SYNTHESIS, CHARACTERIZATION AND REACTIONS OF DIOXO- MOLYBDENUM(VI) AND TUNGSTEN(VI) SCHIFF BASE COMPLEXES

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CERTIFICATE

Certified that the work incorporated in the thesis SYNTHESIS, CHARACTERIZATION AND REACTIONS OF DIOXO- MOLYBDENUM(VI) AND TUNGSTEN(VI) SCHIFF BASE COMPLEXES *submitted by Ms. Deena Antony. C, M.Sc was carried out by the candidate in the Inorganic Chemistry Division, National Chemical Laboratory, Pune 411 008, under my supervision for the Degree of Doctor of Philosophy in Chemistry, University of Poona. This work is not submitted so far for any other degree.*

(C. Gopinathan)

Research Guide

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Deena Antony. C

Pune
(Deena Antony C.)

Date 30-1-1996

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CHAPTER 1

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1.1 GENERAL INTRODUCTION TO THE CHEMISTRY OF GROUP VIB METALS

Chromium, molybdenum and tungsten belong to the VIB group of *d*-block transition metals. Being a member of the same periodic group, they have the general electronic configuration $(n-1)d^5ns^1$ and show many common characteristic properties. However, they differ markedly in certain properties which are dependent on their atomic and ionic radii. The chemistry of molybdenum and tungsten (which are quite similar chemically) differs in many respects from that of chromium. Thus chromium forms several compounds that are unknown or rare in molybdenum and tungsten chemistry.[1]

In their lower oxidation states, stabilized by π bonding ligands, chromium, molybdenum and tungsten show their greatest chemical similarity. They form innumerable organometallic compounds, a stable hexacarbonyl and many substituted carbonyls. However, in the higher oxidation states the three metals show similarities to a smaller degree. Chromium has a well defined +II oxidation state and many chromium(II) salts and complexes are readily prepared. Mo(II) and W(II) compounds are generally not analogous to those of Cr(II) though there are similarities between molybdenum and tungsten compounds. Mo(II) and W(II) form metal atom clusters with an octahedral array of six metal atoms exhibiting metal-metal bonding; a type of struoture apparently unknown for chromium. The most stable oxidation state of chromium is +III and a good effort has been made in the development of chromium(III) coordination chemistry. In contrast, very little is known about the coordination chemistry of Mo(III) and W(III). Finally, though the aqueous chemistry of chromium in +IV and +V oxidation states are not well established, the solution chemistry of Mo and W in +IV and +V oxidation states are well described in literature, in which the metal has even coordination number 8 which is unknown in chromium chemistry.

1.2 CHEMISTRY OF MOLYBDENUM AND TUNGSTEN

Molybdenum and tungsten exist in oxidation states of -II to +VI. Their coordination number ranges from 4 to 8 and accordingly the metal has a varied stereochemistry.[2] The coordination chemistry of molybdenum and tungsten in which the metal is in its higher oxidation state is dominated by oxo and sulphido species which may be terminal, bridging or both.[1,3] The strong σ and π electron donations by oxo ligand neutralize much of the effective positive charge of the metal and destroy its acidity enhancing effect. The most important feature of the terminal oxo species is multiple bonding between oxygen and the metal atom (Mo or W) with bond orders ranging from 2 to 3.[4,5]

X-ray crystallographic data of several oxo-complexes have shown that terminal molybdenum-oxygen bonds ($Mo-O_t$) are shorter (1.65 - 1.85 Å) than those of bridging oxygen (1.88 Å) and much shorter than Mo — O and Mo — N single bonds(2.33 Å). The bonds between Mo and ligand atoms which are *trans* to terminal Mo — O bonds are exceptionally long due to labilisation effect.[6]

The +IV, +V and +VI oxidation states of molybdenum show greater affinity for oxygen, although nitrogen and sulphur containing complexes are also known. While lower oxidation states have tendency to bind nitrogen, sulphur ligands display an intermediate range of ligational behaviour.[7] Lowering of oxidation state experiences an increased affinity for sulphur with concomitant decrease in affinity for oxygen. This is well reflected in the coordination environment found in natural molybdenum. In sea-water molybdenum is found mostly as MoO_4^{2-} (oxidation state +VI) and an exclusive sulphur coordination is observed in molybdenite, a mineral where the metal is found as sulphide, MoS_2 (oxidation state +IV). In biological systems (except in nitrogenase) both oxygen and sulphur are known to be coordinated where oxidation states of molybdenum cycle between +IV and +VI states.

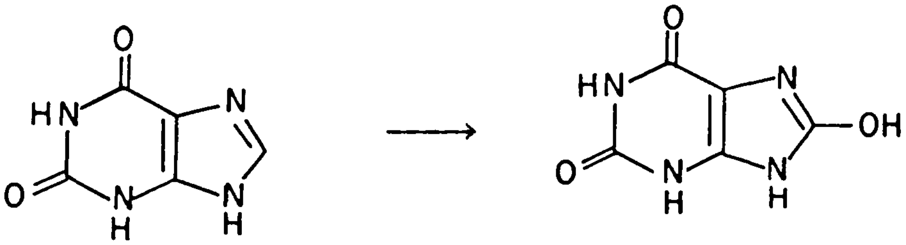
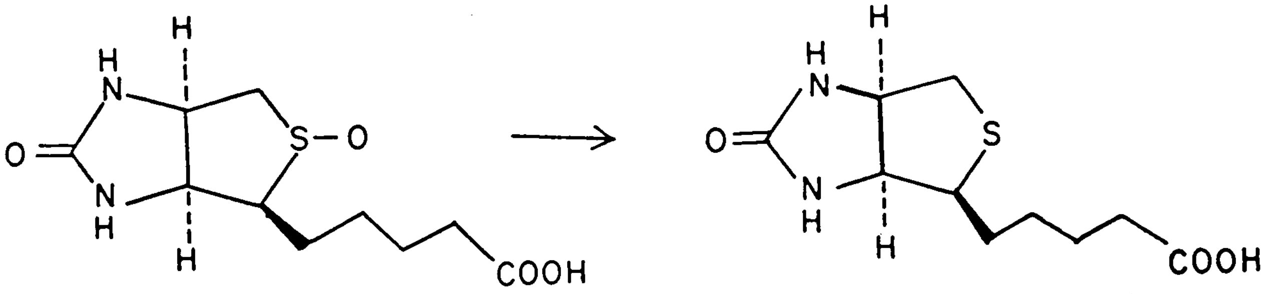
1.3 BIOLOGICAL IMPORTANCE OF MOLYBDENUM

Molybdenum is the only element among the second and third transition series known to be essential for life.[8] Though the presence of molybdenum in the ashes of plants was discovered in 1900, it was not until 1930 when the role of molybdenum in nitrogen metabolism was realized, with the discovery that the metal was essential for the growth of the nitrogen-fixing organism Azotobacter.[9] Since then various molybdenum dependent enzymes have been identified in several species of living systems. The enzymes are found in simple bacteria as well as in complex mammalian systems.

Burgmayer et. al.[10] have grouped the molybdoenzymes according to their primary function in the metabolism of nitrogen, sulphur or carbon. Molybdenum has an important role in the cycle of nitrogen in biological system.[11] Molybdoenzymes participate in the initial reduction reactions of inorganic nitrogen ($N_2 \longrightarrow NH_3$ and $NO_3^- \longrightarrow NO_2^-$) and in the oxidation of organic nitrogen compounds such as purines and pyrimidines.[12] Clearly, molybdoenzymes play a direct role in the entry of nitrogen into most plant and bacterial systems. Sulphite oxidase oxidizes the toxic SO_3^{2-} ion to the harmless SO_4^{2-} ion. The sulphite ion itself can arise from the interesting and important reaction catalyzed by the enzyme rhodanese.
$CN^- + S_2O_3^{2-} \longrightarrow SCN^- + SO_3^{2-}$ which is crucial in the detoxification of cyanide. The biotin sulphoxide reductase reduces oxybiotin to biotin, latter being a growth factor (vitamin) for the bacterium Escherichia Coli. Carboxidobacteria uses the oxidation of CO to CO_2 as an energy source for metabolic processes. Anaerobes such as clostridia can use CO_2 reductase

(the reverse reaction of formate dehydrogenase) to effect CO_2 fixation as part of their assimilatory metabolism.

The substrates and products of selected molybdoenzymes are given below.[13]

Molybdoenzyme	**Substrate**		**Product**
Xanthine Oxidase/ dehydrogenase.			
Aldehyde oxidase	RCHO	→	RCOOH
Carbonmonoxide oxidase	CO	→	HCO_3^-
Sulphite oxidase	SO_3^{2-}	→	SO_4^{2-}
Formate dehydrogenase	HCO_2^-	→	HCO_3^-
Nitrate reductase	NO_3^-	→	NO_2^-
D-Biotin S-oxide reductase			
S-Oxide reductase	R_2SO	→	RSR
N-Oxide reductase	R_3NO ArNO	→	R_3N ArN

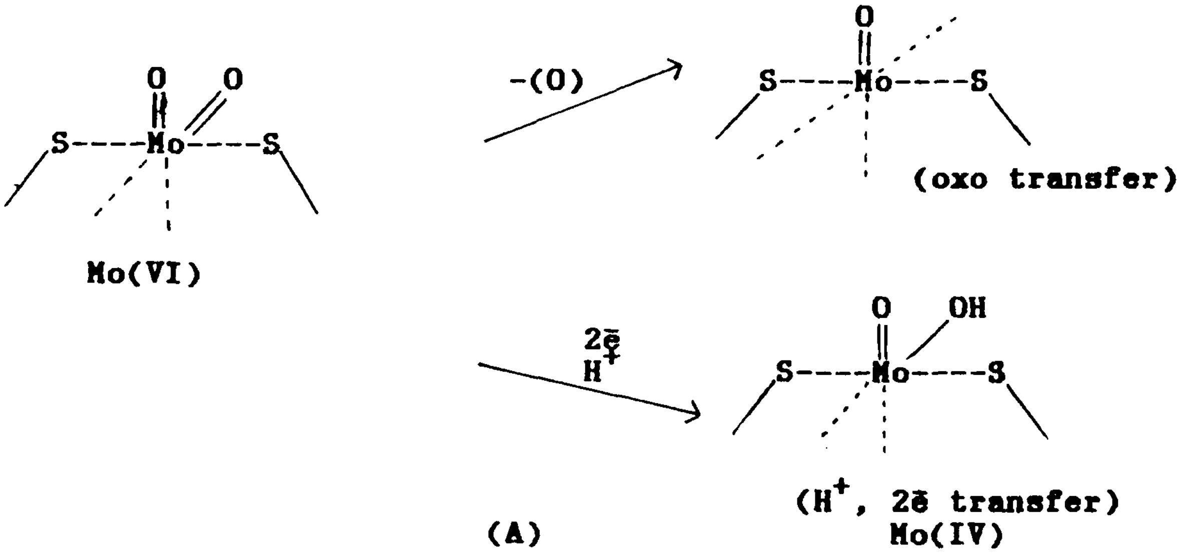
1.3.1 Composition and Redox Potentials of Molybdoenzymes

Each molybdoenzyme contains other electron-transfer active prosthetic groups in addition to Mo. In the case of sulphite oxidase, sulphite is oxidized to sulphate at the Mo site by a two electron process. The two electrons transferred to the Mo site are transmitted (one electron at a time) to the heme site from which they are donated to the ultimate electron acceptor (oxidant), cytochrome C. Other prosthetic groups transfer electrons (again one at a time) between the Mo group and the external oxidant or reductant. The action of Mo site is to affect the redox reaction of the substrate. Mo site is the substrate transforming active site of the protein. In nitrogenase a complex system is present. Here, two distinct proteins, designated Fe-Mo and Fe are involved.

The reactions, however, are fundamentally similar, essentially involving the addition or removal of hydroxyl group, by using or producing a molecule of water. The lack of crystallographic results on molybdenum proteins has led to an even heavier reliance on other physical measurements to deduce the details of the structures of the metal sites. The techniques which have been most useful for probing the molybdenum sites of diverse enzymes are electron paramagnetic resonance (EPR) and extended X-ray absorbance fine structure (EXAFS) analyses. Redox potentials of Mo centers also in many cases carry valuable informations about the electron transfer behaviours of these multifunctional enzymes. The observed differences in potentials could be either because of the effect of the individual proteins on the molybdenum center, or due to differences in the oxidation states of the co-factor or both.

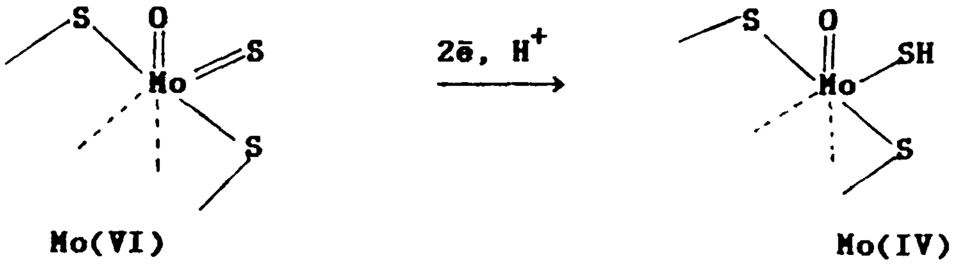
Molybdenum environments in (A) Sulphite oxidase (B) Xanthine oxidase consistent with EXAFS studies.[10]

(A) Sulphite oxidase



(A)

(B) Xanthine oxidase



(B)

1.3.2 The Molybdenum Co-factor

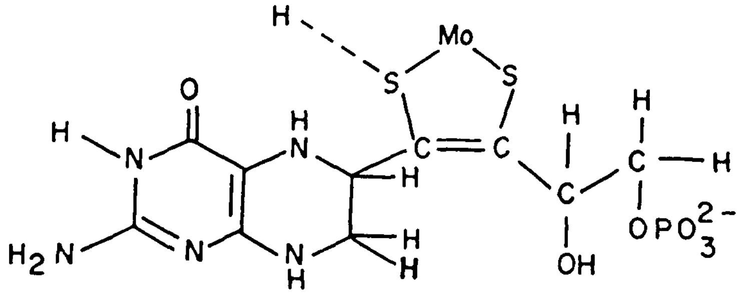
An alternative method of classification considers the molybdoenzymes comprising of two classes, each possessing a particular type of molybdenum centre or co-factor. Co-factor designates a prosthetic group that binds to the larger "apo" protein, the enzymatically active entity. The larger class of molybdoenzymes is designated as oxo-Mo enzymes. These enzymes catalyze two electron oxidation or reduction of the substrate and most of them are formally hydroxylases.[14]

All the molybdoenzymes have atleast one oxo group bound to molybdenum centre where the characteristic oxidation or reduction of the substrate takes place. All oxo Mo enzymes contain a type of molybdenum centre called the molybdenum cofactor, Mo-Co. The remaining class currently consists of a single enzyme, nitrogenase. This enzyme contain, within its Fe-Mo protein, a unique cluster of iron, molybdenum and sulphur designated as the iron molybdenum co-factor, FeMo-Co.[10]

EXAFS data on Mo-Co containing enzymes[15] demonstrate that molybdenum may exist in different forms within different enzymes though all these forms once removed from the protein, have the same activity in the nit-1 assay. In xanthine oxidase, xanthine dehydrogenase, sulphite oxidase and nitrate reductase the Mo is coordinated by sulphur donor ligands.[16] The oxidized forms of nitrate reductase and sulphite oxidase appear to have the familiar dioxomolybdenum(VI) $[MoO_2]^{2+}$ core. Oxidized xanthine oxidase and xanthine dehydrogenase show a mixed oxo-sulphido coordination. The changes in the number of (=X) ligands during enzyme turnover is particularly informative as a mechanistic indicator. Both sulphite oxidase and nitrate reductase lose one oxo ligand upon reduction. The protonation of sulphides to form an -SH group on reduction of xanthine oxidase is supported by EPR studies where proton superhyperfine coupling to Mo(V) was detected.[17]

1.3.3 The Pterin Component of Mo-Co

The discovery of a pterin component associated with Mo-Co was made through the isolation of degraded organic fragments whose precursor was apparently part of the cofactor. "Pterin" is a biologically prevalent N-heterocycle which has the 2-amino-4-oxypteridine structure.[18] The initial evidence for the presence of pterin was the appearance of a strongly fluorescent material upon degradation of Mo-Co.[19] The metabolism of Mo-Co in humans may proceed through urothione since it was observed that Mo-Co deficient children have no urothione present in their urine. The pterin component of Mo-Co has been suggested to be 5,6,7,8-tetrahydropterin, substituted in the 6-position by an α, β-unsaturated four carbon chain terminated by a phosphate and having two thiols on adjacent (α and β) carbon. It is postulated that Mo may be coordinated through these two sulphur atoms, since molybdenum forms very stable complexes with dithiolene ligands.[20] However, alternative Mo-binding modes are also possible. For example, Mo may be tri chelated by the 4-oxo, 5-nitrogen and only sulphur of the proposed dithiolene. The function of the second thiol could be to bind the co-factor to the protein through a disulphide linkage. Although pterin compounds are present in other biological processes, they are less well-known than other biologically important nitrogen heterocycles (purines, pyrimidines, flavins, nicotinamides). It chelates molybdenum in a unique way to block dimerizations. The 2-amino-4-oxy pteridine core possesses sites that may be used to bind the co-factor to the protein or to the substrates *via* the heterocyclic nitrogens, amino group or oxo-substituent.



Proposed structure of the pterin component of Mo-Co

The composition of the molybdenum iron cluster extruded from nitrogenase has been analyzed by numerous methods although no definitive stoichiometry could be assigned at present.[21] The range of values obtained, 1 Mo : 6-8 Fe : 4-9 S reflects this uncertainty. Further information about the FeMo-Co cluster has come from its physical and chemical properties. The cluster possesses an EPR signal characteristic of an $S = 3/2$ species.[22] The FeMo-Co cluster is negatively charged since it is observed to stick to anion-exchange resins but not to cation one.[23]

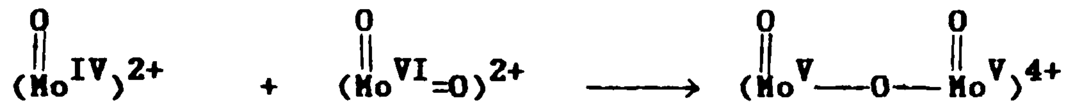
1.3.4 Functional Models of Molybdoenzyme Active Sites: A Bioinorganic Approach.

The principal area of current bioinorganic chemistry research is the isolation and characterization of synthetic analogues of molybdoenzymes which by definition is to reproduce ligation modes and to approach or achieve the stereochemistry of metalloenzyme active sites. Success in this endeavour has proven particularly useful for interpreting the properties and reactions of many metal containing macromolecules. This is especially true for iron and to a lesser extent, copper biomolecules.

Model studies for molybdenum have suffered, by comparison, because of lack of sufficient biochemical data. This is due, in large measure, to the high molecular weights and great complexity of the molybdenum enzymes, which make their purification difficult and precludes, at present X-ray crystallographic investigation.[24] In addition, the lack of distinctive biological molybdenum chromophores with large molar absorptivity such as found with heme iron complexes and blue copper proteins, has been a considerable barrier. However, application of new EXAFS technique and isolation[25] and characterization[26-28] of the low molecular weight molybdenum co-factor, has made the mononuclear active sites of these enzymes structurally more defined.

Synthetic representations of such sites must fulfill the following conditions. (1) approach the ligand native set (2) execute the forward or reverse reaction with X/XO and (3) not undergo the μ-oxo dimerization reaction. For fulfilling the first requirement, the ligand set L_n must contain atleast two thiolate ligands. Requirement (2) is offered in terms of the overall reaction(a), with the allowance that the oxygen atom actually transferred may be derived from solvent water. Reaction (b) is prevented by protein structural constraints, there by leading to requirement (3). A number of interesting structural models of Mo enzyme active sites,[29-62] especially those contain, MoO_2 unit, have been reported recently. Unfortunately none of these satisfies the requirements (1) to (3) simultaneously.

$$\mathrm{Mo^{VI}O_2L_n} \quad + \quad \mathrm{X} \quad \rightleftharpoons \quad \mathrm{Mo^{IV}OL_n} \quad + \quad \mathrm{XO} \qquad \text{(a)}$$



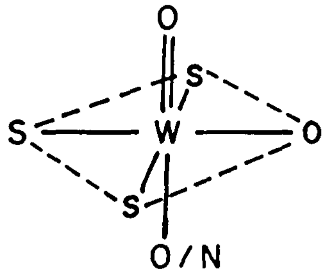
$$(\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}{}^{\mathrm{IV}})^{2+} \quad + \quad (\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}{}^{\mathrm{VI}}{=}\mathrm{O})^{2+} \quad \longrightarrow \quad (\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}{}^{\mathrm{V}}{-}\mathrm{O}{-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}{}^{\mathrm{V}})^{4+} \qquad \text{(b)}$$

The second reaction (conproportionation to µ-oxo dioxomolybdenum(V) species) often makes the oxo-transfer reaction more complicated. In addition to the steric factor a recent report[58,59] indicates that the association of solvent on five coordinated Mo(IV) species, $\mathrm{Mo^{IV}O(t\text{-}BuL\text{-}NS)_2}$ (t-BuL-NS = bis(4-tert-butyl phenyl)-2-pyridyl methane thiolate) suppresses µ-oxo bridge formation in donor solvents such as acetonitrile, THF and DMF.

1.4 BIOLOGICAL IMPORTANCE OF TUNGSTEN

Although tungsten and molybdenum possess quite similar chemistry, only recently a variety of tungsten containing enzymes have been found[63,64,65], e.g., formate dehydrogenase, carboxylic acid reductase (aldehyde oxidase) and aldehyde oxidoreductase (aldehyde ferredoxin oxidoreductase). However, in comparison to molybdenum, the lack of well characterized $\mathrm{W^{VI}O_2}$ and $\mathrm{W^{IV}O}$ compounds has hampered the acquisition of information on tungsten-mediated oxo-transfer reactions.[66] The apparent disparity between tungsten and molybdenum may be due to the low environmental abundance of tungsten, rather than to some inadequacy in a catalytic role. Tungsten, like iron and manganese may be rather more available in the extreme environments of shallow and deep sea hydrothermal vents, which are inhabited by hyperthermophilic bacteria. These remarkable archaebacteria grow optimally at temperatures near or even 100°.

Aldehyde-ferredoxin oxidoreductase obtained from hyperthermophile which catalyzes aldehydes to carboxylic acids, is a monomeric protein of approximate molecular weight 85,000 that contains approximately one tungsten, seven iron and five sulphides. EXAFS study of the tungsten site of this enzyme show that the tungsten possesses an oxo-thiolate coordination which is isostructural to the most common molybdenum enzymes.[67] The W-O bond length of 1.74 Å, clearly indicates that this is a terminally bound oxygen or oxo ligand.[68,69] Furthermore, the presence of two such oxo ligands suggest that the tungsten is present in the formal oxidation state W +VI, as no dioxotungsten compounds are known for any other oxidation states.

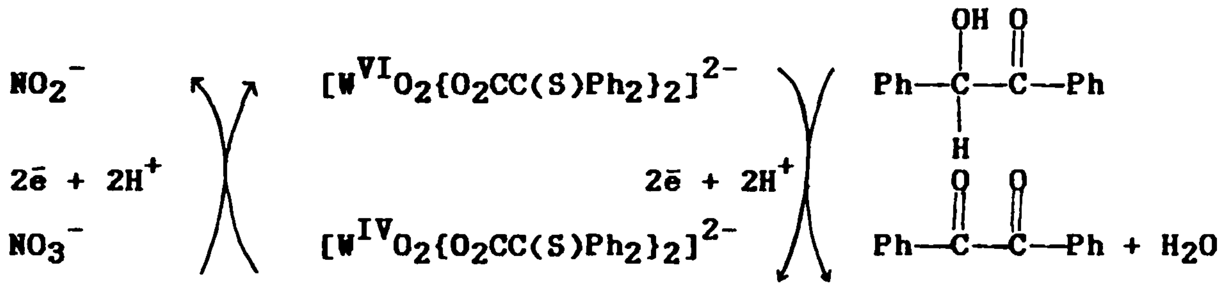


Proposed structure for the tungsten site of aldehyde oxidoreductase in which octahedral geometry is assumed for the metal atom.

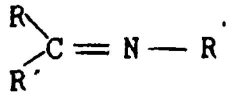
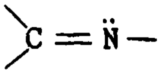
Another tungsten enzyme which has been characterized is the formate dehydrogenase from Clostridium thermoaceticum.[63(a)] Cramer et. al.[15(e)] have suggested that it is possible that the C. thermoaceticum may have a tungsten site analogous to that present in Escherichia Coli enzyme.[70] This enzyme contains, in molar ratios, 2 tungsten, 2 selenium, 36 iron and 50 inorganic sulphur and has a molecular weight of about 340,000. In clostridium thermoaceticum, the first reaction in the reduction of CO_2 to the methyl group of acetate is catalyzed by an NADP-dependent formate dehydrogenase [$NADP^+$]. An apparent tungsten co-factor was found after denaturation by boiling the formate dehydrogenase in the presence or in the absence of iodine at pH 2.5. From the fluorescence spectra it is found that the tungsten co-factor contains a pterin compound which may be similar or identical with the novel pterin found in the molybdenum co-factor from nitrate reductase, sulphite oxidase and xanthine oxidase.[27,71]

Another tungsten containing enzyme carboxylic acid reductase (aldehyde dehydrogenase) seems to be the first which is able to reduce non-activated carboxylic acids to aldehydes.[63(b)] There is no further reduction of the aldehydes to the corresponding alcohols. The tungsten does not seem to be bound very strongly to the enzyme, since part of it was easily lost during electrophoresis. It remains to be established why certain acetogenic eubacteria use tungsten rather than molybdenum as an essential catalytic component which is contrast to the remainder of the microbe world.

Model compounds for the tungsten enzymes are rare.[72-74] The structural characterization and reactivity of tungsten -(VI), -(V) and -(IV) complexes containing benzene dithiolate ligands has focused on proposing models for oxo-tungsten active sites of enzymes.[72] It is worth noting that $[W^{IV}O(S_2C_6H_4)_2]^{2-}$ complex is capable of reacting with benzoin to regenerate the starting $W^{IV}O$ complex. Recently, Cervilla et. al.[74] have synthesized and characterized the complex $(NH_4)_2[W^{IV}O_2(O_2CC(S)Ph_2)_2]$. It is the first example of a non-dithiolene tungsten complex capable of oxidizing benzoin to benzil in methanol. The reduced monomeric $W^{IV}O$ species, was reoxidised with nitrate ions, regenerating the starting $W^{VI}O_2$ complex which then act as a true homogeneous catalyst. The catalytic cycle of the oxygen atom transfer reactions is as shown below.



1.5 IMPORTANCE OF SCHIFF BASES

In 1864[75] Schiff prepared a series of compounds by the condensation of primary amines and active carbonyl compounds and since then they are known as Schiff bases. The Schiff bases have a general structure  $RR'C=\ddot{N}-R''$ (where R, R′ and R″ are alkyl, aryl, cyclohexyl, hydroxyalkyl, hydroxyaryl groups etc.). The Schiff bases contain an azomethine group and have a tendency to donate the lone pair of electrons present on the nitrogen atom of the azomethine moiety ( $>C=\ddot{N}-$). The donating property of the lone pair of electrons increases when a functional group such as SH or OH is sufficiently near to the azomethine group and this facilitates the formation of a stable metal complex.

Metal complexes of Schiff bases represent an important and interesting class of coordination compounds. Schiff bases containing polyfunctional groups have not only produced stable metal complexes of transition, non-transition , inner transition, and actinide metal ions, but these ligands and their metal complexes have also played a significant role in the domains of stereochemistry, structure, isomerism, magnetism, spectroscopy, kinetics, and mechanism of reactions, reaction of coordinated ligands, model systems of biochemical interest, catalysis, stabilizers, polymers, pigments and dyes, photography, electro-optical devices and agriculture.

The Schiff bases exhibit important properties such as anti-inflammatory activity,[76] antibiotic activity,[77] antimicrobial activity,[78] and antitumor activity.[79] Hodnett et. al.[80] have reported that the carbonyl part of the Schiff bases play the key role in antitumor activity. It has been observed that the Schiff bases prepared by the condensation of arylamine and *o*- and *p*- substituted benzaldehyde are potential anticancer agents.[81] The Schiff base pyridine-4-carboxaldehydeisonicotinoyl hydrazone and its transition metal complexes show good antibacterial activity[82] against klebsilla pneumonia, E. Coli and staphylococcus.

Several transition metal complexes have been used for increasing the weather resistance of polyethylene, polypropylene and polystyrene.[83] A number of Schiff bases and their transition metal complexes have been used in dyeing and pigment industries.[84] There are many reports in literature where transition metal complexes of Schiff bases[85,86] have been used as pigments due to their good colour, strength, solvent resistance and light stability.

Polymeric Schiff bases have been reported to exhibit photoconductive properties[87,88] and have been used as electrophotographic materials.[89] The Schiff base obtained by the condensation of 3-methoxy-4-hydroxy benzaldehyde, 3,4-dimethoxy benzaldehyde and *p*-phenylene diamine have been used as antioxidants in lubricating oils.[90] The aromatic Schiff bases and their metal complexes have been used as catalysts in polymerization, oxidation and decomposition reactions.[91] Thus Schiff bases and their metal complexes play a key role in various fields such as in industry, medicine and agriculture.

1.6 LITERATURE SURVEY OF DIOXOMOLYBDENUM(VI) SCHIFF BASE COMPLEXES

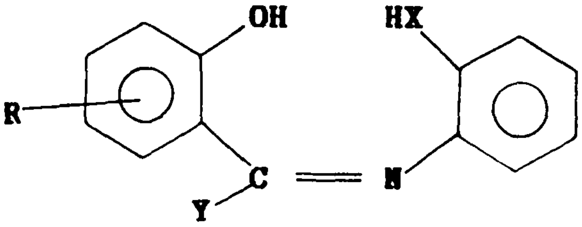
The literature survey presented here covers only those dioxomolybdenum(VI) and tungsten(VI) complexes of Schiff bases which appeared in the last few years in the literature and are relevant to the work reported in this thesis.

The survey mainly deals with the complexes of tridentate ONO and ONS donor ligands, their reactivity and use in the epoxidation of olefins.

The starting materials for the $[MoO_2]^{2+}$ complexes are MoO_2Cl_2, $MoO_2(acac)_2$, $MoO_2(sal)_2$, Na_2MoO_4 or $(NH_4)_2MoO_4$ of which $MoO_2(acac)_2$ is extensively used for the preparation of dioxomolybdenum(VI) complexes. $MoO_2(acac)_2$ was prepared by Jones by the reaction of molybdic anhydride or ammonium para molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ with acetylacetone in the presence of HNO_3.[92] Gehrke,Jr and Veal[93] modified the above procedure by using sodium molybdate dihydrate instead of molybdic anhydride or ammonium para molybdate. Recently, Chen et. al. used another procedure to obtain $MoO_2(acac)_2$ in a better yield.[94] This compound slowly decomposes to μ-oxo dioxo tetrakis(2,4-pentane dionato) dimolybdenum(V) with the simplest formula $[(C_5H_7O_2)_2MoO]_2O$.[95]

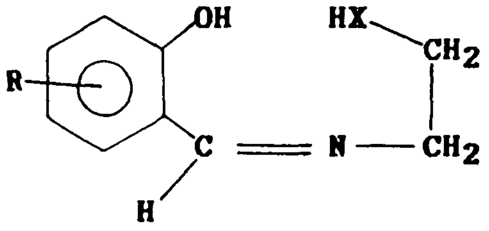
Yamanouchi and Yamada [96] have synthesized and characterized new dioxomolybdenum(VI) complexes with quadridentate Schiff bases derived from salicylaldehyde, substituted salicylaldehyde and polymethylenediamines. On the basis of infrared and proton magnetic spectra, it was concluded that the MoO_2 group in them has *cis* structure, in which the quadridentate ligand, bis(salicylaldehyde)polymethylenediiminates assume non-planar coordination instead of planar one. Hill et. al. have reported a large number of bidentate, tridentate and tetradentate Schiff base ligands containing oxygen, nitrogen and sulphur donor atoms and these ligands were complexed to the *cis*- MoO_2 moiety.[97]

The complexes of the type MoO_2L_2 and $MoO_2L.D$(where LH_2 = tridentate Schiff base, D = monodentate ligand) have been prepared with the Schiff bases (I) and (II) starting from MoO_2Cl_2, $MoO_2(acac)_2$, $MoO_2(sal)_2$, Na_2MoO_4 or $(NH_4)_2MoO_4$.[98-109]



(I)

R= H, 5- CH_3, 3- C_4H_9, 5- C_4H_9, 5,6- C_4H_4, 5- NO_2, 5- Br, 5- Cl, 5- OCH_3 X= O, S Y= H, CH_3.

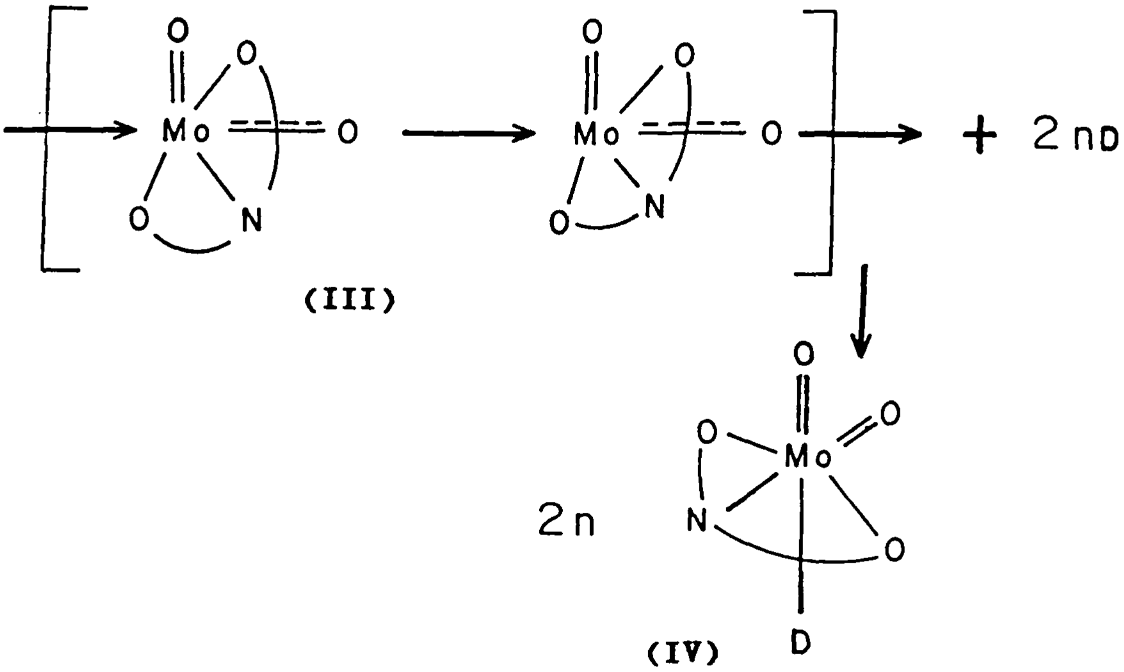


(II)

R= H, 5- Cl, 5- NO_2, 5- CH_3, 5- OCH_3, 3- C_4H_9, 5- C_4H_9, 5,6- C_4H_4.

X= O, S.

Rajan et. al.[88] have synthesized and characterized Mo(VI) complexes of type $MoO_2(L)$ where L is tridentate dianionic Schiff base ligands. IR data suggest oligomerization *via* a $Mo = O \longrightarrow Mo$ bridge **(III)**. These oligomeric complexes undergo cleavage with a wide variety of monodentate ligands (D) such as CH_3CHO, C_6H_5CHO, EtOH, *p*- anisaldehyde, DMSO, DMF, picoline, imidazole, pyridine N-oxide to produce $MoO_2(L)(D)$ **(IV)**.



(III)

(IV)

In **(IV)**, the tridentate Schiff bases occupy the meridional coordination sites about the $[MoO_2]^{2+}$ unit, and D occupies the labile coordination site trans to an oxo oxygen. The $MoO_2L.D$ complexes undergo substitution reactions according to the following equation:

$$\mathbf{MoO_2L.D + D' \longrightarrow MoO_2L.D' + D}$$

where D and D′ are different unidentate ligands and a large number of complexes with D′ = methanol, DMSO, DMF, pyridine, ν-picoline, pyridine N-oxide, methylamine, triphenylphosphine, triphenylphosphine oxide($OPPh_3$), hexamethyl phosphonic acid amide, imidazole, substituted imidazoles, acetaldehyde, benzaldehyde and *p*-anisaldehyde have been synthesized and characterized. The order of D′ binding is as follows: CH_3OH < C_6H_5OH < *p*-anisaldehyde < DMF < ν-picoline < DMSO < imidazoles < pyridine N-oxide. The $MoO_2L.D$ complexes exhibit two *cis*-MoO_2 stretches in the region 880-950 cm^{-1} and the species having nitrogen donors exhibit $\nu(O=Mo=O)$ at lower energies than those having oxygen donors. However, the MoO_2L complexes exhibit only one $\nu(Mo=O)$ at 930 cm^{-1} and a strong band at 800 cm^{-1} due to ---Mo=O---Mo=O--- interactions. On heating $MoO_2(L)(D)$ readily gets converted to $MoO_2(L)$ in a single endothermic step. The temperature at which the loss of D occurs depends on the nature of D.

The MoO_2L, $MoO_2L.D$ and $MoO_2L.D'$ are non electrolytes and diamagnetic as expected for the $4d^0$ system. The electronic spectra of the complexes are dominated by a strong band in the region 22400-28800 cm^{-1} due to the ligand to metal charge transfer transition (LMCT). Topich and Lyon[102] have observed that the energy of this transition shifts to higher levels as the R group becomes more electron withdrawing. The ability of molybdenum to bind to the sulphur donors is of great importance in the chemistry of molybdenum. It is this affinity for sulphur which fixes molybdenum in biological systems. Many more experiments on relatively small molecules containing the Mo-S linkage are needed to gain insight into the gross mechanism of enzyme activity.

The cyclic voltammetric behaviour of the dioxomolybdenum(VI) complexes of the Schiff bases has been reported by Topich et.al.[99,102,105] and Rajan et.al.[98,106] Irreversible behaviour has been observed for all the *cis*- dioxomolybdenum(VI) complexes. The plot of E_{pc} *vs*. Hammet parameter σ_p indicates that a linear relationship exists between E_{pc} and σ_p for each series of dioxomolybdenum(VI) complexes. The parameter Δ has been calculated using the relation,[102]

$$\Delta = E_{pc}\text{ (comp)} - E_{pc}\text{ (stand)}$$

where E_{pc} (comp) is the cathodic reduction potential of the molybdenum complex under consideration and E_{pc} (stand) is the cathodic reduction potential of the standard molybdenum complex.

A positive Δ value indicates that the dioxomolybdenum(VI) complex is easier to reduce than the standard. However, a negative Δ value signifies the more difficult reducible nature of dioxomolybdenum(VI) complex in comparison with the standard. E_{pc} is dependent on (1) the substitution on the salicylaldehyde moiety (2) the substitution of a sulphur atom for an oxygen in the ligand (3) the degree of ligand electron delocalization. An electron withdrawing group withdraws the electron density away from the molybdenum and forces the molybdenum to be more easily reduced. The E_{pc} values are in the order of the substituents: $OCH_3 < H < Cl \simeq Br < NO_2$.

The substitution of a sulphur atom in place of an oxygen atom in the ligand lowers the charge on the molybdenum and as a result the molybdenum complexes with sulphur donor ligands are more easily reduced than the molybdenum complexes with oxygen donor ligands. Dioxomolybdenum(VI) complexes can be reduced to the corresponding oxomolybdenum(IV) complexes MoOL using phosphine and substituted phosphines[110] according to the following equation,

$$Mo^{VI}O_2L + PEtPh_2 \longrightarrow Mo^{IV}OL + OPEtPh_2$$

The kinetic study of the oxygen transfer reaction reported by Topich and Lyon[107, 108, 109] shows that the reactions are first order with respect to both $PEtPh_2$ and the molybdenum(VI) complex and the rate law follows the equation

$$-d\,[MoO_2L]/dt \quad = \quad +d[MoOL]/dt \quad = \quad k_1[MoO_2L]\ [PEtPh_2]$$

The electronic spectral studies show that the molybdenum(V) dimer, $Mo_2O_3L_{2n}$ is not formed during the reaction

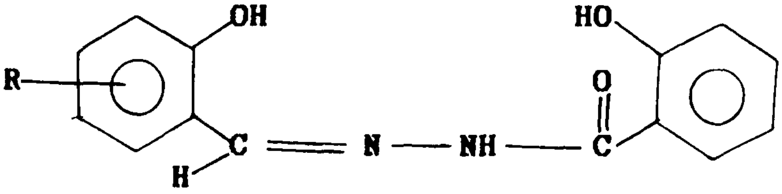
$$Mo^{VI}O_2L_n \quad + \quad Mo^{IV}OL_n \quad \xrightarrow{\qquad} \quad Mo^{V}{}_2O_3L_{2n}$$

Although the R substituents are not directly bonded to the metal, their electronic effect is transmitted to the Mo-oxo core through the ligand. k_1 is in the order Br > Cl > H > OCH_3. The electron donating group removes the electron density from the $[MoO_2]^{2+}$ moiety and makes the oxo oxygen atoms the most electrophilic in the series. The reactivity of dioxomolybdenum(VI) complexes with $PEtPh_2$ depends on the donor atoms of the ligand. The order of reactivity is found to be ONO < ONS < NNSS < SSSS (where ONO, ONS, NNSS and SSSS are the donor atoms of the ligand).[108] The molybdenum(VI) complex with a Schiff base having a sulphur donor atom, an extended π electron system and an effective electron-withdrawing substituent is more effective in oxidizing $PEtPh_2$. A linear dependence exists between the Hammet σ_p parameter for the substituents R in the ligand and $\log(K_{1R}/K_{1H})$ and between K_1 and cathodic reduction potential E_{pc} within each series of complexes.

