-): 518 (100%, m/z) [C\textsubscript{18}H\textsubscript{12}S\textsubscript{6}Mo\textsubscript{1}, (M)\textsuperscript{−}, 518].

Reaction between L\textsuperscript{t-bu}Mo (CO)\textsubscript{4} and bdt\textsuperscript{2−} at −78 °C

In a schlenk flask, Bis(3-tertbutyl pyrazolyl)borate (0.10g, 0.35 mmol) and Mo(CO)\textsubscript{6} (0.09g, 0.35 mmol) were dissolved in dry N,N-dimethylacetamide (20 mL), stirred and heated at 120 °C for 22hrs. Carbonyl gas was evolved during the reaction. The
color of reaction mixture changed from yellow to yellow-brown after 22 hrs. The solution was evaporated and the residue was redissolved in dry tetrahydrofuran (10 mL). In another schlenk flask, H₂bd (0.50 g, 0.35 mmol) was dissolved in dry tetrahydrofuran and triethylamine (0.10g, 0.98 mmol) was added in it. The whole mixture was then transferred to the mixture of LMo(CO)₄ by using cannula at -78°C. The color of reaction mixture was changed from yellow-brown to dark reddish-brown after addition of H₂bd-Et₃N solution. The reaction mixture was then stirred for 3 hrs at -78 °C and gradually warmed up to room temperature. The color of reaction mixture changed to dark green and solvent was evaporated to get a green colored residue. The residue was redissolved in DCM and PPh₄Cl (0.13g, 0.35 mmol) in methanol was added into the solution to obtain a reddish violet colored compound.

**Reaction of L⁠₄⁻⁰⁴⁰⁰Mo (CO)₄ with mnt at -78°C:**

In a schlenk flask, Bis(3-tertbutyl pyrazolyl)borate (0.10g, 0.35 mmol) and Mo(CO)₆ (0.10 g, 0.35 mmol) were dissolved in dry DMAC (20 mL), stirred and heated at 120 °C for 22hrs. Carbonyl gas was evolved during the reaction. The color of reaction mixture changed from yellow to yellow-brown after 22 hrs. The solution was evaporated and the residue was redissolved in dry tetrahydrofuran (10 mL). The solution was cooled at -78 °C and the solution of Na₂mnt (0.07g, 0.35 mmol) in dry tetrahydrofuran was added into it. The color of the reaction mixture changed from yellow brown to reddish brown. The mixture was gradually brought up to the room temperature that changed the color of the mixture to green. The solvent was evaporated and the residue was
redissolved in DCM to precipitate the dirty green colored compound using hexane as precipitant.

**Reaction of MoO$_2$Cl$_2$(OPPh$_3$)$_2$ + bdt+ KL$^{t\text{-bu}}$:**

In a schlenk flask, MoO$_2$Cl$_2$(OPPh$_3$)$_2$ (0.27g, 0.35 mmol) was dissolved in tetrahydrofuran and stirred at –78 °C. H$_2$bdt (0.50 g, 0.35 mmol) and triethylamine (0.10 g, 0.98 mmol) dissolved in dry tetrahydrofuran were added into the reaction mixture. The color of reaction mixture changed to greenish brown. The reaction mixture was stirred for 1hr at –78 °C. After 1 hr, the ligand KL$^{t\text{-bu}}$ (0.10 g, 0.35 mmol) was added into the reaction mixture at –78 °C and stirred for 1 hr. The color of reaction mixture changed to red. The mixture was warmed to room temperature at which point the color of the reaction mixture changed to green. The solvent was evaporated and residue was redissolved in DCM. The methanolic solution of PPh$_4$Cl (0.13g, 0.35 mmol) was added to the reaction mixture to precipitate the compound as green colored solid.

