1. INTRODUCTION

The structural study of Schiff base coordination complexes, especially Schiff base derived from hydroxyaryl aldehyde has been investigated extensively in the last two decades. This class of compounds can be derived by condensing aliphatic, aromatic or heterocyclic aldehyde or ketone with thiosemicarbazide or hydrazide compounds. The recent literature shows that a variety of three dimensional supramolecular arrays such as helicate, grid, cages, ladder and rings have been prepared by the Schiff base ligand and transition metal ions [1-10]. It is because of the azomethine linkage (-N=CH-) which is a prominent feature that makes the Schiff base an interesting ligand for complexation. Of the second series of transition metals, molybdenum is the only trace element important for living organisms. The importance of molybdenum as a biological trace element has been investigated in various molybdenum containing enzymes as *cis*-MoO_2^{2+} group in the stable oxidized form which is coordinated to ligands containing heteroatoms like ONS has been found useful in various oxidation reaction such as epoxidation and hydroxylation of olefins [11-13] and oxidation of alcohol [14]. The easy conversion between Mo(VI) and Mo(IV) and a large accessible oxidation states make oxomolybdenum complexes a decent precursor as the active site of oxotransfer reaction in molybdoenzyme such as xanthine oxidase, sulphite oxidase, nitrate reductase and aldehyde oxidase. Since the structural chemistry of Schiff base metal complexes have taken the forefront position in the development of coordination chemistry, this project was directed towards the synthesis and structural characterization of new dioxomolybdenum(VI) Schiff base complexes.

1.1 A short introduction of the Schiff base ligands

Schiff base (*N*-substituted imine) is a compound which consists of an azomethine functional group, -RHC=N-R' (where R'≠H), as a result of condensation reaction between primary amine/ carboxylic hydrazide compounds and carbonyl compounds. It was firstly developed by a German chemist, Hugo Schiff, in 1864. Thereafter, Schiff bases have been widely used as synthetic intermediate in organic chemistry and as multidentate ligands in coordination chemistry. In the past 50 years, a multitude number of Schiff bases derived from hydroxyaryl aldehyde (2-hydroxy-1-napthaldehyde, 3-hydroxy-2-napthaldehyde, salicylaldehyde, 3-ethoxysalicylaldehyde, 5-nitrosalicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde and *o*-vanilin) have been synthesized. These ligands have been studied extensively due to their relative easiness of preparation and the presence of lone pair electrons in the sp^2 hybridized orbital of nitrogen atom of the azomethine group as chelating agents. The conjugation effect of the aromatic ring in the Schiff base, the adjustable electronic and steric properties due to various substitutions at the aromatic ring, and the presence of other ligating groups such as -OH and -SH close to the azomethine group have made the Schiff base of this group cut out for complexation of metal (Fig.1).

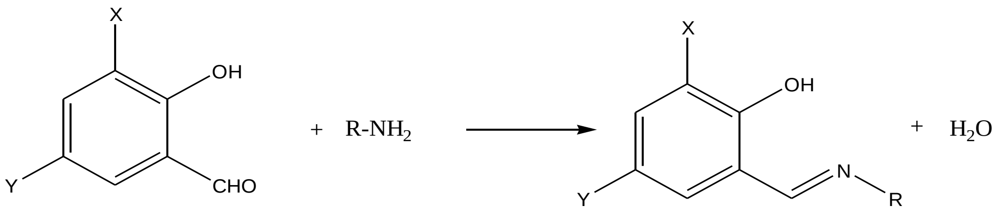


Figure 1: **Formation of Schiff base ligands** Salicylaldehyde (X=H, Y=H), 3-ethoxysalicylaldehyde (X=OCH_3, Y=H), 5-chlorosalicylaldehyde (X=H, Y=Cl), 5-bromosalicylaldehyde (X=H, Y=Br), 5-nitrosalicylaldehyde (X=H, Y=NO_2), o-vanilin (X=OCH_3, Y=H); RNH_2 is primary amine (where R is alkyl or aryl group); RNH_2 is carboxylic hydrazide (R= R'CONH where R' is alkyl or aryl group)