^{95}Mo NMR spectra of the dioxomolybdenum(VI) complexes have been reported[111,112] and the chemical shifts referenced to 2M Na_2MoO_4 are in the range 28 - 543 ppm. The replacement of an oxygen atom of the Schiff base by a sulphur atom causes deshielding of the ^{95}Mo NMR signal from 34 to 231 ppm.[113] Least shielding occurs in the case of electron donating methoxy substituent which causes significant downfield shift compared to nonsubstituted dioxomolybdenum(VI) Schiff base complexes.

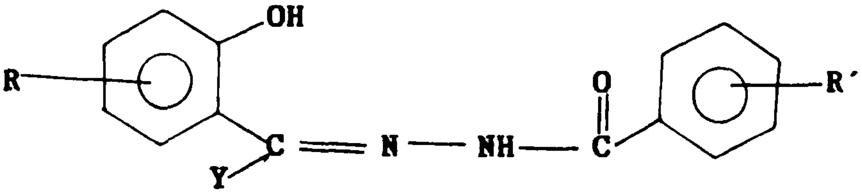
Wang et. al.[114] have reported the synthesis of a dioxomolybdenum(VI) complex of the type MoO_2L (where LH_2 is the Schiff base derived from salicylaldehyde and isonicotinoyl hydrazide). The single crystal X-ray diffraction studies indicate that the complex $[MoO_2(o\text{-}C_6H_4\text{=NN=COC}_5H_4N)MeOH]$ is monoclinic, space group $P2_1/n$, with cell dimensions a = 8.188(1), b = 12.422(1), c = 15.078(1) Å, V = 1518.84 Å and Z = 4. The structure resembles that of the *cis*-dioxomolybdenum(VI) complex $[MoO_2$(5-t-Busap)(MeOH)].MeOH of the tridentate 2-(5-t-butyl salicylideneamino) phenolate(2-)ligand.[115] Berg et. al.[116] have reported structural proofs of ligated and polymeric dioxomolybdenum(VI) tridentate complexes. The polymeric chains of the Mo complexes have a distorted octahedral environment and an oxo group unsymmetrically bridges from an adjacent complex to satisfy the sixth vacant coordination site in the octahedral arrangement.

The Schiff base ligands [(V) and (VI)] produced from salicylaldehyde, substituted salicylaldehyde and salicylhydrazide are dibasic tridentate. On complexation, enolization of the ligand takes place followed by coordination of the enolic oxygen after deprotonation to the metal atom, resulting in the formation of complexes of the type $MoO_2L.X.$(where X = H_2O or THF).[117,118] Dutta and Pal[119] also prepared the dioxomolybdenum(VI) complexes with the ligand **(VI)** (R = H, 5,6-C_4H_4, R′= Y = H) by reacting $MoO_2(acac)_2$ and the ligand in MeOH. The crystal structure of the complex $MoO_2L.C_2H_5OH$ (LH_2 = **(VI)**, R = R′= Y = H) prepared from Na_2MoO_4 and LH_2 in ethanol confirms the coordination of ethanol.[120]



(V)

R = H, 5-Cl, 5-Br, 5-NO_2, 3-OCH_3, 3-OC_2H_5, 3,5-Cl_2, 5,6-C_4H_4



(VI)

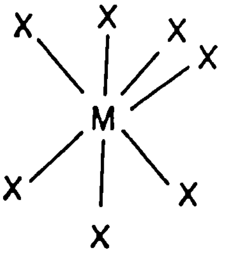
R =H, 5-Cl, 5-Br, 5-NO_2, 3-OCH_3, 3-OC_2H_5, 3,5-Cl_2, 5,6-C_4H_4.
R′ =H, 2-NH_2, 4-NH_2. Y = H, CH_3.

Prabhakaran and Nair[121] have reported the synthesis of dioxomolybdenum(VI) complexes of the Schiff base **(VI)** (R = R′ = H, Y = CH_3) of the type $MoO_2L.X$ (X = H_2O, DMF, THF, pyridine N-oxide). The separation between $\nu_{sym}(O = Mo = O)$ and $\nu_{asym}(O = Mo = O)$, $\Delta\nu$ is in the order H_2O > DMF > pyridine N-oxide > THF > DMSO and is consistent with the donor power of X. The thermal stability of the complexes is in the order H_2O > pyridine N-oxide > DMSO > DMF >THF . Abramenko et. al.[122] have reported dioxomolybdenum(VI) complexes of the type $MoO_2L.MeOH$ with salicylaldehyde hydrazone ligands. The hydrazones are tridentate dibasic ligands coordinating through the nitrogen atom and two oxygen atoms.

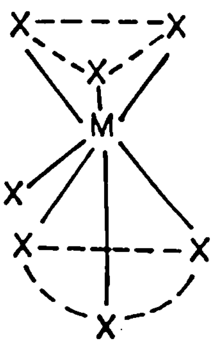
Havanur et. al.[123] have synthesized binuclear Mo(VI) complexes of the hexadentate ligands derived from the condensation of salicylaldehyde or 3- methoxy salicylaldehyde and various dihydrazides. The complexes have the composition $[(MoO_2)_2L(py)_2]$ where (LH_4 = Schiff base). The thermal study indicates the loss of both pyridine molecules in the temperature range 150-200°. A six coordinate dimeric structure has been suggested for the complexes.

Bis(acetyl acetonato) dioxomolybdenum(VI), $MoO_2(acac)_2$ reacts with the Schiff bases derived from salicylaldehyde and thiocarbohydrazide or carbohydrazide [(*o*- $HOC_6H_4CH{=}NNH)_2CX$ (X = S,O)] and salicylaldehyde in MeOH to afford mono and binuclear complexes respectively.[124] All the complexes exhibit an irreversible cyclic voltammetric peak at ~-0.90 V *vs.* SCE which is attributed to an electron transfer centered at molybdenum.

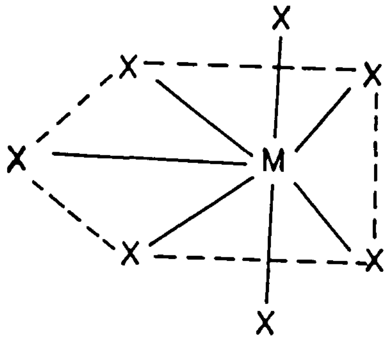
Dioxomolybdenum(VI) complexes of the formula $MoO_2L.CH_3OH$ has also been reported with the Schiff base derived from salicylaldehyde and 5-methyl pyrazole-3-carbohydrazide.[125] The IR and NMR spectral studies show that the Schiff base behaves as a dibasic tridentate ligand coordinating through the deprotonated phenolic oxygen, enolic oxygen and the azomethine nitrogen. Dioxomolybdenum(VI) complexes $[MoO_2L]H_2O$ and oxomolybdenum(V) complexes $[Mo_2O_3L_3]H_2O$ and $[Mo_2O_3(LH)_2(OH)_2(H_2O)_2]$ (where LH_2 = thiocarbohydrazones derived from thiocarbohydrazide with salicylaldehyde, 5-methyl, 5-chloro, 5-bromo, 3-methoxy salicylaldehyde and 2-hydroxy-1-naphthaldehyde) have been prepared and characterized.[126] The elemental analysis and other relevant data suggest that molybdenum(VI) complexes are non electrolytes, diamagnetic and have monomeric distorted octahedral geometry, whereas the molybdenum(V) complexes are non electrolytes, paramagnetic, and have distorted octahedral structures possibly with metal interaction *via* oxo bridging. Several hydrazide based Schiff base complexes of dioxomolybdenum(VI) have been synthesized and studied by IR, electronic spectra and molecular weight measurements.[127,128] The nitrogen donor bidentate ligands such as ethylenediamine, trimethylenediamine, 1,10-phenanthroline, 2,2′-bipyridine, *o*-phenylenediamine, 2-amino ethyl pyridine react with the labile six coordinated $MoO_2L.H_2O$ and as a result the seven coordinated heterochelates $[MoO_2L(AA)]$ are formed. [129-131] The replacement of the aquo molecule in $MoO_2L.H_2O$ by the bidentate ligands was accompanied by an increase in coordination number and by a shift of the ν_{sym} (O═Mo═O) and ν_{asym}(O═Mo═O) stretches to lower energy. These shifts are in accordance with an increase in electron density at molybdenum leading to an increase in repulsive forces with the non bonding electrons of the Mo-O bond. The $\Delta\nu$ ($\nu_{sym}-\nu_{asym}$) values are in the order en $\simeq$ tn $\simeq$ bn $<$ bipy $\simeq$ *o*-phen $\simeq$ aepy $\simeq$ phen and are in line with the weaker donor character of aliphatic amines compared with the aromatic amines. Three different structures are possible for seven coordinate complexes (1) capped octahedron (VII) (2) capped triagonal prism (VIII) and (3) pentagonal bipyramid (IX). The pentagonal bipyramid is the most regular arrangement of these structures.



(VII)



(VIII)



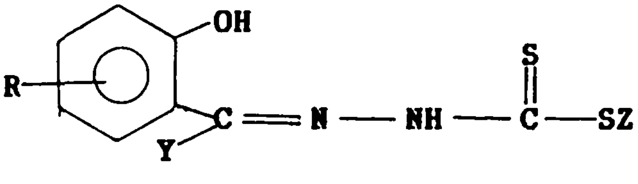
(IX)

Representative dioxomolybdenum(VI) complexes of N-salicylidene-L- amino acids (the amino acids are valine, leucine and histidine) have been synthesized and characterized by various spectroscopic techniques.[132] Dioxomolybdenum(VI) complexes of the type MoO_2L.DMSO with ligands derived by the condensation of 2-hydroxy-1-naphthaldehyde, 2,4-pentanedione and 2-hydroxy acetophenone with glycine or β-alanine were synthesized and characterized.[133] A pseudooctahedral and octahedral structure is proposed to MoO_2L and MoO_2L. DMSO respectively.

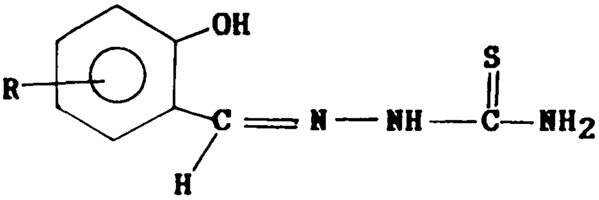
Tarafder et.al.[134] have synthesized and characterized several new peroxocomplexes of Mo and W containing different organic ligands and found that these complexes can be used for the oxidation of allylalcohol, PPh_3 and $AsPh_3$ to their oxides. Subramanian et. al.[135] have synthesized dioxomolybdenum(VI) complexes with sterically bulky ligands to prevent dimerization upon one electron coloumetric reduction.

Mohanty et . al.[136,137] have prepared and characterized dioxomolybdenum(VI) complexes with tridentate Schiff base ligands and imidazole bases. The thermogravimetric measurements support the labile binding of the imidazole molecule in these complexes. $MoO_2(acac)_2$ reacts with polydentate dioxime based Schiff base ligands obtained by the condensation of biacetylmonoxime with various diamines such as ethylenediamine, propylenediamine, diethylenetriamine and triethylenetetramine to form binuclear, ligand-bridged, six-coordinated, *cis*- dioxomolybdenum(VI) complexes $[(acac)MoO_2(L)O_2Mo(acac)]$.[138]

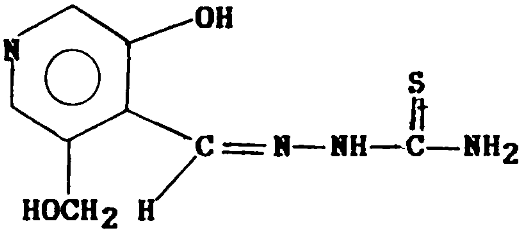
Bis(acetylacetonato) dioxomolybdenum(VI) undergoes a ligand exchange reaction with the Schiff bases **(X, XI and XII)** [R = H, 5,6-C_4H_4, Y = H, CH_3, Z = CH_3, C_6H_5] in MeOH and complexes of the type $MoO_2L.MeOH$ are formed.[139] The complexes are monomers, non-electrolytes, dia-magnetic and six coordinated. The Schiff bases behave as dibasic tridentate ligands and coordinate through the phenolic oxygen, thioenolic sulphur and the azomethine nitrogen. All the complexes exhibit a band at *ca.* 25,000 cm^{-1} due to the ligand to metal charge transfer transition.



(X)



(XI)



(XII)

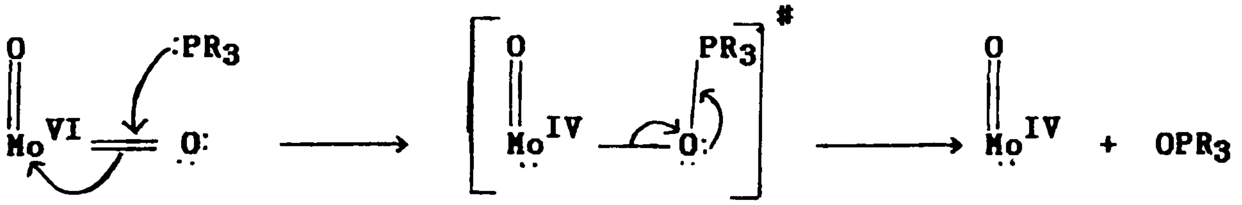
Kanoongo et.al.[140,141] have prepared six coordinated dioxomolybdenum complexes $[MoO_2(Htscz)_2]$ where Htscz = semicarbazone of 2-furan carbaldehyde, 3-indole carbaldehyde, cinnamaldehyde, Me_2CO, PhC(O)Me, BuC(O)Me and studied their fungicidal activities. From the data they obtained, it is evident that the complexes of the type $[MoO_2(Htscz)_2]$ are capable of inhibiting the fungal growth both at high and low dilutions. Purohit et. al.[142,143a] have reported the synthesis and characterization of a number of oxomolybdenum(VI, V, IV) complexes with salicylaldehyde thiosemicarbazones as the SNO-donor metal binding substrates. A number of Mo(VI) complexes with ring substituted 4-phenyl thiosemicarbazides (LH) have also been synthesized and characterized. These compounds are either six coordinated *cis*-dioxo $[MoO_2L_2]$ or seven coordinated $[MoOL_2Cl_2]$ species. In all the complexes the thiosemicarbazides are ligated to the Mo(VI) acceptor centre in the deprotonated enol form.[143b] Sergienko et. al.[144] have synthesized dioxo (salicylaldehyde S-methyl isothiosemicarbazonato)molybdenum(VI) 1:1 solvate with methanol. The complex was found to have distorted octahedral configuration with the two oxygen atoms in *cis* positions.

Condensation of 2-acetylpyridine, 2-acetylfuran, 2-acetyl thiophene and 2-acetylindole with thiosemicarbazide or semicarbazide yields the corresponding Schiff bases. These

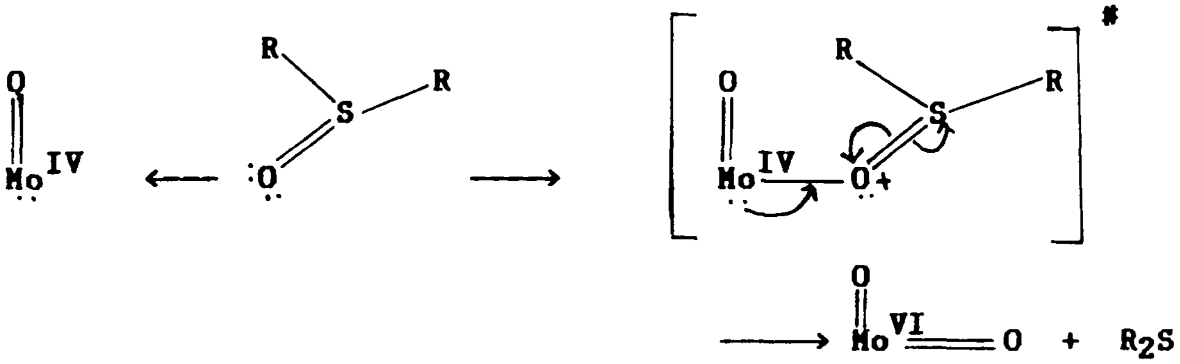
Schiff bases react with $MoO_2(acac)_2$ to give the corresponding dioxomolybdenum(VI) complexes.[145] The reaction of $MoO_2(acac)_2$ [Hacac = acetylacetone] with salicylaldehyde S-methyl thiosemicarbazone (H_2L) yielded [$MoO_2(L)(Q)$] (Q = py, MeOH, EtOH respectively).[146] Topich et. al.[147] investigated a series of complexes of the type [$MoO_2L.DMF$] using FT-IR spectroscopy in DMF solution. The observed variation in $\nu_{asym}(Mo{=}O)$ as the ligand structure is systematically altered and reflects changes in the relative energy of the oxo O_{π^*} antibonding orbital. This energy change contributes to the activation energy in the oxygen atom transfer reaction with $PEtPh_2$. Results support the reaction mechanism of donation of the phosphorus lone pair electrons into the oxo O_{π^*} antibonding orbital.

Molybdenum mediated oxygen atom transfer reactions have become increasingly well-defined with regard to scope, kinetics and mechanism. The first report of this type of oxygen atom transfer reactions appeared in 1972 where oxo transfer between Mo(VI) complexes and PPh_3 was studied.[148] Oxygen atom transfer reactions of dioxomolybdenum(VI) complexes containing sulphur donor ligands are well known, the prototypical reaction being that of $MoO_2({}_2SCNEt_2)_2$ with PPh_3 to yield $OPPh_3$ and $MoO({}_2SCNEt_2)_2$.[52] Such reactions are usually accompanied by the formation of oxo-bridged dimers unless ligands of sufficient steric bulk are used to hinder dimer formation. When dimer formation is inhibited, the resulting Mo(IV) complex can be reacted with an oxygen donor solvent such as DMSO to regenerate the original Mo(VI) complex. Sulphur donor atoms facilitate oxygen transfer reactions, resulting in mononuclear Mo(IV) complexes as products.[108,149] The simple mechanism of oxygen transfer reactions is as follows.[13]

Phosphine oxidation by Mo(VI) dioxo complex.



Oxygen abstraction from DMSO by Mo(IV) oxo complex.



In the most known oxygen atom transfer reactions the molybdenum(IV) complex obtained is five coordinate square pyramidal having a vacant coordination site trans to the oxo ligand. Bhattacharjee and Bhattacharyya[150,151] reacted $[MoO_2L]$ with PPh_3 in CH_2Cl_2, MeOH or MeCN to obtain complexes of the type MoO(L) (where L= S-benzyl- or S-methyl 3-(2-hydroxy phenyl)methylene dithiocarbazate). In donor solvents D (D = DMF or Py), the reaction resulted in the formation of oxomolybdenum(IV) derivatives of the type [MoO(L)(D)], respectively. The kinetics of oxo transfer from MoO_2^{2+} to PPh_3 occurs in a second order process with rate constant 1.32 X 10^{-2} $dm^3mol^{-1}s^{-1}$ at 30°. The rate constant of the reaction from the polymer $[(MoO_2L)_n]$ to the PPh_3 substrate is ~10^2 times higher than that of the corresponding monomer $[MoO_2L(D)]$. The complexes [MoO(L)] in DMF accepts an oxygen atom from DMSO (Me_2SO) affording $[MoO_2L(DMSO)]$ and Me_2S.

Craig et. al.[115] and Moloy et. al.[152] have studied the oxygen atom transfer chemistry of oxomolybdenum(IV, V, VI) complexes of the type $MoO_2(L)(solv)$ [where LH_2 = 2-(salicylideneamino)-phenolate(2-)(sap) or 2-(salicylideneamino) benzene thiolato(2-)(ssp)]. Dioxomolybdenum(VI) complex of the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand has also been synthesized and oxygen atom transfer reactions has been studied.[153]

Epoxidation of olefins by organic hydroperoxides in presence of certain transition metal catalysts was first described by Hawkins in 1950.[154] In recent years this area has attracted considerable attention essentially because of industrial interest such as in the production of propylene oxide.[155] In general, catalysts based on V(V), Mo(VI), W(VI) and Ti(IV) have been found to be effective, though Mo(VI) catalysts have proved to be generally superior,[156] except when the substrate is an allyl alcohol for which V(III) showed outstanding performance.[157]

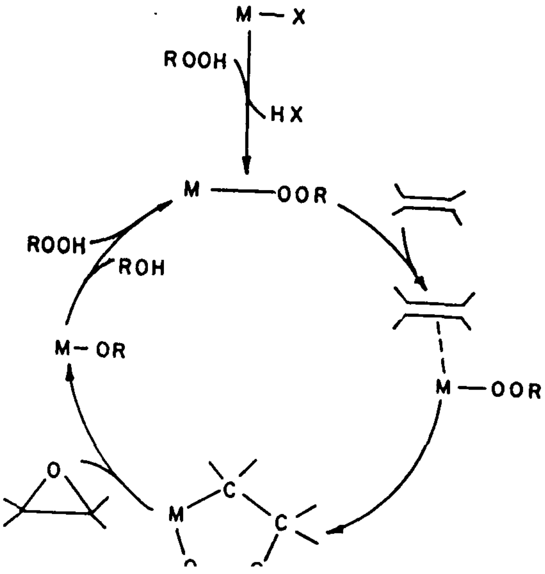
The main function of the catalyst is to withdraw electrons from the peroxidic oxygens of the hydroperoxide. In doing so the catalyst acts as a Lewis acid; the Lewis acidity increases with increasing oxidation state of the metal. The Lewis acidity of transition metal oxides decreases in the order CrO_3, MoO_3 >> WO_3, TiO_2, V_2O_5, VO_3. Thus Mo(VI) seems to be the most effective epoxidation catalyst. On the basis of its strong Lewis acidity Cr(VI) would also be expected to be a good catalyst. But it is not so due to the fact that Cr(VI) is a strong oxidant and readily causes the decomposition of the hydroperoxides. Lewis acidity will also be influenced by the nature of the ligands surrounding the metal. In practice, however, a ligand effect should be observable only in the initial stages of the reaction in view of the rapid oxidative destruction of the original ligands by reaction with the hydroperoxide. Thus a good catalyst for the hydroperoxide epoxidation of olefins should be both a strong Lewis acid and a poor oxidizing agent.[158]

Sapunov et. al.[159] stated that the reaction between hydroperoxides ROOH and olefins catalyzed by Mo compounds involves the formation of a complex (catalyst-ROOH) which reacts with olefins. During the formation of the catalytic complex an electron transfer takes place from the π^* orbital of the hydroperoxide to the corresponding π^* orbital of the Mo. There are many reports in literature where Mo(VI) complexes can be used for the oxidation of olefins and other substrates and mechanism of these oxidation reactions have also been suggested.[160-187]

Dawoodi and Kelly[188] prepared a series of MoO_2L_2 (L = ligand having N$\frown$O donor sites) complexes and examined their activity as catalysts for the epoxidation of ethylene by *t*-butyl hydroperoxide. Improvements in selectivity and reproducibility for these catalysts have been shown to result from the addition of cyclohexene oxide to the reaction mixture. They have classified the mechanisms of the transition metal catalyzed hydroperoxide epoxidation of olefins into two types.

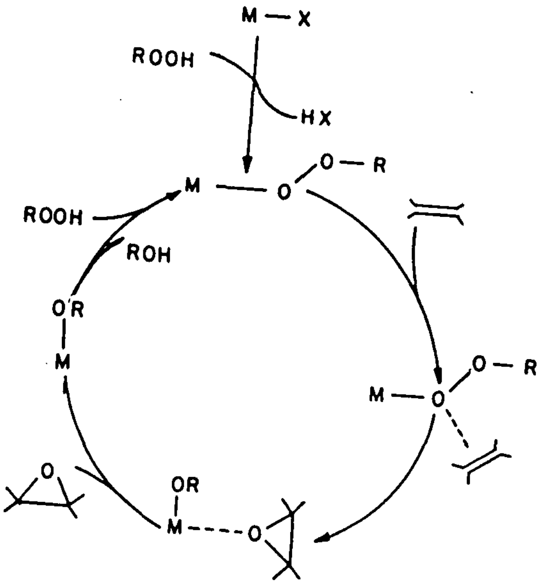
(1) Olefin insertion mechanism.

This proceeds via prior coordination of the olefin to the metal hydroperoxide followed by insertion to form a cyclic intermediate and then the elimination of the epoxide.

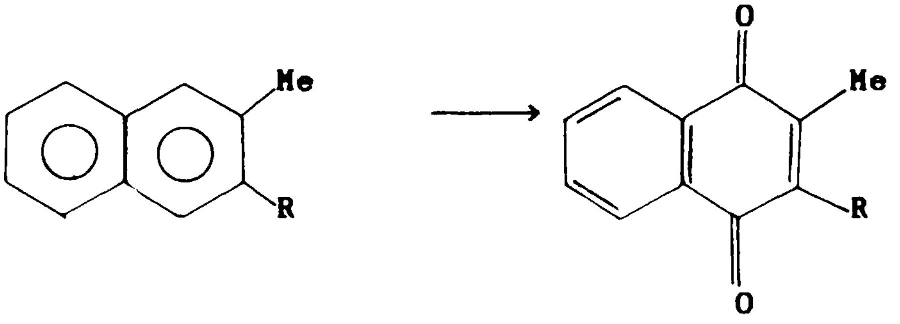


(2) Metal activated hydroperoxide mechanism.

In this type of mechanism the role of the metal catalyst is that of a Lewis acid which seems to activate the oxygen atoms of the hydroperoxide ligand by electronic induction.



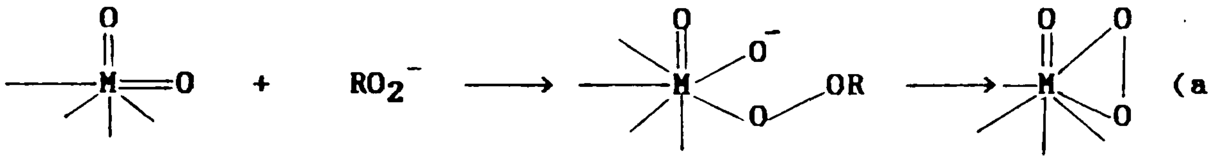
Chen et. al.[189] carried out the oxidation of methyl naphthalenes (XIII) with Me_3COOH in the presence of $MoO_2(acac)_2$ to give quinones.



(XIII)

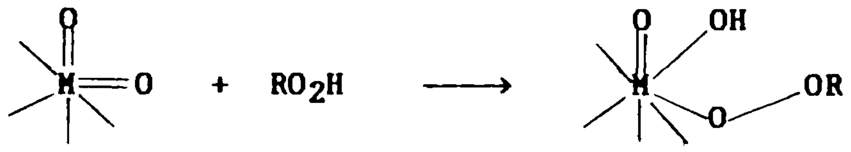
Agarwal et. al.[190] have prepared *cis*-dioxomolybdenum complexes having tetradentate ligands and have used them as catalyst with *t*-butylhydroperoxide. These complexes give epoxides from olefins in good yield. The steric environment due to the ligand around the metal center plays a significant role in the epoxidation of olefins such as isoprene and 1,2-dimethyl-1,4-cyclohexadiene and *cis* and *trans*-2-hexene. The effect of pH was studied by carrying out the reaction (1) without buffer and (2) using Na_2HPO_4. It was observed that the reaction was very slow and selectivity was very poor when Na_2HPO_4 was used. The reaction was considerably fast when no buffer was used. This can be explained on the basis of the reaction shown in equations(a) and (b).

basic pH



(a)

acidic pH



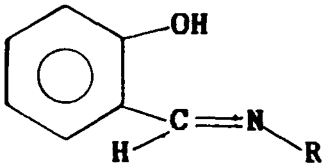
(b)

This shows that the basic pH of the reaction medium leads to the formation of a peroxo complex (a) which has weaker catalytic activity than the *cis*-dioxomolybdenum complex. A mechanism similar to that proposed by Sharpless et. al.[158] can be proposed for the *cis*-dioxomolybdenum complexes, where hydroperoxide first coordinates to the metal centre and then oxygen atom transfer to the olefin takes place.

1.7 LITERATURE SURVEY OF DIOXOTUNGSTEN(VI) SCHIFF BASE COMPLEXES.

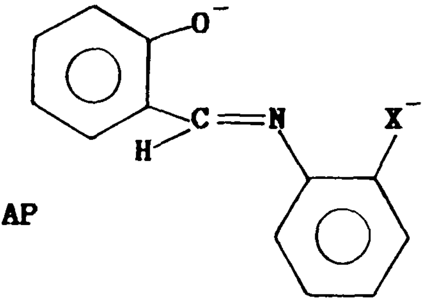
Although there has been considerable interest in the chemistry of coordination compounds of Schiff bases with the $4d^0$ system, comparatively very little has appeared on the compounds of Schiff bases with the $5d^0$ tungsten(VI).

In 1967, Brisdon et. al.[191] synthesized complexes of type $WO_2Cl_2(L)_2$, L being neutral ligands such as DMSO, DMF, MeCN, $OPPh_3$ etc. Yamanouchi et. al.[192] studied the reaction of WO_2Cl_2 with various N-aryl salicylaldimines [abbreviated as (sal-R)H] **(XIV)** to yield tungsten(VI) complexes of the type WO_2Cl_2[(sal-R)H]. These complexes involved the Schiff bases as neutral unidentate ligands to coordinate the tungsten(VI) ion. Infrared spectra indicate that the tungstyl group WO_2^{2+} in these complexes has a *cis*-configuration, according to the criterion proposed earlier.[193]



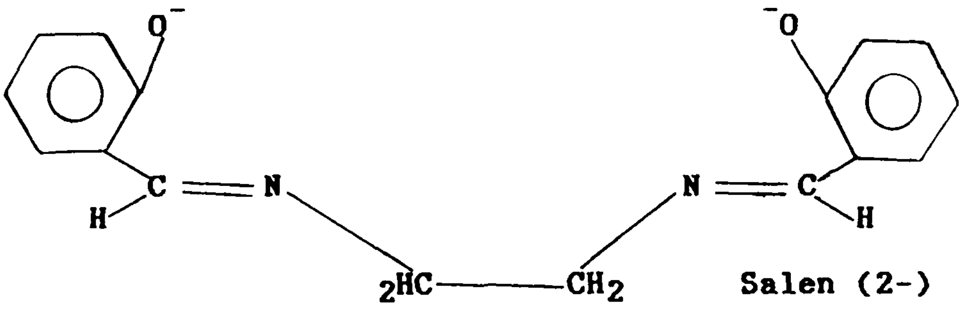
(XIV)

All the complexes obtained are diamagnetic as expected for a $5d^0$ system. Absence of a band in the region 700 - 800 cm^{-1} due to a bridging $W \cdots O \rightarrow W$ structure in the IR spectra of the complexes clearly prove the octahedral geometry around the WO_2^{2+} core. The high tendency of the tungstyl group WO_2^{2+} to assume a *cis*-configuration is explained in terms of the multiple-bonding between the oxygen and the tungsten atoms as proposed for the molybdenyl ion. It is assumed that maximum overlap of dative-bonding between the oxygen and the metal ion is attained for the *cis*-MO_2 rather than for the *trans* MO_2 configuration. The data obtained are in agreement with the octahedral geometry with the two oxygen atoms, two chloride ions and two oxygen atoms from two neutral Schiff bases being bound to the tungsten(VI) ion. The same authors[184] have also synthesized oxo tungsten(VI) complexes with bi-, ter- and quadridentate Schiff bases obtained from salicylaldehyde and various amines. The following type of complexes have been isolated: (1) $[WOCl_3(bidentate)]$ (2) $[WOCl_2(terdentate)]$ and (3) $[WO_2(terdentate).L]$ (L being N,N-dimethyl formamide and pyridine). With quadridentate ligand N,N-ethylene bis(salicylaldiminate), $[WOCl_3(quadridentate)_{1/2}]$ has been obtained.



(XV) Sal-OAP

(X=O, NH)



(XVI)

Although a large number of $MoO_2(R_2dtc)_2$ complexes have been synthesized and characterized, only three tungsten species[185] of $WO_2(R_2dtc)_2$ (R = Me, Et, n-Pr) have been reported with some characterization data. These compounds were prepared by the intermetal oxo transfer reaction between $W(CO)_2PPh_3(R_2dtc)_2$ and $Mo_2O_3(Et_2dtp)_4$. The μ-oxo dimer $Mo_2O_3(Et_2dtp)_4$ exists in labile equilibrium with $MoO(Et_2dtp)_2$ and $MoO_2(Et_2dtp)_2$ according to the equation,

$$MoO_2(Et_2dtp)_2 + MoO(Et_2dtp)_2 \rightleftharpoons Mo_2O_3(Et_2dtp)_4$$

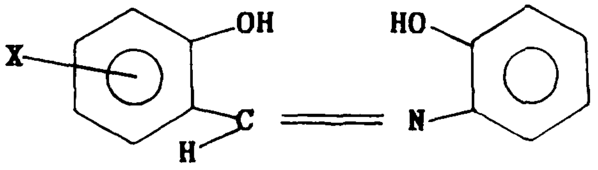
$$W(CO)_3(R_2dtc)_2 + 2\ MoO_2(Et_2dtp)_2 \longrightarrow WO_2(R_2dtc)_2 + 3\ CO + 2MoO(Et_2dtp)_2$$

The lack of reactivity of the *cis*-WO_2 complexes with respect to oxo transfer may be a significant factor in the inactivity of a variety of tungsten substituted molybdoenzymes. The inactivity of the tungsten substituted oxidases could result from the inability of W(VI) = O to undergo oxotransfer to substrate, while in the reductases, either the apparent instability of W(IV) or the difficulty in removing oxygen atom from tungsten to reactivate the catalytic site, may be responsible for the lack of activity.

Rice et. al.[196] have synthesized six new oxo tungsten(V) and tungsten(VI) complexes and studied by IR and EPR spectra and their electrochemical properties. Cyclic voltammograms of both tungsten(V) and (VI) complexes show reduction peaks that are considerably more negative than those of the corresponding molybdenum complexes, and the reductions are less reversible. Their results supported the hypothesis that tungsten occupies the same binding site as that of molybdenum when substituted in the enzyme sulphite oxidase. The lack of catalytic activity of the tungsten enzyme is attributed to the lower reduction potential of tungsten compared with that of molybdenum. Major differences between the two metals are found, however, in the cyclic voltammetric peak potentials and the degree of reversibility of the reductions. The tungsten complexes have reduction peaks -0.30 to -0.50 V more negative than those of the molybdenum complexes and the reductions are less reversible.

Syamal and Maurya[197] have synthesized several dioxotungsten(VI) complexes of the types WO_2L, $WO_2L.X$ and $WO_2L.BB$ (where LH_2 = Schiff base derived from *o*-aminophenol and salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde and 3-ethoxysalicylaldehyde, X = DMF, DMSO, BB = 1,10-

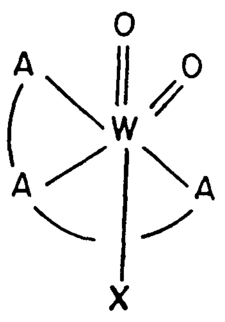
phenanthroline and 2,2′- dipyridyl. While WO_2L and $WO_2L.X$ are hexa coordinated octahedral, $WO_2L.BB$ are seven coordinated pentagonal bipyramidal complexes.



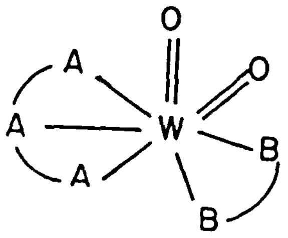
(XVII)

X = H, 5- Cl, 5- Br, 3- ethoxy.

The IR spectra of the complexes $WO_2L.X$ and $WO_2L.BB$ exhibit bands in the region 890 - 905 cm^{-1} and 925 - 940 cm^{-1} due to ν_{asym} and ν_{sym} $(O{=}W{=}O)$ modes, respectively. On the other hand, WO_2L exhibits one $\nu(W{=}O)$ in the range 935 - 940 cm^{-1} and a strong band at ~740 cm^{-1} due to ---W=O---W=O--- interaction and IR data suggest the presence of an oligomeric structure for WO_2L. In the oligomer each W(VI) ion achieves a pseudooctahedral structure *via* oxo bridging.[198]



(XVII)



(XIX)

The first synthesis of bis(pentane-2,4 dionato) *cis*-dioxotungsten(VI), [$WO_2(acac)_2$] was reported by Nikolovski.[199] McDonell prepared $WO_2(acac)_2$ and reacted with N,N-dialkyl hydroxylamines in presence of Et_3N.[200]

Recently Yu and Holm [5] reported a rather simple reproducible preparation of $WO_2(acac)_2$ and its reaction with the Schiff bases H_2sap and H_2ssp [sap = 2-(salicylideneamino)-phenolate(2-) and ssp = 2-(salicylideneamino)benzene thiolate(2-)]. The single crystal X-ray diffraction studies showed that the complex [WO_2(5-*t*-Busap)(MeOH)] to be monoclinic $P2_1$ with a = 6.832 (2)Å, b = 11.299(4)Å, c = 13.354(7)Å, β = 99.02(4) and Z = 2. The complex contains a *cis*- dioxo group, a coordinated methanol molecule *trans* to one oxo ligand and a *mer* arrangement of the tridentate ligand, whose oxygen atoms are mutually *trans* and are *cis* to the oxo ligands. The two W = O bond lengths differ by 0.12Å. In contrast to their Mo analogues the complexes are not reactive to reductive oxo transfer with a number of basic tertiary phosphines under moderately forcing conditions. The compounds do undergo O/S substitution with $(Me_3Si)_2S$ yielding $WS_2(sap)$ and $WS_2(ssp)$. The reaction proceeds according to the equation

$$\mathbf{WO_2L(MeOH) \ + \ 2\ (Me_3Si)_2S \longrightarrow WS_2L(MeOH) \ + \ 2\ (Me_3Si)_2O}$$

Upon exposure to water they are immediately hydrolyzed to the corresponding dioxo species. The complexes obtained are having a *cis*-disulphido stereochemistry. Although oxygen atom transfer chemistry of molybdenum is extensively studied, there are very few documented oxo-transfer reactions of tungsten. One cause of the lack of information about tungsten mediated oxo transfer is the dearth of well characterized $W^{VI}O_2$ and $W^{IV}O$ compounds. Organometallic W^{VI} complexes have been described,[201,202] but their oxo transfer reactivity has not been tested.

1.8 PEROXO COMPLEXES OF MOLYBDENUM AND TUNGSTEN

Peroxo complexes have received considerable attention due to their applications in synthetic organic chemistry.[203-213] The complexes of transition metals are sources of active oxygen atoms and many of these complexes can be used as efficient stoichiometric or catalytic oxidants for inorganic and organic substrates.[210-214]

Jacobson et.al.[215] have prepared oxo-peroxo complexes of molybdenum with pyridine-2-carboxylic acid [C_5H_4NCOOH] and pyridine 2,6-dicarboxylic acid [$C_5H_3N(COOH)_2$] by the reaction of peroxomolybdic acid and ligand. The complex $H[MoO(O_2)_2(C_5H_4NCOO)]$ has two peroxo groups while $[MoO(O_2)(C_5H_3N(COO)_2).H_2O]$ has only one, however, both the complexes are seven coordinated and have pentagonal bipyramidal structure.

Westland et.al.[208] have prepared several diperoxo complexes of the type $[MO(O_2)_2.LL']$ (where M = Mo or W, L = amine oxide, tertiary phosphine oxide or tertiary arsine oxide and L′ = L or H_2O). These complexes stoichiometrically oxidize olefins to epoxides and catalyze the epoxidation of olefins by *tert*-butylhydroperoxide.

Tarafder et.al.[212] have reported peroxo complexes of molybdenum and tungsten containing different organic ligands. The complexes have the compositions $[Mo(O)(O_2)L_2]$, $[Mo(O)_2(O_2)L(H_3O)]^+$, $[Mo(O)(O_2)L']$ and $[W(O)(O_2)L_2]$ [LH = oxoquinoline, aniline-2-carboxylic acid, 2-aminophenol, picolinic acid or quinoline-2-carboxylic acid ligand, L′ = N-(2-oxophenyl) salicylidenimino ligand], respectively. The complexes were found to oxidize allyl alcohol to glycerol and PPh_3 and $AsPh_3$, to their respective oxides. The IR spectra of the complexes indicate that ν_1-mode of the $M(O_2)$ grouping which is essentially an O-O stretch, decreases with increase in atomic number of metals within a particular group.

Peroxo complex of tungsten with ethylenediamine tetraacetic acid (H_4edta) has been synthesized and characterized.[214] Ethylene diaminetetraacetic acid behaves as a quadridentate ligand in the complex $[WO(O_2)(H_2EDTA)]$.

Tarafder et.al.[216] have prepared organo peroxo complex of Mo^{VI} containing monobasic bidentate and dibasic bidentate ligands such as pthalic acid, *o*-phenylene diamine, 2-

aminopyridine, 2-aminophenol, ethanolamine, ethylene glycol and malonic acid. They have also synthesized peroxomolybdenum(VI) complexes of glycine, leucine or tyrosine and have studied the oxygen-atom transfer reactions of these peroxo complexes.[217]

Griffith et.al.[218] have isolated the complexes $[WO(O_2)_2(pyO)_2]$ and $[MoO(O_2)_2(pyO)_2]$ (pyO = pyridine-N-oxide) from the reaction of pyridine and $[WO_4]^{2-}$ or $[MoO_4]^{2-}$ in the presence of H_2O_2. The X-ray crystal structure of the complex $[WO(O_2)_2(pyO)_2]$ reveals that the complex has a pentagonal bipyramidal geometry in which the axial positions are occupied by oxo ligands and the equatorial positions are occupied by the two peroxo groups and the pyridine-N-oxide.

A few peroxo complexes of molybdenum(VI) and uranium(VI) containing diphenicacid and heterocyclic amines such as pyridine, quinoline, isoquinoline, 2-picoline, 4-picoline have been synthesized and characterized.[219] The complexes were found to be inert towards oxidation of allylalcohol, but oxidized triphenylphosphine and triphenylarsine to their respective oxides.