**Reaction of MoO$_2$Cl$_2$(OPPh$_3$)$_2$ with Na$_2$Mnt and KL$^{t\text{-bu}}$**

In a schlenk flask, MoO$_2$Cl$_2$(OPPh$_3$)$_2$ (0.25g, 0.34 mmol) was dissolved in tetrahydrofuran and stirred at –78°C. Solid Na$_2$mnt (0.06g, 0.34 mmol) was added in argon atmosphere into the reaction mixture. The color of the reaction mixture changed to orange. The reaction mixture was stirred for 1hr. at –78°C. Now the ligand KL$^{t\text{-bu}}$ (0.10 g, 0.34 mmol) was added to it and stirred for 1 hr. The color of the reaction mixture changed to red, which was then brought up to the room temperature. After warming the reaction mixture the color changed to green. The solvent was evaporated to get dark
green colored residue, which was dissolved in DCM and hexane was added as a precipitant to get a dirty green colored compound.

**Reaction between (Phen)Mo(CO)$_4$ and bdt$^2-$**

In a Schlenk flask, PhenMo(CO)$_4$ (0.14g, 0.35 mmol) was dissolved in dry tetrahydrofuran (10 mL). In another schlenk flask, H$_2$bdt (0.50g, 0.35 mmol) was dissolved in dry tetrahydrofuran and triethylamine (0.10 g, 0.98 mmol) was added in it. The whole mixture was then transferred to the red solution of (Phen)Mo(CO)$_4$ by using cannula. The color of the reaction mixture darkens after addition of the mixture of H$_2$bdt and Et$_3$N. The reaction mixture was then stirred for 3.5 hrs at 50 °C and then solvent was evaporated to get a dark bluish green colored residue. The purification was done using silica gel column inside the dry box. The first band was dark red in color, which was eluted, in pure toluene and the second green band was eluted with toluene/ acetonitrile (2:1) mixture.

3.5. Results and Discussion

3.5.1. Synthesis and Characterization of Ligands and Complexes

3.5.1.1. Pyrazole ligand and its Mo-complexes

3(5)-tert butyl pyrazole and bis-(3-pyrazole)borate were synthesized by using the procedure described by Trofimenko et al.$^{86}$ A detailed reaction is shown in Scheme 1, which describes the stepwise progress of the reaction. In the first step pinacolone and ethyl formate were stirred with sodium methoxide in dry toluene, which gave a 1,3-dicarbonyl compound. The diketone compound reacted without any purification or
characterization with hydrazine monohydrochloride to give 3(5)-tert butyl pyrazole as a clear mass. The $^1$H NMR was matched with the reported one. It was further characterized by $^{13}$C NMR, IR, and mass spectrometry, which showed the signatures of desired compound.

To synthesize the potassium hydrobis-pyrazole borate ligand the above pyrazole was reacted with potassium borohydride at 120 °C in dimethyl acetamide media as shown in Scheme 2. Heating under controlled temperature is the key element in the high yield and purity of this compound. This compound was isolated as a clear thick mass, which was soluble in most of the common organic solvents. The complete characterization of this ligand was done using ESI-MS, $^1$H and $^{13}$C NMR, and IR spectroscopies (Figure 5).