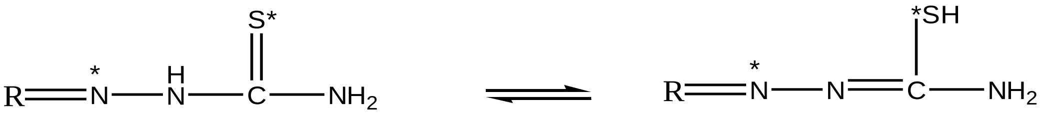
Schiff base ligands derived from the condensation of salicylaldehyde with carboxylic acid hydrazides have become the topic of recent research. Carboxylic acid hydrazide is a compound in which the hydroxyl group in carboxylic acid is substituted by a hydrazine moiety. It is generally prepared from aqueous hydrazine and the corresponding carboxylic acid or ester as shown in the following equation.[15]

$$\text{R-COOH} + NH_2NH_2 \longrightarrow \text{R-CONHNH}_2 + H_2O$$

These carboxylic acid hydrazides are also useful compounds for further synthesis besides being used as polyfunctional ligands in coordination chemistry. Some of the hydrazides and related compounds that are commonly used are: carboxylic hydrazides ($RCONHNH_2$), thiohydrazides ($RCSNHNH_2$), semicarbazides ($NH_2CONHNH_2$), thiosemicarbazides ($NH_2CSNHNH_2$) and sulfonylhydrazides (RSO_2NHNH_2) [16].

It is long since hydrazones and their derivatives have attracted the attention of scientists. Being a Schiff base ligand, hydrazone contains a secondary amido group (R-CO-NH-) in addition to the azomethine (-C=N-) functionality. Although the amido nitrogen atom rarely participates in the complexation, but the inter- and intramolecular hydrogen bonding interaction induced generate supramolecular architecture. Depending on the nature of the hydrazone and the metal as well as the reaction condition, hydrazone may form either mono- or polynuclear coordination complex. When hydrazide compounds react with derivatives salicylaldehydes, these hydrazones may act as bidentate *N,O*-, tridentate *N,O,O*-, *N,O,N*- *N,O,S*-, tetradentate *N,N,O,O*- or hexadentate *N,N,O,O,S,S*- donor ligands, which will be adopted to produce mononuclear complexes. When dihydrazide compounds, which are derived from diester reacts with derivatives salicylaldehyde, bis-aroylhydrazone binucleating ligands will be produced. Bis-acyl-/or aroyl-hydrazones can be obtained from dihydrazide or dialdehyde(or diketone).

Thiosemicarbazone ligands have been investigated widely due to the central role played by sulfur coordination in these compound. The ligand can exist as an equilibrium mixture of thione (I) and thiol (II) tautomers in solution in Figure 2:

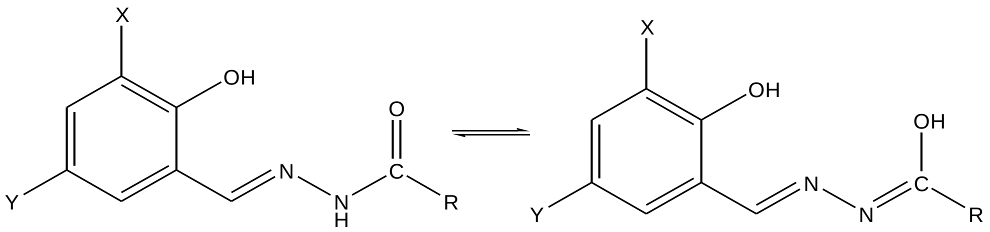


(I) (II)

Figure 2: Tautomerization of thiosemicarbazone ligands

The ONO donor types of Schiff base ligands also show keto-enol tautomerization both in solution and solid state (Fig.3).

\



(a) (b)

Figure 3: **Tautomerization of hydrazone ligands** (a) keto tautomer derived from carboxylic hydrazide and salicylaldehyde derivatives
(b) enol tautomer derived from carboxylic hydrazide and salicylaldehyde derivatives

In general, the number of possible coordinating sites of the Schiff base ligands depend on the carbonyl group, azomethine nitrogen and the suitable substitution on the ligand’s framework and on their tautomeric equilibrium. Consequently, the existence of tautomeric equilibrium in the compounds make it possible to obtain coordination compounds containing either neutral keto form or deprotonated enol form, which allows various structural possibilities for the corresponding metal complexes.