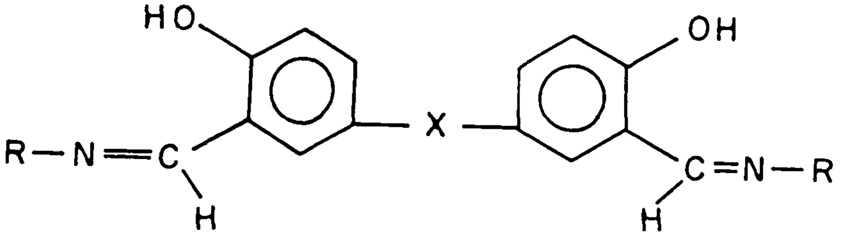
Yang et.al.[220] have synthesized and characterized $W(TPP)(O)(O_2)$ (TPP = tetraphenylporphyrinato) complex by the reaction of H_2O_2 with W(V) porphyrin complexes. Maurya has reported the single-step synthesis of dioxotungsten(VI) and dioxomolybdenum(VI) complexes of N-isonicotiamidosalicylaldimine, by the reaction of the corresponding oxo-peroxo complexes with triphenylphosphine.[221]

1.9 SUMMARY OF THE PRESENT WORK

Among the d^0 systems of chromium group metals the chemistry of mononuclear dioxomolybdenum(VI) complexes has been extensively studied. Although a number of reports are available in the literature dealing with mononuclear dioxomolybdenum(VI) complexes of tridentate Schiff base ligands, such systems with binuclear dioxomolybdenum(VI) complexes are rare. In our endeavor to obtain more knowledge about the coordination chemistry of binuclear dioxomolybdenum(VI) and dioxotungsten (VI) complexes we have prepared several such dioxomolybdenum(VI) and tungsten(VI) complexes and characterized them by elemental analyses, IR, ^1H NMR and electronic spectral studies. Electrochemical studies of these complexes in DMF using 0.1M tetrabutylammonium perchlorate as supporting electrolyte were also carried out. Though we were unable to determine the stereochemistry of the binuclear complexes using single crystal X-ray diffraction studies, we have established the stereochemistry beyond any doubt using various spectroscopic data. Single crystal X-ray diffraction study of one of the mononuclear tungsten(VI) complex clearly proves the ONO donor behaviour of the Schiff bases.

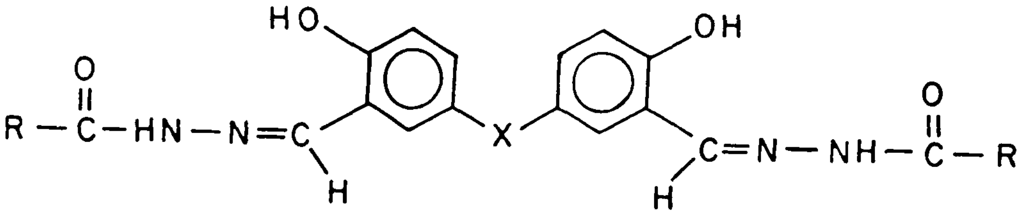
The Schiff bases together with their abbreviations used in the present study are as follows.

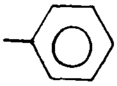
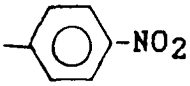
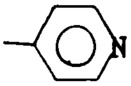
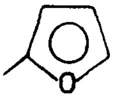
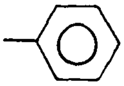
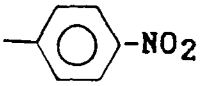
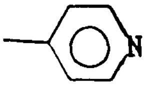
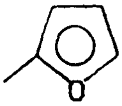
(A) The Schiff bases derived from 5,5′-methylene- or dithio bis(salicylaldehyde) and various amines.



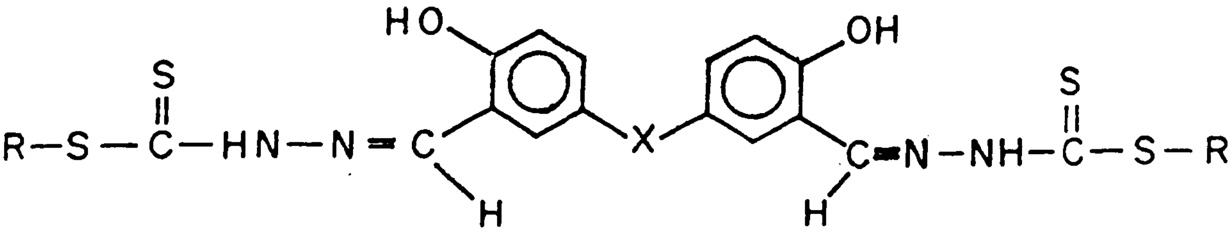
	X	R	Abbreviations
1	CH_2	o-C_6H_4OH	$CH_2(H_2sal\text{-}OAP)_2$
2	CH_2	CH_2CH_2OH	$CH_2(H_2sal\text{-}EA)_2$
3	CH_2	$C(CH_3)_2CH_2OH$	$CH_2(H_2sal\text{-}AMP)_2$
4	CH_2	$CH_2CH(CH_3)OH$	$CH_2(H_2sal\text{-}IPA)_2$
5	S-S	o-C_6H_4OH	$S_2(H_2sal\text{-}OAP)_2$
6	S-S	CH_2CH_2OH	$S_2(H_2sal\text{-}EA)_2$
7	S-S	$C(CH_3)_2CH_2OH$	$S_2(H_2sal\text{-}AMP)_2$
8	S-S	$CH_2CH(CH_3)OH$	$S_2(H_2sal\text{-}IPA)_2$

(B) Schiff bases derived from 5,5′-methylene- or dithio bis(salicylaldehyde) with benzoylhydrazide, *p*-nitrobenzoyl hydrazide, isonicotinoylhydrazide and furoicacidhydrazide.



	X	R	Abbreviations
9	CH_2		$CH_2(H_2sal\text{-}BZH)_2$
10	CH_2		$CH_2(H_2sal\text{-}NO_2BZH)_2$
11	CH_2		$CH_2(H_2sal\text{-}INH)_2$
12	CH_2		$CH_2(H_2sal\text{-}FAH)_2$
13	S-S		$S_2(H_2sal\text{-}BZH)_2$
14	S-S		$S_2(H_2sal\text{-}NO_2BZH)_2$
15	S-S		$S_2(H_2sal\text{-}INH)_2$
16	S-S		$S_2(H_2sal\text{-}FAH)_2$

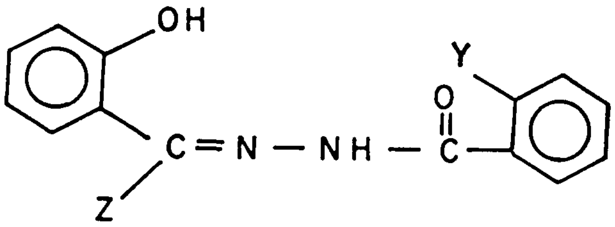
C Schiff bases derived from 5,5′-methylene- or dithio bis(salicylaldehyde) and S-methyl dithiocarbazate or S-benzyl dithiocarbazate.



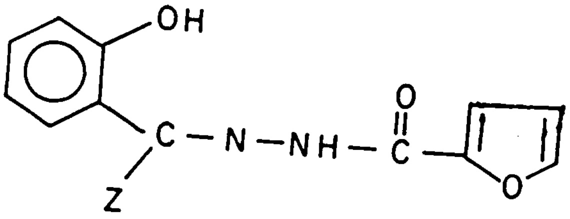
	X	R	Abbreviations.
17	CH_2	CH_3	$CH_2(H_2sal\text{-}SMDTC)_2$

18	CH_2	$CH_2C_6H_5$	$CH_2(H_2sal\text{-}SBDTC)_2$
19	CH_2	CH_3	$S_2(H_2sal\text{-}SMDTC)_2$
20	CH_2	$CH_2C_6H_5$	$S_2(H_2sal\text{-}SBDTC)_2$

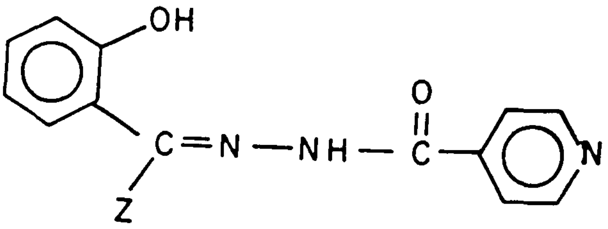
D Schiff bases derived from salicylaldehyde, *o*-vanillin or *o*-hydroxyacetophenone with benzoylhydrazide, salicylhydrazide, isonicotinoylhydrazide and furoicacidhydrazide.



(I)



(II)



(III)

	Ligand	X	Y	Z	Abbreviations.
21	I	H	H	H	$H_2sal\text{-}BZH$
22	I	OMe	H	H	$H_2van\text{-}BZH$
23	I	H	OH	H	$H_2sal\text{-}SZH$
24	I	OMe	OH	H	$H_2van\text{-}SZH$
25	II	H	--	H	$H_2sal\text{-}FAH$
26	II	OMe	--	H	$H_2van\text{-}FAH$
27	III	H	--	H	$H_2sal\text{-}INH$

28	III	OMe	--	H	H_2van-INH
29	I	H	H	CH_3	H_2hap-BZH
30	I	OH	OH	CH_3	H_2hap-SZH
31	II	H	--	CH_3	H_2hap-FAH
32	III	H	--	CH_3	H_2hap-INH

5,5′-Methylene and dithio- bis(salicylaldehyde) behave like salicylaldehyde and react with $-NH_2$ containing organic compounds in a 1:2 molar ratio to form the binucleating tetraanionic Schiff base ligands **1-20**. All the Schiff bases obtained were yellow to orange in colour.

All the flexibly-bridged hexadentate tetraanionic Schiff bases LH_4 [**1-20**] are new and they were characterized by elemental analyses, IR, ^1H NMR, electronic spectral studies. ^1H NMR spectra of Schiff bases derived from the 5,5′-methylene bis(salicylaldehyde) show the singlet due to a $-CH_2$ proton attached to the methylene group even after condensation. Mass spectral studies of some of the ligands were also done and the presence of molecular ion peak m/z of **1** at 438 (calc. 438), **3** at 398 (calc. 398), **5** at 488 (calc. 488) and **7** at 448 (calc. 448) indicate the high degree of stability of the molecular ion to electron impact.

The Schiff bases **21 - 32** were prepared according to the reported procedures[222] and characterized by elemental analyses, IR, ^1H NMR and electronic spectral studies.

The reaction of the flexibly bridged ligands [1 - 20] with $MoO_2(acac)_2$ in a 1:2 molar ratio proceeded according to the equation (1) in refluxing methanol and complexes of the type $[(MoO_2)_2L]$ were formed.

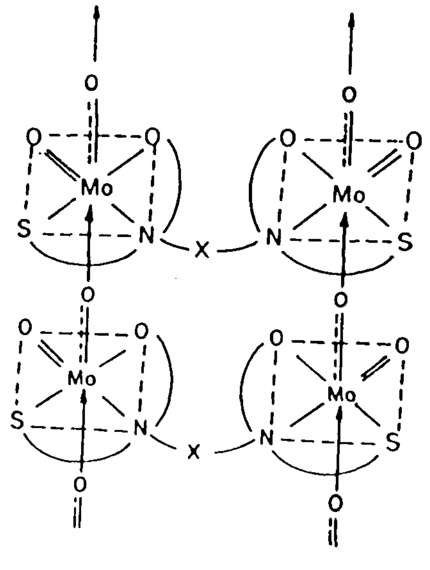
$$2\ MoO_2(acac)_2 \ + \ LH_4 \ \xrightarrow[MeOH]{} \ [(MoO_2)_2L] \ + \ 4\ acacH \qquad (1)$$

The analytical data support the formation of the complexes by complete removal of the coordinated acetylacetone group under the reaction conditions. These complexes do not undergo any weight loss upto 200° which suggests the formation of the five coordinated complex $[(MoO_2)_2L]$ and not the expected octahedral complex $[(MoO_2)_2L.2MeOH]$. However, strong coordinating monodentate ligands (D) like DMSO, pyridine and 4-methyl pyridine do form octahedral complexes $[(MoO_2)_2L(D)_2]$ when the complexes are dissolved in them. The sixth labile coordination site in the binuclear 5-coordinated complexes can also be occupied by an imidazole molecule. All the complexes are non-electrolytes ($\sim 20\,\Omega^{-1}$ mol^{-1} cm^{2}) in DMF and are diamagnetic as expected for the $4d^{0}$ system. They are soluble in coordinating solvents such as DMSO, THF and pyridine. The high decomposition temperature indicates their good thermal stability.

The thermal analysis data for pyridine adducts reveal a well defined endothermic step at around 180°, corresponding to the loss of two molecules of pyridine in $[(MoO_2)_2L(py)_2]$.

The cyclic voltammetric measurements indicated irreversible to quasireversible reduction of the molybdenum(VI) with a cathodic reduction potential of -0.83 to -0.85 V vs. SCE. In some voltammograms one oxidative peak is also seen, but there is a large difference between the reductive and oxidative peak potential indicating that the rate of Mo(VI) to Mo(IV) reductions are irreversible tending to quasireversibility at lower scan rates. Molybdenum complexes of the sulphur containing ligands show no detectible reduction or oxidation waves in their cyclic voltammograms.

The IR spectra of the complexes of the type $[(MoO_2)_2L(D)_2]$ show two IR absorptions at *ca.* 900 cm^{-1}, attributable to a *cis*-MoO_2 structure, whereas the oligomeric complexes usually show an intense $\nu(M{=}O)$ band at 910-938 cm^{-1} and a broad but strong band at 820 cm^{-1} due to a weakened $\nu(Mo{=}O)$ as a result of $Mo{=}O \longrightarrow Mo$ interactions. Thus from IR and NMR spectral data an oligomeric (pseudooctahedral) structure is suggested for these complexes as shown in the figure.



We have reacted the sulphur containing $Mo(VI)O_2$ complexes with PPh_3 to obtain Mo(IV) complexes, according to the following equation.

$$[(Mo^{VI}O_2)_2L] + 2\ PPh_3 \longrightarrow [(Mo^{IV}O)_2L] + 2\ OPPh_3$$

The Mo(IV)O complex obtained shows one IR absorption peak due to M=O stretching and it is observed at higher frequency than in the corresponding $Mo(VI)O_2$ complexes. Since our system is binuclear and the Mo(IV)O species are easily oxidisable to $Mo(VI)O_2$, we could not arrive at any precise determination of the stoichiometry of these oxo Mo(IV)O species.

The olefin epoxidation reactions were tried with these complexes using tertiarybutyl hydroperoxide. But no epoxide formation was observed with all these complexes. We used cyclohexene, *trans*-stilbene and styrene as olefins for epoxidation reactions.

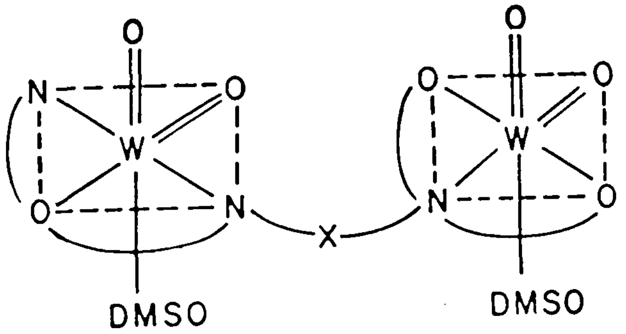
DIOXOTUNGSTEN(VI) COMPLEXES

To explore the chemistry of the dioxotungsten(VI) complexes, we have synthesized several tungsten(VI) complexes and characterized them by elemental analyses and various spectroscopic techniques. The Schiff bases **20-32** were used for the preparation of the mononuclear $W(VI)O_2$ complexes where $WO_2(acac)_2$ was used as the precursor. All the spectroscopic data show the coordination of the solvent methanol in the sixth labile binding site of the tungsten atom forming an octahedral geometry around the metal atom. The single crystal X-ray diffraction study of the complex [WO_2(*o*-OC_6H_4CH=NN=C(O)C_6H_5)(MeOH)]. MeOH] shows that the tungsten atom has a highly distorted octahedral coordination in which anionic oxygen atoms of the tridentate ligand are mutually *trans* and are *cis* to the *cis*-dioxo group. The complex belongs to the space group $Pbc2_1$ with a = 6.992(2), b = 16.190(2), c = 31.390 (4)Å, V = 3553.4(12) $Å^3$, Z = 8, R_F = 0.050 and R_w = 0.054.

In the case of complexes derived from *o*-hydroxyacetophenone, the spectroscopic results do not show the presence of coordinated methanol molecule. A pseudooctahedral geometry is suggested for these complexes where each tungsten atom is coordinated to the oxo group of the adjacent molecule forming a $W \overset{...}{=} O \longrightarrow W$ bridge as in the case of analogous Mo complexes. These oligomeric complexes react with coordinating solvents such as DMSO, DMF, pyridine to form the complexes of the type $WO_2L.(D)$ by breaking the oligomeric bridge through the oxo oxygen.

We have also tried to react the hexadentate Schiff base ligands with $WO_2(acac)_2$ in 1:2 molar ratio in refluxing methanol. From the spectroscopic studies, it can be concluded that the binuclear oligomeric tungsten(VI) complexes are formed using

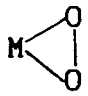
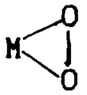
ONO⁀ONO donor flexibly bridged hexadentate tetraanionic Schiff bases. But no reaction was observed with the ONS⁀ONS donor Schiff bases. This lower affinity of W(VI) towards sulphur donor ligands is supported by the previous observation that the molybdenum in the molybdoenzymes can not be replaced by tungsten atom. The oligomeric type of complexes of the form $(WO_2)_2L$ can be converted into $[(WO_2)_2L.(D)_2]$ (D = monodentate ligand) by reacting with monodentate ligands such as pyridine, 4-methyl pyridine and DMSO. The following structure in which each metal atom has an octahedral coordination environment is proposed for the binuclear tungsten(VI) complex $[(WO_2)_2L.(DMSO)_2]$.



$x = CH_2$ or S_2

SYNTHESIS OF BINUCLEAR ORGANO OXO-PEROXO COMPLEXES OF TUNGSTEN(VI) AND MOLYBDENUM(VI) AND THEIR CONVERSION TO CORRESPONDING DIOXO COMPLEXES USING PPh_3.

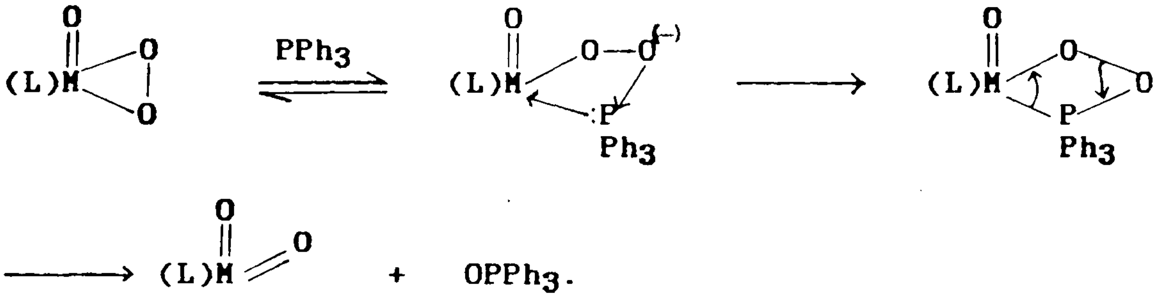
In order to extend the feasibility of the single-step synthesis of dioxo complexes from the corresponding oxo-peroxo complexes, we have synthesized some new binuclear oxo-peroxo complexes of molybdenum(VI) and tungsten(VI). Attempt has also made to find the application of these oxo-peroxo complexes as catalysts for the oxidation of olefins in presence of *t*-butylhydroperoxide. The binucleating Schiff bases **11** and **15** have been used for the preparation of the peroxo complexes. We could not prepare the oxo-peroxo complexes with other Schiff bases derived from benzoylhydrazide and furoylhydrazide under similar reaction conditions.

Agitation of WO_3 or MoO_3 in excess of 30% aqueous H_2O_2 generates *insitu* peroxotungstic acid or peroxomolybdic acid. These peroxo species readily react with alcoholic solution of the Schiff base ligand H_4L to give the corresponding binuclear oxoperoxo complexes which on crystallization from 95% alcohol have the general formula $[\{MO(O_2)\}_2L(H_2O)_2]$ (M = Mo or W). These oxo-peroxo complexes exhibit three IR active vibrational modes namely, O—O stretching(ν_1), the symmetric  stretch (ν_2) and the antisymmetric  stretch(ν_3). There is a decrease in the ν_1 upon passing from molybdenum complexes to the corresponding tungsten one. In addition, the oxo-peroxo complexes exhibit ν(M=O) at *ca*.960 cm^{-1}. These oxoperoxo complexes readily undergo oxygen transfer reactions with PPh_3 in anhydrous methanol to give the corresponding dioxo complexes of formula $[(MO_2)_2L]$. The formation of dioxo complex may be represented by the equation:

$$[\{MO(O_2)\}_2L(H_2O)_2] \quad + \quad 2\ PPh_3 \longrightarrow [(MO_2)_2L] \quad + \quad 2\ OPPh_3 \quad + \quad 2\ H_2O$$

(M = Mo or W)

The presence of a sharp band at *ca*.950 cm^{-1} due to ν(O=M=O) stretch and one broad band at *ca*.810 cm^{-1} due to weakened ν(M=O) as a result of $M\cdots O \longrightarrow M$ interaction and the absence of bands due to metal-peroxo group in the IR spectra clearly indicate the formation of $[MO_2]^{2+}$ complexes. A pseudo-octahedral geometry is suggested for the complexes, $[(MO_2)_2L]$. The formation of *cis*-dioxo group around each metal atom from the binuclear oxoperoxo complex using PPh_3 can be easily explained through the following reaction path:



(where M = W or Mo and L = ligand(s) coordinated to M)

To explore the reactivity of the newly prepared peroxo complexes we have reacted these complexes with various olefins such as cyclohexene, styrene and *trans*-stilbene. These complexes failed to give the epoxides of the olefins. This negative result outline the enhanced stability of the metal peroxide moiety in the presence of tridentate dibasic ligands. However, the formation of cyclohexanol to cyclohexanone was observed using these complexes as catalysts in presence of tertiarybutylhydrogen peroxide both by GC and TLC.

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CHAPTER 2

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DIOXOMOLYBDENUM(VI) COMPLEXES OF NEW BINUCLEATING SCHIFF BASES DERIVED FROM 5,5′-METHYLENE OR DITHIO- BIS(SALICYLALDEHYDE) AND VARIOUS AMINES

2.1 INTRODUCTION

The discovery of molybdenum in a number of enzymes has led to the continued growth of coordination chemistry of molybdenum.[1] The potential for biological and physiological activity, and the industrial use of these complexes have also stimulated the discovery of a variety of molybdenum complexes in various oxidation states.[2] Amongst the -II to +VI oxidation states, the most stable one is +VI and is associated with the dioxo group. Although a number of reports are available in the literature dealing with the mononuclear dioxomolybdenum(VI) complexes of tridentate Schiff base ligands where one labile binding site allows the binding and displacement of various substrate molecules, such systems with binuclear dioxomolybdenum(VI) complexes are rare.[2c]

Marvel et. al.[3] have prepared 5,5′-methylene bis(salicyl aldehyde) by the reaction of salicylaldehyde with trioxane and sulphuric acid in acetic acid solution. They converted this dialdehyde to a polymeric Schiff base having a molecular weight of about 10,000 by heating with *o*-phenylenediamine. The polymeric Schiff base obtained was converted to the polymeric chelates of the metal ions like copper(II), cobalt(II), zinc(II), nickel(II), iron(II) and cadmium(II) and their thermal stabilities were studied.

Awasarkar et. al.[4] have prepared 5,5′-dithio bis(salicyl aldehyde) by the reaction of sulphur monochloride with salicylaldehyde. The replacement of a proton which is *para* to the hydroxyl group of salicylaldehyde takes place similar to the reaction in the case of aromatic hydroxy ketones.[5,6] The hydroxyl group is still intact in all these cases. They have prepared octahedral polymeric complexes of the disulphide, $[C_6H_3(OH)(CHO)]_2S_2$ by reacting it with $TiCl_4$ and Bu_2SnO.

$$\mathbf{TiCl_4 + [C_6H_3(OH)(CHO)]_2S_2 \longrightarrow [C_6H_3(O)(CHO)]_2S_2TiCl_2 + 2HCl}$$

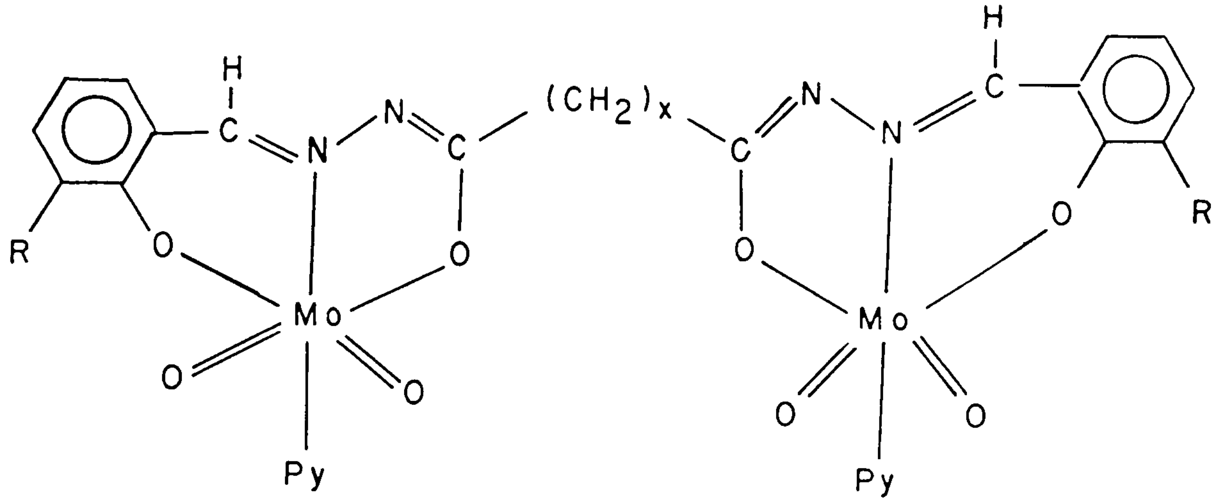
$$\mathbf{Bu_2SnO + [C_6H_3(OH)(CHO)]_2S_2 \longrightarrow Bu_2Sn[C_6H_3(O)(CHO)]_2S_2 + H_2O}$$

The reaction of 5,5′-dithio bis(salicylaldehyde) and salicylaldehyde hydrazone or 2-hydroxy acetophenone hydrazone resulted in the formation of new dithio bis(diazine) derivatives containing four OH, two N-N and one S-S groups. These diazines (H_4L) react with $TiCl_4$ and Bu_2SnO forming pentacoordinated binuclear titanium(IV) and tin(VI) complexes, respectively.[7]

$$\mathbf{2TiCl_4 + H_4L \longrightarrow Cl_2Ti(L)TiCl_2 + 4\ HCl}$$

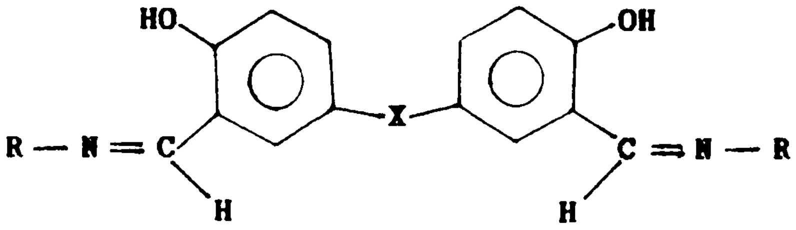
$$\mathbf{2Bu_2SnO + H_4L \longrightarrow Bu_2Sn(L)SnBu_2 + 2\ H_2O}$$

There is only one report in the literature dealing with binuclear dioxomolybdenum(VI) complexes. Havanur et. al.[2d] have prepared a series of binuclear dioxomolybdenum(VI) complexes with various dihydrazones. The complexes prepared were of the type $[(MoO_2)_2L(py)_2]$ in which ligands coordinate in the enol form. Octahedral structures (I) containing *cis*-MoO_2 groups were proposed for the complexes.



(I)

In order to explore the area of binuclear dioxomolybdenum(VI) chemistry, we have synthesized and characterized some binuclear dioxomolybdenum(VI) complexes of flexibly bridged hexadentate tetraanionic Schiff base ligands. The following tetraanionic Schiff base ligands (structure II) have been selected for the present study.



	X	R	Abbreviations
1	CH_2	o-C_6H_4OH	$CH_2(H_2$sal-OAP$)_2$
2	CH_2	CH_2CH_2OH	$CH_2(H_2$sal-EA$)_2$
3	CH_2	$C(CH_3)_2CH_2OH$	$CH_2(H_2$sal-AMP$)_2$
4	CH_2	$CH_2CH(CH_3)OH$	$CH_2(H_2$sal-IPA$)_2$
5	S-S	o-C_6H_4OH	$S_2(H_2$sal-OAP$)_2$
6	S-S	CH_2CH_2OH	$S_2(H_2$sal-EA$)_2$
7	S-S	$C(CH_3)_2CH_2OH$	$S_2(H_2$sal-AMP$)_2$
8	S-S	$CH_2CH(CH_3)OH$	$S_2(H_2$sal-IPA$)_2$

2.2 EXPERIMENTAL

All reagents and solvents used were of analytical grade. *o*-Aminophenol, salicylaldehyde and acetylacetone were used after purification. 5,5′-Methylene bis(salicylaldehyde)[3] and 5,5′-dithio bis(salicylaldehyde)[4] were prepared following the literature procedures. $[MoO_2(acac)_2]$ was synthesized by the method described previously.[8]

Molybdenum was determined gravimetrically as dioxobis(8-quinolinolato)molybdenum(VI) after decomposing the complex with con.HNO_3 and then precipitating with 8-hydroxyquinoline.[9] Other elemental analyses were performed by the microanalytical section of National Chemical Laboratory. IR spectra were recorded as nujol mulls and as KBr discs on a Perkin-Elmer model 1620 FT-IR spectrophotometer. Electronic spectra were recorded in DMF on a

Shimadzu model UV-2101PC UV-VIS scanning spectrophotometer. ^1H NMR spectra were obtained on Bruker WH-200 spectrometer in DMSO-d_6 and $CDCl_3$. Chemical shifts (δ in ppm) are reported relative to DMSO-d_6 (2.40 ppm) or $CDCl_3$ (7.24 ppm). The electrical conductance measurements were performed in 1×10^{-3} M DMF solutions using a Biochem model DC 808 digital conductivity bridge calibrated with potassium chloride solution. Mass spectra of ligands were recorded on a Finnigan Mat model 1020 Automated GC-MS spectrometer.

The following binucleating hexadentate tetraanionic Schiff bases and their binuclear dioxomolybdenum(VI) complexes have been prepared. The elemental analyses, m.p. and colour have been presented in Table 2.1.

(1) Preparation of 5,5′-methylene bis(salicylideneamino-2-phenol) [$CH_2(H_2sal\text{-}OAP)_2$]

A solution of 2-aminophenol (0.218 g, 0.002 mol) in methanol (10 ml) was added to a hot solution of 5,5′-methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) in methanol (10 ml) and the reaction mixture was refluxed for 2 h on a water bath. After reducing the solvent to 5 ml, the solution was cooled to 10° overnight. The separated orange solid was filtered, washed with cold methanol and dried under reduced pressure at ambient temperature and finally it was recrystallized from methanol. Yield 0.346 g (79%); m.p. 232°.

(2) Preparation of 5,5′-methylene bis(salicylideneamino-1-ethanol) [$CH_2(H_2sal\text{-}EA)_2$]

2-Amino ethanol (0.122 g, 0.002 mol) in methanol (10 ml) and 5,5′-methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) were mixed in 20 ml methanol and refluxed for 3h. After reducing the solvent to 10 ml, the solution was cooled to 0° overnight. The separated yellow solid product was filtered, air dried and recrystallized from methanol. Yield 0.200 g (58%); m.p. 92°.

(3) Preparation of 5,5′-methylene bis(salicylideneamino-2-methyl-1-propanol) [$CH_2(H_2sal\text{-}AMP)_2$]

2-Amino-2-methyl propanol (0.178 g, 0.002 mol) was dissolved in methanol (20 ml) and to this solution 5,5′-methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) was added and refluxed for 3h. The resulting solution upon concentration and cooling deposited yellow crystalline solid which was filtered and dried in air and recrystallized from methanol. Yield 0.250 g (62%); m.p. 190°.

(4) Preparation of 5,5′-methylene bis(salicylideneamino-2-propanol) [$CH_2(H_2sal\text{-}IPA)_2$]

1-Amino-2-propanol (0.150 g, 0.002 mol) was dissolved in methanol (10 ml) and to this a solution of 5,5′-methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) dissolved in 10 ml methanol was added and refluxed for 3h. Upon concentration and cooling the yellow crystals separated were filtered and recrystallized from methanol. Yield 0.260 g (70%); m.p.: 102°.

(5) Preparation of 5,5′-dithio bis(salicylideneamino-2-phenol) [$S_2(H_2sal\text{-}OAP)_2$]

2-Amino phenol (0.218 g, 0.002 mol) in methanol (10 ml) and 5,5′-dithio bis(salicylaldehyde) (0.306 g, 0.001 mol) in methanol (10 ml) were mixed and refluxed for 3h. Upon cooling a red solid product was separated, which was filtered air dried and finally recrystallized from methanol. Yield 0.388 g (79%); m.p. 220°.

(6) Preparation of 5,5′-dithio bis(salicylideneamino-1-ethanol) [$S_2(H_2sal\text{-}EA)_2$]

2-Amino ethanol (0.122 g, 0.002 mol) was dissolved in methanol (10 ml) and to this solution 5,5′-dithio bis(salicyl aldehyde) (0.306 g, 0.001 mol) was added and refluxed for 3h. After reducing the solvent to 5 ml, the solution was cooled to 0° overnight. The separated orange solid product was filtered, air dried and recrystallized from methanol. Yield 0.260 g (66%); m.p. 108°.

(7) Preparation of 5,5′-dithio bis(salicylideneamino-2-methyl propanol) [$S_2(H_2sal\text{-}AMP)_2$]

2-Amino-2-methyl propanol (0.178 g, 0.002 mol) was dissolved in methanol (10 ml) and and to this solution 5,5′-dithio bis(salicylaldehyde) (0.306 g, 0.001 mol) was added and refluxed for 3h. The resulting solution upon concentration and cooling deposited orange coloured solid product which was filtered and dried in air. Yield: 0.300 g (67%); m.p. 160°.

(8) Preparation of 5,5′-dithio bis(salicylideneamino-2-propanol) [$S_2(H_2$sal-IPA$)_2$]

1-Amino-2-propanol (0.150 g, 0.002 mol) was dissolved in methanol (10 ml) and mixed with 5,5′-methylene bis(salicyl aldehyde) (0.306 g, 0.001 mol) and the contents refluxed for 3h. On concentration and cooling the orange crystals separated were filtered and recrystallized from methanol. Yield 0.218 g (52%); m.p. 52°.

(1a) Preparation of [$(MoO_2)_2(CH_2\{$sal-OAP$\}_2)$]

The Schiff base [$CH_2\{H_2$sal-OAP$\}_2$] (0.219 g, 0.0005 mol) was dissolved in methanol (50 ml) by heating on a water bath and to this was added $MoO_2(acac)_2$ (0.330 g, 0.001 mol) as a solid with vigorous shaking. The resulting turbid solution was filtered and the clear filtrate refluxed on a water bath for 6 h. After concentrating the solution to 10 ml and cooling to 10° overnight, the separated solid was filtered, washed with methanol and dried at 100° in air. Yield 0.244 g (71%); m.p. >250°.

(2a) Preparation of [$(MoO_2)_2(CH_2\{$sal-EA$\}_2)$]

$MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added to a refluxing solution of the ligand [$CH_2\{H_2$sal-EA$\}_2$] (0.171 g, 0.0005 mol) in methanol (50 ml). The resulting mixture was filtered immediately and the solution refluxed on a water bath for 6h. After reducing the solvent to 10 ml, the solution was cooled to room temperature. The separated orange solid product was filtered, washed with hot methanol and dried at 100°. Yield 0.300 g (71%); m.p. >250°.

(3a) Preparation of $[(MoO_2)_2(CH_2\{sal\text{-}AMP\}_2)]$

To a refluxing solution of the ligand $[CH_2\{H_2sal\text{-}AMP\}_2]$ (0.199 g, 0.0005 mol) in methanol (50 ml) $MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added as a solid. The resulting solution was filtered while hot and again refluxed for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated orange solid was filtered, washed with hot methanol and dried at 100°. Yield 0.312 g (69%); m.p. >250°.

(4a) Preparation of $[(MoO_2)_2(CH_2\{sal\text{-}IPA\}_2)]$

$MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added to a refluxing solution of the ligand $[CH_2\{H_2sal\text{-}IPA\}_2]$ (0.185 g, 0.0005 mol) in methanol (50 ml). The resulting solution was filtered and the filtrate was again refluxed on a water bath for 6h. After reducing the volume of the solvent, the mixture was cooled at 0° overnight. The separated yellow coloured complex was filtered and dried at 100°. Yield 0.330 g (70%); m.p.>250°.

(5a) Preparation of $[(MoO_2)_2(S_2\{ sal\text{-}OAP\}_2)]$

The Schiff base $[S_2\{H_2sal\text{-}OAP\}_2]$ (0.244 g, 0.0005 mol) was dissolved in methanol (50 ml) by heating on a water bath and to it was added $MoO_2(acac)_2$ (0.330 g, 0.001 mol) as a solid with vigorous shaking. The resulting turbid solution was filtered and then refluxed on a waterbath for 6h. After concentrating the solution to 10 ml and cooling to 10° overnight, the separated orange solid was filtered and dried at 100° in air. Yield 0.326 g (66%); m.p. >250°.

(6a) Preparation of [$(MoO_2)_2(S_2\{sal\text{-}EA\}_2)$]

$MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added to a refluxing solution of the ligand [$S_2\{H_2sal\text{-}EA\}_2$] (0.196 g, 0.0005 mol) in methanol (50 ml). The resulting mixture was filtered immediately and refluxed on a water bath for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated orange solid product was filtered, washed with hot methanol and dried at 100°. Yield 0.310 g (69%); m.p. >250°.

(7a) Preparation of [$(MoO_2)_2(S_2\{sal\text{-}AMP\}_2)$]

To a refluxing solution of the ligand [$S_2\{H_2sal\text{-}AMP\}_2$] (0.224 g, 0.0005 mol) in methanol (50 ml) $MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added as a solid. The refluxing solution was filtered while hot and again refluxed for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated orange solid was filtered, washed with hot methanol and dried at 100°. Yield 0.320 g (67%); m.p. >250°.

(8a) Preparation of [$(MoO_2)_2(S_2\{sal\text{-}IPA\}_2)$]

$MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added to a refluxing solution of the ligand [$S_2\{H_2sal\text{-}IPA\}_2$] (0.210 g, 0.0005 mol) in methanol (50 ml). The resulting solution was filtered and the filtrate was again refluxed on a water bath for 6h. After reducing the volume of the solvent, the mixture was cooled at 0° overnight. The separated yellow coloured complex was filtered and dried at 100°. Yield 0.314 g (67%); m.p. >250°.

Preparation of complexes of the type $[(MoO_2)_2L(py)_2]$.

These complexes were prepared in quantitative yield by dissolving the respective complexes of the type $[(MoO_2)_2L]$ in slightly more than the stoichiometric amount of pyridine with heating on a water bath and then evaporating the excess of pyridine under vacuum. Yield (80-85%).

2.3 RESULTS AND DISCUSSION

5,5′-Methylene- and dithio- bis(salicylaldehyde) ligands behave like salicylaldehyde and react with primary amines in 1:2 molar ratio to give binucleating tetraanionic Schiff base ligands 1 - 8. The mass spectral data of some of the representative Schiff base ligands [e.g., molecular ion peak m/e of 1 at 438 (Calc. 438), 3 at 398 (Calc. 398), 5 at 488(Calc. 488) and 7 at 448 (Calc. 448)] indicate the high degree of stability of the molecular ion to electron impact. These data also indicate that *para*-substituted methylene or disulphide groups are intact and still attached to two salicylaldehyde moieties. These ligands are further characterized by elemental analysis and other spectral techniques.

These tetraanionic binucleating Schiff base ligands **1** – **8** react with [$MoO_2(acac)_2$] in 1 : 2 molar ratio in refluxing methanol and complexes of the type [$(MoO_2)_2L$] are formed as follows:

$$2\ [MoO_2(acac)_2] + LH_4 \xrightarrow[MeOH]{} [(MoO_2)_2L] + 4\ acacH$$

Under these reaction conditions complete replacement of the bidentate acetylacetone groups occurs. The analytical data support the formulation of the complexes as [$(MoO_2)_2L$] and not as [$(MoO_2)_2L.2MeOH$], an expected binuclear octahedral complex. However the coordination of methanol was noticed in some complexes when they were dried only at ambient temperature. But on drying at 100° they are invariably converted into a stable species [$(MoO_2)_2L$]. Treatment of [$(MoO_2)_2L$] with pyridine results in the formation of [$(MoO_2)_2L(py)_2$] in which pyridine occupies the sixth coordination position in both $[MoO_2]^{2+}$ units. The [$(MoO_2)_2L$] complexes do not lose weight on heating up to 200°. However, thermal analysis data for pyridine adducts reveal a well-defined endothermic step at around 180°, corresponding to the loss of two molecules of pyridine; an information which confirms the coordination of pyridine in [$(MoO_2)_2L(py)_2$]. The coordinated monodentate ligand in complexes of the type [$MoO_2L.X$] (X = monodentate ligand) is known to undergo cleavage on heating due to weak coordination and hence confirms its labile nature.[10]

All the complexes reported here are diamagnetic as expected for the 4d^0 molybdenum ion. The low molar conductance values (3.0 - 9.0 mho mole^{-1} cm^2) of the complexes in DMF indicate their non-electrolytic behaviour. They are soluble in coordinating solvents like pyridine, DMSO and DMF. The high decomposition temperature (>250°) indicates the good thermal stability of the complexes.