Molybdenum carbonyl complex of pyrazolylborate $L^{1-Bu}_2$Mo(CO)$_4$, $L = \text{bis(tert-butylpyrazole)borate}$ was synthesized by following the methodologies of Trofimenko\textsuperscript{87} as shown in Scheme 2. A mixture of pyrazole borate and Mo(CO)$_6$ was heated at 120 °C in DMAC media under anaerobic condition. CO-gas was evolved during the reaction and was seen in an oil trap that was attached to the condenser. After the reaction the solvent was distilled under reduced pressure and an aqueous solution of Et$_4$NBr was added to the above mixture under anaerobic atmosphere, which yielded a light yellowish solid compound upon stirring. The solid was filtered and washed with water and dried under anaerobic atmosphere. This compound was found to be very sensitive to air and light. In the presence of light it changes to a brown mass probably because of the labile CO ligands. In the air it forms a green colored compound. It must be noted that these types of complexes are reported to be very unstable and therefore they were not isolated from the reaction mixture and used as in situ precursors for further syntheses.\textsuperscript{87} Here, we tried to
isolate and characterize this complex by using IR, ESI MS, and $^1$H NMR spectroscopy. IR showed strong stretches between 1750 and 2045 cm$^{-1}$ region, which indicates the presence of CO groups (Figure 6). This region is matching very well with the known tetra carbonyl complexes of Mo(0).$^{89}$ A weak stretch at 2517 cm$^{-1}$ can be assigned to the B-H stretch of pyrazole. It is interesting to see only one stretch for the BH$_2$ group. Trofimenko have also reported such observations in H$_2$B(3-R$_1$,5-R$_2$-pyrazolyl)borateMo(CO)$_2$(allyl) type of complexes, where R$_1$ and R$_2$ are different or same alkyl groups.$^{87}$ They have also observed a triplet in the $^{11}$B NMR spectra around (+) 33ppm with the coupling constant ($J$) = 80-100 Hz range confirming the presence of a BH$_2$ group. Mass spectrum of the complex showed a peak cluster at 473 (m/z) at cone voltage 10 mV, which was 4 mass units different than that calculated for the parent molecular ion (molecular weight = 469, C$_{18}$H$_{24}$O$_4$N$_4$BMo). It is interesting to note that by changing the cone voltage a pattern for the dissociation of four CO ligands was observed, which indicated that the compound has at least four CO ligands, which was consistent with the IR information. The four mass unit differences may therefore be related to the formylation of CO groups in the mass spectral conditions. It must be noted that this result was reproducible from several sets of reactions. The isotope distribution pattern was also not matching with the expected molecular ion, which may be due to the combination of the molecular ions containing carbonyl and formyl groups (different in one or two mass units). $^1$H NMR of the complex has protons signals from pyrazole ring and tert-butyl groups. There were small signals from tetraethyl ammonium cation. In addition to the above analysis a conductivity experiment was also carried out in an acetonitrile solution of complex, which showed the 1:1 electrolytic nature of the complex. Because this complex was not very stable and was
decomposing with time, we decided to follow the methodologies, where in situ synthesis of \( \text{L}^{\text{t-Bu}}\text{Mo(CO)}_4 \) was used for synthesizing further complexes.

3.5.1.1. Synthesis of Mo complexes consisting \( \text{L}^{\text{t-Bu}} \) and dithiolene ligands

Ligand Exchange Reactions

As discussed in chapter 2 (section 2.1.4.4), molybdenum carbonyl complexes \( \text{Mo(CO)}_6 \) or \( \text{Mo(CO)}_3(\text{CH}_3\text{CN})_3 \) show a ligand exchange reaction with neutral Ni-dithiolene complex first reported by Schrauzer et al\(^{92}\) and later modified by Holm et al\(^{93}\) to synthesize bis(dithiolene) monooxo molybdenum complexes:

\[
[\text{Mo(CO)}_3(\text{MeCN})_3] + 2[\text{Ni(S}_2\text{C}_2\text{R}_2)_2] \rightarrow [\text{Mo(CO)}_2(\text{S}_2\text{C}_2\text{R}_2)_2] + [\text{Ni}^{\text{II}}_2(\text{S}_2\text{C}_2\text{R}_2)_2] + 3\text{MeCN} + \text{CO}
\]