1.2 A Short Introduction of Dioxomolybdebum(VI) Schiff Base Complexes

In recent years, coordination chemistry research work on Mo(VI) complexes has focused on molybdo-containing enzyme that catalyze oxygen transfer reaction. They mainly consist of mononuclear high oxidation state molybdenum atom that is coordinated by at least one oxygen and one or two molybdopterine (N/S-donor atom) ligands.

Hydrazide Schiff base ligand is one of the tridentate ligands that has been used for the preparation of dioxomolybdenum(VI) complexes. The Schiff base ligands can form complexes of the type [*cis*-MoO_2(L)D], where L is dianionic tridentate ligand and D is donor solvent molecule. Thus, various dioxomolybdenum(VI) hydrazide Schiff base complexes of different **R** functional groups can be prepared (fig.4).

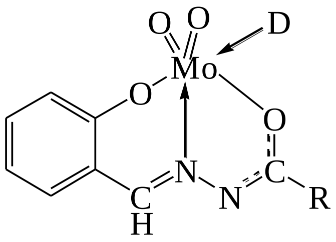


Figure 4: Various dioxomolybdenum(VI) hydrazide Schiff base complexes of different R functional groups

Molybdenum-based supramolecular network is important in material science due to their potential application in catalysis and optoelectronics [17-18]. In addition to the coordinate bond, one of the strategies for preparing extended structures with metal building block is based on the use of intermolecular hydrogen bonds or π-π interaction [19-20]. In that sense, hydrazide Schiff base ligand cause interesting building block to form extended structures. History has shown that different Schiff base environment in the dioxomolybdenum(VI) complexes providing the steric and electronic effect that will influence the performance of catalyst in terms of rate and selectivity. According to Luan *et.al*, dioxomolybdenum(VI) complexes with bridging ligand containing nitrogen donor atoms has been proven to be good catalyst for the epoxidation of olefins [21].

The aim of this project involves the synthesis and structure study of different types of mononuclear dioxomolybdenum(VI) complexes as well as some new dinuclear and polynuclear molybdenum hydrogen bonded polymers that contain 4,4-bipyridne and 4,4-bipyridine N,N’dioxide.

1.3 Spectroscopic Techniques for Structural Analysis

1.3.1 IR Spectroscopy

Infrared spectroscopy is an essential technique in the characterization of *cis* dioxomolybdenum complexes. The O=Mo=O unit exhibits two strong bands generally at 905-948 cm^{-1} and 875 – 914 cm^{-1} assignable to the symmetric and assymetric stretching of Mo=O. These are the diagnostic values for the *cis*-MoO_2 unit as a *trans* MoO_2 structure would have shown one υ (O=Mo=O) band due to the asymmetric stretch. On the other hand, the *cis*-trioxo fragments, formulated $Mo(O_t)_2O_b$ or $Mo_2(O_t)_4O_b$, for example $Mo_2O_5(\eta\text{-}C_5H_5)_2$, are reported to give $\upsilon_{asymm}(Mo\text{-}O_t)$ at 920 cm^{-1}, $\upsilon_{sym}(Mo\text{-}O_t)$ at 898 and υ_{asymm} $(Mo\text{-}O_b\text{-}Mo)$ at 770 cm^{-1}. Thus, the characteristic IR bands for Mo=O are as follow: MoO_2 (dioxo), $\upsilon(Mo\text{-}O_t)$ at 885-950; Mo_2O_3, $\upsilon(Mo\text{-}O_t)$ at 920-950, $\upsilon(Mo\text{-}O_b)$ at 750-760; ; Mo_2O_5, $\upsilon(Mo\text{-}O_t)$ at 900-930, $\upsilon(Mo\text{-}O_b)$ at 750-790, but with the possibility of intermediate bands. As a general conclusion, IR spectra can serve for the identification of MoO_2, Mo_2O_3 and Mo_2O_5, in which the presence of a broad band at 750 – 800 cm^{-1} provides evidence in support of oxo bridging and the presence of polymeric structure in molybdenum complexes.