IR Spectral Studies

The IR spectral data of the new Schiff bases and their metal complexes are summarized in Table 2.2. The Schiff bases $CH_2(H_2sal\text{-}OAP)_2$ (1) $S_2(H_2sal\text{-}OAP)_2$ (5) show one broad band at *ca.*2700 cm^{-1} due to intramolecular hydrogen bonded phenolic hydroxyl groups. Other Schiff bases 2, 3, 4, 6, 7 and 8 show one more band at ~3200 cm^{-1}, in addition to the former one, due to the ν(OH) of the alcoholic hydroxyl group.

In the IR spectra of the complexes $[(MoO_2)_2(CH_2\{sal\text{-}OAP\}_2)]$ and $[(MoO_2)_2(S_2\{sal\text{-}OAP\}_2)]$ the band at 2700 cm^{-1} is absent suggesting the coordination of both phenolic oxygen atoms to the metal ion after deprotonation. Similarly, the absence of bands at *ca.* 3200 and 2700 cm^{-1} in the other complexes indicates the deprotonation of the alcoholic as well as phenolic hydroxyl groups and coordination of the oxygen atoms to molybdenum. The strong band in the region 1630-1645 cm^{-1} due to ν(C=N) stretch shifts to a lower frequency by 2-36 cm^{-1}, indicating the participation of the azomethine nitrogen atom in coordination.[11] Thus the IR data suggests the dibasic tridentate and ONO donor behaviour of each Schiff base unit.

$MoO_2(acac)_2$ (Hacac = acetylacetone) exhibits only one band at 904 cm^{-1} due to ν_{asym}(O=Mo=O) stretch.[12] The other band due to ν_{sym}(O=Mo=O) is masked due to strong absorbance of several other ligand bands. The binuclear complex $[(MoO_2)_2(CH_2\{sal\text{-}OAP\}_2)]$ exhibits two bands at 931 and 911 cm^{-1} due to ν_{sym} and ν_{asym} (O=Mo=O) stretches respectively and a strong band at 851 cm^{-1} due to $Mo\cdots O\longrightarrow Mo$ interaction.[1b] The IR spectrum of the pyridine adduct $[(MoO_2)_2(CH_2\{sal\text{-}OAP\}_2)(py)_2$ exhibits two bands due to ν_{sym} and ν_{asym} stretches at 936 and 906 cm^{-1} respectively. In the other metal complexes of the type $[(MoO_2)_2L]$ only a sharp single band is observed at 910-938 cm^{-1} due to ν(O=Mo=O)stretch and a broad band at 820 cm^{-1} due to weakened ν(Mo=O) as a result of $Mo\cdots O\longrightarrow Mo$ interaction. However, in the case of pyridine adducts two bands in the regions 920-934 and 905-915 cm^{-1}, due to the ν_{sym} and ν_{asym} (O=Mo=O) stretches, respectively are observed. These data indicate the presence of a *cis*-MoO_2 structure as a *trans*-MoO_2 structure would only show one ν(O=Mo=O) band due to the asymmetric stretch.[1b]

These observations suggest the presence of an oligomeric (pseudo-octahedral) structure for $[(MoO_2)_2L]$ in which each molybdenum ion achieves a pseudooctahedral structure *via* oxo bridging.[10] Adduct formation with pyridine essentially shows the breaking of this bridge as the band at 820 cm^{-1} disappears and a new band appears at *ca.* 910 cm^{-1} due to $\nu_{asym}(O{=}Mo{=}O)$ stretch. This observation suggests bridging through the $Mo{=}O{\rightarrow}Mo$ moiety. The occurrence of the ν(C-O) (phenolic) band at almost identical positions in $[(MoO_2)_2(CH_2\{sal\text{-}OAP\}_2)]$ (1551 cm^{-1}) and $[(MoO_2)_2(CH_2\{sal\text{-}OAP\}_2)(py)_2]$ (1552 cm^{-1}) also suggests the presence of oligomeric bridges only through $Mo{=}O{\rightarrow}Mo$ as oligomerization *via* the phenolic oxygen bridge would be expected to produce substantial increase in the ν(C-O)(phenolic) stretch.[13]

The coordination of pyridine is characterized by the shift of the ring breathing mode of pyridine, which occurs at 990 cm^{-1} in free pyridine,[14] to a higher frequency by 15-20 cm^{-1}. In addition, the shift of the totally symmetric ring stretching mode at 1587 cm^{-1}, in-plane anti-symmetric ring stretching mode at 1438 cm^{-1} and in-plane totally symmetric ring breathing mode at 1030 cm^{-1} to higher energy are indicative of the pyridine coordination to molybdenum ion.

^{1}H NMR Studies

Further evidence for the coordinating mode of the Schiff base ligands is obtained from the study of their ^{1}H NMR spectra.

The NMR spectra of the ligands and complexes are presented in Table 2.3. In the ^{1}H NMR spectrum of the ligands [$CH_2(H_2$sal-OAP$)_2$] and [S_2(sal-OAP$)_2$)] the phenolic protons of the salicylaldehyde residue resonate at 13.61 and 14.15 ppm, respectively with an additional signal due to phenolic proton of the *o*-aminophenol residue at 9.71 and 9.56 ppm respectively. Similarly all other Schiff bases exhibit a signal due to the phenolic protons in the range 13.50 - 14.85 ppm. The Schiff bases do not show alcoholic protons in $CDCl_3$ solution which may be possibly due to intramolecular hydrogen bonding between alcoholic proton and azomethine group.[15] However, the spectra of Schiff bases (2, 3, 6 and 7) in DMSO show alcoholic proton signal at ~ 4.26-5.10 ppm which is confirmed by D_2O exchange studies.

In the metal complexes, the absence of both phenolic and alcoholic proton signals indicates the coordination of both the phenolic and alcoholic oxygen atoms to molybdenum after proton replacement.[16] A downward shift of the azomethine proton is observed in the case of all complexes (see Table 2.3) suggesting the coordination of the lone pair of the nitrogen of azomethine group to the molybdenum atom. The coordination of pyridine to the molybdenum ion in [$(MoO_2)_2L(py)_2$] is evidenced by the appearance of two to three new signals in the aromatic region. Other signals in the complexes due to aromatic protons, $-CH_3$ protons, -CH- protons, $-CH_2-$ protons and $-CH_2CH_2-$protons are observed nearly in the same positions as in the respective Schiff bases. The occurrence of a singlet due to $-CH_2-$ protons attached to two aromatic rings at 3.80-3.97 ppm in the Schiff bases derived from 5,5′-methylene bis(salicylaldehyde) and in their complexes indicates that the two Schiff base groups are still attached to methylene group. Thus the NMR data agree well with the conclusion drawn from the IR data.

Electronic Spectral Studies

The electronic spectra of the complexes are recorded in DMF and the data are listed in Table 2.2. The Schiff bases exhibit two to three electronic spectral bands in the regions 34960 - 37740, 27860-31060 and 23980-24690 cm^{-1}. These bands are assigned to $\pi \rightarrow \pi_1^*$, $\pi \rightarrow \pi_2^*$ and $n \rightarrow \pi^*$ transitions, respectively.[17] There is no band due to hydrogen bonding and association in any ligand which indicates the breaking of the hydrogen bonding in DMF. Usually this band appears in non-coordinating solvents. These ligand bands are also observed in the complexes but there is no systematic trend in change of energy. In addition, some complexes show a new band at 20220-23580 cm^{-1} which is assigned to the ligand to metal charge transfer transition between the highest occupied ligand molecular orbital and the lowest empty d-orbital of molybdenum.

2.4 CONCLUSION

From all the spectroscopic and elemental analyses data it can be concluded that all the newly prepared Schiff bases act as flexibly bridged hexadentate tetraanionic $\mathrm{ONO}\frown\mathrm{ONO}$ donor ligands, coordinating through azomethine nitrogen, phenolic oxygen and alcoholic oxygen, resulting in the formation of the oligomeric complexes of the type $(MoO_2)_2L$. A pseudo-octahedral geometry around each metal atom is suggested for the complexes of the type $(MoO_2)_2L$. However, complexes of the type $(MoO_2)_2L(py)_2$ have octahedral geometry where the sixth labile binding site around each metal atom is occupied by a pyridine molecule. The coordination of pyridine molecule is confirmed by a well-defined endothermic step at around 180°, corresponding to the loss of two molecules of pyridine.

Table 2.1 Analytical and physicochemical data of the ligands and complexes.[a]

S. No.	Compound/ stoichiometry	Colour	m.p. (°)	Found(Calc.) %			Λ_M^{b}
				C	H	N	
1	$CH_2(H_2sal\text{-}OAP)_2$ $C_{27}H_{22}N_2O_4$	Orange	232	73.5 (74.0)	5.2 (5.1)	6.2 (6.4)	
2	$CH_2(H_2sal\text{-}EA)_2{}^{c}$ $C_{19}H_{22}N_2O_4$	Yellow	92				
3	$CH_2(H_2sal\text{-}AMP)_2$ $C_{23}H_{30}N_2O_4$	Yellow	190	69.1 (69.3)	7.3 (7.6)	7.2 (7.0)	
4	$CH_2(H_2sal\text{-}IPA)_2$ $C_{21}H_{26}N_2O_4$	Yellow	102	68.3 (68.1)	6.9 (7.1)	7.3 (7.6)	
5	$S_2(H_2sal\text{-}OAP)_2$ $C_{26}H_{20}N_2O_4S_2$	Red	220	64.2 (63.9)	4.1 (4.1)	5.8 (5.7)	
6	$S_2(H_2sal\text{-}EA)_2$ $C_{18}H_{20}N_2O_4S_2$	Orange	108	55.3 (55.1)	5.3 (5.1)	7.0 (7.1)	
7	$S_2(H_2sal\text{-}AMP)_2$ $C_{22}H_{28}N_2O_4S_2$	Orange	160	58.5 (58.9)	6.1 (6.3)	6.4 (6.2)	
8	$S_2(H_2sal\text{-}IPA)_2{}^{c}$ $C_{20}H_{24}N_2O_4S_2$	Orange	52				
1a	$[(MoO_2)_2(CH_2(sal\text{-}OAP)_2)]$ $C_{27}H_{18}N_2O_8Mo_2$	Red	>250	47.3 (47.0)	2.9 (2.6)	4.0 (4.1)	5.6
1b	$[(MoO_2)_2(CH_2(sal\text{-}OAP)_2)(py)_2]$ $C_{37}H_{28}N_4O_8Mo_2$	Orange	>250	52.8 (52.4)	3.5 (3.3)	6.9 (6.6)	4.0
2a	$[(MoO_2)_2(CH_2(sal\text{-}EA)_2)]$ $C_{19}H_{18}N_2O_8Mo_2$	Orange	>250	38.2 (38.4)	3.2 (3.0)	4.7 (4.7)	8.0
2b	$[(MoO_2)_2(CH_2(sal\text{-}EA)_2)(py)_2]$ $C_{29}H_{28}N_4O_8Mo_2$	Yellow	>250	46.1 (46.3)	3.5 (3.8)	7.8 (7.5)	6.0
3a	$[(MoO_2)_2(CH_2(sal\text{-}AMP)_2)]$ $C_{23}H_{26}N_2O_8Mo_2$	Yellow	>250	42.2 (42.5)	4.0 (4.0)	4.1 (4.3)	5.0

contd..

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..contd

4a	$[(MoO_2)_2(CH_2(\text{sal-IPA})_2)]$ $C_{21}H_{22}N_2O_8Mo_2$	Yellow	>250	40.2 (40.5)	3.8 (3.6)	4.5 (4.5)	5.5
5a	$[(MoO_2)_2(S_2(\text{sal-OAP})_2)]$ $C_{26}H_{16}N_2O_8S_2Mo_2$	Red	>250	42.5 (42.2)	2.2 (2.2)	3.5 (3.8)	7.0
5b	$[(MoO_2)_2(S_2(\text{sal-OAP})_2)(py)_2]$ $C_{36}H_{26}N_4O_8S_2Mo_2$	Orange	>250	48.5 (48.1)	3.9 (3.9)	6.5 (6.2)	3.5
6a	$[(MoO_2)_2(S_2(\text{sal-EA})_2)]$ $C_{18}H_{16}N_2O_8S_2Mo_2$	Yellow	>250	33.1 (33.6)	2.3 (2.5)	4.7 (4.4)	9.0
6b	$[(MoO_2)_2(S_2(\text{sal-EA})_2)(py)_2]$ $C_{28}H_{26}N_4O_8S_2Mo_2$	Yellow	>250	42.2 (41.9)	3.5 (3.3)	6.8 (7.0)	6.0
7a	$[(MoO_2)_2(S_2(\text{sal-AMP})_2)]$ $C_{22}H_{24}N_2O_8S_2Mo_2$	Yellow	>250	37.9 (37.7)	3.2 (3.5)	4.4 (4.0)	3.0
8a	$[(MoO_2)_2(S_2(\text{sal-IPA})_2)]$ $C_{18}H_{20}N_2O_8S_2Mo_2$	Yellow	>250	33.1 (33.3)	3.3 (3.1)	4.1 (4.3)	4.0

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[a] Abbreviations as under structure (II).

[b] Conductance values are in mho mol^{-1} cm^2.

[c] Elemental analysis could not be recorded.

Table 2.2 IR and electronic spectral data (cm^{-1}).

Compounds[a]	IR			Electronic spectra
	$\nu(C = N)$	$\nu(O = Mo = O)$	$\nu(Mo \cdots O \rightarrow Mo)$	$(\epsilon)^b$
1	1631			35090(35350), 27860(48330)
1a	1611	931, 911	851	37880(29000), 32310(38500), 28410(17437), 23360(9875)
1b	1613	936, 906		37880(37976),31055(11156), 27250(4855), 23470(462)
2	1634			37170(2663), 30860(9695), 23810(1413)
2a	1630	917	808	36900(25000),30770(4895), 29240(4845)
2b	1598	920, 902		36500(30120),30580(5204), 28820(5204)
3	1630			37740(14490), 30860(9140), 23980(720)
3a	1626	928	820	37240(18750), 29850(4836)
4	1644			37660(14198), 30960(8521), 24070(354)
4a	1612	913	838	37520(1550), 30170(2480)
5	1633			34720(18867), 28090(18773)
5a	1606	938, 915	821	37800(38062), 32570(38875), 27930(18757), 23580(8500)
5b	1609	922, 905		36970(7790), 32260(13680), 27780(8173), 23470(3250)
6	1645			37590(11539), 31060(6157)
6a	1643	910	820	34720(15110), 31250(10800)
6b	1640	922, 905		37740(3775), 31450(1259)
7	1643			34960(10751), 30400(10451),24690(8105)
7a	1633	934	829	34600(16850), 31250(12136)
8	1643			37380(12609), 30260(9160), 26320(6470)
8a	1641	924	823	37740(4700), 31550(1474)

[a] For abbreviations see Table 2.1.

[b] ϵ in $dm^3 mol^{-1} cm^{-1}$.

Table 2.3 ^{1}H NMR spectral data (δ in ppm).^{a,b}

Compounds^{c}	-CH = N	Aromatic protons	$-CH_2CH_2-$	$-CH_2-$	$-CH_3$	-OH
1	8.90 (s, 2H)	6.88(m, 6H), 7.13(t, 2H), 7.29(d, 2H), 7.36(d, 2H), 7.45(s, 2H)		3.88(s, 2H)		9.71(s, 2H), 13.61(s, 2H)
1a	9.23(s, 2H)	6.88(m, 6H), 7.21(t, 2H), 7.45(d, 2H) 7.63(s, 2H), 7.80(d, 2H)		3.97(s, 2H)		
1b	9.23(s, 2H)	6.92(m, 6H), 7.20(t, 2H), 7.41(m, 6H), 7.61(s, 2H), 7.81(t, 4H), 8.59(b, 4H)		3.97(s, 2H)		
2	8.47(s, 2H)	6.80(d, 2H), 7.15(d, 2H), 7.26(s, 2H)	3.35(m,8H)	3.80(s, 2H)		4.26(b,2H)^{d}
2a	8.70(s, 2H)	6.82(d, 2H), 7.32(d, 2H), 7.35(s, 2H)	3.95(t, 4H), 4.35(t, 4H)	3.88(s, 2H)		
2b	8.70(s, 2H)	6.85(d, 2H), 7.40(m, 8H), 7.82(t, 2H), 8.57(b, 4H)	3.97(t, 4H), 4.37(t, 4H)	3.90(s, 2H)		
3	8.41(s, 2H)	6.77(d, 2H), 7.15(d, 2H), 7.27(s, 2H)	3.44(s, 4H)	3.80(s, 2H)	1.20(s, 12H)	14.10(s, 2H) 4.90(b, 2H)^{d}
3a	8.60(s, 2H)	6.83(d, 2H), 7.37(d, 2H), 7.48(s, 2H)	4.23(s, 4H)	3.87(s, 2H)	1.32(s, 12H)	
4	8.43(s, 2H)	6.76(d, 2H), 7.17(d, 2H), 7.25(s, 2H)	3.82(b, 4H)	4.75(s, 2H)	1.07(s, 3H), 1.12(s, 3H)	13.50(s, 2H)
4a	8.62(s, 2H)	6.81(d, 2H), 7.29(d, 2H), 7.35(s, 2H)	4.12(m, 4H)	3.90(s, 2H)	1.23(s, 3H), 1.27(s, 3H)	
5	8.80(s, 2H)	6.72 - 7.77(m, 14H)				9.56(s, 2H), 14.15(s, 2H)
5a	9.30(s, 2H)	6.82(t, 2H), 6.95(m, 4H), 7.26(t, 2H), 7.73(d, 2H), 7.85(q, 2H), 8.06(d, 2H)				
5b	9.30(s, 1H)	6.95(m, 6H), 7.25(m, 2H), 7.40(t, 3H) 7.75(m, 6H), 8.02(m, 2H), 8.10(d, 1H) 8.55(b, 4H)				
6	8.35(s, 2H)	6.60(d, 2H), 6.81(d, 2H), 7.20(s, 2H)	3.25(t, 8H)			4.70(b, 2H)^{d}
6a	8.75(s, 2H)	6.90(m, 2H), 7.58(t, 2H), 7.72(s, 2H)	4.08(t, 4H), 4.45(t, 4H)			

contd ..

... contd

6b	8.75(s, 2H)	6.95(d, 2H), 7.38(t, 2H), 7.62(d, 4H), 7.73(d, 2H), 7.81(m, 2H), 8.55(b, 4H)	3.97(t, 4H) 4.40(t, 4H)			
7	8.50(s, 2H)	6.70(d, 2H), 7.45(d, 2H), 7.65(s, 2H)	3.35(s, 4H)		1.25(s, 12H)	14.85(s, 2H) 5.10(b, 2H)[d]
7a	8.70(s, 2H)	6.90(d, 2H), 7.67(d, 2H), 7.95(s, 2H)	4.32(s, 4H)		1.38(s, 12H)	
8	8.10(s, 2H)	6.25(d, 1H), 6.50(d, 1H), 6.95(d, 1H), 7.12(d, 1H), 7.18(s, 1H), 8.15(s, 1H)	3.55(m, 2H) 4.40(m, 2H)		0.75(s, 3H)	14.0(b, 2H)
8a	8.65(s, 2H)	6.92(d, 2H), 7.56(d, 2H), 7.71(s, 2H)	4.12(m, 2H), 4.50(m, 2H)		1.26(s, 3H), 1.29(s, 3H)	

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[a] Letters given in parentheses indicate the type of signal. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

[b] CH resonance at 3.43(m, 2H) in 4, 4.44(m, 2H) in 4a, 3.07(m, 1H) and 3.20(m, 1H) in 8 and 3.57(m, 2H) in 8a.

[c] For abbreviation see Table 2.1.

[d] Alcoholic OH resonance.

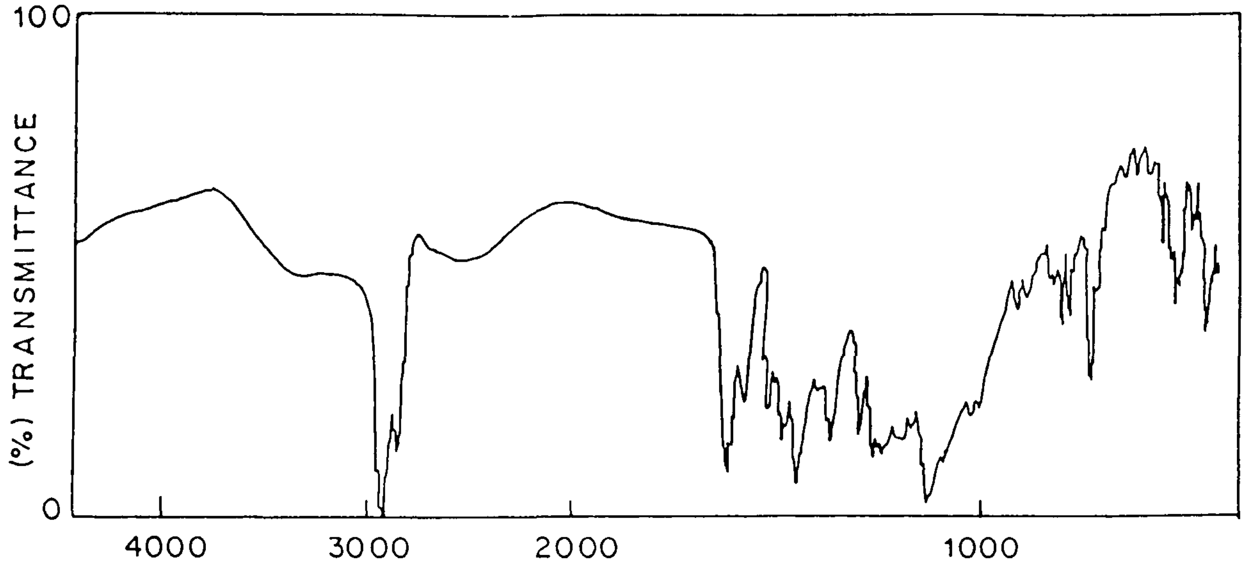

FIG. 2.1: IR SPECTRUM OF $[CH_2(H_2Sal\text{-}OAP)_2]$ IN NUJOL.

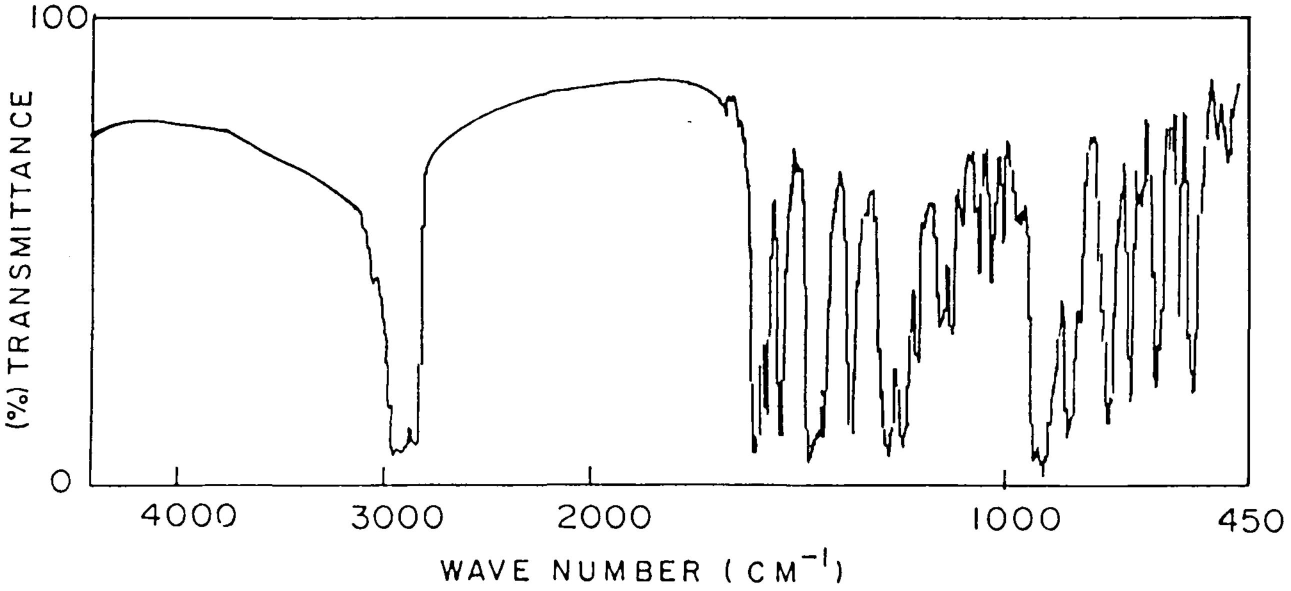

FIG. 2.2: IR SPECTRUM OF $[(MoO_2)_2(CH_2\{Sal\text{-}OAP\}_2)(PY)_2]$ IN NUJOL.

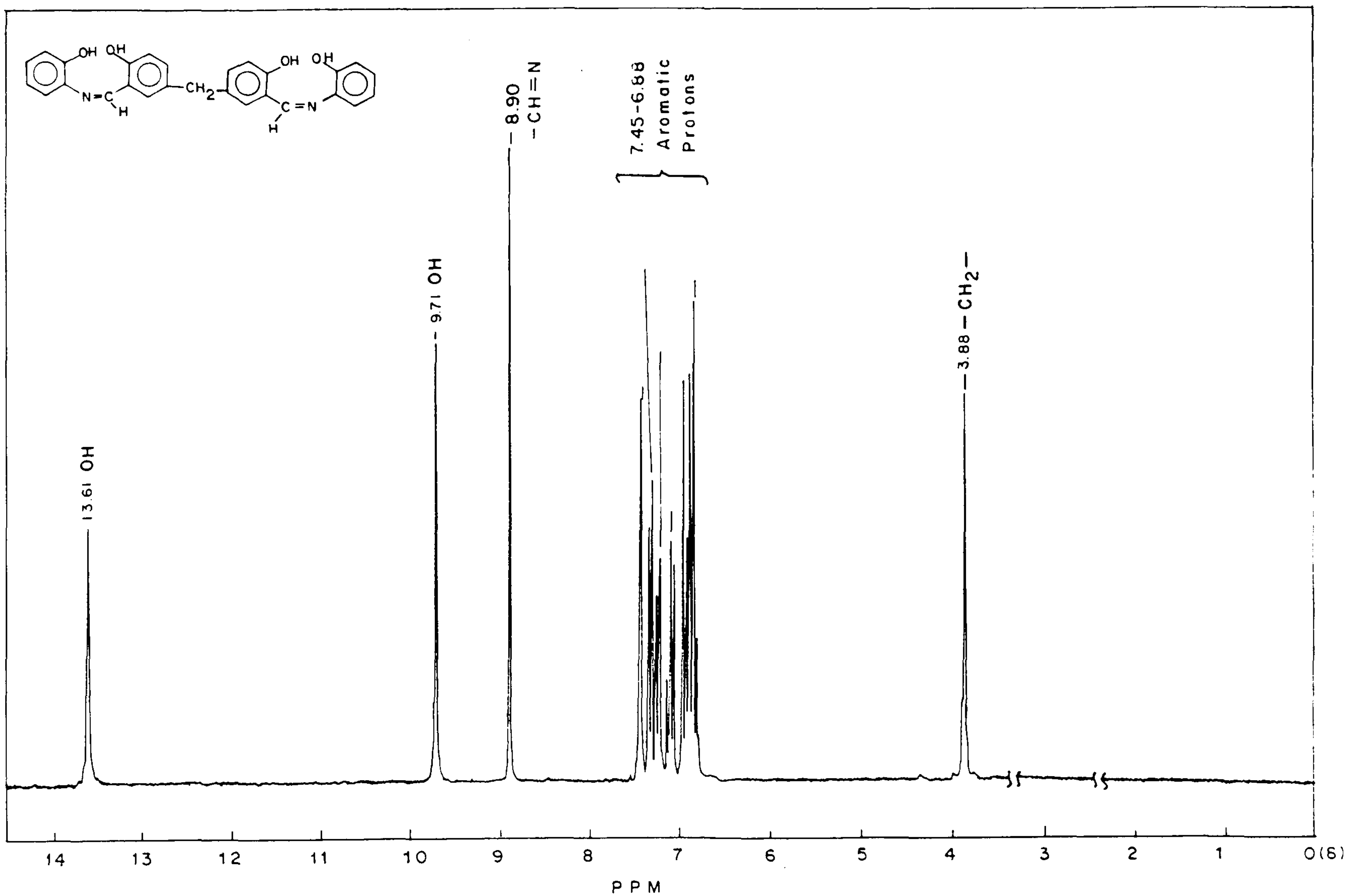

FIG. 2.3 : ^{1}H-NMR SPECTRUM OF [$CH_2(H_2Sal-OAP)_2$] IN DMSO- d_6

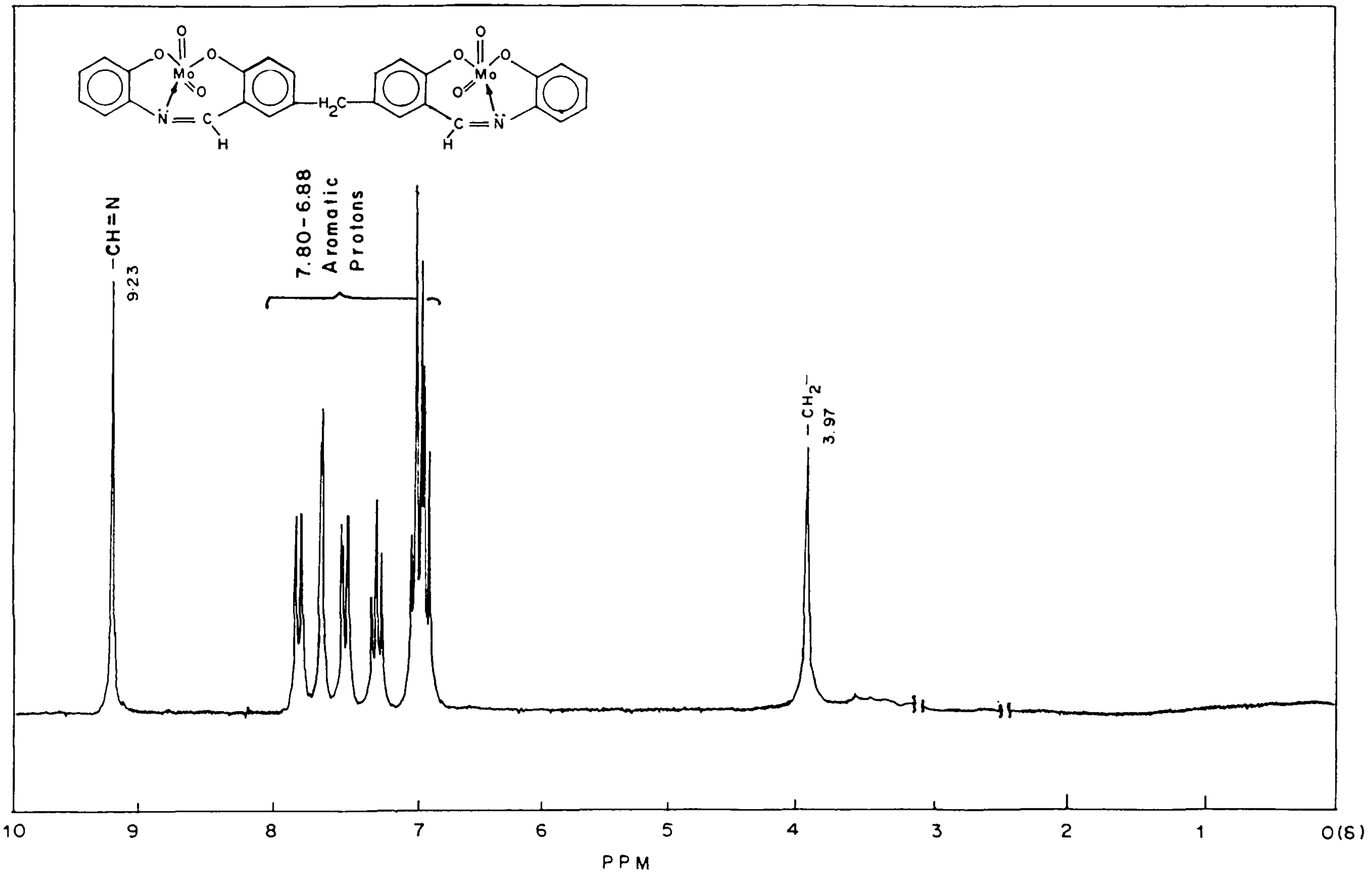

FIG.2.4 : ^{1}H-NMR SPECTRUM OF [$(MoO_2)_2$ $(CH_2$ {Sal -OAP}$_2$] IN DMSO-d_6.

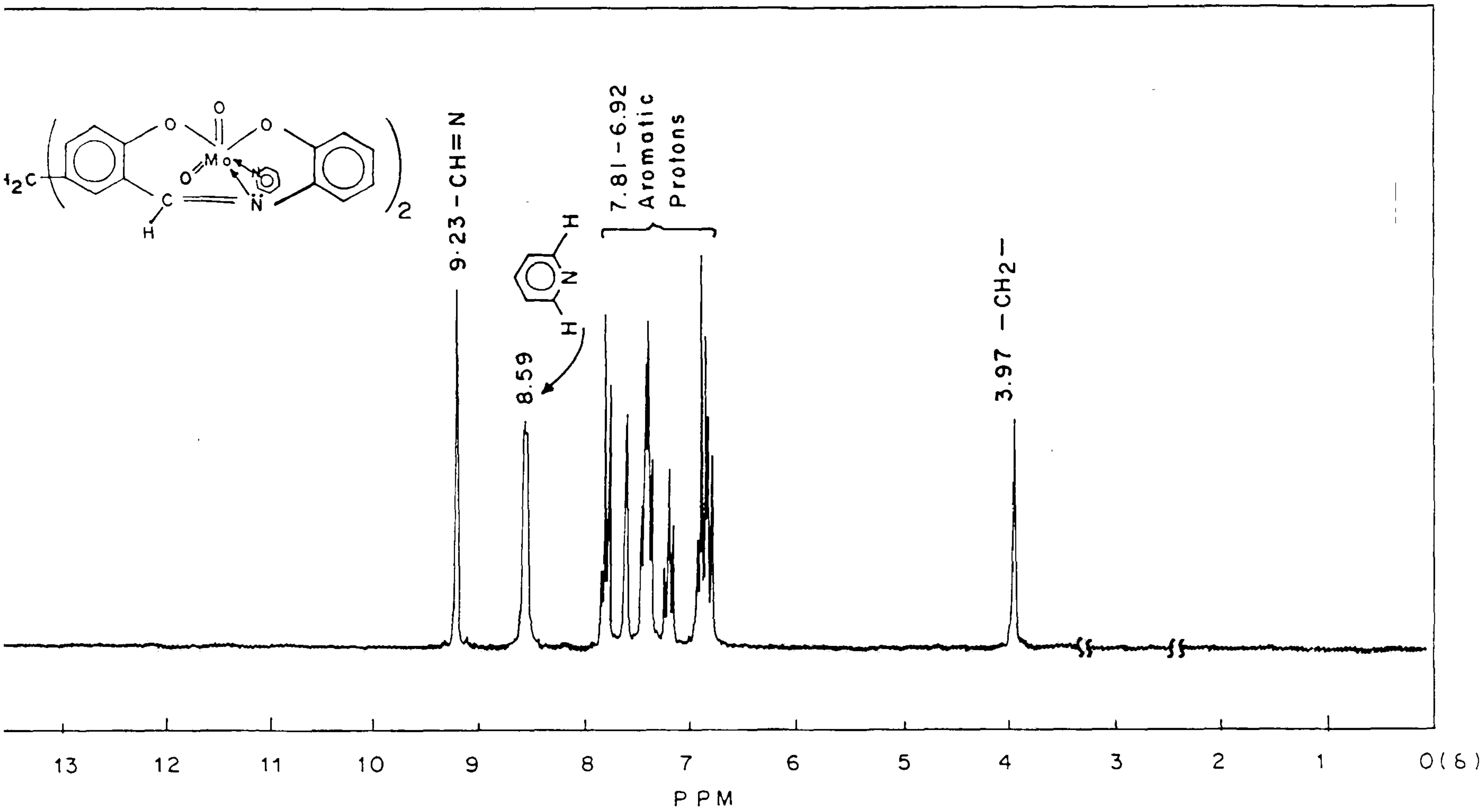

FIG.2.5 : ^{1}H-NMR SPECTRUM OF $[(MoO_2)_2(CH_2\{Sal-OAP\}_2)(PY)_2]$ IN DMSO-d_6

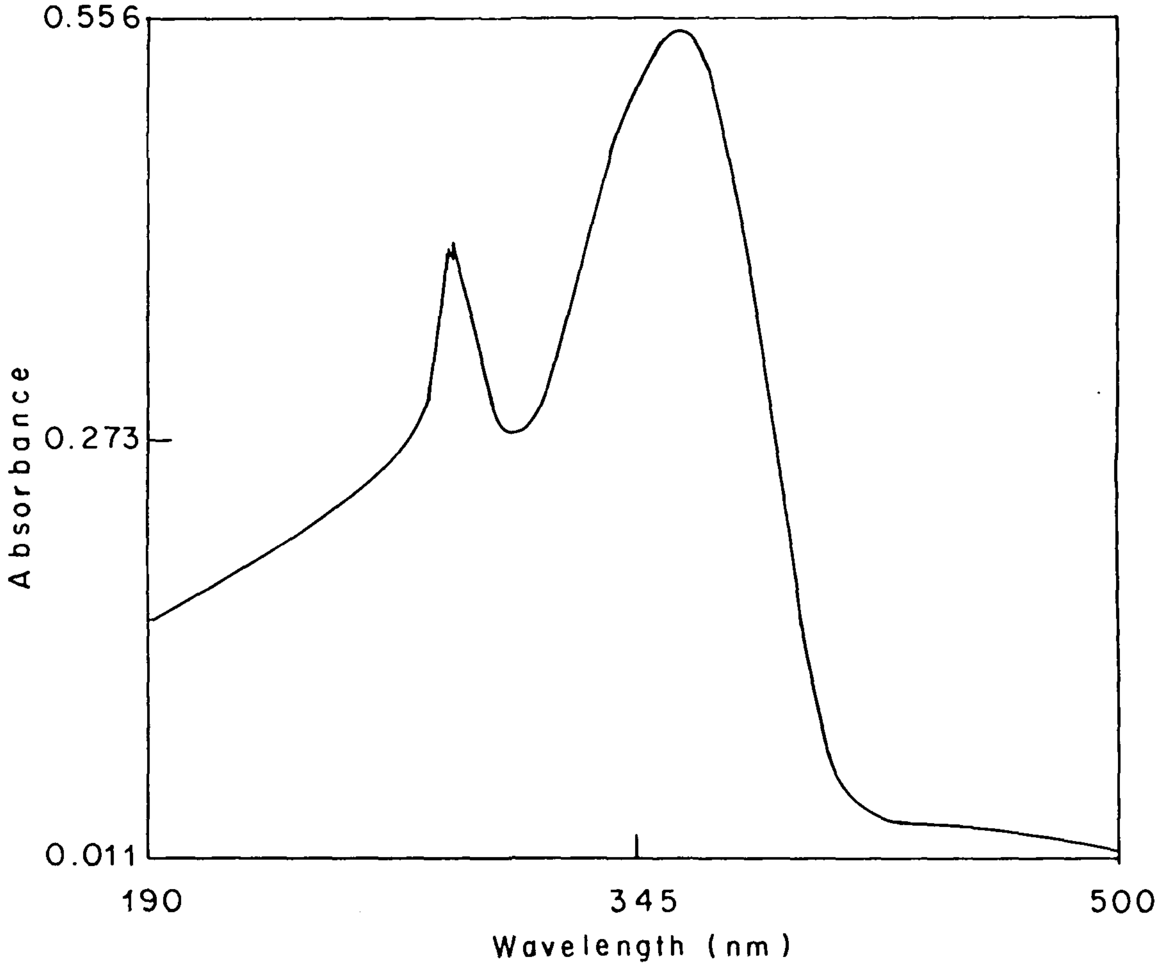

FIG. 2.6 : UV-VISIBLE SPECTRUM OF $[CH_2\{H_2Sal\text{-}OAP\}_2]$ IN DMF.