Here the oxidation state of molybdenum changes from zero to four. The dicarbonyl precursor can be reacted with \( \text{Et}_4\text{NOH} \) to give monooxo bis(dithiolene) molybdenum complex, a model complex for molybdenum oxotransferases. Utilizing such reactivity of molybdenum carbonyl complexes we decided to react \( \text{L}^{\text{t-Bu}}\text{Mo(CO)}_4 \) with different nickel dithiolene complexes as shown in Scheme 3. An stoichiometric amount of \( \text{L}^{\text{t-Bu}}\text{Mo(CO)}_4 \) and neutral \([\text{Ni(S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2]\) was reacted in dry tetrahydrofuran under strict anaerobic conditions. The dark green color solution of \([\text{Ni(S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2]\) changed immediately into red-violet after the addition of brownish-yellow solution of \( \text{L}^{\text{t-Bu}}\text{Mo(CO)}_4 \). The reaction was monitored by TLC analysis where unreacted Ni-complex showed a prominent spot in addition to the immobile Mo-precursor. After 1 day of stirring the color of the reaction mixture changed to bluish green, but TLC still showed unreacted Ni-complex along with two other spots. The reaction was stopped and the product was isolated by precipitation using DCM/MeOH and acetonitrile/ether, which gave a green
colored compound and brown colored filtrate. Further TLC analysis of precipitate and filtrate showed spots of unreacted Ni-complex along with two different spots. Purification was then done with preparative TLC and the NMR of these spots was recorded, where only the peaks of phenyl rings and no other peaks due to pyrazolyl borate ligands were obtained. Further ESI MS analysis identified the green colored compound as a tris(dithiolene) complex of molybdenum \([\text{Mo}(\text{S}_2\text{C}_2\text{C}_6\text{H}_5)_2)_3]\) (Figure 7). In addition, unreacted \(\text{L}^{\text{t}}\text{-BuMo(CO)}_4\) and \([\text{Ni}(\text{S}_2\text{C}_2\text{C}_6\text{H}_5)_2)_2]\) were also detected. It suggests that the carbonyl groups were replaced during the reaction. Therefore we adopted a different route to get the same target product.

\(\text{Mo(CO)}_6\) was first converted to \(\text{Mo(CO)}_3(\text{CH}_3\text{CN})_3\) by refluxing it in acetonitrile for 3 hours under anaerobic condition.\(^{88}\) This compound was not stable, therefore only a quick IR was recorded on KBr pellet, which showed multiple CN and CO stretches around \(2260\ \text{cm}^{-1}\) and \(1850\ \text{cm}^{-1}\) respectively (Figure 8). \(\text{Mo(CO)}_3(\text{CH}_3\text{CN})_3\) was redissolved in tetrahydrofuran and to this solution was added the solution of \(\text{KL}^{\text{t}}\text{-Bu}\), which changed the color of reaction mixture to amber. After the stirring of two days the solvent was evaporated and a solid product was obtained, which was found to be unstable in air and light. Before using it for further reactions an IR was recorded that showed a shifted signal at \(2441\ \text{cm}^{-1}\) for B-H stretch (Figure 9). Other stretches were two strong CO vibrations at \(1932\ \text{cm}^{-1}\) and \(1899\ \text{cm}^{-1}\) and C-H stretches around \(2953\ \text{cm}^{-1}\), however, no prominent peak of CN was observed.

\(\text{L}^{\text{t}}\text{-BuMo(CO)}_3(\text{CH}_3\text{CN})_3\) was redissolved in tetrahydrofuran and a stoichiometric amount of neutral \([\text{Ni}(\text{S}_2\text{C}_2\text{C}_6\text{H}_5)_2)_2]\) dissolved in dry tetrahydrofuran was added to the above solution under strict anaerobic conditions. The brownish-yellow solution changed
to red-violet. The reaction was monitored by TLC analysis where a similar spot pattern was seen as described above. This mixture was stirred for 2 days at room temperature and the ESI MS was recorded for the crude reaction mixture. The result obtained was exactly the same as obtained from the above reaction, where tris-dithiolene Mo complex and unreacted [Ni(S$_2$C$_2$C$_6$H$_5$)$_2$]$_2$ was obtained. Purification was attempted using precipitation of a solid by using a mixture of DCM and hexane but the target compound was not obtained.

It may be concluded from the failure of above reactions that ligand exchange reactions using nickel-dithiolene complexes with LMo(CO)$_n$ type complexes may not be a useful under the conditions tried here. We therefore planned to use a direct reaction between a dithiolene ligand and L$^{1}$Bu Mo(CO)$_4$.