Electron-withdrawing or donating substituent on the salidene ring can induce electron density changes at the molybdenum atom, thereby influencing the Mo=O stretching frequencies. Since the oxo oxygen are electron donors, greater electron density in the Mo π orbitals (arising from electron donating substituent) would increase electron repulsion between the Mo π electrons and the oxo oxygen electrons, decreasing the Mo=O overlapping, resulting in lower frequency Mo=O stretches. Conversely, the electron withdrawing substituent will increase the Mo=O stretching frequencies. Trends in the $\upsilon_{Mo=O}$ are also observed as a function of the ligands donor set (ONO vs ONS). When a sulphur is substituted for an oxygen atom, one observes a decrease in the Mo=O stretching frequencies. This is due to the reduction of the electron density within the Mo=O bond as a result of the increase in Mo dπ–S pπ interaction [22]. Coordination of neutral bidentate N-N donor ligands to the Mo atom lowers the Mo=O stretching frequency [23-24].

The Schiff base ligands carry a few potential donor sites: (i) phenoxyl oxygen, (ii) carbonyl oxygen, (iii) acyclic azomethine nitrogen (iv) thioketone sulphur and (v) amine nitrogen. In order to study the binding mode of Schiff base ligand to the MoO_2^{2+} ion in the complexes, the IR spectra of the free ligands were compared with the spectra of the corresponding complexes. For instance, the azomethine C=N stretching vibration of the Schiff base are usually observable in the region of 1585 – 1650 cm^{-1}. As a corollary of the coordination of the ligands to the molybdenum atom *via* the azomethine nitrogen atom, a slight decrease or increase in the frequency of C=N stretching vibration could be observed. The C-O stretching vibration of the phenolic group could be found in *ca.* 1280 cm^{-1} region. Similarly, the stretching frequency of C-O is shifted to a higher wave-number when the ligands are involved in complexation. The IR spectra of the complexes show a negative shift of 15-20 cm^{-1} in $\upsilon_{C=O}$ absorption indicating the decrease in stretching force constant of C=O as a result of coordination through oxygen atom of the ligand.

The dioxomolybdenum(VI) complexes also exhibit IR absorption bands that is associated to the stretching frequencies of donor solvent molecules. Drago and Meek have assigned υ_{S-O} at 1025-985 cm^{-1} when DMSO is coordinated to molybdenum center through oxygen atom [25]. The $\upsilon(P\text{-}O)_{HMPA}$ is usually noticeable at 1100 – 1200 cm^{-1} . In free imidazole, absorption peaks were observed at *ca*. 1600-1675 cm^{-1} as reported by Otting [26]. On the other hand, free 4,4-bipyridine and free pyridine N-oxide exhibit absorption bands at *ca*. 990 and 1234 cm^{-1}, respectively [27-28].

1.3.2 NMR Spectroscopy

NMR spectroscopy technique has been used as an auxiliary tool to elucidate the structural formula of the dioxomolybdenum(VI) complexes. It is noteworthy to comment some points regarding ^{1}H NMR and ^{13}C NMR spectra feature of the ligands and complexes.

In ^{1}H NMR, sharp singlet is observed in 8.00 - 9.30 ppm due to the azomethine proton in the ligands. The azomethine proton signals, on an average shows chemical shift that is attributed to the drainage of the electron density from nitrogen atom of azomethine group to metal center [29-31]**.** The peaks observed at *ca*. 12.50 and 11.50 ppm which are assigned to δ OH and δNH proton in the free ligands disappear in the complexes suggesting that the ligands are coordinated to the metal center through phenoxyl and enolate oxygen. The multiplets due to aromatic protons normally appear in the 6.50 to 8.30 ppm region [32-33]. In addition, the signals reported for the *ortho* and *meta* protons of pyridyl ring of 4,4-bipyridine are located at 8.80 and 7.40 ppm [34].

The coordination of O and N atoms could be confirmed by comparison of ^{13}C NMR of the ligands and the complexes. This has further given information on the structure of the complexes in solution from comparison of complexes and ligands. For example, the resonance due to the azomethine carbon and carbonyl carbon is much downfield shifted since they are closer to the coordinated oxygen and nitrogen atom. The signals of these carbons which are usually found in the regions of 155-160 ppm in free ligands could be in the region 170-185 ppm in the complexes. The chemical shift, δ, accompanying the coordination of the ligands in the complexes is reported and the numbering scheme for the carbon atoms for the ligands has been shown.