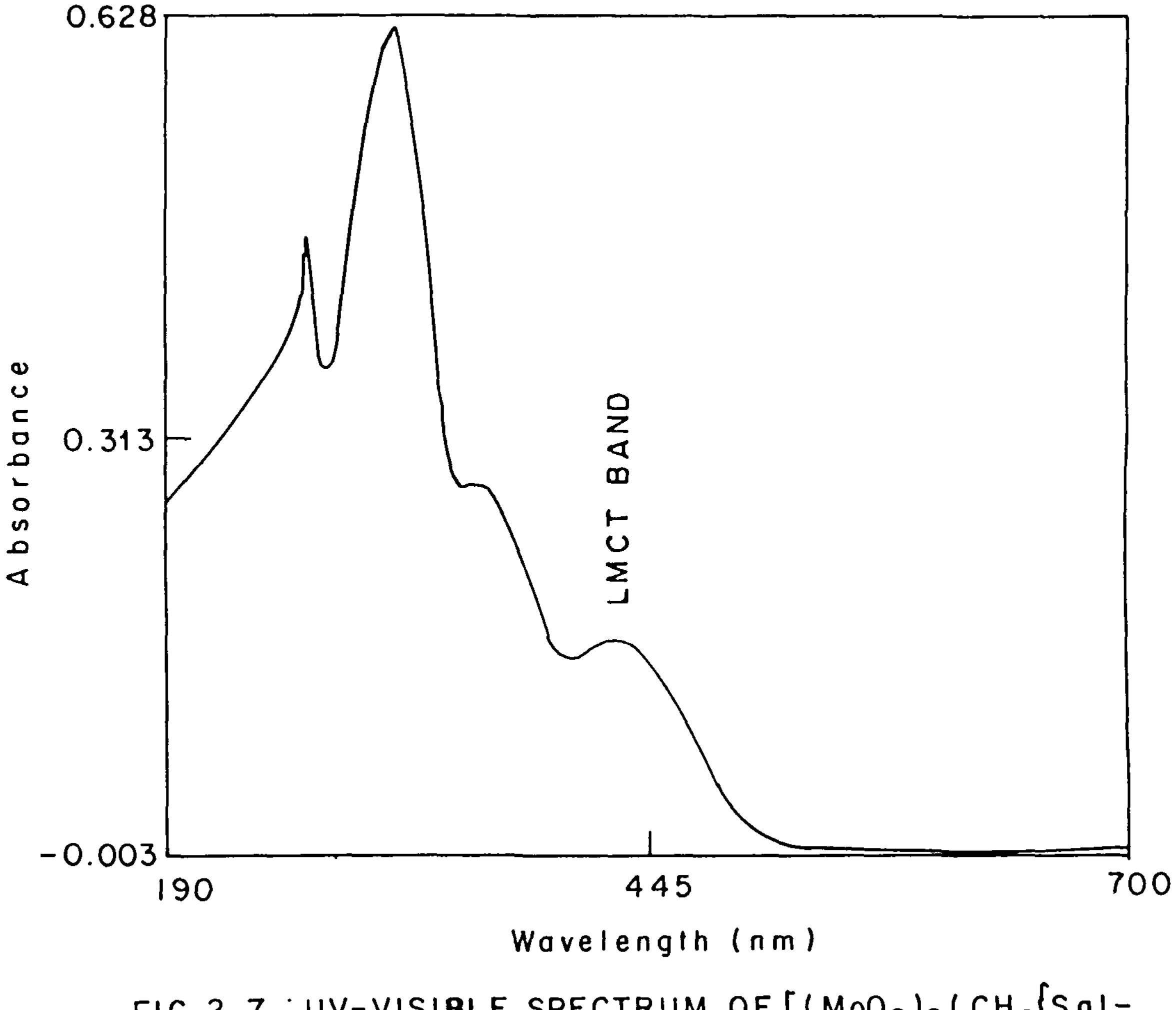

FIG.2.7 : UV-VISIBLE SPECTRUM OF $[(MoO_2)_2(CH_2\{Sal\text{-}OAP\}_2)]$ IN DMF.

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CHAPTER 3

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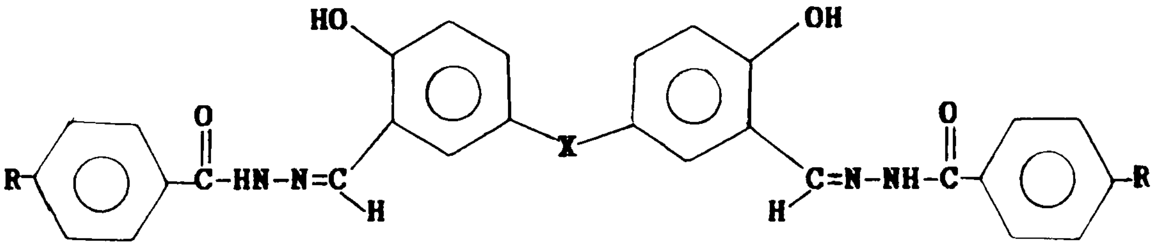
SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMISTRY OF BINUCLEAR DIOXOMOLYBDENUM(VI) COMPLEXES OF VARIOUS ONO⌒ONO DONOR LIGANDS.

3.1 INTRODUCTION

The coordination chemistry of dioxomolybdenum(VI) cation has attracted attention due to its presence in the oxidized form of certain molybdoenzymes.[1] Some of the dioxomolybdenum(VI) complexes have also been proposed as models for the active site of oxo-transfer molybdoenzymes.[2] Most dioxomolybdenum(VI) complexes, using starting materials such as Na_2MoO_4, MoO_2Cl_2, $MoO_2(acac)_2$ (acacH = acetylacetone), etc., are octahedral and have *cis*-$[MoO_2]^{2+}$ core. Design and synthesis of such mononuclear *cis*-dioxomolybdenum(VI) complexes with Schiff bases having one labile binding site are well documented in the literature.[3] The available binding site may allow the binding and displacement of various substrate molecules during a catalytic cycle. Although two labile binding sites may be rare to access within the mononuclear complex, such a system is possible in binuclear dioxomolybdenum(VI) complexes.

In Chapter 1 we have reported the binuclear dioxomolybdenum(VI) Schiff base complexes and have shown that two labile binding sites are easily accessible within the molecule in polar solvents.[4] These labile binding sites may also act as active sites to bind biologically active molecules such as urea, thiourea, pyridine, imidazole, etc. In the enzyme urease, urea is proposed to bind to the active site via. C $=$ O---Ni^{2+} coordination.[5]

To further elucidate the coordination chemistry of binucleating ligands we have synthesized and characterized some new binuclear *cis*-dioxomolybdenum(VI) complexes of the ligands (structure I). In order to demonstrate the acceptor behaviour and selectivity of these molybdenum complexes towards neutral donor molecules, we have carried out the reaction of these complexes with pyridine, 4-methylpyridine and imidazole. Spectroscopic and electrochemical data for these complexes are reported in this chapter.



(I)

	X	R	Abbreviations
1	CH_2	H	$CH_2(H_2sal\text{-}BZH)_2$
2	CH_2	NO_2	$CH_2(H_2sal\text{-}NO_2BZH)_2$
3	S-S	H	$S_2(H_2sal\text{-}BZH)_2$
4	S-S	NO_2	$S_2(H_2sal\text{-}NO_2BZH)_2$

3.2 EXPERIMENTAL

All the chemicals used were of analytical reagent grade. Salicylaldehyde and acetylacetone were used after purification. Dioxobis(acetylacetonato)molybdenum(VI),[6] 5,5′-methylene bis-(salicylaldehyde)[7] and 5,5′-dithio bis(salicylaldehyde)[8] were prepared by the methods described previously. Dimethylformamide (DMF) used for the electrochemical studies was distilled from CaH_2 and stored under dry nitrogen over molecular sieves.

All electrochemistry experiments were made on an ultramicro-electrode using a conventional three compartment cell with a platinum gauze (2.5 X 4 cm^2) as counter electrode, and a reference electrode of precalibrated saturated calomel. The ultramicro-electrode was prepared from a 10 μm Pt wire, which was washed with 30 % nitric acid, etched in aqua regia, dried overnight and then placed in a 10 cm long (3 mm diameter), Pyrex tube. After high vacuum cleaning the wire was sealed and subsequently etched with HF, washed and then dried. Electrical connection to the Pt wire was made by immersing copper wire through a mercury column in the capillary. All the cyclic voltammograms (CV) were recorded at ambient temperature (25 ± 1°) with nitrogen bubbling using 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte. The CV were corrected for the solvent background[9] and the measurements were performed with a PAR model 175 Universal Programmer and PAR model 173

Potentiostat coupled with a Houston Instrument Model RE 0081 4 recorder.

Elemental analyses were performed for all the newly prepared Schiff bases and their metal complexes. Details of other techniques are reported in the Chapter 1.[4]

(1) Preparation of 5,5′-methylene bis(salicylideneaminobenzoyl hydrazine) [$CH_2(H_2sal-BZH)_2$]

A solution of benzoylhydrazine (0.272 g, 0.002 mol) in methanol (10 ml) was added to 5,5′-methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) dissolved in 10 ml of hot methanol and the reaction mixture was refluxed on a water bath for 2h. After reducing the solvent to 10 ml and cooling to room temperature, the separated yellow solid product was filtered, washed with hot methanol and dried in *vacuo* at ambient temperature. Yield 0.400 g (81%); m.p. 265°.

(2) Preparation of 5,5′-methylene bis(salicylideneamino -5-nitrobenzoylhydrazine) [$CH_2(H_2sal-NO_2BZH)_2$]

5-Nitrobenzoylhydrazine (0.362 g, 0.002 mol) in methanol (10 ml) and 5,5′-methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) were mixed in 20 ml of methanol and the reaction mixture was refluxed for 3h. Upon cooling, the orange crystals separated were filtered, dried in air and recrystallized from methanol. Yield 0.516 g (89%); m.p. 270°.

(3) Preparation of 5,5′-dithio bis(salicylideneamino benzoylhydrazine) [$S_2(H_2sal\text{-}BZH)_2$]

Benzoylhydrazine (0.272 g, 0.002 mol) was dissolved in methanol (10 ml) and to this a solution of 5,5′-dithio bis(salicylaldehyde) (0.306 g, 0.001 mol) was added and the resulting mixture was refluxed for 3h. The resulting solution upon cooling gave an yellow solid which was collected and dried in air. Yield 0.488 g (80%); m.p. 240°.

(4) Preparation of 5,5′-dithio bis(salicylideneamino -5-nitrobenzoylhydrazine) [$S_2(H_2sal\text{-}NO_2BZH)_2$]

A solution of 5-nitrobenzoylhydrazine (0.362 g, 0.002 mol) dissolved in methanol (10 ml) was mixed with 5,5′-dithio bis(salicylaldehyde) (0.306 g, 0.001 mol) and the contents were refluxed for 3h. On cooling the yellow crystals separated were filtered and recrystallized from methanol. Yield 0.564 g (89%); m.p. 310°.

(1a) Preparation of [$(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)$]

$MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added as a solid to a well stirred hot solution of [$CH_2(H_2sal\text{-}BZH)_2$] (0.246 g, 0.0005 mol) in 50 ml of methanol. The resulting turbid solution was filtered immediately and the filtrate was refluxed on a waterbath for 6h. The separated orange solid was filtered, washed with hot methanol and dried at 100° in air. Yield 0.400 g (80%); m.p. >250°.

(2a) Preparation of [$(MoO_2)_2(CH_2\{sal\text{-}NO_2BZH\}_2)$]

To a hot and well stirred solution of the ligand [$CH_2(H_2sal\text{-}NO_2BZH)_2$] (0.291 g, 0.0005 mol) in methanol (50 ml) $MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added as a solid. The resulting solution was filtered while hot and again refluxed on a waterbath for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated orange solid was filtered, washed with hot methanol and dried at 100°. Yield 0.478 g (88%); m.p. >250°.

(3a) Preparation of [$(MoO_2)_2(S_2\{sal\text{-}BZH\}_2)$]

$MoO_2(acac)_2$ (0.330g, 0.001 mol) was added to a refluxing solution of the ligand [$S_2(H_2sal\text{-}BZH)_2$] (0.271 g, 0.0005 mol) in methanol (50 ml). The resulting solution was filtered and the filtrate was again refluxed on a water bath for 6h. After reducing the volume of the solvent to 10 ml, the mixture was cooled at room temperature. The separated orange solid was filtered, washed with hot methanol and dried at 100° in air. Yield 0.456 g (84%); m.p. >250°.

(4a) Preparation of [$(MoO_2)_2(S_2\{sal\text{-}NO_2BZH)_2$

The Schiff base [$S_2(H_2sal\text{-}NO_2BZH)_2$] (0.318 g, 0.0005 mol) was dissolved in methanol (50 ml) by heating on a water bath and to it was added $MoO_2(acac)_2$ (0.330 g, 0.001 mol) as a solid with vigorous shaking. The resulting turbid solution was filtered and then refluxed on a waterbath for 6h. After concentrating the solution to 10 ml and cooling to 10° overnight, the separated orange solid was filtered and dried at 100° in air. Yield 0.500 g (87%); m.p. >250°.

Preparation of the Complexes of the Type *$[(MoO_2)_2L(py)_2]$* and *$[(MoO_2)_2L(pic)_2]$* (py = pyridine, pic = 4-methylpyridine).

These complexes were prepared in quantitative yield by dissolving $[(MoO_2)_2L]$ (0.10 g) in excess of pyridine or 4-methylpyridine (2 ml) while heating on a water bath followed by removing the excess of solvent under vacuum. The complexes were finally washed with diethyl ether and dried in *vacuo* at ambient temperature. Yield (80%).

Preparation of the complexes of the type $[(MoO_2)_2L(im)_2]$ (*im = imidazole*)

Procedure a. The appropriate Schiff base (0.001 mol) and imidazole (0.140 g, 0.002 mol) were dissolved in hot methanol (60 cm^3) and to this $[MoO_2(acac)_2]$ (0.660 g, 0.002 mol) was added in one portion with vigorous shaking. The resulting solution was filtered and then refluxed on a water bath for 6 h. After cooling the flask to ambient temperature, the precipitate was filtered, washed with methanol and dried *in vacuo* at ambient temperature. Yield: 85%.

Procedure b. A solution of imidazole (0.140 g, 0.002 mol) dissolved in 5 ml of methanol was added to a solution of appropriate molybdenum complex (0.001 mol) in 10 ml of DMSO and the resulting reaction mixture was refluxed for 6 h on a water bath. After cooling the solution to 10° for 1 h, the separated solid was filtered, washed with methanol and dried *in vacuo* at room temperature. Yield (65%).

The analytical and physico-chemical data of all Schiff bases, and their $[(MoO_2)_2L]$ and $[(MoO_2)_2L(D)_2]$ complexes are presented in Table 3.1.

3.3 RESULTS AND DISCUSSION

The reaction of hydrazines with 5,5′-methylene- or dithio-bis(salicylaldehyde) in 2:1 molar ratio results in the formation of binucleating tetraanionic hydrazone derivatives of Schiff base ligands **1-4** (see structure I). Elemental analyses and spectral data (Tables 3.1 and 3.2) of these Schiff bases are consistent with their structure.

$[MoO_2(acac)_2]$ has been used extensively as a precursor to prepare dioxomolybdenum(VI) complexes of the Schiff bases and other ligands.[3] $[MoO_2(acac)_2]$ undergoes single-step ligand exchange reaction (equation (i)) with the Schiff base ligands **1-4** also in 2:1 molar ratio in refluxing methanol to yield the corresponding *cis*-dioxomolybdenum(VI) complexes of the type $[(MoO_2)_2L]$ (where LH_4 = Schiff base)

$$2\ [MoO_2(acac)_2] \quad + \quad LH_4 \xrightarrow[MeOH]{} [(MoO_2)_2L] \quad + \quad 4\ acacH \qquad (i)$$

Under these reaction conditions complete removal of the coordinated acetylacetone groups occurs. Analytical data support the above formulation of complexes. Further, complexes of the type $[(MoO_2)_2L]$ form molecular addition compounds with monodentate Lewis bases such as DMF, DMSO, pyridine, 4-methylpyridine and imidazole to form complexes of the type $[(MoO_2)_2L(D)_2]$ in which D the Lewis base occupies the sixth coordination position in both $[MoO_2]^{2+}$ units. The complexation ability of $[(MoO_2)_2L]$ with imidazole is found to be very poor. However, the complexation ability with imidazole could be improved to nearly quantitative when reaction of Schiff base with $[MoO_2(acac)_2]$ in presence of imidazole was tried *in situ* in methanol.

The complexes are soluble in coordinating solvents like pyridine, DMF and DMSO. They are non-electrolytes (3.5-4.7 ohm^{-1} mol^{-1} cm^2) in DMF and are diamagnetic as expected for the $4d^0$ molybdenum ion. The high decomposition temperature (>250°) of the complexes indicates their good thermal stability.

The thermal analysis data of the complex $[(MoO_2)_2(sal\text{-}BZH)_2]$ does not indicate any weight loss upto 200°. But the pyridine adduct $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)(py)_2]$ reveal a well defined endothermic step at 190° indicating the loss of pyridine from the complex. In all the complexes of the type $[(MoO_2)_2L(D)_2]$, a well defined endothermic step around 200° is observed corresponding to the loss of two monodentate ligands, confirming the coordination of respective Lewis bases to the metal atom . The coordinated monodentate ligands in complexes of the type [$MoO_2L(D)$] are known to undergo cleavage on heating due to weak coordination and their labile nature.[10]

IR Spectral Studies

A partial listing of the IR spectra of the ligands and their complexes is given in Table 3.2. The hydrazone ligand $CH_2(H_2sal\text{-}BZH)_2$ exhibits intramolecularly hydrogen bonded ν(OH) stretch at 2815 cm^{-1}. The bands at 1651 cm^{-1} due to ν(C=O) and at 3201 cm^{-1} due to ν(NH) suggest the existence of the ligand in the keto form. The IR spectra of the rest of the hydrazone Schiff base ligands (2-4) exhibit a similar broad band in the region ~2850 cm^{-1} attributable to the intramolecularly hydrogen bonded ν(OH) stretch and bands due to ν(C=O) and ν(NH) appear in the regions 1645-1675 and 3200-3300 cm^{-1}, respectively.

In the IR spectrum of the metal complex [$(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)$] the band at 2815 cm^{-1} due to intramolecularly hydrogen bonded ν(OH) is absent suggesting the coordination of the phenolic hydroxyl group after proton replacement. The bands at 1651 cm^{-1} due to ν(C=O) and at 3201 cm^{-1} due to ν(NH) disappear in the complex suggesting the destruction of the carbonyl moiety due to enolization and consequent proton replacement with the molybdenum. A new band which appears at 1248 cm^{-1} is assigned to to the ν(C-O) (enolic) mode. The ν(C=N) of the ligand at 1609 cm^{-1} shifts to a lower frequency indicating the participation of azomethine nitrogen in coordination.[11] But the ν(C=N) band of the pyridine adduct $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)(py)_2]$ shifts to higher energy which may be due to the coupled effect of ν(C=N) of the coordinated Schiff base and pyridine molecule's ν(C=N) stretches. A similar pattern of bands is observed in the IR spectra of the other complexes. Thus, the IR data suggest the hexadentate and tetraanionic nature of the Schiff bases where each Schiff base unit behaves as ONO donor dibasic tridentate ligand.

The metal complexes of the type $[(MoO_2)_2L]$ exhibit a sharp single band (sometimes two bands, which may be due to crystal packing effect) at 930-950 cm^{-1} due to ν(O=Mo=O) stretch and a strong but broad band at 850 cm^{-1} due to weakened ν(Mo=O) as a result of $\mathrm{Mo\overset{---}{-}O\longrightarrow Mo}$ interaction. The band due to ν_{asym}(O=Mo=O) is absent in the complexes of the type $[(MoO_2)_2L]$ since it is shifted to lower frequency and appear at 850 cm^{-1} as a broad band due to weak interaction of Mo of one $[MoO_2]^{2+}$ group to the other $[MoO_2]^{2+}$ group. However, the complex $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)]$ exhibits two bands at 950 and 912 cm^{-1} due to ν_{sym} and ν_{asym}(O=Mo=O) stretches together with a broad but strong band at 855 cm^{-1} is due to weakened (Mo=O) as a result of $\mathrm{Mo\overset{---}{-}O\longrightarrow Mo}$ interaction. These observations suggest the presence of an oligomeric (pseudo-octahedral) structure for the complex in which each molybdenum ion achieves a pseudo-octahedral structure *via* $\mathrm{Mo}\overset{\cdots}{-}\mathrm{O}\longrightarrow\mathrm{Mo}$ bridging[3,10] (Fig. 3.1). The occurrence of the (C-O)(phenolic) band at nearly identical positions in $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)]$ and its adducts $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)(D)_2]$ suggest the presence of oligomeric bridges only through $\mathrm{Mo}\overset{\cdots}{-}\mathrm{O}\longrightarrow\mathrm{Mo}$ as oligomerization via phenolic oxygen bridges would be expected to produce substantial increase of the ν(C-O) (phenolic stretch).[10]

On the other hand, the hexa-coordinated complexes of the type $[(MoO_2)_2L(D)]$ show two bands in the 930-950 and 910-920 cm^{-1} regions due to ν_{sym} and ν_{asym} (O=Mo=O) modes respectively.[10] The complexation of neutral Lewis bases with $[(MoO_2)_2L]$ essentially shows the breaking of the oligomeric structure to discrete monomer as the band at *ca.* 850 cm^{-1} disappears and a new band appears at *ca.* 920 cm^{-1} due to ν_{asym}(O=Mo=O) stretch. The coordination of a Lewis base is characterized by the shift of their characteristic vibrational modes. For example, pyridine and 4-methyl pyridine exhibit totally symmetric ring breathing mode of vibration at 990 and 1000 cm^{-1}, respectively. In the IR spectra of the complexes, this band shifts to higher frequency by 18-30 and 20-30 cm^{-1}, respectively. Similarly, the higher frequency shift of the totally symmetric stretching mode of vibration, which appears at 1587 cm^{-1} in pyridine and 1574 cm^{-1}

in 4-methyl pyridine, is indicative of the pyridine coordination to the molybdenum ion.[12] In the case of the complex $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)(im)_2]$ the NH band of the imidazole molecule is observed at 3272 cm^{-1}. The reason for the shifting of the NH frequency from 3480 cm^{-1} in free imidazole to 3272 cm^{-1} in coordinated imidazole is the absence of strong intermolecular hydrogen bonding which occurs in the solid state.[13] In the metal complexes no hydrogen bonding can occur because the pyridine nitrogen is coordinated to the metal ion.[14] This will result in different frequencies for the N-H vibration compared with that for imidazole itself.

^1H NMR Studies

Table 3.3 summarizes the ^{1}H NMR spectra of the ligands and their complexes. The Schiff base ligand $CH_2(H_2sal\text{-}BZH)_2$ exhibits a singlet due to phenolic proton at 12.0 ppm. The presence of NH proton signal at 11.05 ppm suggests that the ligand exists in its keto form. A sharp singlet due to azomethine proton appears at 8.80 ppm. The signal due to bridging $-CH_2-$ group is observed at 3.85 ppm as a sharp singlet. Other Schiff base ligands (**2**, **3** and **4**) show signals due to NH and phenolic protons in the regions 11.0-11.5 and 12.0-12.3 ppm respectively, suggesting the existence of these ligands also in their keto form.

In the metal complex $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)]$ the signals at

11.05 and 12.0 ppm due to NH and phenolic protons, respectively are absent suggesting the enolization and subsequent coordination of both phenolic and enolic OH groups to the metal atom after deprotonation. The sharp singlet due to azomethine proton at 8.60 ppm shifts downfield and appears at 8.95 ppm as a sharp singlet.[15] A similar pattern of signals is observed in the ^1H NMR spectra of the other complexes. The aromatic protons are observed at nearly identical positions both in the complexes and their respective Schiff bases. The occurrence of a singlet due to $-CH_2-$ protons attached to two aromatic rings in the complexes derived from 5,5′-methylene bis(salicylaldehyde) indicates that the two Schiff base groups are still attached to methylene group.

In the 4-methyl pyridine adduct $[(MoO_2(CH_2\{sal\text{-}BZH\}_2)(pic)_2]$, the characteristic pyridine proton signal is observed at 8.40 ppm. A sharp singlet due to methyl protons of the 4-methyl pyridine is observed at 2.32 ppm suggesting the coordination of 4-methyl pyridine to the metal atom in the complex $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)(pic)_2]$. In the case of imidazole adduct $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)(im)_2]$, the characteristic signals due to imidazolyl protons are observed at 7.85 and 7.01 ppm as broad bands in the aromatic region.[16] Thus the ^1H NMR data agree well with the conclusion drawn from the IR data.

Electronic Spectral Studies

The electronic spectra of the complexes are recorded in DMF and the λ_{max} obtained are collected in Table 3.2 together with their respective extinction coefficient. The Schiff bases obtained from *p*-nitro benzoylhydrazine exhibit three electronic spectral bands at about 39000, 36000 and 29000 cm^{-1} which are assigned to $\phi \rightarrow \phi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. However, in the case of Schiff bases obtained from benzoylhydrazine, the band due to $\pi \rightarrow \pi^*$ splits into two bands $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$ and appear at about 34000 and 33000 cm^{-1}, respectively. There is no band due to hydrogen bonding and association in the ligands which indicates the breaking of the hydrogen bonding in the coordinating solvent. Usually this band appears in non-coordinating solvents. On complexation the $\phi \rightarrow \phi^*$ band of the Schiff bases shifts to lower energy, the $n \rightarrow \pi^*$ shifts to higher energy and the $\pi \rightarrow \pi^*$ transition remains almost constant. A new band in the complexes at about 24000 cm^{-1} is assigned to the ligand to metal charge transfer transition (l.m.c.t.) between the highest occupied ligand molecular orbital to the lowest empty *d*-orbital of the molybdenum.

Electrochemical Studies

Fig. 3.5 shows the cyclic voltammograms of Mo(VI) complexes (**1a**, **1b**, **3a** and **3b**) used in the present investigation. Use of ultramicro-electrode enables one to have negligible uncompensated resistance and nonfaradaic interference in these cyclic voltammograms[17]. Remarkable difference in the electron-transfer reaction of the metal centre are observed depending upon the ligand structure. For example, the reductive peak potential is very sharp for **1a** indicating a kinetically facile Mo(VI) to Mo(IV) reduction in comparison with others and the appearance of a discernible oxidative peak becomes much clearer at lower scan rates (see Fig.3.6). This in turn, helps to calculate the formal potential, $E^{0'}$ (*ca.* -0.78 V vs. SCE)[9] in DMF. This oxidative peak cannot be clearly distinguished in other complexes. The voltammograms corresponding to **3b** (Fig.3.5) show the other extreme, where even the reductive peak potential is not clearly seen. These voltammograms, where reductive and oxidative peaks can be separately seen, generally show large difference between the reductive peak potential and oxidative peak potential indicating that the rate of Mo(VI) to Mo(IV) reduction is slow, *i.e.*, quasireversible or irreversible as reported for various molybdenum complexes.[10,18] The reduction potential (E_{pc}) values of **1a** (-0.83 V) and **3a** (-0.85 V) indicate that the bridging methylene ($-CH_2-$) or dithio (-S-S-) group has very little effect on the thermodynamic stability of these complexes. This can be explained by considering the similar ONO donor system in both the complexes as well as the absence of powerful electron withdrawing groups such as $-NO_2$ in the immediate vicinity of the metal centre. In the case of pyridine adducts, (especially with **3b**) the voltammograms do not reveal clear features although Mo(VI) to Mo(IV) reduction is indicated as a hump when the ligand contains bridging methylene group.

The facile kinetics of Mo(VI) to Mo(IV) reduction of $[(MoO_2)_2(CH_2\{sal\text{-}BZH\}_2)]$ **1a** in DMF in comparison with **1b**, **3a** and **3b** prompted us to study the feature of this in detail at various scan rates. These voltammograms, displayed in Fig.3.6, indicate the dependence of Mo(VI) to Mo(IV) reduction kinetics on the time window of experiment. The faster kinetics of the two electron-transfer reduction of each molybdenum centre in **1a** can be clearly inferred from the larger peak current and the well defined peak shape. Furthermore, as the scan rate increases the reductive peak potential (E_{pc}) progressively becomes more negative (*ca*. 140 mV for each ten fold increase in scan rate) indicating a quasireversible behavior. The absence of linearity in I_{pc} *vs*. $\sqrt{\nu}$ (ν = scan rate) plot further supports the quasireversibility of Mo(VI) reduction. From all these voltammograms, it can be concluded that Mo(VI) to Mo(IV) reductions are irreversible tending to quasireversibility at lower scan rates.

3.4 CONCLUSION

The foregoing results indicate that binuclear dioxomolybdenum(VI) complexes reported here are oligomeric in nature. However, two binding sites within a molecule are easily accessible in donor solvents. We were unable to get suitable crystals for X-ray analysis due to solubility problems. These complexes are good acceptors towards nitrogen donor molecules than oxygen or sulphur donors. However, weak oxygen donor molecules such as urea, benzaldehyde etc. are coordinated to the uranium in dioxouranium(VI) complexes of not only simple ONNO donor ligands but even of macrocyclic ligands.[19] Thus, the new molybdenum(VI) complexes are only selective for nitrogen donor molecules. The redox behaviour of the complexes indicates that complex **1a** is more facile from Mo(VI) to Mo(IV) reduction in comparison to **1b**, **3a** and **3b** and at lower scan rates the oxidative peak is clearer. There is no indication of the electrochemical reduction of dioxomolybdenum(VI) species to oxomolybdenum(V). The methylene or dithio bridging group has very little effect on the rate of reduction of the molybdenum centre.

Table3.1. Analytical[a] and physicochemical data of the ligands and complexes[b]

S.No	Compound/ Stoichiometry	Color	M.p. (°C)	Analysis % C	 H	 N	Λ_M[c]
1	$CH_2(H_2sal\text{-}BZH)_2$ $C_{29}H_{24}N_4O_4$	Yellow	265	70.2 (70.7)	5.0 (4.9)	11.1 (11.4)	
2	$CH_2(H_2sal\text{-}NO_2BZH)_2$ $C_{29}H_{22}N_6O_8$	Orange	270	59.5 (59.8)	3.5 (3.8)	14.6 (14.4)	
3	$S_2(H_2sal\text{-}BZH)_2$ $C_{28}H_{22}N_4O_4S_2$	Yellow	240	62.1 (62.0)	3.9 (4.1)	10.0 (10.3)	
4	$S_2(H_2sal\text{-}NO_2BZH)_2$ $C_{28}H_{20}N_6O_8S_2$	Yellow	310	53.4 (53.1)	3.2 (3.2)	13.4 (13.3)	
1a	$[(MoO_2)_2(CH_2(sal\text{-}BZH)_2)]$ $C_{29}H_{20}N_4O_8Mo_2$	Orange	>250	46.4 (46.8)	2.5 (2.7)	7.7 (7.5)	3.8
1b	$[(MoO_2)_2(CH_2(sal\text{-}BZH)_2)(py)_2]$ $C_{39}H_{30}N_6O_8Mo_2$	Orange	>250	52.2 (51.9)	3.6 (3.3)	9.2 (9.3)	3.6
1c	$[(MoO_2)_2(CH_2(sal\text{-}BZH)_2)(pic)_2]$ $C_{41}H_{34}N_6O_8Mo_2$	Yellow	>250	53.3 (52.9)	3.9 (3.7)	9.3 (9.0)	4.4
1d	$[(MoO_2)_2(CH_2(sal\text{-}BZH)_2)(im)_2]$ $C_{35}H_{28}N_8O_8Mo_2$	Orange	>250	47.5 (47.7)	3.0 (3.2)	13.0 (12.7)	4.6
2a	$[(MoO_2)_2(CH_2(sal\text{-}NO_2BZH)_2)]$ $C_{29}H_{18}N_6O_{12}Mo_2$	Orange	>250	41.4 (41.7)	2.1 (2.1)	9.9 (10.1)	3.9
3a	$[(MoO_2)_2(S_2(sal\text{-}BZH)_2)]$ $C_{28}H_{18}N_4O_8S_2Mo_2$	Orange	>250	42.2 (42.3)	2.2 (2.2)	6.9 (7.1)	4.3
3b	$[(MoO_2)_2(S_2(sal\text{-}BZH)_2)(py)_2]$ $C_{38}H_{28}N_6O_8S_2Mo_2$	Orange	>250	47.9 (47.9)	3.2 (3.0)	8.8 (8.8)	3.5
3c	$[(MoO_2)_2(S_2(sal\text{-}BZH)_2)(pic)_2]$ $C_{40}H_{32}N_6O_8S_2Mo_2$	Yellow	>250	49.3 (49.0)	3.5 (3.3)	8.5 (8.6)	4.5
3d	$[(MoO_2)_2(S_2(sal\text{-}BZH)_2)(im)_2]$ $C_{34}H_{26}N_8O_8S_2Mo_2$	Orange	>250	43.6 (43.9)	2.8 (2.8)	12.2 (12.0)	3.9
4a	$[(MoO_2)_2(S_2(sal\text{-}NO_2BZH)_2]$ $C_{28}H_{16}N_6O_{12}S_2Mo_2$	Brown	>250	37.7 (38.0)	1.6 (1.8)	9.2 (9.5)	4.7

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[a] Calculated values are given in parentheses.

[b] Abbreviations as under structure (I).

[c] Conductance values are in Ω^{-1} mol^{-1} cm^{2}.

Table3.2. IR and electronic spectral data (cm^{-1}).

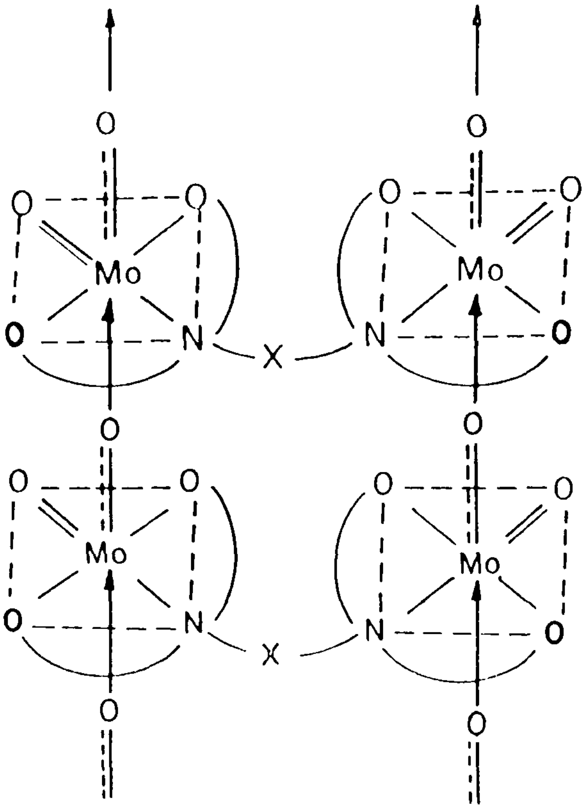
Compound[a]	IR			λ_{max} (ϵ/l mol^{-1} cm^{-1})
	ν(C=N)	ν(O=Mo=O)	(Mo$\cdots$O→Mo)	
1	1609			38910(35980), 34480(63175), 33110(62710), 29850(42445)
1a	1595	950, 912	855	37880(38155), 34480(42570), 33110(44030), 30580(38880), 24815(6700)
1b	1614	933, 915		37870(33810), 34365(32615), 33005(34000), 30960(34110), 24630(6547)
1c	1613	930, 915		37735(38870), 34130(34075), 32575(36040), 30960(38710), 24450(8225)
1d	1613	915, 882		37735(43414), 34482(41123), 33003(44013), 31152(45275), 24691(9793)
2	1604			39215(24400), 36490(27500), 29070(18700)
2a	1590	933, 917	852	37880(45490), 35090(37070), 29325(39195), 24940(10490)
3	1607			38000(25690), 34130(29575), 33005(26730), 29850(15690)
3a	1606	936, 919	826	37735(53500), 34015(47450), 32785(46000), 31545(39220), 24815(6790)
3b	1613	930, 913		37455(54480), 34720(52355), 33220(49885), 31250(40862), 23960(6655)
3c	1613	933, 915		37350(53880), 34500(54070), 32170(52550), 31250(44730), 24440(8250)
3d	1613	934, 912		37455(54380), 34250(53960), 32160(51660), 31100(43650), 24350(8100)
4	1609			37880(36665), 35210(29505), 28985(16320)
4a	1603	931, 919	865	37735(55615), 34130(42190), 29760(38775), 24155(8945)

[a] For abbreviations see Table 3.1.

Table 3.3. ^1H NMR spectral data (δ in ppm).[a]

Compound	-CH = N	Aromatic protons	-CH$_2$-	-NH	-OH	Neutral molecule
1	8.60(s, 2H)	6.80 - 7.95(m, 16H)	3.85(s, 2H)	11.05(s, 2H)	12.00(s, 2H)	
1a	8.95(s, 2H)	6.98 - 8.15(m, 16H)	4.05(s, 2H)			
1b	8.90(s, 2H)	6.85 - 8.00(m, 22H)	3.94(s, 2H)			8.40(b, 4H)
1c	8.90(s, 2H)	6.90 - 8.00(m, 20H)	3.93(s, 2H)			8.30(b, 4H), 2.32(s, 6H)
1d	8.85(s, 2H)	6.82 - 8.00(m, 16H)	3.90(s, 2H)			7.85(b, 2H), 7.01(b, 4H)
3	8.60(s, 2H)	6.95 - 7.95(m, 16H)		11.55(s, 2H)	12.17(s, 2H)	
3a	8.97(s, 2H)	6.95 - 8.00(m, 16H)				
3b	9.05(s, 2H)	6.95 - 8.05(m, 22H)				8.45(b, 4H)
3c	9.05(s, 2H)	6.95 - 8.05(m, 20H)				8.40(b, 4H), 2.40(s, 6H)
3d	9.00(s, 2H)	6.95 - 8.05(m, 16H)				7.85(b, 2H), 7.01(b, 4H)
4	8.65(s, 2H)	6.95 - 8.35(m, 14H)		11.30(s, 2H)	12.35(s, 2H)	
4a	9.03(s, 2H)	6.95 - 8.35(m, 14H)				

[a] letters given in parentheses indicate the type of signal, s = singlet, m = multiplet, b = broad.



$X = CH_2$ or S_2

FIG. 3. I : PROPOSED OLIGOMERIC STRUCTURE OF $[(MoO_2)_2 L]$ TYPE COMPLEXES.

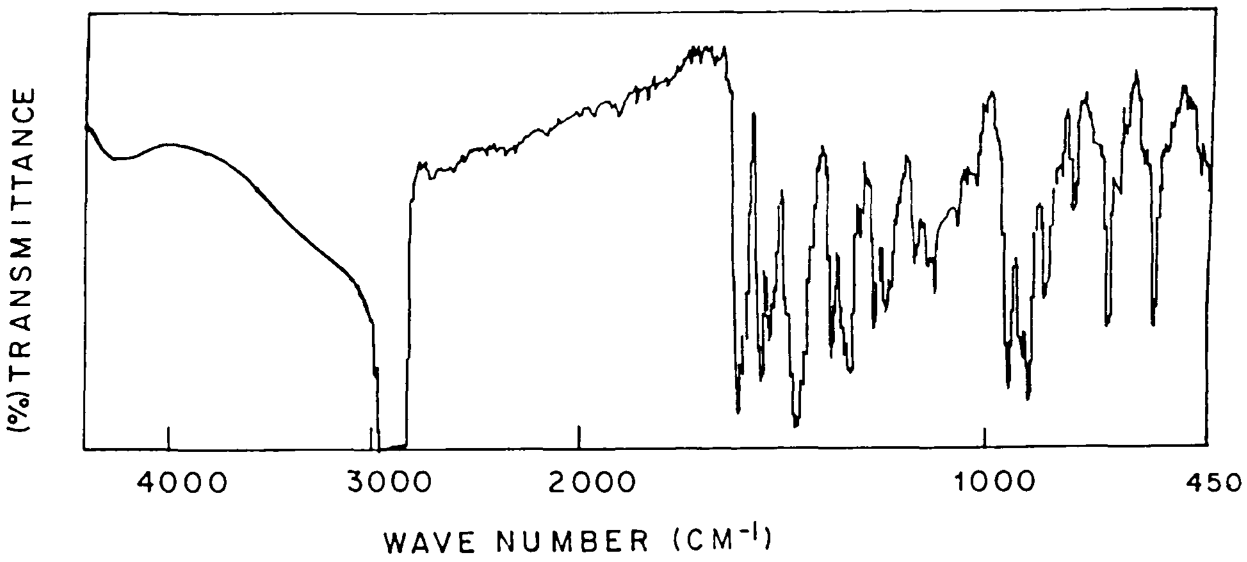


FIG. 3. 2 : IR SPECTRUM OF $[(MoO_2)_2(CH_2\{Sal-BZH\}_2)]$ IN NUJOL.

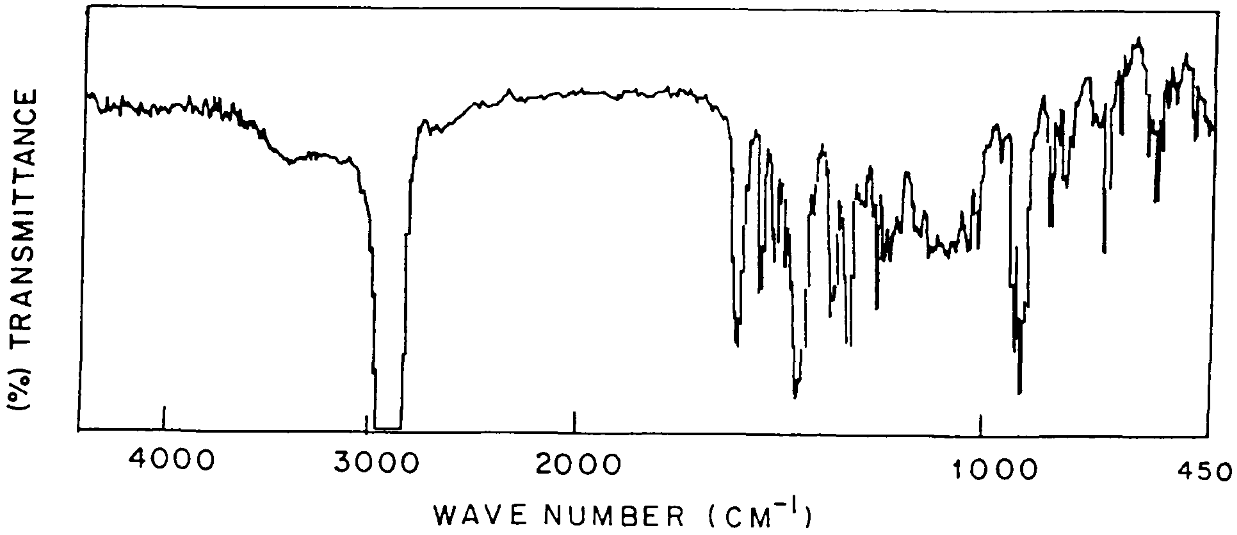


FIG. 3. 3 : IR SPECTRUM OF $[(MoO_2)_2(CH_2\{Sal-BZH\}_2(Pic)_2)]$ IN NUJOL.