3.5.1.1.2. Reactions of L$^{1}$Bu Mo (CO)$_4$ with dithiolenes

We selected two popular dithiolene ligands: ‘maleonitrile (mnt)’ and ‘benzenedithiolate (bdt)’ for trying these reactions. One of the examples is shown in Scheme 4. L$^{1}$Bu Mo(CO)$_4$ was prepared in situ as described above and dissolved in dry tetrahydrofuran. To this solution a mixture of H$_2$bdt and triethylamine in tetrahydrofuran was added slowly at room temperature. The color of reaction mixture changed from yellow-brown to burgundy after the addition of the mixture of H$_2$bdt and Et$_3$N. The reaction mixture then stirred for 3.5 hrs at 50°C and then solvent was evaporated and the residue was purified using adsorption chromatography on silica gel column inside the dry box using a mixture of toluene and acetonitrile. The first band was dark green in color eluted in 35% of acetonitrile in toluene and the second band was orange in color, which
was eluted in 50% acetonitrile in toluene. Both compounds were analyzed by using IR and Mass spectrometry. The mass spectral studies showed that the orange band was the molybdenum monooxo bis-dithiolene [MoO(S$_2$C$_2$(C$_6$H$_4$)$_2$)$_2$]$^{2-}$ complex (Figure 10). The presence of monooxo ligand was further confirmed by IR spectrum, which has a peak at 906 cm$^{-1}$ that was matching with the reported [Mo$^{IV}$O(S$_2$C$_2$(C$_6$H$_4$)$_2$)$_2$]$^{2-}$ complex.$^{46}$ Green compound was found to be a tris-dithiolene molybdenum complex [Mo(S$_2$C$_2$(C$_6$H$_4$)$_2$)$_3$] by the mass spectral studies (Figure 10). These results were further confirmed by matching the UV-vis spectra of these compounds with the reported ones. The similar reaction was tried again under similar conditions but at $-78^\circ$C to subsidize the high reactivity of dithiolate ligand. Here again a dark green solution was obtained. During the workup a methanolic solution of PPh$_4$Cl was added in the reaction mixture and a green color product was isolated as [Mo$^{V}$O(S$_2$C$_2$(C$_6$H$_4$)$_2$)$_2$]$^-$, which had similar mass value as [Mo$^{IV}$O(S$_2$C$_2$(C$_6$H$_4$)$_2$)$_2$] $^{2-}$ but the M=O stretch came at 930 cm$^{-1}$ (Figure 11), which matched with the reported [Mo$^{V}$O(S$_2$C$_2$(C$_6$H$_4$)$_2$)$_2$] complex. The green color residue showed a peak for [Mo(S$_2$C$_2$(C$_6$H$_4$)$_2$)$_3$] in the ESI MS.

Under the similar conditions, ‘Na$_2$mnt’ was used instead of ‘bdt’ and the reaction was carried out at $-78^\circ$C in tetrahydrofuran. The results were consistent as the [MoO(mnt)$_2$]$^{2-}$ and [Mo(mnt)$_3$] were obtained as major products from the reaction mixture. This reaction was then not tried at elevated temperatures.

These reactions failed to yield any L$_{^{1-Bu}}$Mo(CO)$_2$(dt) complex. It may be due to the displacement of ligand L$_{^{1-Bu}}$ by dithiolate ligand, which form stronger bonds with Mo center. It is also important to note that an oxo-group is inserting to form complexes of type [Mo$^{V}$O(S$_2$C$_2$(C$_6$H$_4$)$_2$)$_2$]$^-$ and [MoO(mnt)$_2$]$^{3-}$, which points out that there might be
some oxygen or water contamination inside the dry box atmosphere (including solvents and silica gel used for purifications).

Based on the above analysis, we concluded that \( \text{L}^{\text{t-Bu}}\text{Mo(CO)}_4 \) may not be a good starting complex to synthesize the target \( \text{L}^{\text{t-Bu}}\text{Mo(CO)}_2(\text{dt}) \) complexes because of its unstable nature. Therefore, we followed other methodologies, where high valent Mo-complexes would be used as the starting materials; however, during this time we had also changed the anionic nitrogen donor ligand \( \text{KL}^{\text{t-Bu}} \) to a neutral nitrogen donor ligand like phenanthroline (Phen).