1.3.3 UV-Vis Spectroscopy

Ultraviolet-visible spectroscopy involves the spectroscopy of photons in the UV-visible region. This technique produces absorption that measures electronic transition from the ground state to the excited state and is commonly used in the quantitative determination of solution containing transition metal ion and conjugated organic substances.

A charge transfer complex is a connection of several portions of a molecule in which a fraction of electrostatic charge is transfered from electron donor to electron acceptor moieties of the molecules, producing electrostatic force that stabilizes the molecular complex. When ultraviolet or visible radiation interact with the complex molecule, electronic transition occurs and a number of absorption bands will be observable. Ultraviolet region falls in the range between 190-380 nm while the visible region falls between 380-750 nm. The possible electronic transitions are: σ to σ* (<200 nm), n to σ* (150-250 nm), n to π* (200-700 nm) and π to π* (200-700 nm). σ to σ* electronic transition occurs at wavelength less than 200 nm in molecule which contains single bond (C-H) and s orbital. Molecules with single bond and non bonding lone pair electrons tend to give n to σ* electronic transition band. Unsaturated molecules such as benzene ring containing molecules will give absorption for electronic transition π–π* while unsaturated molecules with atoms such as oxygen or nitrogen (nitrate, carbonate, and nitrite ions) may undergo electronic transition n–π* other than π–π*. Both σ to σ* and n to σ* transition require a great deal of energy and therefore occur in the far ultraviolet region or weakly in the region below 200 nm. Transition of n to π* and π to π* occur at higher wavelength as they require less energy. Aromatic system, which contains π electron such as C_5H_5N (250 nm) and C_4H_4O (210 nm) absorb strongly in the ultraviolet region

1.3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is the most widely used method in material science in which the measurement is based on the mass loss of material as a function of temperature. As a result, a continuous graph of mass change against temperature is obtained when the compound is heated at uniform rate.

The TG curve is used to determine the thermal stability of a material by providing information concerning thermal decomposition behavior of the material. A typical TG curve is shown below (fig.5).

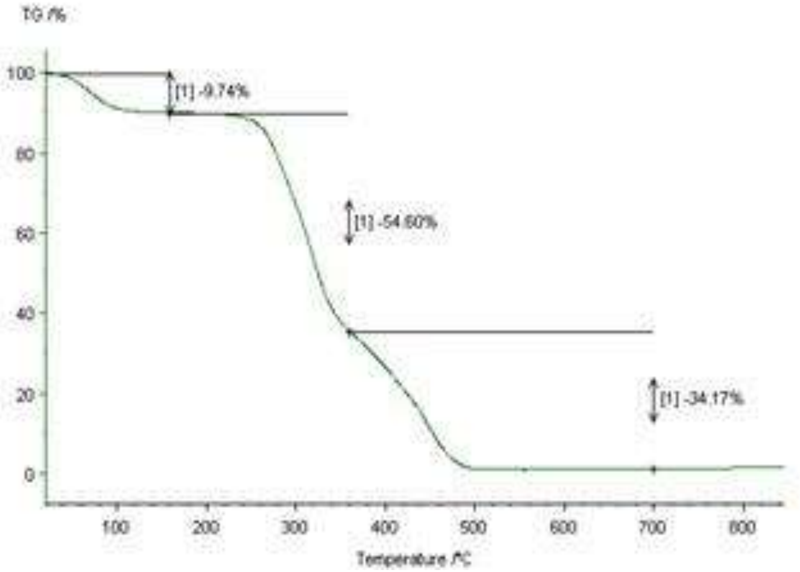


Figure 5: Example of TG curve

From the thermogram, we can determine the temperature at which the onset of a mass changes and the final temperature at which the particular decomposition appears to complete as well as the percentage of mass loss due to decomposition. In short, TG curve gives quantitative interpretation and qualitative comparison on thermal stability of a substance.

1.3.5 Cyclic Voltammetry (CV)

CV is one of the versatile analytical techniques available to the electrochemist. The technique allows identification of reversible couple, study of mechanism and rate of oxidation-reduction process and provide a tool to help at unraveling complex electrochemical system. In a cyclic voltammogram, an electrolyte solution component is allowed to be in contact with an electrode surface to undergo redox reaction, enabling the surface of the electrode to gain sufficient positive and negative voltage to induce electron transfer.