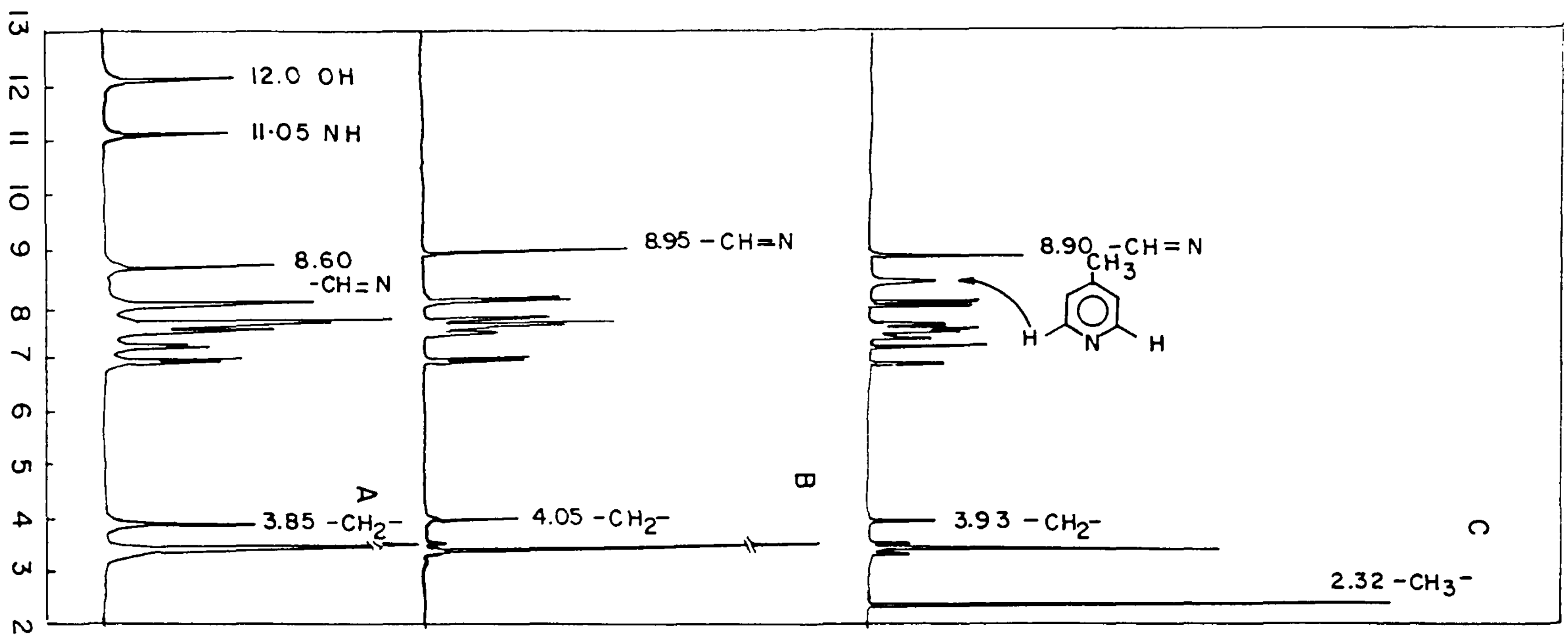


FIG. 3.4 : ^{1}H-NMR SPECTRUM OF (A) $[CH_2\{H_2Sal-BZH\}_2]$ (B) $[(MoO_2)_2(CH_2\{Sal-BZH\}_2)]$ (C) $[(MoO_2)_2(CH_2\{Sal-BZH\}_2(Pic)_2)]$ IN DMSO-d_6.

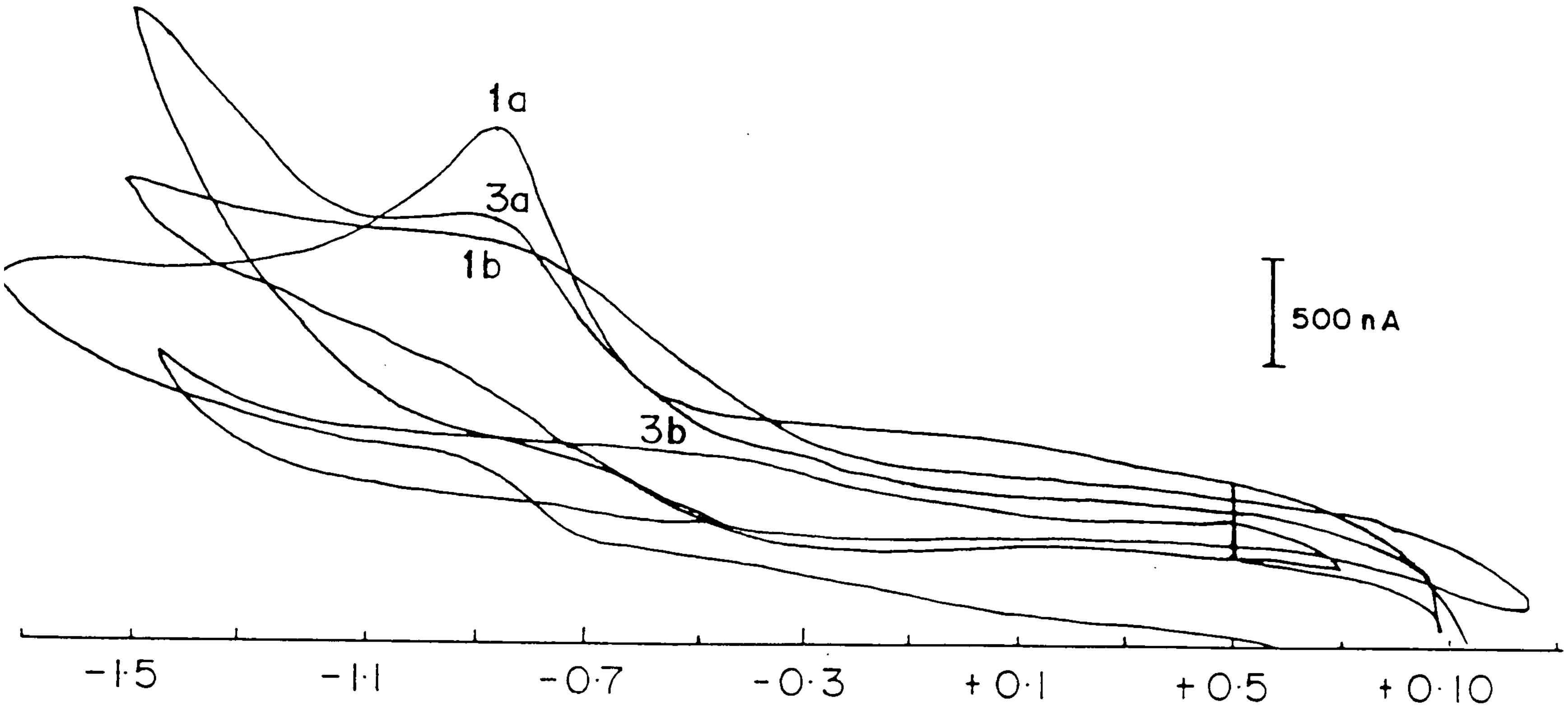


FIG. 3. 5 : CYCLIC VOLTAMMOGRAMS FOR $[(MoO_2)_2L]$ TYPE COMPLEXES IN DMF AT SCAN RATE 200 mV/S.

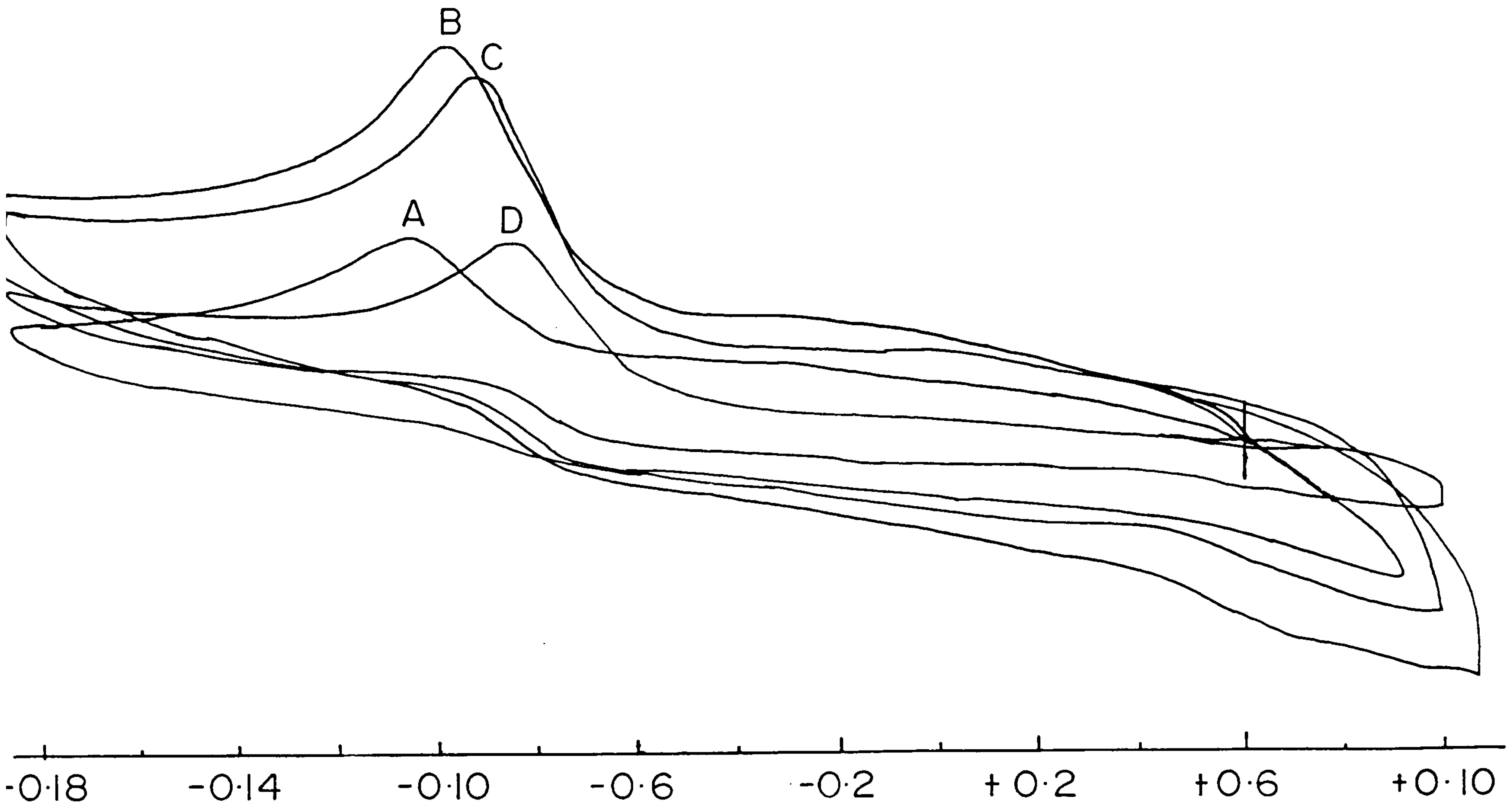


FIG. 3.6 : CYCLIC VOLTAMMOGRAMS FOR $[(MoO_2)_2(CH_2\{Sal-BZH\}_2)]$ IN DMF SCAN RATE (A) 500mV/S, (B) 200 mV/S, (C) 50mV/S, (D) 10mV/S.

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CHAPTER 4

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BINUCLEAR DIOXOMOLYBDENUM(VI) COMPLEXES OF FLEXIBLY BRIDGED HEXADENTATE TETRAANIONIC SCHIFF BASES DERIVED FROM 5,5′-METHYLENE- OR DITHIO- BIS(SALICYLALDEHYDE) AND S-METHYL DITHIOCARBAZATE OR S-BENZYLDITHIOCARBAZATE

4.1 INTRODUCTION

The coordination complexes of molybdenum in higher oxidation states are generally associated with oxo-group.[1-3] The oxo-molybdate unit ($\mathrm{Mo{=}O}$ or $\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Mo}}\mathrm{{=}O}$) is shown to be present in various enzymes.[4] In these enzymes molybdenum cycles between +VI and +IV oxidation states by reversible oxo-transfer reaction.[5,6] Although mononuclear dioxomolybdenum(VI) complexes of Schiff bases are well documented in the literature and their chemical properties are well understood,[3] very little is known about such binuclear dioxomolybdenum(VI) complexes.[7]

Dithiocarbazic acid and its derivatives have received considerable attention over the past few years. The chemistry of such ligands warrants further studies because of the following reasons (1) Dithiocarbazic acid and the Schiff bases derived from its S-alkyl esters form an interesting series of ligands, whose properties can be greatly modified by introducing organic substituents into the ligand molecule thereby inducing different stereochemistry in the metal complexes (2) biological activities may be expected for some of the metal complexes. Carcinostatic activities have readily been found for some metal complexes of dithiocarbazic acid and the Schiff bases derived from its methyl ester.[8] Dithiocarbazate $NH_2NHCS_2^-$ and its substituted derivatives have been less widely investigated as a ligand than other well-known dithioanions such as dithiocarbamates $R_2NCS_2^-$ xanthates $ROCS_2^-$, dithiophosphates $(RO)_2PS_2^-$ and dithiocarboxylates RCS_2^-.[9]

A number of these chelates derived from the dithiocarbazic acid ligands has been tested for anticancer activity: the palladium(II) and copper(III) complexes are found to show moderate anti-tumour activity.[10] The carcinostatic and antiviral activity of metal chelates is quite markedly altered by minor changes in the ligand.

Syamal et. al.[11] have reported the syntheses of several new dioxomolybdenum(VI) with composition $MoO_2L.MeOH$(where LH_2 = Schiff base derived from salicylaldehyde, 2-hydroxy-1-naphthaldehyde, *o*-hydroxyacetophenone, *o*-hydroxybenzophenone, pyridoxal and thiosemicarbazide, S-methyldithiocarbazate or S-benzyldithiocarbazate.

Bhattachargee et. al.[12] have also synthesized *cis*-dioxomolybdenum(VI) complexes of the above ligands or its derivative having a 5-methyl substituent on the phenyl ring of salicylaldehyde. But these complexes have general formula $[MoO_2L]$. All these complexes undergo oxo transfer reaction with

PPh_3 at room temperature, furnishing oxomolybdenum(IV) derivatives MoO(L) and $OPPh_3$. The complexes [MoO(L)] in DMF accepts an oxygen atom from DMSO, affording $[MoO_2(L)(D)]$ and Me_2S.

The oxo transfer from $[MoO_2L]$ (unsubstituted salicoyl ring) to PPh_3 occurs in a second-order process with rate constant 1.32×10^{-2} dm^3 mol^{-1} s^{-1} at 30°. The oxo transfer from DMSO to the MoO^{2+} core is much faster. The reaction between PPh_3 and DMSO furnishing $OPPh_3$ and Me_2S becomes highly facile in the presence of $[MoO_2L]$ as catalyst. Thus, these oxo transfer reactions can be expressed by two general equations (1) and (2).

$$[Mo^{VI}O_2(ligand)] + X \longrightarrow [Mo^{IV}O(ligand)] + XO \quad (1)$$

$$[Mo^{IV}O(ligand)] + YO \longrightarrow [Mo^{VI}O_2(ligand) + Y \quad (2)$$

Since $[Mo^{IV}O(ligand)]$ type complexes are generally reconverted into $[Mo^{VI}O_2(ligand)]$ in aqueous aerobic media, the net effect caused by oxo-transfer molybdoenzymes which as oxidases or reductases catalyze the transfer or abstraction of an oxygen atom to or from substrate X or YO respectively, can be represented by equation (3).

$$X + H_2O \longrightarrow XO + 2H^+ + 2\bar{e} \quad (3)$$

The oxo-transfer ability of the MoO_2^{2+} core depends on the functionalities present in the ligands. Bhattacharjee et. al.[13]

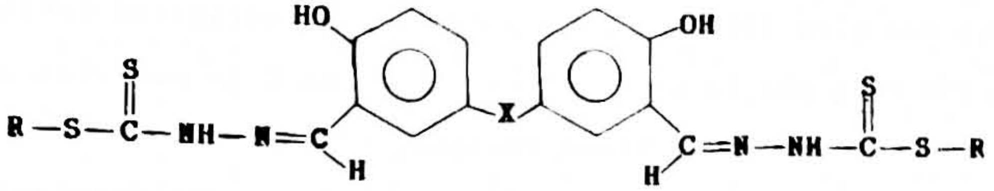
have observed for the first time that the rate constant of the oxo-transfer reaction from the oligomer $[(MoO_2L)_n]$ to the PPh_3 substrate is 10^2 times higher than that of the corresponding monomer $[MoO_2L(D)]$. Both $[MoO(L)]$ and $[MoO(L)(DMF)]$ react with the Me_2SO substrate in CH_2Cl_2 or DMF in a two-stage process.

$$\begin{tikzcd} {[MoOL]_n + nMe_2SO} \arrow[r, shift left, "k"] & {n[MoOL.Me_2SO]} \arrow[l, shift left] \arrow[d, "k_{-1}"] \\ & {n[MoO_2L] + nMe_2S} \end{tikzcd}$$

$$\begin{tikzcd} {[MoOL.DMF] + Me_2SO} \arrow[r, shift left, "k"] & {[MoOL.Me_2SO] + DMF} \arrow[l, shift left] \arrow[d, "k_{-1}"] \\ & {[MoO_2L] + Me_2S} \end{tikzcd}$$

Roberts et.al.[14] have prepared dioxomolybdenum(VI) complexes of the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand and studied the oxygen atom transfer reactions. When the ligand set of the starting Mo(VI) complex contains only oxygen and nitrogen donor atoms, oxygen atom transfer reactions are uncommon and usually produce binuclear complexes as products. $MoO_2(acac)_2$ and $MoO_2(ox)_2$ react with PPh_3 in refluxing dichloroethane to produce the binuclear $Mo_2O_3L_4$ complexes. In general sulphur donor atoms facilitate oxygen atom transfer reactions, resulting in mononuclear Mo(IV) complexes as products.

In this chapter we report the binuclear dioxomolybdenum(VI) complexes of new flexibly-bridged hexadentate tetraanionic (SNO$\frown$ONS donor) Schiff base ligands (structure I). Spectral and electrochemical properties of the isolated complexes are presented here.



(I)

	X	R	Abbreviations
1	CH_2	CH_3	$CH_2(H_2sal\text{-}SMDTC)_2$
2	CH_2	$CH_2C_6H_5$	$CH_2(H_2sal\text{-}SBDTC)_2$
3	S-S	CH_3	$S_2(H_2sal\text{-}SMDTC)_2$
4	S-S	$CH_2C_6H_5$	$S_2(H_2sal\text{-}SBDTC)_2$

4.2 EXPERIMENTAL

S-Methyldithiocarbazate,[15] S-benzyldithiocarbazate,[16] 5,5′-methylene bis(salicylaldehyde),[17] 5,5′-dithio bis(salicylaldehyde)[18] and $[MoO_2(acac)_2]$[19] (acacH = acetylacetone) were prepared following the literature procedures. Other chemicals were used as mentioned in previous chapters.

Elemental analyses of all the new binucleating SNO⁀ONS donor ligands and their complexes are given in Table 4.1. Details of other techniques are reported in the previous chapters.[7]

(1) Preparation of 5,5′-methylene bis[(S-methyl-β-N(2-hydroxy phenyl)methylenedithiocarbazate] [$CH_2(H_2sal\text{-}SMDTC)_2$

A hot methanolic solution (10 ml) of the 5,5′-methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) was added to a hot solution of S-methyldithiocarbazate (0.244 g, 0.002 mol) in methanol (10 ml) and the reaction mixture was refluxed for 3 h on a waterbath. After reducing the solvent to 10 ml the solution was cooled to 10° overnight. The separated yellow solid was filtered, washed with methanol, dried at ambient temperature and finally recrystallized from hot methanol. Yield 0.320 g (68%); m.p. 222°.

(2) Preparation of 5,5′-methylene bis[(S-benzyl-β-N(2-hydroxy phenyl)methylenedithiocarbazate] [$CH_2(H_2sal\text{-}SBDTC)_2$]

S-Benzyldithiocarbazate (0.396 g, 0.002 mol) and 5,5′-methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) were mixed in 50 ml of methanol and the reaction mixture was refluxed for 3h. Upon cooling the pale yellow solid separated was filtered, dried and recrystallized from methanol. Yield 0.420 g (68%); m.p. 220°.

(3) Preparation of 5,5′-dithio bis[(S-methyl-β-N(2-hydroxy phenyl)methylenedithiocarbazate] [$S_2(H_2sal\text{-} SMDTC)_2$]

S-Methyldithiocarbazate(0.244 g, 0.002 mol) was dissolved in methanol (10 ml) and to this a solution of 5,5′-dithio bis(salicyladehyde) (0.306 g, 0.001 mol) was added and then refluxed for 3 h. The resulting solution upon cooling deposited an yellow solid which was collected and recrystallized from methanol. Yield 0.350 g (68%); m.p. 226°.

(4) Preparation of 5,5′-dithio bis[(S-benzyl-β-N(2-hydroxy phenyl)methylenedithiocarbazate] [$S_2(H_2sal\text{-}SBDTC)_2$]

S-Benzyldithiocarbazate(0.396 g, 0.002 mol) was dissolved in methanol (10 ml) and mixed with 5,5′-dithio bis(salicylaldehyde) (0.306 g, 0.001 mol) dissolved in methanol (10 ml). The reaction mixture was refluxed for 3h. On cooling the yellow crystals separated were filtered and recrystallized from methanol. Yield 0.470 g (70%); m.p. 198°.

(1a) Preparation of [$(MoO_2)_2(CH_2\{sal\text{-}SMDTC\}_2)$]

To a hot solution of the ligand [$CH_2(H_2sal\text{-}SMDTC)_2$] (0.232 g, 0.0005 mol) in methanol (40 ml), $MoO_2(acac)_2$ (0.306 g, 0.001 mol) was added with vigorous shaking. The resulting turbid solution was filtered and then refluxed on a water bath for 6 h. After reducing the volume of the solution to 10 ml, it was cooled to 10° overnight. The separated brown solid was filtered, washed with methanol and dried in air at 100°. Yield 0.400g (78%); m.p. >250°.

(2a) Preparation of [$(MoO_2)_2(CH_2\{sal\text{-}SBDTC\}_2)$]

The binucleating Schiff base [$CH_2(H_2sal\text{-} SBDTC)_2$] (0.308 g, 0.0005 mol) was dissolved in methanol (50 ml) by heating on a water bath and to that was added $MoO_2(acac)_2$ (0.306 g, 0.001

mol) as a solid with vigorous shaking. The resulting turbid solution was filtered and the clear filtrate refluxed on a waterbath for 6h. After concentrating the solution to 10 ml, the separated orange solid product was filtered, washed with hot methanol and dried at 100° in air. Yield 0.440 g (78%); m.p. >250°.

(3a) Preparation of [$(MoO_2)_2(S_2\{sal\text{-}SMDTC\}_2)$]

$MoO_2(acac)_2$ (0.330 g, 0.001 mol) was added to a refluxing solution of the ligand [$S_2(sal\text{-}SMDTC)_2$] (0.257 g, 0.0005 mol) in methanol (50 ml). The resulting mixture was filtered immediately and the solution refluxed on a water bath for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated brown solid product was filtered, washed with hot methanol and dried at 100°. Yield 0.400 g (78%); m.p.>250°.

(4a) Preparation of [$(MoO_2)_2(S_2\{sal\text{-}SBDTC\}_2)$]

To a refluxing solution of the ligand [$S_2(H_2sal\text{-}SBDTC)_2$] (0.330 g, 0.0005 mol) in methanol (50 ml) $MoO_2(acac)_2$ (0.306 g, 0.001 mol) was added as a solid. The resulting solution was filtered while hot and again refluxed on a water bath for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated orange solid was filtered, washed with hot methanol and dried at 100°. Yield 0.440 g (75%); m.p. >250°.

Preparation of the complexes of the type $[(MoO_2)_2(CH_2\{sal-SMDTC\}_2)(D)_2)]$ (D = DMSO, py, pic)^{20}

$[(MoO_2)_2(CH_2\{sal-SMDTC\}_2)]$ (0.20 g) was dissolved in a respective solvent (5 ml) by heating on a water bath. Partial evaporation of the solvent to about 2 ml under vacuum produced a solid compound which was filtered, washed with ether, and dried under vaccum. Yield (80-85%).

The analytical and other physicochemical data of all the new Schiff bases and their dioxomolybdenum(VI) complexes are presented in Table 4.1.

Oxo-transfer reactions with triphenyl phosphine and dimethylsulphoxide.

Reaction with PPh_3

The complex $[(MoO_2)_2(CH_2\{sal-SBDTC\})_2$ or $[(MoO_2)_2(S_2\{sal-SBDTC\})_2$ (0.001mol) was taken in either dry ethanol or acetonitrile (50 ml) and the solution was heated on a water bath under nitrogen. Triphenylphosphine (1.5 mol) was added as a solid to the solution with constant stirring. The reaction mixture was heated on a water bath for 20 min producing a dark brown compound. The resulting binuclear oxomolybdenum complex of the type $[(Mo^{IV}O)_2L]$ was filtered off and washed with ethanol. Yield: 80%.

Reaction with DMSO.

The above obtained binuclear $[(Mo^{IV}O)_2L]$ complex was dissolved in 2 ml DMSO and the solution was heated on a water-bath for 30 min. Excess DMSO was removed in *vacuo* and the solid product obtained was washed with ethanol and was identified as $[(Mo^{VI}O_2)_2L]$ type complex. Yield (85%).

Procedure Used for the Epoxidation of Olefins

Cyclohexene (0.0324 mol), *t*-butylhydroperoxide (0.0648 mol), catalyst $[(MoO_2)_2CH_2\{sal\text{-}SMDTC\}_2)]$ (0.000324 mol) and dry benzene (20 ml as solvent) were placed in an RB flask. The contents were stirred' well using a magnetic stirrer and heated at 70° for 5h. and then cooled. The contents after reaction were extracted with diethylether and the samples so obtained were dried over anhydrous magnesium sulphate. The samples were analyzed both by GC and TLC to get the olefin back. The other olefins such as geraniol, *trans*-stilbene and styrene were also used for the epoxidation reaction. The reaction was carried out in homogeneous condition also using DMF as solvent.

4.3 RESULTS AND DISCUSSION

The synthetic procedure for the preparation of the flexibly-bridged hexadentate tetraanionic Schiff bases is straight forward. While elemental and physicochemical data demonstrate the formation of Schiff bases, the spectral data (vide infra) confirm the existence of these in their thione form as shown by structure (I). The reaction of flexibly-bridged ligands **1** – **4** with $[MoO_2(acac)_2]$ in 1:2 molar ratio proceeds as follows [equation (i)] in refluxing methanol and complexes of the type $[(MoO_2)_2L]$ are formed.

$$2\ [MoO_2(acac)_2] + LH_4 \xrightarrow[MeOH]{} [(MoO_2)_2L] + 4\ acaoH \quad (i)$$

Analytical data support the formation of the complexes by the complete removal of the coordinated acetylacetone group under the reaction conditions. These complexes do not undergo any weight loss on heating upto 200° which suggests the formation of the five coordinated complex $[(MoO_2)_2L]$ and not the expected octahedral complex $[(MoO_2)_2L.2MeOH]$. The weakly coordinated monodentate ligands like methanol in complexes of the type $[MoO_2L.MeOH]$ are known to undergo dissociation even at room temperature.[4] The complexes are non-electrolytes (4.4 - 5.5 ohm^{-1} $mole^{-1}$ cm^2) in DMF and are diamagnetic as expected for the $4d^0$ system. These complexes react with coordinating solvents such as DMSO, DMF, THF and pyridine giving molecular addition complexes of the type $[(MoO_2)_2L.(D)_2]$. The high decomposition temperature (>250°) of complexes of the type $[(MoO_2)_2L]$ indicates their increased thermal stability.

IR Spectral Studies.

A partial listing of the IR spectra of the ligands and their complexes is given in Table 4.3. The Schiff base $[S_2(H_2sal-$

SBDTC)$_2$] exhibits an absorption band at 3261 cm^{-1} due to νNH, indicating the thione nature of the ligand. This is further supported by the presence of a strong absorption band at 1040 cm^{-1} due to ν(C=S).[21] The bands due to ν(OH) and ν(C=N) are observed at 3380 and 1607 cm^{-1}, respectively. A similar pattern of bands is observed in the IR spectra of the ligands **1**, **2** and **3**. The presence of a strong band at 1030-1052 cm^{-1} due to ν(C=S) in all these ligands indicates their thione nature.[22] This is further supported by the presence of a band in the region 3095-3248 cm^{-1} due to ν(NH) of the hydrazide residue. A broad band at around 3400 cm^{-1} is assigned to the ν(OH)(phenolic) band in the free Schiff bases.

In the IR spectrum of the metal complex [(MoO$_2$)$_2$(S$_2${sal-SBDTC}$_2$)],the bands due to ν(C=S) and ν(NH) at 1040 and 3261 cm^{-1} respectively are absent, supporting thioenolization of the C=S group and coordination of the sulphur to molybdenum. The band due to phenolic OH at 3380 cm^{-1} is also absent in the complex suggesting the coordination of the phenolic oxygen after deprotonation. This is further supported by the shift of the ν(C-O) (phenolic) band from 1539 cm^{-1} of the Schiff base to 1552 cm^{-1} in the complex.[23] The strong band due to azomethine group at 1607 cm^{-1} in the free Schiff base is shifted to lower frequency and is observed at 1591 cm^{-1}, indicating the participation of azomethine nitrogen atom in the coordination.[22]

A similar pattern of bands is observed in the IR spectra of the rest of the metal complexes of the type $[(MoO_2)_2L]$. Thus the IR data suggest that both the Schiff base units attached to $-CH_2$ or -S-S- group behave as dibasic tridentate and ONS donor ligands. The coordination of the monodentate ligands in the adducts has also been confirmed by the appearance of their characteristic vibrational mode(s).[24,25]

The $[(MoO_2)_2L]$ type complexes exhibit a sharp single band (some times two bands) at 924 - 948 cm^{-1} due to $\nu(O{=}Mo{=}O)$ stretch and a strong but broad band at *ca.* 850 cm^{-1} due to $Mo\cdots O\rightarrow Mo$ interaction.[1] However, the complex $[(MoO_2)_2(S_2\{sal\text{-}SBDTC\}_2)]$ exhibits two bands at 947 and 910 cm^{-1} due to $\nu(O{=}Mo{=}O)$ stretches. A broad band is observed at 837 cm^{-1} due to weakened $\nu(Mo{=}O)$ as a result of $Mo\cdots O\rightarrow Mo$ interaction, indicating an oligomeric (pseudo-octahedral) structure of the complex. Each molybdenum atom achieves pseudo-octahedral structure through oxo-bridging from the adjacent molecule. A probable oligomeric structure through $Mo\cdots O\rightarrow Mo$ bridging is shown in Fig. 4.1. Similar oligomeric structure for other dioxomolybdenum(VI) and dioxotungsten(VI) complexes having tridentate dibasic ONS and ONO donor ligands have been suggested.[4,26]The observation of $\nu(C\text{-}O)$ (phenolic) at identical positions in **1a** and its adducts (e.g.$[(MoO_2)_2(CH_2\{sal\text{-}SMDTC\}_2)]$, 1552; $[(MoO_2)_2(CH_2\{sal\text{-}SMDTC\}_2)(DMSO)_2]$, 1551; $[(MoO_2)_2(CH_2\{sal\text{-}SMDTC\}_2)(py)_2]$, 1552;

$[(MoO_2)_2CH_2\{sal\text{-}SMDTC\}_2(pic)_2]$, 1552cm^{-1}) further supports the presence of an oligomeric bridge *via* an oxygen of the MoO_2 group as oligomerization *via* phenolic oxygen bridging would show a significant change in the C-O stretch.[27]

^{1}H NMR studies.

The ^{1}H NMR spectra of the Schiff bases and complexes are recorded in DMSO-d_6 and chemical shift (δ in ppm) are reported relative to DMSO-d_6 (2.40 ppm). The binucleating Schiff base $[S_2(H_2sal\text{-}SBDTC)_2]$ exhibits NH proton resonance at 10.65 ppm suggesting its thione nature. The OH proton resonance of the salicylaldehyde residue appears at 13.35 ppm. The spectral data presented in Table 4.2 show that all the Schiff bases exist in their thione form as only a singlet at 10.05 - 10.65 ppm due to -NH proton is observed in the spectra of the Schiff bases. Usually -SH proton resonance is observed when such ligands exist in their tautomeric thiolo form. In all the free Schiff bases, the phenolic protons are observed in 13.27 - 13.35 ppm region.

In the complex $[(MoO_2)_2(S_2\{sal\text{-}SBDTC\}_2)]$, the resonance due to NH proton at 10.65 ppm is absent, indicating thioenolization and subsequent coordination of the thioenolic sulphur to the metal atom. The disappearance of the signal due to phenolic OH of the salicylaldehyde residue at 13.35 ppm indicates the coordination of the phenolic oxygen to molybdenum. The sharp singlet at 8.47 ppm due to azomethine proton shifts downfield after coordination to the metal and is observed at 9.05 ppm as sharp singlet.[28] In the rest $[(MoO_2)_2L]$ complexes, a similar ^1H NMR pattern is observed. The complexes do not exhibit any signal due to coordinated methanol, supporting their oligomeric structure. In the 4-methylpyridine adduct $[(MoO_2)_2(S_2\{sal\text{-}SBDTC\}_2)(pic)_2]$, the methyl protons are observed at 2.30 ppm as a sharp singlet in addition to all the signals present in the complex $[(MoO_2)_2(S_2\{sal\text{-}SBDTC\}_2)]$ indicating the coordination of 4-methyl pyridine to molybdenum. The coordination of pyridine and 4- methyl pyridine to the molybdenum in the adducts is also evidenced by the appearance of two or three new signals in the aromatic region. Other resonances due to $-CH_2-$ protons, $-SCH_2-$ protons, $-SCH_3$ protons and aromatic protons in the complexes appear almost in the same positions as in the respective Schiff bases. The presence of a singlet at 3.75 - 3.95 ppm due to $-CH_2-$ protons attached to two benzene rings in the Schiff bases $[CH_2(H_2sal\text{-}SMDTC)_2]$ and $[CH_2(H_2sal\text{-}SBDTC)_2]$ and their complexes indicates that the two dibasic tridentate Schiff base units are still attached to the methylene group.

Electronic Spectral Studies

The spectral data presented in Table 4.3 also show that all these Schiff bases exhibit three or four electronic spectral bands. These bands are also observed in the complexes. In addition, a broad shoulder observed at around 24000 cm^{-1} is assigned to the ligand to metal charge transfer (lmct) band between the lowest empty d-orbital of molybdenum and the highest occupied ligand molecular orbital. The appearance of lmct band as shoulder with relatively high extinction coefficient is probably due to influence of ligand band which appear at 25700-27472 cm^{-1} in the ligands and merges with lmct band in the complexes.

Electrochemical Study.

The cyclic voltammetry measurements of the complexes were carried out at different temperatures (25 - 50°) and at various scan rates in DMF under dry nitrogen using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. However, no detectible reduction or oxidation waves were noticed in any cyclic voltammogram. This is contrary to the observation reported for mononuclear dioxomolybdenum(VI) complexes of very similar ONS donor ligands where all the complexes show irreversible to quasi-reversible single electron reduction waves in their cyclic voltammograms.[12,13] The cyclic voltammograms of even dioxomolybdenum(VI) complexes of flexibly-bridged ligands having $ONO\frown ONO$ donor system show irreversible to quasi-reversible reduction of the molybdenum(VI) to molybdenum(IV) species.[7]

Oxidation Reactions using $[(MoO_2)_2CH_2\{sal\text{-}SMDTC\}_2)]$ and $[(MoO_2)_2S_2\{sal\text{-}SMDTC\}_2)]$ as catalysts.

The reaction of the above complexes with PPh_3 (large excess) produced $OPPh_3$ and the corresponding $(MoO)_2L$ complexes. The IR spectra of the $Mo^{IV}O$ complexes show only one ν(Mo=O) stretching frequency at *ca*. 975 cm^{-1} which is higher than in the corresponding $Mo^{VI}O_2$ complexes. Since the system is binuclear, we could not arrive at any precise stoichiometry of these complexes.

Olefin epoxidation reactions using these complexes as catalysts in presence of molecular oxygen or *t*-butyl hydroperoxide as oxidants did not show any epoxide formation both by GC and TLC. The procedure used for the epoxidation reactions is given in the experimental section.

4.4 CONCLUSION

From IR and ^1H NMR spectroscopic data it can be concluded that the Schiff bases exist in their thione form. On complexation thioenolization followed by deprotonation occurs leading to the formation of oligomeric dioxomolybdenum(VI) complexes with $SNO\frown ONS$ ligation. Though the complexes were shown to be resistant towards electrochemical reduction, they undergo oxo-transfer reaction with PPh_3 leading to the formation of oxo-molybdenum(IV) complexes . Since all these complexes are binuclear the exact stoichiometry of these oxomolybdenum(IV) complexes could not be established. But IR spectra of the complexes obtained after oxo-transfer reaction with PPh_3 strongly suggest the formation of oxomolybdenum(IV) species.

Table 4.1. Analytical and Physicochemical Data of the Ligands and Complexes[a]

	Compound/			Found (Calcd) %			
S. No.	Stoichiometry	Color	M.p. (°)	C	H	N	S
1	$CH_2(H_2sal-SMDTC)_2$ $C_{19}H_{20}N_4O_2S_4$	Yellow	222	49.49 (49.11)	4.68 (4.34)	12.21 (12.06)	27.81 (27.60)
2	$CH_2(H_2sal-SBDTC)_2$ $C_{31}H_{28}N_4O_2S_4$	Pale yellow	220	59.97 (60.36)	4.90 (4.58)	9.23) (9.08)	20.62 (20.79)
3	$S_2(H_2sal-SMDTC)_2$ $C_{18}H_{18}N_4O_2S_6$	Yellow	226	42.26 (42.00)	3.82 (3.52)	10.62 (10.88)	37.15 (37.38)
4	$S_2(H_2sal-SBDTC)_2$ $C_{30}H_{26}N_4O_2S_6$	Yellow	198	53.76 (54.02)	3.71 (3.93)	8.57 (8.40)	28.59 (28.85)
1a	$[(MoO_2)_2(CH_2\{sal-SMDTC\}_2)]$ $C_{19}H_{16}N_4O_6S_4Mo_2$	Brown	>250	31.81 (31.85)	1.97 (2.25)	7.53 (7.82)	17.61 (17.90)
2a	$[(MoO_2)_2(CH_2\{sal-SBDTC\}_2)]$ $C_{31}H_{24}N_4O_6S_4Mo_2$	Orange	>250	42.45 (42.86)	2.84 (2.78)	6.23 (6.45)	14.93 (14.76)
3a	$[(MoO_2)_2(S_2\{sal-SMDTC\}_2)]$ $C_{18}H_{14}N_4O_6S_6Mo_2$	Brown	>250	28.49 (28.20)	1.97 (1.84)	7.06 (7.31)	25.06 (25.10)
4a	$[(MoO_2)_2(S_2\{sal-SBDTC\}_2)]$ $C_{30}H_{22}N_4O_6S_6Mo_2$	Orange	>250	39.03 (39.22)	2.29 (2.41)	6.01 (6.10)	21.10 (20.88)

[a] Abbreviations: As under Structure (I)

Table 4.2. ^1H NMR Spectral Data (δ in ppm)[a]

Compounds[b]	-CH=N-	Aromatic protons	$-SCH_2$	$-CH_2-$	$-CH_3$	-NH	-OH
1	8.45(s, 2H)	6.75(d, 2H), 7.13(d, 2H), 7.45(d, 2H)		3.80(s, 2H)	2.47(s, 6H)	10.05(s, 2H)	13.30(s, 2H)
1a	8.95(s, 2H)	6.93(d, 2H), 7.45(d, 2H), 7.70(d, 2H)		3.95(s, 2H)	2.55(s, 6H)		
2	8.50(s, 2H)	6.80(d, 2H), 7.50(d, 2H), 7.35(m, 12H)	4.50(s, 4H)	3.75(s, 2H)		10.10(s, 2H)	13.35(s, 2H)
2a	8.95(s, 2H)	6.92(d, 2H), 7.30(m, 6H), 7.45(d, 6H), 7.70(d, 2H)	4.40(s, 4H)	3.80(s, 2H)			
3	8.45(s, 2H)	6.88(d, 2H), 7.42(d, 2H), 7.85(d, 2H)			2.50(s, 6H)	10.60(s, 2H)	13.27(s, 2H)
3a	8.95(s, 2H)	7.00(d, 2H), 7.70(d, 2H), 8.00(d, 2H)			2.65(s, 6H)		
4	8.47(s, 2H)	6.88(d, 4H), 7.32(m, 10H). 7.77(d, 2H)	4.50(s, 4H)			10.65(s, 2H)	13.35(s, 2H)
4a	9.05(s, 2H)	7.00(d, 2H), 7.28(m, 6H), 7.45(d, 4H), 7.68(d, 2H), 8.05(d, 2H)	4.45(s, 4H)				

[a] Letters given in parentheses indicate the type of signal. s = singlet, d = doublet, m = multiplet.

[b] For abbreviations see Table 4.1.