### 3.5.1.1.3. Reactions of \( \text{MoO}_2\text{Cl}_2(\text{OPPh}_3)_2 \) with \( \text{KL}^{\text{t-Bu}} \) and dithiolenes

Nicholas et al have reported the synthesis of a mono dithiolene complex with tertiary phosphine ligands (see section 3.3.3.3). Following the same concept we planned to synthesize our target \( \text{L}^{\text{t-Bu}}\text{MoO(dt)} \) type complexes, where dt = dithioline as shown in Scheme 5.

Here we chose \( \text{MoO}_2\text{Cl}_2(\text{OPPh}_3)_2 \) as the starting complex, which was synthesized according to the literature procedure. In the first trial \( \text{MoO}_2\text{Cl}_2(\text{OPPh}_3)_2 \) dissolved in tetrahydrofuran was reacted with \( \text{H}_2\text{bdt} \) and \( \text{Et}_3\text{N} \) in tetrahydrofuran solution at \(-78^\circ\text{C}\). The color of reaction mixture changed to greenish brown, which was stirred for 1 hr at \(-78^\circ\text{C}\) and ligand \( \text{KL}^{\text{t-Bu}} \) was added by dissolving in tetrahydrofuran into it that changed the color to red. The reaction mixture was stirred for another 1 hr with the gradual increase in the temperature to room temperature, which changed the color of reaction mixture to green. A methanolic solution of \( \text{PPh}_4\text{Cl} \) was added to the reaction mixture and a green color product was isolated. ESI MS showed a peak cluster for \([\text{MoO(bdt)}_2]\) at
394 (m/z). The Mo=O stretch at 930 cm\(^{-1}\) was also matched with the reported [Mo\(^{V}\)O(bdt)]\(^2\) complex (Figure 12). Under the similar conditions, the same reaction was tried with mnt instead of bdt and the similar results were obtained where ESI MS showed a peak cluster for [MoO(mnt)]\(^2\) at 394 (m/z) (Figure 13).

Having seen the displacement of anionic nitrogen donor ligands we decided to study the neutral nitrogen based bis-chelating ligands complexes. Here the starting point was the tetra carbonyl (Phen)Mo(CO)\(_4\) complex, which was then extended to the high valent (Phen)MoO\(_2\)Cl\(_2\) complex, where phen = phenanthroline ligand.

3.5.1.2. Phenanthroline based Mo-dithiolene Complexes

3.5.1.2.1. Reactions of (Phen)Mo(CO)\(_4\) with dithiolenes (Scheme 6)

The starting precursor (Phen)Mo(CO)\(_4\) was synthesized by following the literature procedures (Figure 14).\(^8^9\) It was a red colored crystalline compound, which has a good stability in air. This complex was reacted with bdt in the similar fashion as described for \(\text{L}^{1-\text{Bu}}\text{Mo(CO)}_4\) and bdt. The reaction mixture was stirred for 3.5 hrs at 50°C and then solvent was evaporated to get a dark bluish green colored residue. The purification was done using a silica gel column inside the dry box. The first dark red band was eluted in toluene and the second green band was eluted with 35% of acetonitrile in toluene. The compounds were analyzed using IR and Mass spectrometry. The first red band was the unreacted (Phen)Mo(CO)\(_4\) complex and the second green band was identified as [Mo (bdt)]\(_3\)] based upon the ESI MS analysis (Figure 15).

Once again we obtained the L (phen) displaced molybdenum complex from a Mo(0) complex. We therefore decided to try high valent Mo precursor, where a bis
nitrogen ligand is already associated to the molybdenum center. Our choice of precursor was (Phen)MoO₂Cl₂, which is a structurally and spectroscopically characterized Mo(VI) complex. It must be noted that in all the above trials we have either used low valent Mo(0) complex (Section 3.5.1.1.1 and 3.5.1.1.2) with L₅-Bu ligand or the ligand was added separately (Section 3.5.1.1.3) (Phen)MoO₂Cl₂ was a promising candidate to try these reaction due to the following reasons: (1) Mo is in highest oxidation state and it can not be further oxidized, (2) it is a hexa-coordinated molecule with two labile Cl-groups and a already attached chelating nitrogen donor, and (3) it will provide a controlled reaction with dithiolene where dithiolate ligand will replace two Cl-groups and does not break the Mo-N bond.