Consider a reversible reaction: $O + e^- \rightarrow R$.

Initially the electrode is at a particular voltage. The electrode voltage is either increased or reduced at a linear rate and finally the voltage is returned to the original value. When the surface becomes sufficiently positive or negative, electron transfer occurs between the solution and the electrode. This is signaled by the appearance of anodic current, I_p^a. The reversed voltage cycle happen when the concentration of the transferring species near the surface drops and the anodic current falls off, leading to an *inverse c*urrent peak. This phenomenon is illustrated in figure 6.

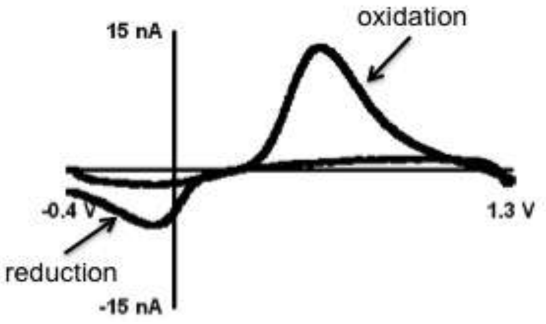


Figure 6: Cyclic Voltammogram

Parameters that characterize reversible process are:

a) The difference between the cathodic and anodic peak potential is about 58 mV at 25°C.

b) The ratio of the cathodic and anodic peak current is 1.

1.4 Oxomolybdenum Compounds as Catalysts/ Molybdoenzyme

The study of molybdenum complexes with dianionic tridentate ligands is particularly significant because of the coordination atmosphere of the MoO_2^{2+} metal center produces an open active site on molybdenum for catalytic oxidation process [35-44]. Hiller has classified the molybdenum enzyme based on their distinct active-site structure into three families. They are molybdenum hydroxylase such as xanthine oxidase and molybdenum oxotransferases such as sulfite oxidase and dimethyl sulfoxide reductase. These molybdenum containing hydroxylase and oxotransferase which posses a mononuclear active site and exist as oxidized form with at least one terminal oxo-group, play an important role in the metabolism of nitrogen, carbon, sulphur and arsenic elements. Figure 7 below shows a proposed mechanism of DMSO reductase [45] reduce DMSO to DMS.

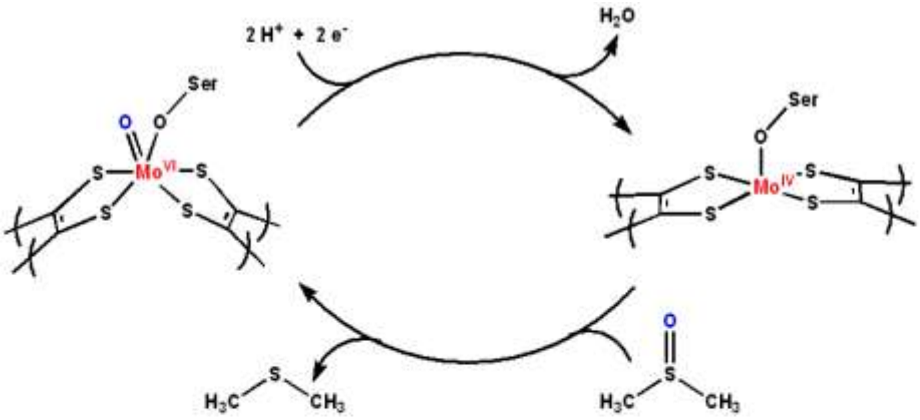


Figure 7: Mechanism of DMSO reductase reduce DMSO to DMS.

As shown in the diagram, H^+, OH^- and electron that transfer between substrate molecules and DMSO reductase occur at the molybdenum center. The chemistry involved is the acid-base reaction and redox chemistry which involve oxidation of Mo(IV) and reduction of Mo(VI). The active site is a coordinately unsaturated molybdenum atom in a sulfur-ligand environment. Mo=O groups are found to be surprisingly labile, allowing the metal center to act as a catalyst for oxygen atom transfer to and from suitable acceptors and donors. A number of MoO_2^{2+} complexes have been prepared as structural and functional model of molybdenum active site. This achievement provided a better insight for the reactivity of the oxomolybdenum (VI) complexes.