Table 4.3. IR and Electronic Spectral Data (cm^{-1})

			IR		λ_{max} (logϵ)
Compounds[a]	$\nu(C = N)$	$\nu(C = S)$	$\nu(O = Mo = O)$	$\nu(Mo \doteq O \rightarrow Mo)$	
1	1039	1623			38,000(4.43), 30,864(4.63), 27,932(4.75)
1a		1605	924	816	37,735(4.65), 31,153(4.68), 24,449(4.07)
2	1030	1624			38,022(4.67), 33,444(4.77), 30,769(4.70), 26,455(5.00)
2a		1606	948	853	37,735(4.69), 31,055(4.68), 24,691(4.08)
3	1052	1608			37,878(4.54), 30,674(4.58), 27,472(4.61)
3a		1592	931	888	37,735(4.46), 34,965(4.36), 24,691(3.82)
4	1040	1607			38,168(4.59), 33,557(4.70), 25,706(4.75)
4a		1591	947, 910	837	37,593(4.86), 30,769(4.76), 24,570(4.18)

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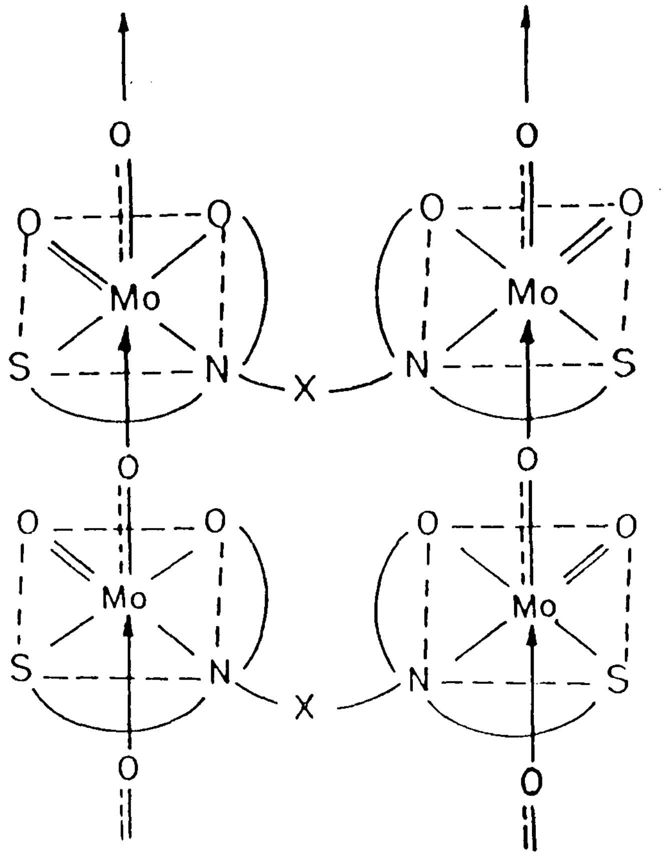
[a] For abbreviations see Table 4.1.



X = CH_2 or S_2

FIG. 4.1 : PROPOSED OLIGOMERIC STRUCTURE OF $[(MoO_2)_2L]$ TYPE COMPLEXES.

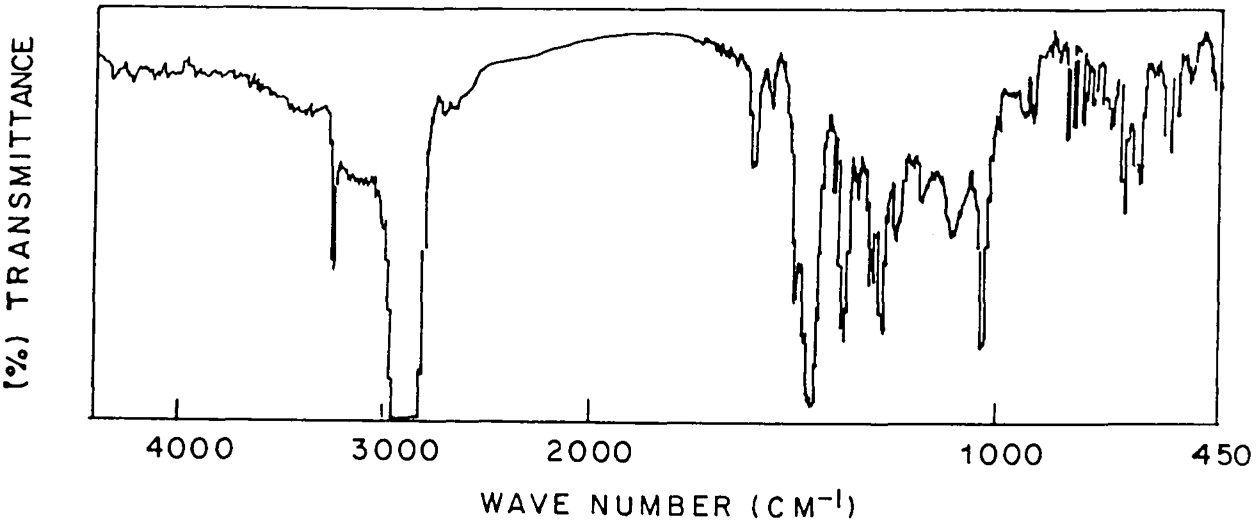


FIG. 4.2 : IR SPECTRUM OF $[S_2(H_2Sal\text{-}SBDTC)_2]$ IN NUJOL.

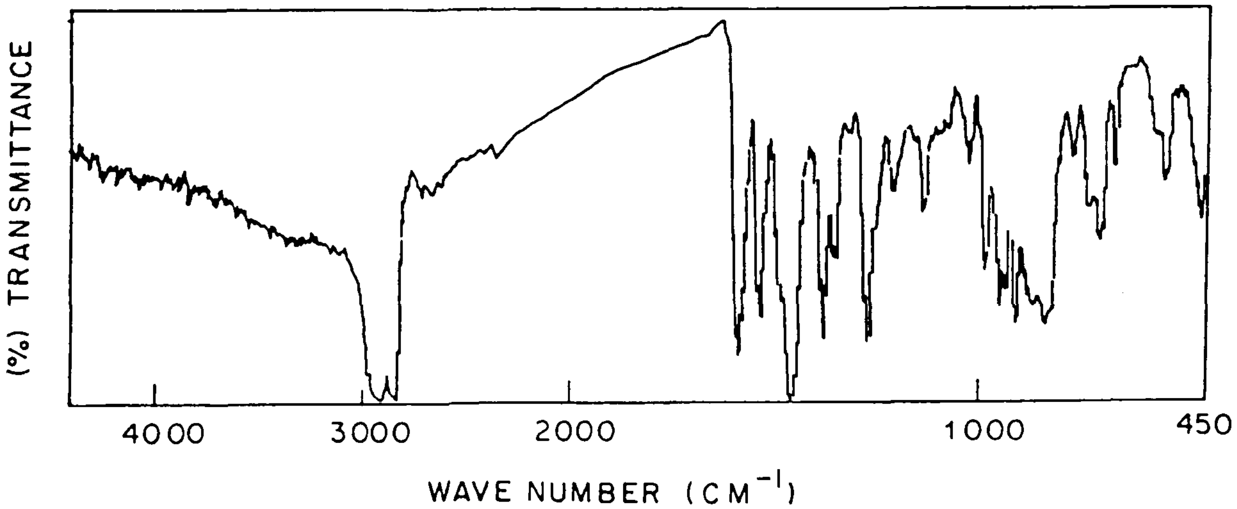


FIG. 4.3 : IR SPECTRUM OF $[(MoO_2)_2(S_2\{Sal\text{-}SBDTC\}_2)]$ IN NUJOL.

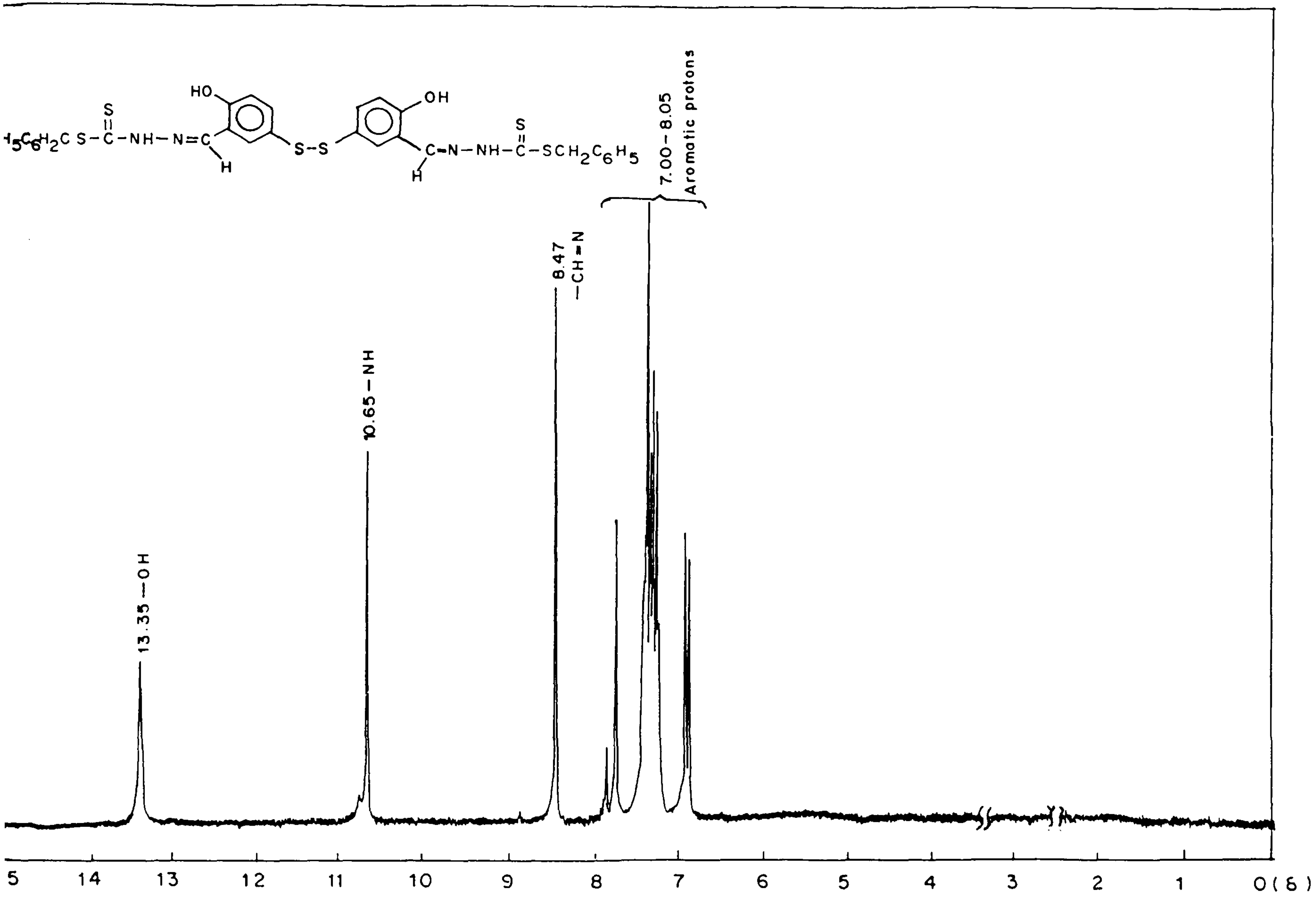


FIG. 4.4 : ^{1}H-NMR SPECTRUM OF $[S_2(H_2Sal-SBDTC)_2]$ IN DMSO-d_6.

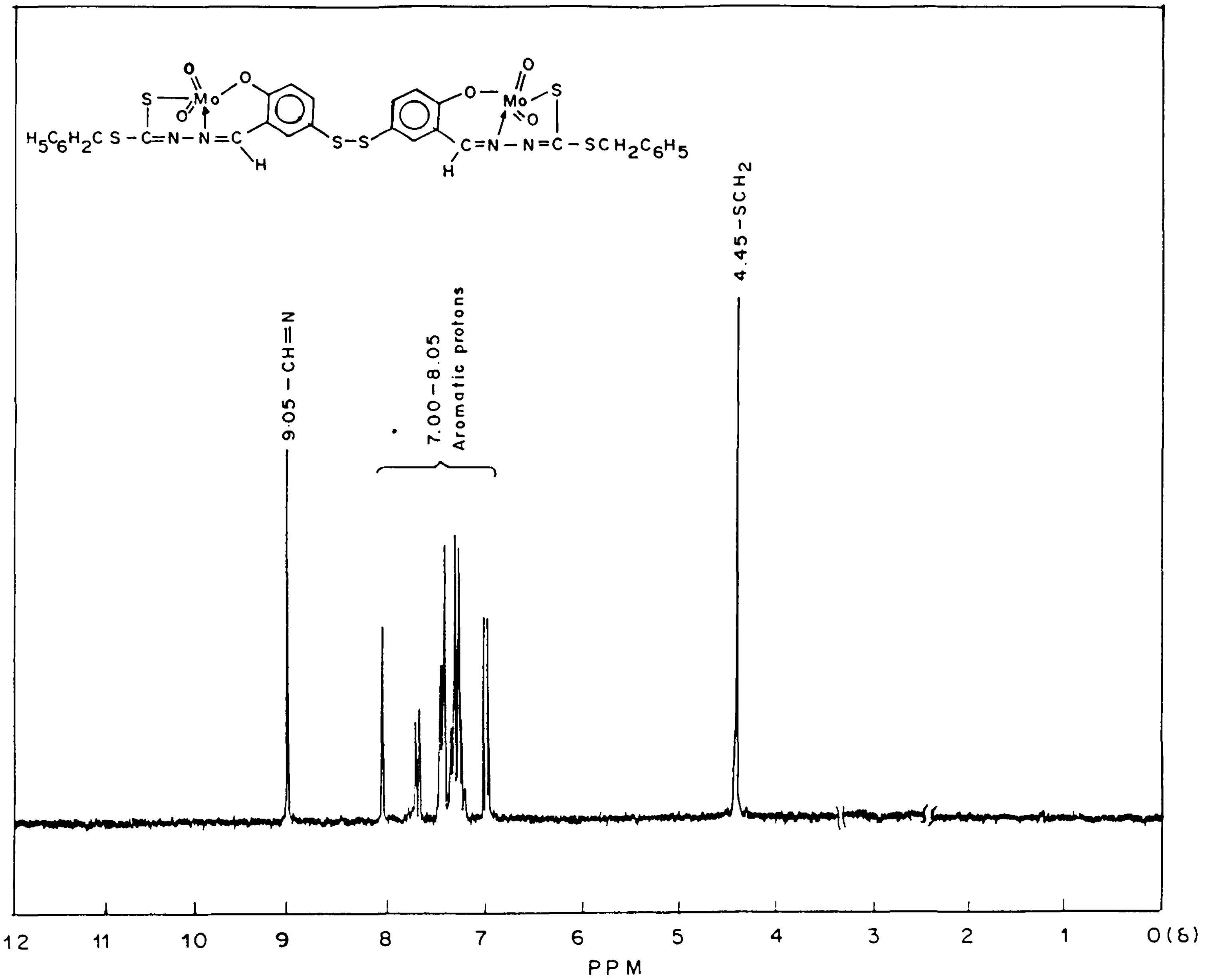


FIG. 4.5 : ^{1}H-NMR SPECTRUM OF $[(MoO_2)_2(S_2\{Sal\text{-}SBDTC\}_2)]$ IN DMSO-d_6 .

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CHAPTER 5

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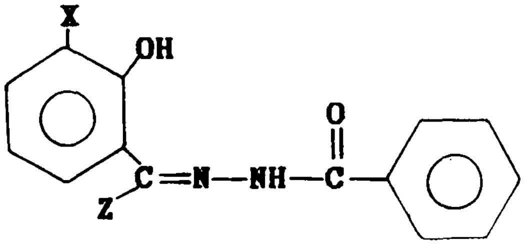
DIOXOTUNGSTEN(VI) COMPLEXES OF ONO DONOR LIGANDS AND THE X-RAY CRYSTAL STRUCTURE OF [WO_2(*o*-$OC_6H_4CH=NN=C(O)C_6H_5$)(MeOH)].MeOH

5.1 INTRODUCTION

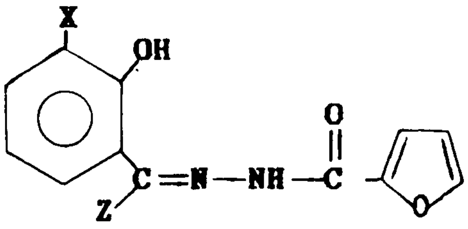
Amongst the d^0 ions of chromium group metals the chemistry of dioxomolybdenum(VI) complexes has been extensively studied possibly due to presence of this cation in the oxidized form of certain molybdoenzymes.[1] The active site of oxo-transfer molybdoenzymes viz. sulphite and aldehyde oxidase, xanthine oxidase, nitrate reductase and xanthine dehydrogenase has also been modeled using some *cis*-dioxomolybdenum(VI) complexes.[2] However, such dioxotungsten(VI) complexes are very limited; mostly organometallics[3] and only a few dealing with the dioxotungsten(VI) complexes of Schiff base ligands[4-7] are reported. The main reason for the lack of dioxotungsten(VI) complexes is the non-availability of a suitable starting material.

Yamanouchi et. al.[4,5] have used WO_2Cl_2 or $WOCl_4$ as the starting material while Syamal et. al. tried the reactivity of Na_2WO_4 towards Schiff bases in aqueous medium with a limited success.[6] Recently Yu and Holm[7] have successfully used [$WO_2(acac)_2$] (acacH = acetylacetone) to prepare dioxotungsten(VI) complexes. The versatility of other similar precursors, having coordinated acetylacetone groups like, [$MoO_2(acac)_2$] for the synthesis of dioxomolybdenum(VI) complexes[8], $[UO_2(acac)_2]$ for dioxouranium(VI)[9] and even $[Mo(NO)_2(acac)_2]$ for dinitrosylmolybdenum(0) complexes[10] are well established and documented in literature.

To establish the suitability of $[WO_2(acac)_2]$ as a precursor and explore the chemistry of dioxotungsten(VI) complexes, we have studied its reactivity towards Schiff bases of general formula I, II and III. Some dioxotungsten(VI) complexes studied here have been isolated in a single-step process. A single crystal X-ray analysis of one representative complex has also been reported.



(I)



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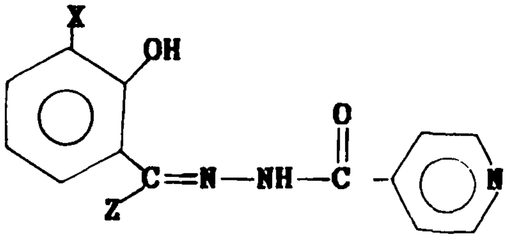

(III)

No.	Ligand	X	Y	Z	Abbreviation
1	I	H	H	H	H_2sal-BZH
2	I	OMe	H	H	H_2van-BZH
3	I	H	OH	H	H_2sal-SZH

4	I	OMe	OH	H	H_2van-SZH
5	II	H	-	H	H_2sal-FAH
6	II	OMe	-	H	H_2van-FAH
7	III	H	-	H	H_2sal-INH
8	III	OMe	-	H	H_2van-INH
9	I	H	H	CH_3	H_2hap-BZH
10	I	H	OH	CH_3	H_2hap-SZH
11	II	H	-	CH_3	H_2hap-FAH
12	III	H	-	CH_3	H_2hap-INH

5.2 EXPERIMENTAL

The chemicals and solvents used were procured from standard sources. Salicylaldehyde and acetylacetone were distilled under reduced pressure before use. [$WO_2(acac)_2$] was prepared by following the method described by Yu and Holm.[7] The Schiff bases were prepared by the literature methods.[11]

Elemental analyses were performed for all the Schiff bases and their metal complexes by the microanalytical section of the National Chemical Laboratory. Details of other techniques are reported in earlier chapters.[12]

(1a) Preparation of [WO_2(sal-BZH)(MeOH)]

The Schiff base [H_2sal-BZH] (0.120 g, 0.0005 mol) was dissolved in 25 ml of methanol by heating on a water bath. A solution of [$WO_2(acac)_2$] (0.207 g, 0.0005 mol) in 10 ml of methanol was added to the above solution with vigorous shaking and the resulting turbid solution was filtered immediately. The filtrate was refluxed on a water bath for 6 h. After reducing the solvent to 10 ml, the solution was cooled to 10° overnight and the separated yellow crystals were filtered, washed with methanol and finally recrystallized from methanol. Yield 0.205 g (80%); m.p. >250°.

(2a) Preparation of [WO_2(van-BZH)(MeOH)]

$WO_2(acac)_2$ (0.207 g, 0.0005 mol) in 10 ml methanol was added to a refluxing solution of the ligand [H_2van-BZH] (0.132 g, 0.0005 mol) in methanol (25 ml). The resulting mixture was filtered immediately and the solution refluxed on a water bath for 6h. After reducing the solvent to 5 ml, the solution was cooled at room temperature. The separated brown solid product was filtered, washed with hot methanol and dried at 100°. Yield 0.215 g (80%); m.p. >250°.

(3a) Preparation of [WO_2(sal-SZH)(MeOH)]

To a refluxing solution of the ligand [H_2sal-SZH] (0.128 g, 0.0005 mol) in methanol (50 ml) a solution of $WO_2(acac)_2$ (0.207g, 0.0005 mol) dissolved in methanol (10 ml) was added. The resulting solution was filtered while hot and again refluxed for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated yellow solid was filtered, washed with hot methanol and dried at 100°. Yield 0.235 g (81%); m.p. >250°.

(4a) Preparation of [WO_2(van-SZH)(MeOH)]

The yellow coloured complex [WO_2(van-SZH)(MeOH)] was prepared according to the above procedure **(3a)** by the reaction of the ligand [H_2van-BZH] (0.143 g, 0.0005 mol) in methanol (50 ml) and $WO_2(acac)_2$ (0.207 g, 0.0005 mol) in 10 ml methanol. Yield 0.230 g (82%); m.p. >250°.

(5a) Preparation of [WO_2(sal-FAH)(MeOH)]

The Schiff base [H_2sal-FAH] (0.112 g, 0.0005 mol) was dissolved in methanol (10 ml) by heating on a water bath and to it was added $WO_2(acac)_2$ (0.207 g, 0.0005 mol) in 10 ml methanol with vigorous shaking. The resulting turbid solution was filtered and then refluxed on water bath for 6h. After concentrating the solution to 10 ml, the solution was cooled at room temperature. The separated yellow solid was filtered, washed with hot methanol and dried at 100°. Yield 0.200 g (91%); m.p. >250°.

(6a) Preparation of [WO_2(van-FAH)(MeOH)]

The yellow coloured complex [WO_2(van-FAH)(MeOH)] was prepared following the above mentioned procedure **(5a)** by the reaction of the ligand [H_2van-FAH] (0.130 g, 0.0005 mol) in 25 ml methanol and $WO_2(acac)_2$ (0.207 g,0.0005 mol) in 10 ml methanol. Yield 0.225 g (95%); m.p. >250°.

(7a) Preparation of [WO_2(sal-INH)(MeOH)]

To a refluxing solution of the ligand [H_2sal-INH] (0.120 g, 0.0005 mol) in methanol (10 ml) $WO_2(acac)_2$ (0.207 g, 0.0005 mol) was added in 10 ml methanol. The refluxing solution was filtered while hot and again refluxed for 6h. After reducing the solvent to 5ml, the solution was cooled at room temperature. The separated yellow solid was filtered, washed with hot methanol and dried at 100°. Yield 0.210 g (92%); m.p. >250°.

(8a) Preparation of [WO_2(van-INH)(MeOH)]

The orange coloured complex [WO_2(van-INH)(MeOH)] was prepared according to the above procedure **(7a)** by the reaction of the ligand [H_2van-INH] (0.135 g. 0.0005 mol) in 25 ml methanol and $WO_2(acac)_2$ (0.207 g, 0.0005 mol) in 10 ml methanol. Yield 0.230 g (94%); m.p. >250°.

(9a) Preparation of [WO_2(hap-BZH)]

$WO_2(acac)_2$ (0.207g, 0.0005 mol) in 10 ml methanol was added to a refluxing solution of the ligand [H_2hap-BZH] (0.127 g, 0.0005 mol) in methanol (25 ml). The resulting solution was filtered and the filtrate was again refluxed on a waterbath for 6h. After reducing the volume of the solvent, the mixture was cooled at 0° overnight. The separated orange coloured complex was filtered and dried at 100°. Yield 0.210 g (90%); m.p. >250°.

(10a) Preparation of [WO_2(hap-SZH)]

The orange coloured complex [WO_2(hap-SZH)] was prepared by the reaction of the ligand [H_2hap-SZH] (0.135 g, 0.0005 mol) in 50 ml methanol and $WO_2(acac)_2$ (0.207 g, 0.0005 mol) in 10 ml methanol according to the above mentioned procedure **(9a)**. Yield 0.210 g (87%); m.p. >250°.

(11a) Preparation of [WO_2(hap-FAH)]

$WO_2(acac)_2$ (0.207 g, 0.0005 mol) in 10 ml methanol was added to a refluxing solution of the ligand [H_2hap-FAH] (0.122 g, 0.0005 mol) in 25 ml of methanol. The resulting mixture was filtered immediately and the solution refluxed on a waterbath for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated orange solid product was filtered, washed with hot methanol and dried at 100°. Yield 0.210 g (87%); m.p. >250°.

(12a) Preparation of [WO_2(hap-INH)]

The orange coloured complex [WO_2(hap-INH)] was prepared by the reaction of the ligand [H_2hap-INH] (0.127 g, 0.0005 mol) in 25 ml methanol and $WO_2(acac)_2$ (0.207 g, 0.0005 mol) in 10 ml methanol according to the above mentioned procedure **(11a)**. Yield 0.215 g (82%); m.p. >250°.

The analytical and physicochemical data of the complexes are presented in Tables 5.1, 5.2 and 5.3.

X-ray data collection and analysis

A single crystal of [WO_2(sal-BZH)(MeOH)].MeOH suitable for X-ray structure determination was grown by slow evaporation of MeOH solution of [WO_2(sal-BZH)(MeOH)] at room temperature. A bright yellow crystal having dimensions of 0.2 X 0.4 X 1.2 mm was mounted on a glass fiber for data collection. Accurate unit cell parameters were determined by least squares fit of 25 machine centered reflections 30 < 2θ < 44°. Data were collected at 293 K on a Nonius CAD-4F single crystal X-ray diffractometer using MoK$_\alpha$ radiation (λ = 0.7107 Å). Three standard reflections measured after every hour showed < 4% variation in average intensity. The structure was solved by direct methods using MULTAN-80. Least squares refinement of the scale factor, positional and anisotropic thermal parameters for nonhydrogen atoms converged to final R = 0.050. Weights based on counting statistics were used. Coordinates of hydrogen atoms were geometrically determined and held fixed during the refinement. The hydrogen atom scattering contribution was included in all subsequent calculations. For structure solution and refinement NRCVAX programs were used.[13] The crystal data, data collection and refinement parameters are summarized in Table 5.4. Final atomic parameters along with their esd's and equivalent isotopic thermal parameters for non-hydrogen atoms are given in Table 5.5. Table 5.6 gives bond lengths and bond angles.

5.3 RESULTS AND DISCUSSION

The use of [$WO_2(acac)_2$] as a starting material for the dioxotungsten(VI) complexes has only recently been reported.[7] The [$WO_2(acac)_2$] undergoes ligand exchange reaction with the Schiff bases I, II and III in refluxing methanol to yield the corresponding dioxotungsten(VI) complexes of the type

$[WO_2L(MeOH)]$ or $[WO_2L]$ (where LH_2 = Schiff base) as follows:

$$[WO_2(acac)_2] + LH_2 \xrightarrow[MeOH]{} [WO_2L(MeOH)]/[WO_2L] + 2acacH$$

The analytical data support the above formulation of the complexes. Under the present reaction conditions complete removal of two bidentate acetylacetone groups occurs; as the Schiff bases are tridentate, the sixth position is occupied by the solvent. The analytical and spectroscopic data suggest an octahedral arrangement around the tungsten atom in complexes **(1a-8a)**. In the case of complexes derived from *o*-hydroxy acetophenone **(9a-12a)** there is no indication of coordination of methanol molecule. Thus an oligomeric type of structure may be suggested for these complexes as in the case of analogous Mo(VI) complexes.[8] In DMSO this oligomeric bridge breaks and the sixth coordination site is occupied by DMSO molecule, thus giving a regular octahedral geometry around the tungsten atom. These complexes are soluble in coordinating solvents like methanol, ethanol, pyridine, DMF and DMSO.

All the complexes are non-electrolytes (11-20 ohm^{-1} mol^{-1} cm^2) in DMF and are diamagnetic as expected for the $5d^o$ tungsten ion. The thermal analysis data for $[WO_2(sal\text{-}INH)(MeOH)]$ shows a well defined endothermic step at around 200°, corresponding to the loss of one molecule of methanol. This information is in agreement with the coordination of the methanol molecule at the sixth position of the metal complexes.

IR Spectral studies

A partial listing of the IR spectra of the ligands and their dioxotungsten(VI) complexes is given in Table 5.2. In the Schiff base [H_2sal-BZH], a broad band due to intramolecularly hydrogen bonded phenolic hydroxyl group is observed at 2880 cm^{-1}. The presence of ν(C=O) band at 1671 cm^{-1} and ν(NH) band at 3260 cm^{-1} indicates the existence of the ligand in the keto form. The ν(C=N) band is observed at 1604 cm^{-1} as a sharp band. A similar pattern of bands is observed in rest of the Schiff bases **(2a-12a)**.

In the dioxotungsten(VI) complex [WO_2(sal-BZH)(MeOH)] **(1a)**, the ligand bands due to ν(C=O) and ν(NH) at 1671 and 3260 cm^{-1}, respectively are absent indicating the destruction of the carbonyl moiety due to enolization and subsequent proton replacement with the tungsten.[14] The band due to ν(OH) at 2680 cm^{-1} is also absent in the complex suggesting the coordination of phenolic oxygen after deprotonation. The band due to ν(C=N) at 1604 cm^{-1} in the Schiff base shifts to lower frequency and is observed at 1601 cm^{-1} indicating the coordination of the lone pair of electrons present in the azomethine nitrogen atom.[15] A new band appearing at 1269 cm^{-1} is assigned to the ν(C-O)(enolic mode). A broad band is observed in the complex at 3380 cm^{-1} due to ν(OH) of the coordinated methanol. This is further supported by the appearance of another new band at 986 cm^{-1} due to ν(C-O) stretch; ν(C-O) band in methanol occurs at 1034 cm^{-1}. The characteristic bands due to ν(O=W=O) stretches are observed at 929 and 896 cm^{-1}, respectively suggesting the presence of a *cis*-WO_2 structure as the *trans*-WO_2 structure would show only one ν(O=W=O) band due to the asymmetric stretch.[8] The other complexes **2a-8a** show coordinated ν(C=N) at ~1600 cm^{-1}, ν(C-O)(phenolic) at ~1550 cm^{-1} and ν(C-O)(enolic) at ~1280 cm^{-1}. The ν(C-O) due to coordinated methanol appears in the region 970-990 cm^{-1}. These complexes show bands due to ν_{sym}(O=W=O) and ν_{asym}(O=W=O) stretches in the region 910-948 and 875-915 cm^{-1}, respectively.

In the case of complexes **(9a-12a)** the ν(OH) bands due to coordinated methanol at ~3400 cm^{-1} and 970-1000 cm^{-1} are absent suggesting the formation of complexes of the type [WO_2L] where the sixth coordination position is satisfied by $W{=}O\rightarrow W$ bridging from the adjacent molecule. This is further supported by the presence of a band due to $\nu(W{=}O\rightarrow W)$ at 800 cm^{-1}, suggesting the formation of $[(WO_2)L]_n$ type complexes. However, in the DMSO adducts **(9b** and **10b)** the band due to $\nu W{=}O\rightarrow W$ is absent suggesting the coordination of DMSO molecule in the vacant coordination site of the metal. The shift of the S-O stretching to lower frequency (~985 cm^{-1}) compared with the value of 1045 cm^{-1} in free sulphoxide, further supports the coordination of

DMSO. The 685 cm^{-1} band of the free sulphoxide due to C-S stretching vibration, undergoes a shift to higher value (~705 cm^{-1}) in the complexes.[16]

^1H *NMR Spectral Studies*

^1H NMR spectra of the Schiff bases and their complexes were recorded in dmso-d_6. The chemical shifts (δin ppm) relative to DMSO (2.40 ppm) are summarized in Table 5.3. The Schiff base [H_2sal-BZH] exhibits a signal at 11.30 ppm due to NH proton which suggests the ligand to be in the keto form. The phenolic OH is observed at 12.10 ppm which is confirmed by D_2O exchange studies. A sharp band due to -CH=N is observed at 8.60 ppm. A similar pattern of signals is observed in the ^1H NMR spectra of the rest of the Schiff bases **(2-12)**. In case of Schiff bases derived from *o*-hydroxyacetophenone **(9-12)** the band due to methyl protons appear in the region 2.30-2.45 ppm. The Schiff bases derived from salicyl hydrazide exhibit a broad band at 11.55 ppm (2H) due to the phenolic proton of the salicyl hydrazide residue and the NH proton.

In the complex [WO_2(sal-BZH)(MeOH)], the signal due to phenolic OH at 12.10 ppm is absent suggesting the coordination of the phenolic oxygen after deprotonation. The resonance due to the NH proton at 11.30 ppm is also absent suggesting the enolization followed by coordination of the enolic oxygen atom after proton replacement. The band due to azomethine proton shifts downfield to 8.95 ppm suggesting the coordination of the lone pair of electrons present in the nitrogen atom.[14] The coordination of methanol molecule is confirmed by the presence of a sharp singlet at 3.30 ppm due to CH_3 protons. In the case of the complexes obtained from salicyl hydrazone Schiff bases (*i.e.* Schiff bases **3** ,**4** and **10**), the presence of a singlet at 11.2 ppm (1H) indicates the existence of one free hydroxyl group in these complexes. Thus the ^1H NMR data also suggest the dibasic tridentate behaviour of the Schiff bases. The absence of methyl proton signals due to coordinated methanol in the complexes **9a–12a** confirms the oligomeric nature of the complexes. Similar conclusion has also been drawn by IR spectral data.

Electronic Spectral Studies

The Schiff bases exhibit two to four electronic spectral bands which are also observed in the complexes (see Table 5.2). In addition, the complexes obtained from isonicotinoyl hydrazone exhibit a new band ~405 nm which is assigned to the ligand ⟶ metal charge transfer (lmct) transition between the lowest empty d-orbital of tungsten and the highest occupied ligand molecular orbital. However, in other complexes, such lmct band could not be located probably due to merging of this band with those of the ligand.

Electrochemical properties

The cyclic voltammograms (CV) of [WO_2(sal-INH)(MeOH)] **(7a)** and [WO_2(van-INH)(MeOH)] **(8a)** were recorded in dmf using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Both complexes show a quasireversible wave with a peak separation of 260 mV and 480 mV at E_{pc} values of -1.48 V and -1.0 V, respectively, vs. SCE. The cyclic voltammogram of **8a** is presented in Fig.5.7. A comparison of the electrochemical data (peak potential) available for similar dioxotungsten(VI) complexes suggests that this is probably due to a W(VI) to W(IV) reduction.[3b] An attempt to do coulometry and isolate the W(IV) complexes was not successful due to decomposition of the latter.

Crystal structure of [WO_2(sal-BZH)(MeOH)]

The X-ray diffraction study of the complex [WO_2(sal-BZH)(MeOH)] **(1a)** reveals that the asymmetric unit consists of two molecules of the coordinated complex along with a solvated methanol and these are related by a pseudocentre. The perspective view of the molecules in asymmetric unit along with the crystallographic numbering of atoms is given in Figure 5.8. The complex contains a usual *cis*-dioxo group and a *mer* arrangement of the tridentate ONO donor ligand, whose anionic oxygen atoms are mutually *trans* and are *cis* to the two oxo ligands. Similar arrangement has also been found in [WO_2(5-*t*-butsal-OAP)(MeOH)] (where 5-*t*-butH_2sal-OAP = Schiff base derived from 5-*t*-butylsalicylaldehyde and *o*-aminophenol).[7] The X-ray structure also shows that the ligand [H_2sal-BZH] forms one five membered ring and one six membered ring. The sixth coordination site around tungsten is occupied by a methanol molecule which is *trans* to the oxygen of the dioxo group. Thus tungsten has a distorted octahedral coordination. The *cis* bond angles range from 79.4(8)^o to 111.3(9)^o and trans angles from 147.6(8)^o to 167.8(8)^o. These distortions are probably due to the incorporation of tungsten into the five membered ring. Thus the structure also resembles that of the known *cis*-dioxomolybdenum(VI) complexes, [MoO_2(sal-INH)MeOH][17] and [MoO_2(5-t-butsal-OAP)].[18] The W-O single bond distances are comparable to those found in other related complexes and even in W(VI) alkoxides.[7,19] W=O bond lengths are 1.59(2) and 1.74(2) Å. An interesting feature is the 0.15 Å difference in the bond lengths of two W=O bonds; a similar difference of 0.12 Å has also been observed in the structure of [WO_2(5-*t*-butsal-OAP)(MeOH)][7]. The structure is stabilized by the intermolecular hydrogen bonding between the oxygen of the solvent molecule and that of coordinated methanol [O(6′).....O(5) (1 + x, y, z) = 2.591(9) Å; O(6) .....O(5′) ($\bar{x}$, $\bar{y}$, 1/2 + z) = 2.624(8) Å] and the bifurcated hydrogen bond between the oxygen of the solvent methanol and oxygen of one of the dioxo group [O(6).....O(2′) ($\bar{x}$, $\bar{y}$, 1/2 + z) = 2.723(9) Å].

5.4 CONCLUSION

From the spectroscopic data, it can be concluded that the complete removal of the two bidendate acetylacetone takes place from the precursor $[WO_2(acac)_2]$ by the ONO donor ligands; the sixth position is occupied by the solvent. In the case of complexes derived from *o*- hydroxyacetophenone, the coordination of the solvent (MeOH) is not observed suggesting a pseudo-octahedral structure as in the case of their dioxomolybdenum(VI) analogues. Electrochemical studies using 10^{-3} M solution of the complexes in DMF indicate a kinetically facile W(VI) to W(IV) reduction. The single crystal X-ray diffraction studies of one of the complexes indicate that the complex contains a usual *cis*-dioxo group and a *mer* arrangement of the tridentate ONO donor ligand whose anionic oxygen atoms are mutually *trans* and are *cis* to the two oxo ligands.

Table 5.1. Analytical and physicochemical data of the dioxo tungsten(VI) complexes.

S. No.	Compound/ stoichiometry	Colour	Found(Cal.)% C	 H	 N	Λ_M ($\Omega^{-1}cm^2\ mole^{-1}$)
1a	$[WO_2(sal\text{-}BZH)(MeOH)]$ $C_{15}H_{14}N_2O_5W$	Yellow	36.91 (37.06)	2.95 (2.90)	5.52 (5.76)	11
2a	$[WO_2(van\text{-}BZH)(MeOH)]$ $C_{16}H_{16}N_2O_6W$	Brown	37.41 (37.23)	3.33 (3.12)	5.19 (5.43)	20
3a	$[WO_2(sal\text{-}SZH)(MeOH)]$ $C_{15}H_{14}N_2O_6W$	Yellow	35.97 (35.88)	2.63 (2.81)	5.32 (5.58)	13
4a	$[WO_2(van\text{-}SZH)(MeOH)]$ $C_{16}H_{16}N_2O_7W$	Brown	36.35 (36.11)	3.14 (3.03)	5.33 (5.26)	12
5a	$[WO_2(sal\text{-}FAH)(MeOH)]$ $C_{13}H_{12}N_2O_6W$	Yellow	32.59 (32.79)	2.54 (2.54)	5.87 (5.88)	14
6a	$[WO_2(van\text{-}FAH)(MeOH)]$ $C_{14}H_{14}N_2O_7W$	Yellow	33.00 (33.22)	2.58 (2.79)	5.36 (5.54)	13
7a	$[WO_2(sal\text{-}INH)(MeOH)]$ $C_{14}H_{13}N_3O_5W$	Yellow	34.50 (34.52)	2.61 (2.69)	8.45 (8.63)	12
8a	$[WO_2(van\text{-}INH)(MeOH)]$ $C_{15}H_{15}N_3O_6W$	Orange	34.81 (34.84)	2.82 (2.92)	8.41 (8.13)	12
9a	$[WO_2(hap\text{-}BZH)]$ $C_{15}H_{12}N_2O_4W$	Orange	38.40 (38.48)	2.40 (2.58)	5.50 (5.98)	4.5
9b	$[WO_2(hap\text{-}BZH)(DMSO)]$ $C_{17}H_{18}N_2O_5SW$	Yellow	37.00 (37.38)	2.80 (3.32)	5.00 (5.13)	
10a	$[WO_2(hap\text{-}SZH)]$ $C_{15}H_{12}N_2O_5W$	Orange	37.00 (37.21)	2.10 (2.50)	5.35 (5.79)	12
10b	$[WO_2(hap\text{-}SZH)(DMSO)]$ $C_{17}H_{18}N_2O_6SW$	Yellow	36.00 (36.31)	2.90 (3.23)	4.55 (4.98)	
11a	$[WO_2(hap\text{-}FAH)]$ $C_{13}H_{10}N_2O_5W$	Orange	33.80 (34.08)	2.00 (2.20)	5.90 (6.12)	9
12a	$[WO_2(hap\text{-}INH)]$ $C_{14}H_{11}N_3O_4W$	Orange	35.40 (35.84)	2.10 (2.36)	8.60 (8.96)	14

Table 5.2. IR[a] and electronic spectral data.

Compound[b]	ν(C=O)	ν(-CH=N)	ν_{sym}(O=U=O)	ν_{asym}(O=U=O)	Electronic spectra (nm) (ϵ = l mole^{-1} cm^{2})
1	1671	1604			380(3048), 327(30518), 298(38292), 286(36959)
1a		1601	928	896	392(4284), 326(24000), 297(29947), 286(30157)
2	1668	1622			348((16891), 317(33851)
2a		1595	944	890	380(13536), 362(19174), 349(19587), 315(31746)
3	1654	1617			380(21839), 362(28846), 349(29487), 301(22916)
3a		1602	949	899	381(4602), 333(14958), 290(14079)
4	1648	1606			380(28823), 365(40441), 349(41397), 316(48345)
4a		1594	917	875	368(5605), 313(14087)
5	1650	1605			328(18173), 300(23923), 289(21096)
5a		1599	910	880	378(2619), 328(18571), 300(25476), 289(23492)
6	1673	1611			341(26115), 311(69736), 303(74276)
6a		1599	951	908	341(15580), 312(35881), 302(38243)
7	1680	1610			332(19935), 300(20215), 289(21293)
7a		1601	930	915	402(2341), 330(21887), 298(24188), 288(26989)
8	1609	1603			342(21527), 305(46631)
8a		1600	948	909	412(1301), 336(12898), 303(30510)
9	1650	1606			385(1404), 322(8553), 281(15574)
9a		1595	949, 883	807	373(5685), 316(9698), 278(15351)

10	1620	1607			381(9049), 333(15135), 296(14162)
10a		1598	951, 884	788	373(9048), 325(11194), 284(14141)
11	1651	1602			327(19265), 296(28979), 286(29551)
11a		1599	953, 883	795	376(6735), 322(9609), 285(13793)
12	1679	1609			382(1702), 330(11382), 285(13851)
12a		1592	961, 878	813	381(2564), 318(5769),280(8974)

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[a] IR data are in cm^{-1}.