3.5.1.2.2. Reactions of (Phen)MoO₂Cl₂ with dithiolenes (Scheme 7)

The air stable (Phen)MoO₂Cl₂ was synthesized using the published procedure (Figure 16).⁹⁰ Only H₂tdt (toluene 3,4-dithiolate) was used as the dithiolene ligand in this set of reactions. A suspension of PhenMoO₂Cl₂ in DCM was reacted with a mixture of tdt and Et₃N in DCM under anaerobic conditions at −78°C. The reaction mixture was stirred only for 15 min and the solvent was evaporated. The residue was redissolved in dry DCM and the compound was precipitated as a reddish violet solid by the addition of dry hexane. The precipitate was filtered and washed with dry dimethoxyethane and dry toluene several times. Analysis of this compound by ESI MS, ¹H NMR and IR spectroscopies gave us favorable results. In the mass spectra the base peak was matched with the molecular ion associated with a [Et₂NH]⁺ ion at 550.2 (m/z), i.e. [M+Et₂NH]⁺ observed in the positive mode of ESI MS (Figure 17). The other prominent peak was assigned as
There were another peaks, which could not be assigned. The association of Et$_3$NH was also observed in $^1$H NMR spectrum where phenanthroline and tdt protons were also present. NH proton was also observed in the expanded window of $^1$H NMR that came at $\sim$11.5 ppm. IR spectrum in the KBr disc showed an oxo stretch at 927 cm$^{-1}$. Combining all these results one can conclude that we must possibly have [Et$_3$NH][(Phen)MoO(tdt)] type complex. We have not checked the oxidation state on the Mo-center that requires conductivity and magnetic moment measurements.

Parallel to the above synthesis, we have also developed an alternative route to synthesize [(Phen)MoO(dt)] type of complexes. This requires synthesis of a Mo(II) carbonyl complex Mo(CO)$_4$Cl$_2$, which can be reacted with dithiolene (like bdt, tdt, mnt etc.) and phenanthroline to generate (Phen)Mo(CO)$_2$(dt) type of complexes. The dicarbonyl group can be replaced by an oxo group using Et$_4$NOH.

3.5.1.2.3. Reactions of Mo(CO)$_4$Cl$_2$ with dithiolenes and bis-N-donor (Scheme 8)

Mo(CO)$_4$Cl$_2$ was synthesized by condensing Cl$_2$ gas on Mo(CO)$_6$ at $–78^\circ$C.$^{94}$ The complex was not purified or analyzed because of its thermal unstability and high reactivity. It was dissolved in dry methanol and a solution of Na$_2$mnt in dry methanol was added into it at $–78^\circ$C, which changed the color of the reaction mixture from yellow to red. At the same time another solution of phenanthroline in dry methanol was added into it, which immediately yielded a reddish violet precipitate. The precipitate was filtered anaerobically and washed with dry methanol. The analysis of the compound obtained was done by IR, NMR and ESI MS (Figure 18). IR showed following signals: CO stretches at 1963 and 1889 cm$^{-1}$; CN stretch at 2206 cm$^{-1}$; aryl C-H stretches at 3070 cm$^{-1}$, which
showed that phen and mnt ligands were present in the complex in addition to the carbonyl groups. 1H NMR showed the proton signals from the phenanthroline ligand, confirming the presence of Phen ligand. Mass spectra showed the base peak at 528, which was predicted as \([\text{M}+2\text{CH}_3\text{CN-CO}]^+\), which is possible because of the labile CO groups. The other prominent peak at 509 was predicted as \([\text{M}+\text{Cl}]^+\), which may be due to the contamination from some chloro- side product. Combining all the observations, we can conclude that the compound is in the form of \((\text{Phen})\text{Mo(CO)}_2(\text{mnt})\).

3.6. Conclusion

We found that low valent Mo complexes were not suitable for the synthesis of mono dithiolene complexes. In our case, we generally obtained bis dithiolene and thermodynamically more stable tris-dithiolene Mo complexes. In our reaction conditions where we used low temperature conditions and also high temperature condition, we could not isolate any mono dithiolene complex either with bis-pyrazole ligand or phenanthroline using low valent Mo precursor. Finally when we reacted Mo(VI) complexes or Mo(II) complexes with dithiolene we were able to isolate complexes, where spectral studies showed the formation of mono-dithiolene complexes with phenanthroline as the other moiety. X-ray crystallography is required to find the structure of these new complexes.
3.7 Figures and Schemes

Figure 1. Structure of iron-molybdenum cofactor of the molybdenum-iron protein of nitrogenase deduced from X-ray crystallography.

Figure 2 Structure of molybdenum cofactor (Moco).

Figure 3. Three major classes of mononuclear molybdenum enzymes according to Hille’s classification.
Figure 4 Important model systems form molybdenum oxo transferases. (A) Dioxo Mo\textsuperscript{VI} ligands that show complete OAT reaction. (B) monooxo Mo\textsuperscript{V} complexes proposed as model complexes for intermediate oxidation state during an OAT reaction. (C) monooxo Mo\textsuperscript{IV} complexes.
Scheme 1

Pinacolone + Ethyl formate → MeO⁻ → 1,3-dicarbonyl compound → NH₂NH₂ → 3-tertbutylpyrazole

K[BH₄] + 3-tertbutylpyrazole → hydrobis(3-tertbutylpyrazole)borate

Scheme 2

H₂B[N=][N=][N=]H₂ + Mo(CO)₆ or Mo(CO)₃(CH₃CN)₃ → hydrobis(3-tertbutylpyrazole)borate → L₄BuMo(CO)₄
Scheme 6

Scheme 7

Scheme 8
Figure 5. Characterization of Potassium Hydrobis(3-tertbutylpyrazole)borate KL\textsuperscript{−}{\textsubscript{Bu}}\textsuperscript{+} ligand.
Figure 6. Characterization data of \( \text{L}^{\text{t-bu}} \text{Mo(CO)}_4 \).
Figure 7. Ligand exchange reaction of Ni(dt)$_2^+$ L$^{tbu}$Mo(CO)$_4$
Figure 8: IR of Mo(CO)$_3$(CH$_3$CN)$_3$

Figure 9: IR of L$^{t}$BuMo(CO)$_3$(CH$_3$CN)
Figure 10: Mass and IR-spectra of \( \text{Lt-bu-Mo(CO)}_4 + \text{bdt} \) at 50 °C
Figure 11: IR of $\text{LMo(CO)}_4 + \text{bdt}$ at $-78 \, ^\circ\text{C}$

Figure 12: IR spectrum of $\text{MoO}_2\text{Cl}_2(\text{OPPh}_3)_2 + \text{bdt} + \text{KL}$ $^{\text{t-Bu}}$ at $-78\, ^\circ\text{C}$.
Figure 12: IR spectrum of MoO₂Cl₂(OPPh₃)₂ + Na₂mnt + KL⁻⁻Bu at – 78°C.
Figure 14: IR (KBr) and $^1$H NMR (solvent: chloroform-d) spectra of (phen)Mo(CO)$_4$. 

PhenMo(CO)$_4$
Figure 15. Mass-spectra of (Phen)Mo(CO)$_4$ + bdt at 50 °C
Figure 16. IR (KBr) and $^1$H NMR (solvent: chloroform-d) spectra of (Phen)MoO$_2$Cl$_2$
Figure 17. IR (KBr), $^1$H NMR (solv: acetonitrile-d$_3$), and mass spectra of (Phen)MoO(tdt).
Figure 18. IR (KBr), $^1$H NMR (solv: acetonitrile-d$_3$), and mass spectra of Mo(CO)$_2$(mnt)Phen complex
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