[b] For abbreviations see Table 5.1.

Table 5.3. ^1H NMR spectral data(δ in ppm)[a]

Compound	-CH=N-	Aromatic protons	$-OCH_3$	$-CH_3$	- NH	-OH
1	8.60(s, 1H)	6.90(m, 2H), 7.25(m, 1H), 7.55(m, 4H), 7.90(m, 2H)			11.30(s, 1H)	12.10(s, 1H)
1a	8.95(s, 1H)	7.05(m, 2H), 7.55(m, 4H), 7.75(d, 1H), 8.00(d, 2H)		3.30(s, 3H)		
3	8.76(s, 1H)	6.96 - 8.02(m, 8H)			10.86(s, 1H)	11.64(s, 2H)
3a	9.10(s, 1H)	7.00(m, 4H), 7.45(m, 1H), 7.60(m, 1H), 7.70(m, 1H), 7.80(m, 1H)		3.15(s, 3H)		
4	8.68(s, 1H)	6.90 - 8.00(m, 7H)	3.74(s, 3H)		10.84(s, 1H)	12.18(s, 2H)
4a	9.05(s, 1H)	7.05(m, 3H), 7.20(m, 2H), 7.50(m, 1H), 7.80(m, 1H)	3.85(s, 3H)	b		
5	8.65(s, 1H)	6.70(s, 1H), 6.90(m, 2H), 7.35(m, 2H), 7.50(d, 1H), 7.95(s, 1H)			11.15(s, 1H)	12.10(s, 1H)
5a	8.95(s, 1H)	6.70(m, 1H), 7.00(m, 2H), 7.25(d, 1H), 7.60(m, 1H), 7.70(d, 1H), 8.00(s, 1H)		3.20(s, 3H)		
6	8.60(s, 1H)	6.70(m, 1H), 6.80(t, 1H), 7.00(m, 1H), 7.10(d, 1H), 7.30(d, 1H), 7.95(d, 1H)	3.85(s, 3H)			
6a	8.85(s, 1H)	6.75(m, 1H), 7.05(t, 1H), 7.30(m, 3H), 7.95(t, 1H)	3.80(s, 3H)	3.15(s, 3H)		
7	8.70(s, 1H)	6.90(m, 2H), 7.25(m, 1H), 7.55(m, 1H), 7.85(d, 2H), 8.80(d, 2H)			11.15(b, 1H)	12.28(b, 1H)
7a	9.05(s, 1H)	7.05(m, 2H), 7.60(t, 1H), 7.75(d, 1H), 7.80(d, 2H), 8.80(d, 2H)		3.20(s, 3H)		
8	8.71(s, 1H)	6.88 - 8.81(m, 7H)	3.83(s, 3H)		10.71(s, 1H)	12.27(s, 1H)
8a	9.00(s, 1H)	7.05(t, 1H), 7.35(d, 2H), 7.85(d, 2H) 8.80(b, 2H)	3.85(s, 3H)	3.20(s, 3H)		
9		6.90 - 7.85(m, 9H)	2.45(s, 3H)[c]		9.05(s, 1H)	12.75(s, 1H)
9a		7.10 - 8.05(m, 9H)	2.93(s, 3H)[c]			

10	6.80 - 7.95(m, 8H)	2.45(s, 3H)[c]	(not located)	11.55(b, 1H) 13.15(s, 1H)
10a	7.00 - 8.00(m, 8H)	2.83(s, 3H)[c]		11.40(s, 1H)
11	6.55 - 7.50(m, 7H)	2.35(s, 3H)[c]	9.25(s, 1H)	12.65(s, 1H)
11a	6.60 - 8.00(s, 7H)	2.85(s, 3H)[c]		
12	6.90 - 8.80(m, 8H)	2.50(s, 3H)[c]	11.60(s, 1H)	13.25(s, 1H)
12a	7.05 - 8.80(m, 8H)	2.95(s, 3H)[c]		

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[a] Letters given in parentheses indicate the type of signal. s = singlet, d = doublet, t = triplet, b = broad, m = multiplet.

[b] CH_3 of MeOH resonance appears underneath of dmso resonance.

[c] CH_3 of the *o*- hydroxy acetophenone residue.

Table 5.4. Crystal and refinement data for 1a.MeOH

Molecular formula	$C_{16}H_{18}N_2O_6W$
Formula weight	518.2
Crystal dimension	0.2 X 0.4 X 1.2 mm
Crystal colour	bright yellow
Space group	$Pbc2_1$
Cell dimensions (Å)	
a	6.992(2)
b	16.190(2)
c	31.390(4)
Cell volume(Å)^3	3553.4(12)
Z	8
F(000)	1999
D_{cal} (gm/cm^3)	1.937
Temperature (K)	293
Radiation	Graphite monochromated MoK$_\alpha$ radiation (λ = 0.7107 Å)
μ(MoK$_\alpha$) (mm^{-1})	6.67
Scan technique	$W/2\theta$
Scan speed (^{o}min^{-1})	1
Scan width (^{o})	$0.80 + 0.35\ tg\theta$
Scan range (^{o})	$0 < 2\theta < 47$
Total no. of unique reflections	2658
Cut of observed data	$3.5\sigma(I)$

No. of observed reflections	2242
No. of parameters refined	450
R_F[a] and R_w[b]	0.050 and 0.054

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[a] $R_F = (\Sigma||F_o| - k|F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma(|F_o|^2)]^{\frac{1}{2}}$.

Table 5.5 Atomic parameters x, y, z and Biso for 1a.MeOH with e.s.d.s. in parentheses.

Atom	x	y	z	Biso(Å)^2
W 1	.1667(1)	.21194(7)	.19047(0)	2.80(5)
O 1	.240(2)	.129(1)	.1688(6)	3.9(9)
O 2	.359(2)	.276(1)	.2037(6)	3.8(10)
O 3	.128(3)	.157(1)	.2468(6)	5.1(11)
O 4	.053(2)	.271(1)	.1424(6)	4.3(10)
O 5	.003(3)	.317(1)	.2261(7)	4.8(10)
N 1	-.141(2)	.166(1)	.1947(7)	2.5(9)
N 2	-.172(3)	.117(1)	.2316(7)	3.1(10)
C 1	-.098(4)	.261(2)	.1144(9)	3.2(13)
C 2	-.085(4)	.308(2)	.0786(10)	4.0(14)
C 3	-.250(5)	.303(2)	.0536(9)	4.4(16)
C 4	-.415(4)	.259(2)	.0641(10)	4.5(16)
C 5	-.412(4)	.213(2)	.1003(10)	4.0(15)
C 6	-.258(4)	.213(2)	.1290(9)	3.5(14)
C 7	-.265(3)	.166(2)	.1661(9)	3.2(13)
C 8	-.022(4)	.118(2)	.2585(9)	3.3(14)
C 9	-.025(4)	.076(2)	.2991(9)	3.3(13)
C10	-.201(5)	.046(2)	.3143(10)	4.7(16)
C11	-.199(4)	.004(2)	.3505(11)	5.0(17)
C12	-.034(6)	-.004(2)	.3753(12)	7.0(22)
C13	.143(5)	.024(2)	.3602(11)	5.9(20)
C14	.141(5)	.066(2)	.3216(11)	5.1(18)
C15	.081(5)	.377(2)	.2534(10)	5.3(18)
O 6	.138(3)	.121(1)	.4755(8)	6.6(15)
C16	.086(5)	.199(2)	.4600(13)	7.2(22)
W 1'	.3648(1)	.04101(7)	.99584(5)	2.67(4)
O 1'	.295(3)	.126(1)	1.0179(7)	4.8(11)
O 2'	.172(3)	-.021(1)	.9827(6)	3.9(9)
O 3'	.408(3)	.101(1)	.9414(6)	4.5(10)
O 4'	.472(3)	-.018(1)	1.0430(6)	4.0(10)
O 5'	.521(3)	.938(1)	.9585(6)	3.6(9)
N 1'	.665(2)	.084(1)	.9908(7)	2.8(10)
N 2'	.714(3)	.128(2)	.9543(7)	3.6(12)
C 1'	.622(4)	-.007(2)	1.0703(9)	3.8(15)
C 2'	.609(4)	-.055(2)	1.1074(9)	4.2(16)
C 3'	.767(4)	-.051(2)	1.1373(10)	4.6(17)
C 4'	.925(4)	-.007(2)	1.1258(9)	4.0(15)
C 5'	.942(4)	.038(2)	1.0882(9)	3.6(14)
C 6'	.780(4)	.035(2)	1.0602(8)	2.7(12)
C 7'	.802(4)	.082(2)	1.0204(8)	2.8(12)
C 8'	.565(4)	.130(2)	.9295(9)	3.7(15)
C 9'	.573(4)	.175(2)	.8825(9)	2.8(12)

C10'	.753(4)	.197(2)	.8703(10)	4.5(16)
C11'	.761(4)	.236(2)	.8317(11)	5.7(19)
C12'	.588(5)	.254(2)	.8116(10)	5.8(20)
C13'	.415(5)	.233(2)	.8267(10)	5.0(18)
C14'	.407(5)	.194(2)	.8658(10)	5.0(17)
C15'	.442(4)	.876(2)	.9369(10)	4.4(16)
O 6'	.667(3)	.375(1)	.2077(8)	6.0(12)
C16'	.620(5)	.452(2)	.2242(13)	6.0(19)

Table 5.6 Bond distances (Å) and bond angles (^{0}) with e.s.d.s. in parentheses.

W(1)-O(1)	1.59(2)	W(1')-O(1')	1.61(2)
W(1)-O(2)	1.74(2)	W(1')-O(2')	1.73(2)
W(1)-O(3)	2.00(2)	W(1')-O(3')	1.99(2)
W(1)-O(4)	1.95(2)	W(1')-O(4')	1.92(2)
W(1)-O(5)	2.34(2)	W(1')-O(5')	2.31(2)
W(1)-N(1)	2.28(2)	W(1')-N(1')	2.22(2)
O(3)-C(8)	1.27(3)	O(3')-C(8')	1.25(3)
O(4)-C(1)	1.38(3)	O(4')-C(1')	1.37(3)
O(5)-C(15)	1.40(3)	O(5')-C(15')	1.34(3)
N(1)-N(2)	1.42(3)	N(1')-N(2')	1.39(3)
N(1)-C(7)	1.25(3)	N(1')-C(7')	1.34(3)
N(2)-C(8)	1.34(4)	N(2')-C(8')	1.30(3)
C(1)-C(2)	1.36(4)	C(1')-C(2')	1.40(4)
C(1)-C(6)	1.43(4)	C(1')-C(6')	1.34(4)
C(2)-C(3)	1.40(4)	C(2')-C(3')	1.45(4)
C(3)-C(4)	1.39(4)	C(3')-C(4')	1.36(4)
C(4)-C(5)	1.36(4)	C(4')-C(5')	1.40(4)
C(5)-C(6)	1.41(4)	C(5')-C(6')	1.43(4)
C(6)-C(7)	1.39(4)	C(6')-C(7')	1.47(4)
C(8)-C(9)	1.45(4)	C(8')-C(9')	1.48(4)
C(9)-C(10)	1.41(4)	C(9')-C(10')	1.43(4)
C(9)-C(14)	1.37(4)	C(9')-C(14')	1.40(4)
C(10)-C(11)	1.32(4)	C(10')-C(11')	1.37(4)
C(11)-C(12)	1.40(6)	C(11')-C(12')	1.40(5)
C(12)-C(13)	1.40(5)	C(12')-C(13')	1.34(5)
C(13)-C(14)	1.39(4)	C(13')-C(14')	1.38(4)
O(6)-C(16)	1.40(4)	O(6')-C(16')	1.40(4)

O(1)-W(1)-O(2)	110.8(9)	O(1')-W(1')-O(2')	111.3(9)
O(1)-W(1)-O(3)	92.4(9)	O(1')-W(1')-O(3')	89.8(10)
O(1)-W(1)-O(4)	102.3(9)	O(1')-W(1')-O(4')	102.3(9)
O(1)-W(1)-N(1)	93.0(8)	O(1')-W(1')-N(1')	92.8(8)
O(2)-W(1)-O(3)	99.2(8)	O(2')-W(1')-O(3')	101.5(8)
O(2)-W(1)-O(4)	102.2(8)	O(2')-W(1')-O(4')	101.3(8)
O(5)-W(1)-O(1)	167.8(8)	O(5')-W(1')-O(1')	166.9(8)
O(5)-W(1)-O(2)	80.3(8)	O(5')-W(1')-O(2')	80.0(8)
O(5)-W(1)-O(3)	80.6(8)	O(5')-W(1')-O(3')	81.3(8)
O(5)-W(1)-O(4)	79.4(8)	O(5')-W(1')-O(4')	81.1(8)
O(2)-W(1)-N(1)	154.9(8)	O(2')-W(1')-N(1')	154.4(9)
O(3)-W(1)-O(4)	147.6(8)	O(3')-W(1')-O(4')	148.2(8)

O(3)-W(1)-N(1)	71.0(8)	O(3')-W(1')-N(1')	69.0(8)
O(4)-W(1)-N(1)	79.5(8)	O(4')-W(1')-N(1')	81.0(8)
O(5)-W(1)-N(1)	75.4(8)	O(5')-W(1')-N(1')	75.1(8)
W(1)-O(3)-C(8)	126(2)	W(1')-O(3')-C(8')	125(2)
W(1)-O(4)-C(1)	139(2)	W(1')-O(4')-C(1')	136(2)
W(1)-O(5)-C(15)	127(1)	W(1')-O(5')-C(15')	128(2)
W(1)-N(1)-N(2)	112(1)	W(1')-N(1')-N(2')	117(2)
W(1)-N(1)-C(7)	128(2)	W(1')-N(1')-C(7')	128(2)
N(2)-N(1)-C(7)	119(2)	N(2')-N(1')-C(7')	115(2)
N(1)-N(2)-C(8)	113(2)	N(1')-N(2')-C(8')	108(2)
O(4)-C(1)-C(2)	114(2)	O(4')-C(1')-C(2')	113(3)
O(4)-C(1)-C(6)	117(2)	O(4')-C(1')-C(6')	123(3)
C(2)-C(1)-C(6)	128(3)	C(2')-C(1')-C(6')	122(3)
C(1)-C(2)-C(3)	112(3)	C(1')-C(2')-C(3')	117(3)
C(2)-C(3)-C(4)	125(3)	C(2')-C(3')-C(4')	118(3)
C(3)-C(4)-C(5)	117(3)	C(3')-C(4')-C(5')	124(3)
C(4)-C(5)-C(6)	123(3)	C(4')-C(5')-C(6')	116(2)
C(1)-C(6)-C(5)	113(3)	C(1')-C(6')-C(5')	122(2)
C(1)-C(6)-C(7)	126(3)	C(1')-C(6')-C(7')	123(2)
C(5)-C(6)-C(7)	121(3)	C(5')-C(6')-C(7')	115(2)
N(1)-C(7)-C(6)	125(2)	N(1')-C(7')-C(6')	122(2)
O(3)-C(8)-N(2)	118(2)	O(3')-C(8')-N(2')	120(3)
O(3)-C(8)-C(9)	120(2)	O(3')-C(8')-C(9')	118(2)
N(2)-C(8)-C(9)	122(2)	N(2')-C(8')-C(9')	120(2)
C(8)-C(9)-C(10)	118(3)	C(8')-C(9')-C(10')	120(2)
C(8)-C(9)-C(14)	119(3)	C(8')-C(9')-C(14')	122(2)
C(10)-C(9)-C(14)	121(3)	C(10')-C(9')-C(14')	118(3)
C(9)-C(10)-C(11)	117(3)	C(9')-C(10')-C(11')	120(3)
C(10)-C(11)-C(12)	122(3)	C(10')-C(11')-C(12')	117(3)
C(11)-C(12)-C(13)	120(3)	C(11')-C(12')-C(13')	124(3)
C(12)-C(13)-C(14)	116(3)	C(12')-C(13')-C(14')	118(3)
C(9)-C(14)-C(13)	120(3)	C(9')-C(14')-C(13')	120(3)

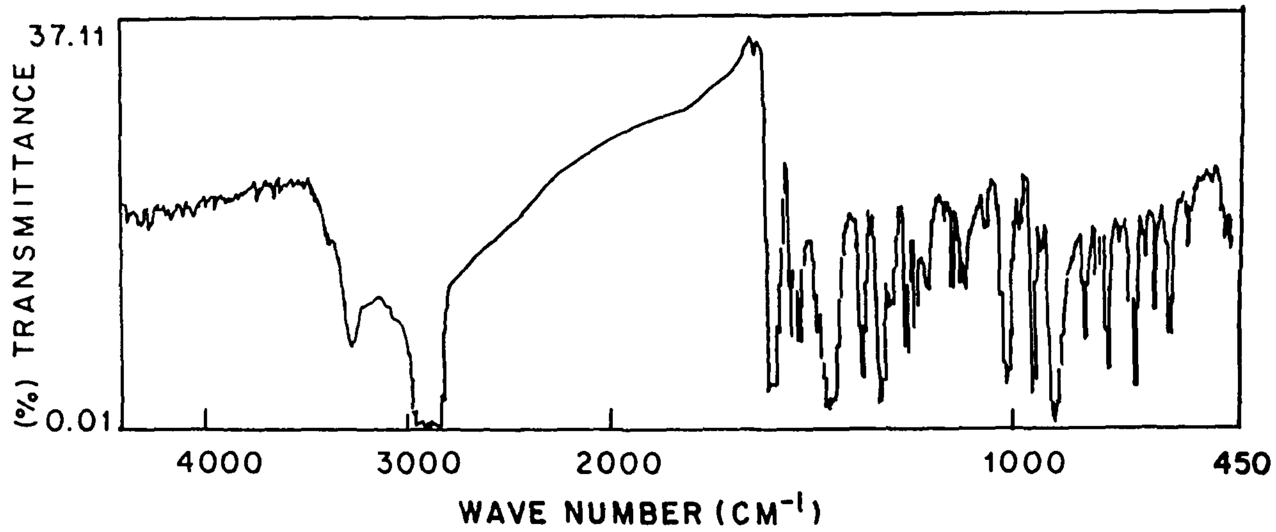

FIG.5.1 : IR SPECTRUM OF [WO_2(Sal-BZH)(MeOH)] IN NUJOL.

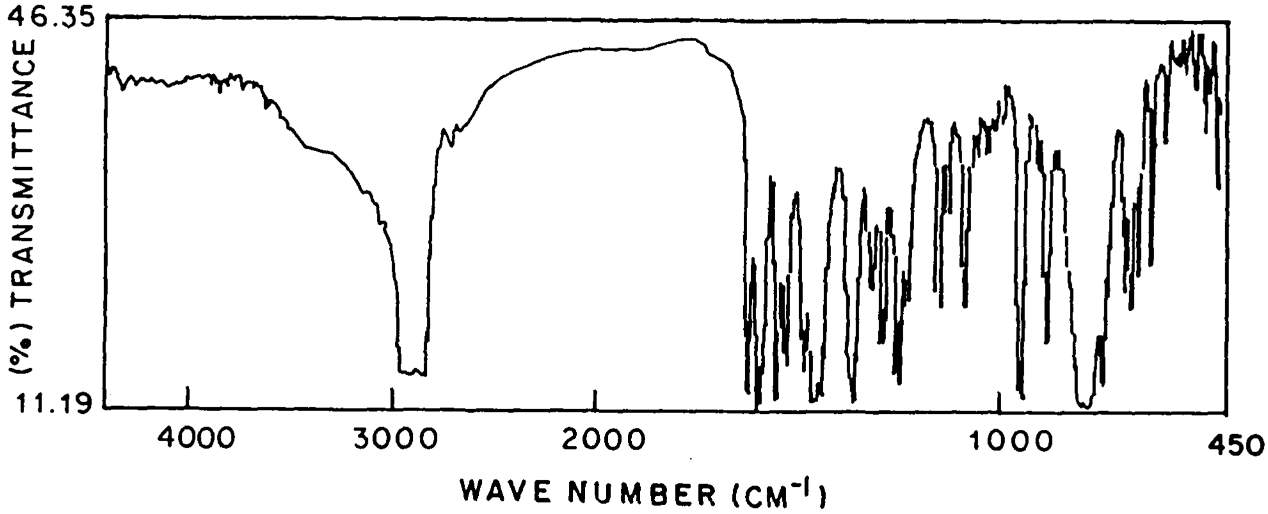

FIG.5.2 : IR SPECTRUM OF [WO_2(hap-SHZ)] IN NUJOL.

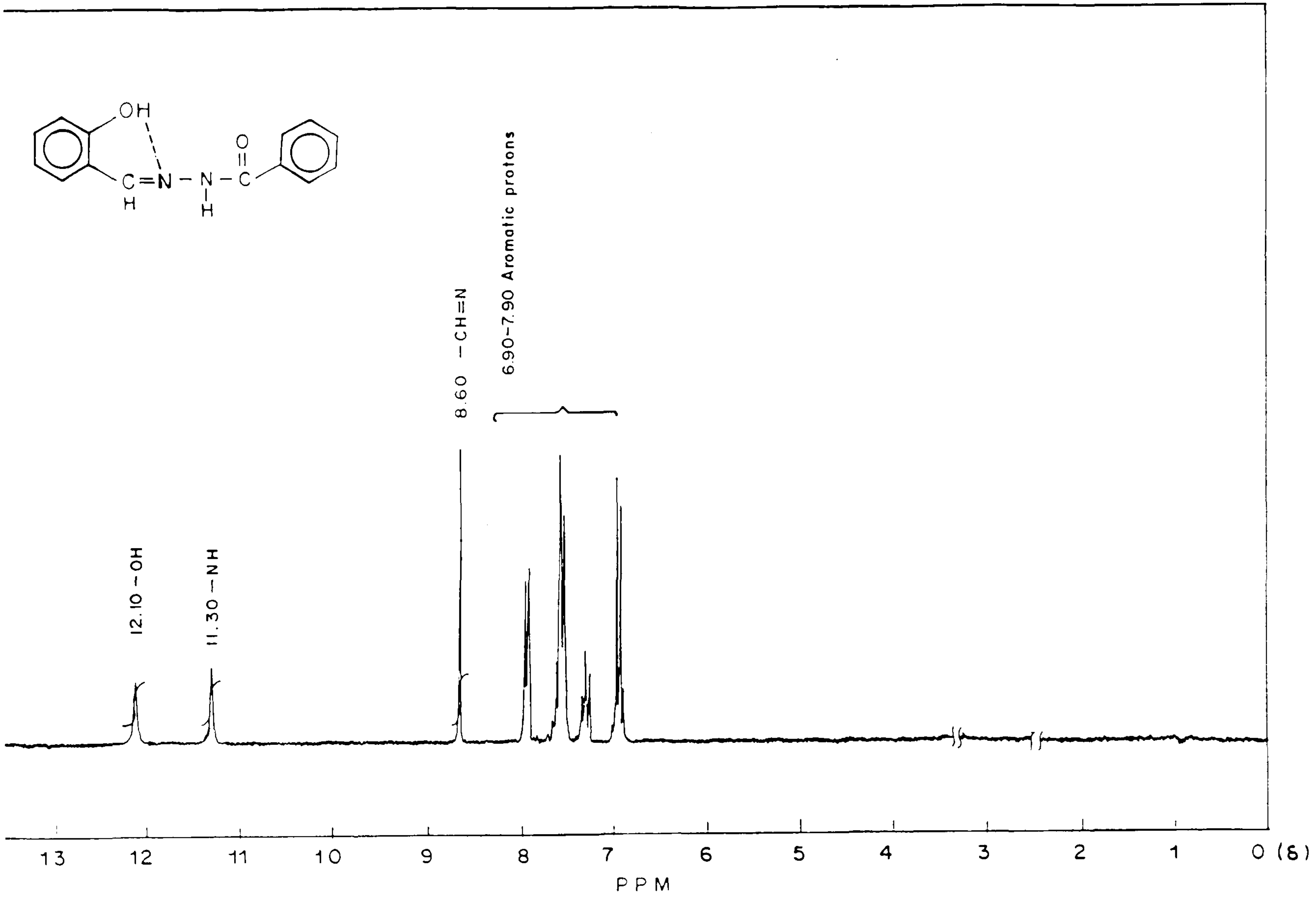

FIG.5.3 : ^{1}H-NMR SPECTRUM OF [H_2Sal - BZH] IN DMSO - d_6.

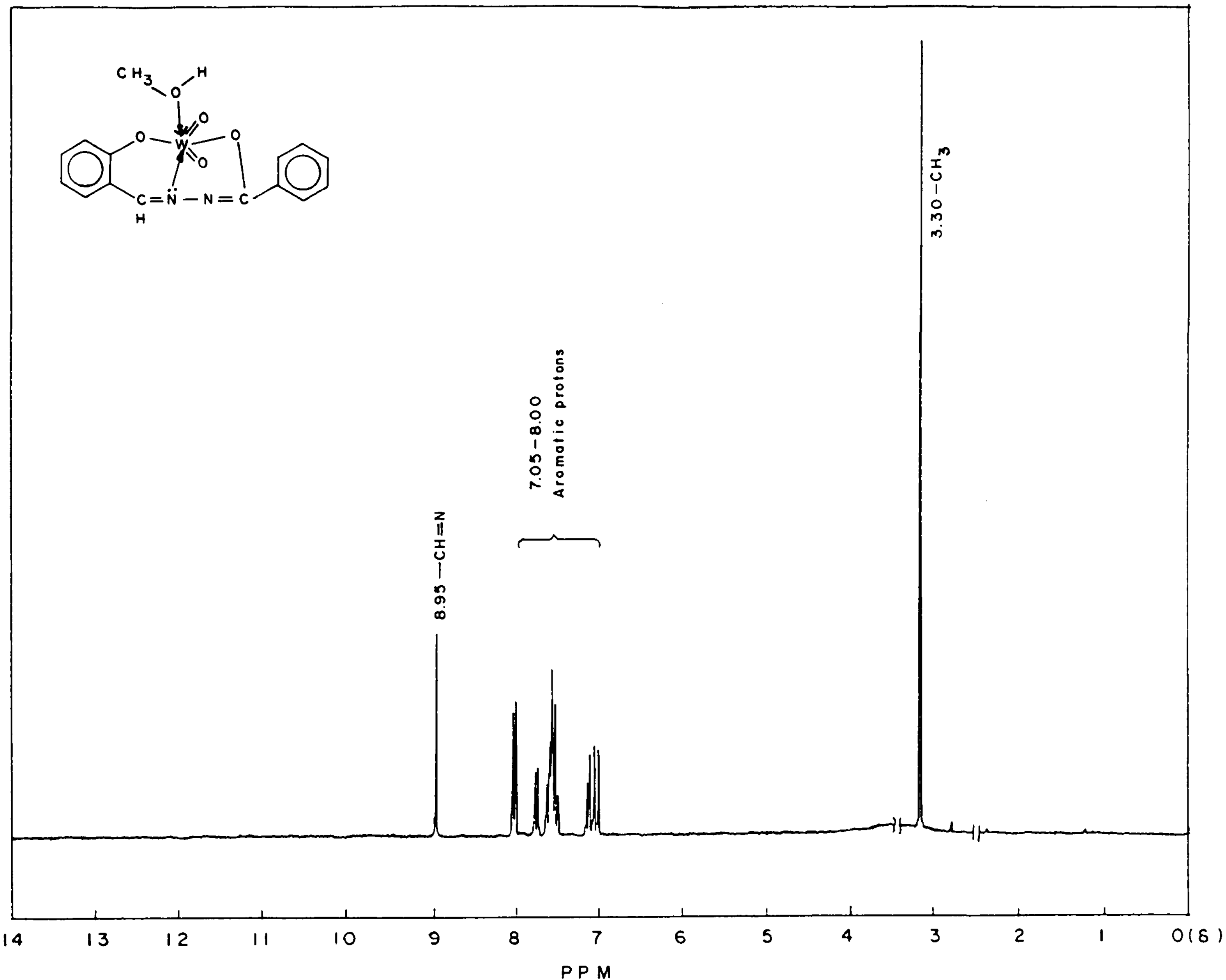

FIG.5.4 : ^1H-NMR SPECTRUM OF $[WO_2(Sal\text{-}BZH)(MeOH)]$ IN DMSO-d_6.

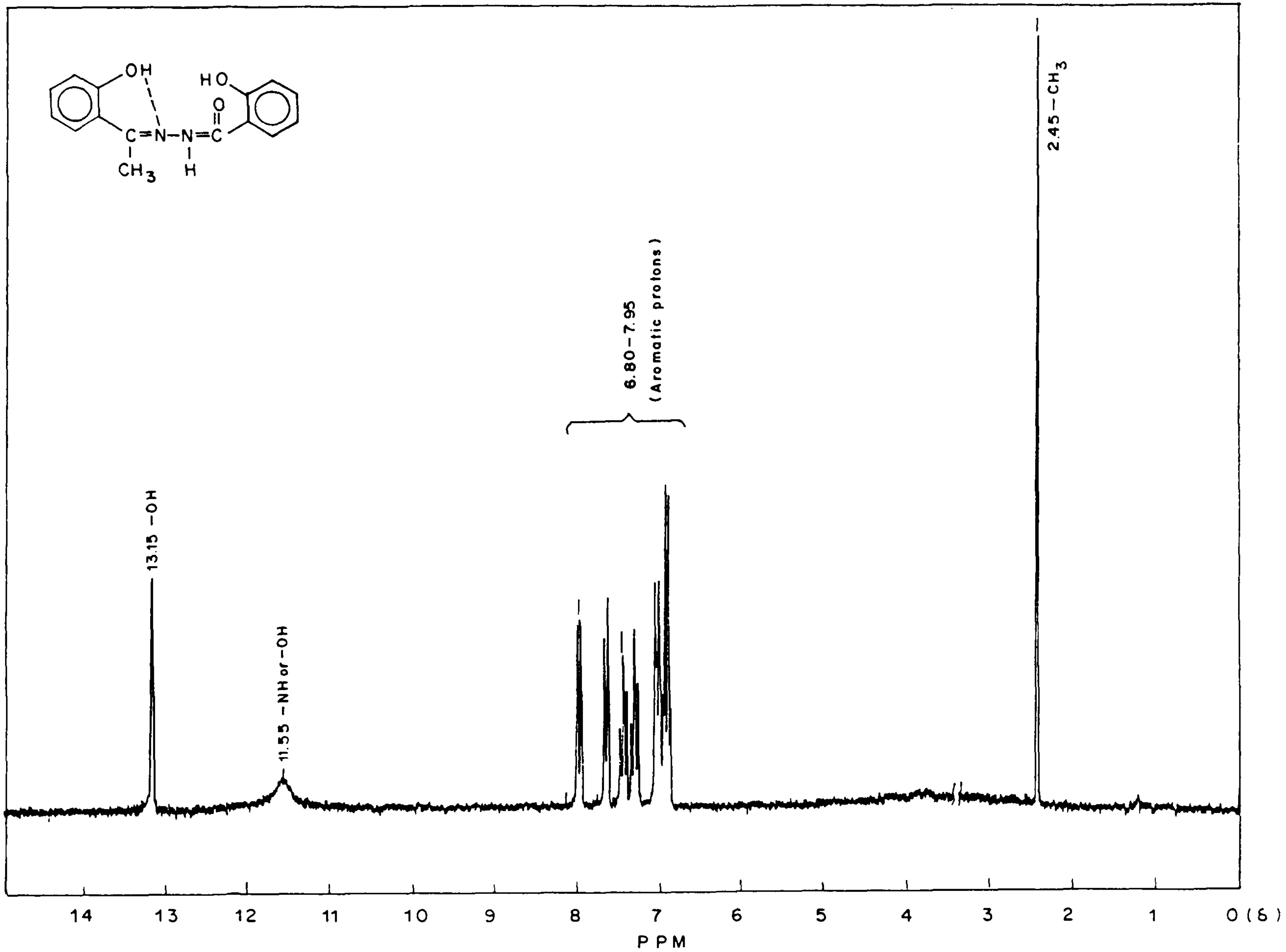

FIG. 5.5 : ^{1}H-NMR SPECTRUM OF [H_2hap-SHZ] IN DMSO-d_6.

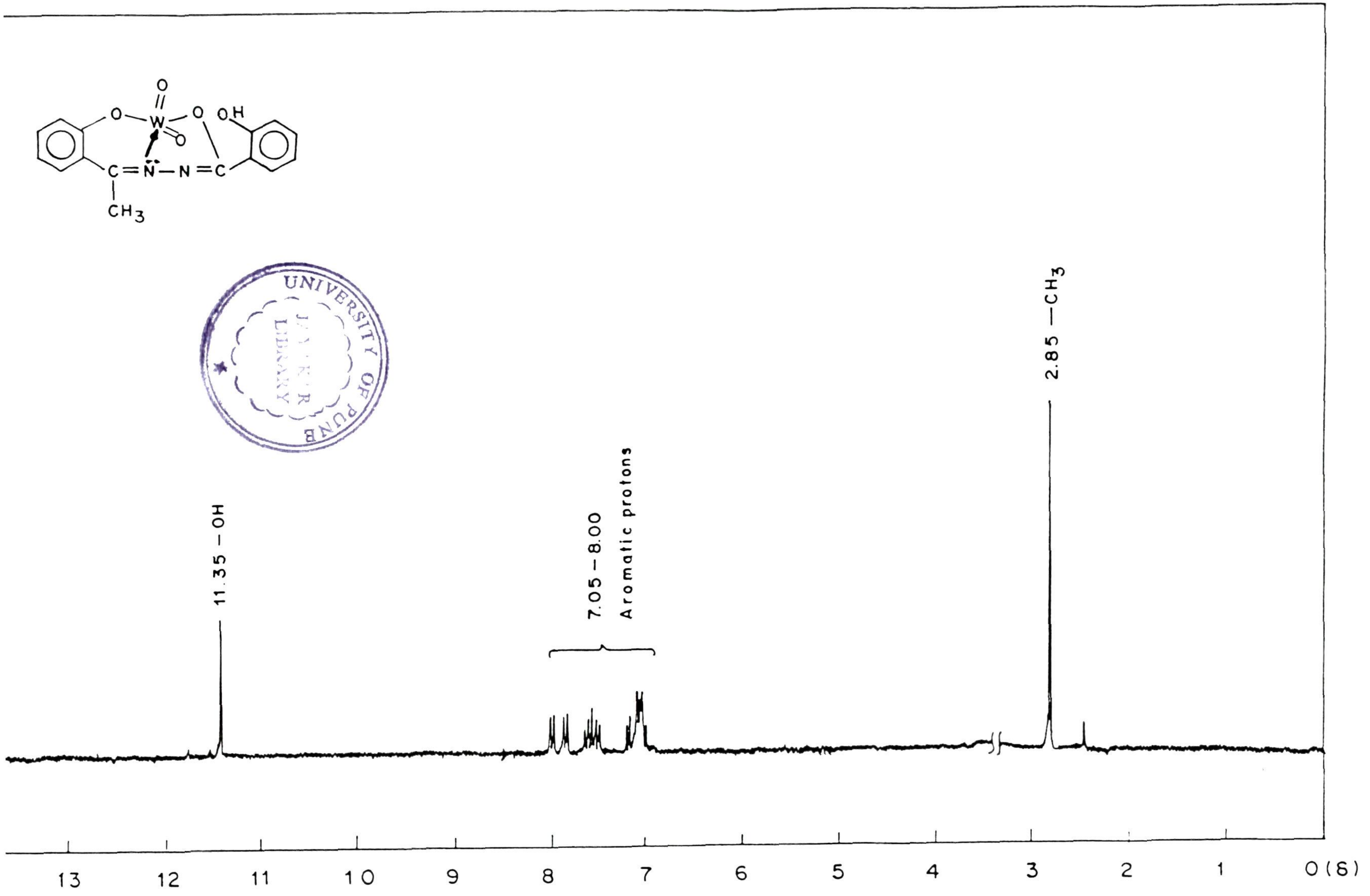

FIG. 5.6 : ^{1}H-NMR SPECTRUM OF [WO_2 (hap-SHZ)] IN DMSO – d6.

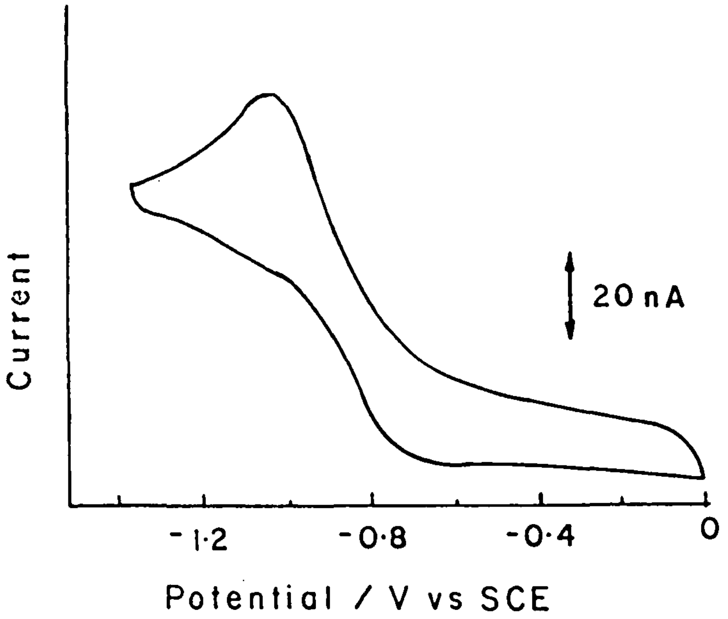

FIG. 5.7 : CYCLIC VOLTAMMOGRAM (1×10^{-3} M IN DMF) OF $[WO_2(VAN-INH)(MeOH)]$ AT SCAN RATE OF 500 mV/S.

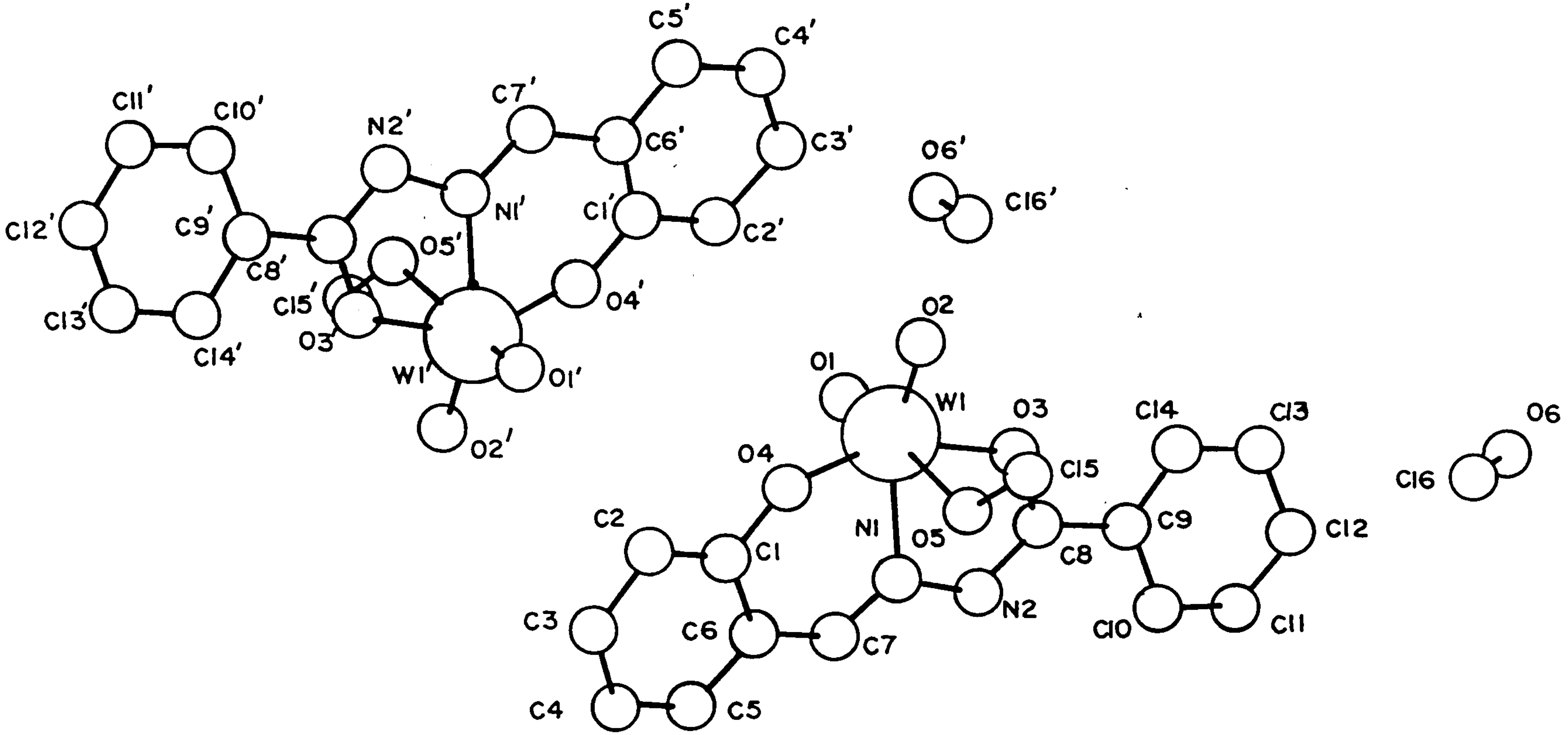

FIG. 5.8 : A PERSPECTIVE VIEW OF THE MOLECULES IN ASYMMETRIC UNIT OF $[(WO_2(o\text{-}OC_6H_4CH{=}NN{=}C(O)C_6H_5)(MeOH)]\cdot MeOH$ ALONG WITH CRYSTALLOGRAPHIC NUMBERING.

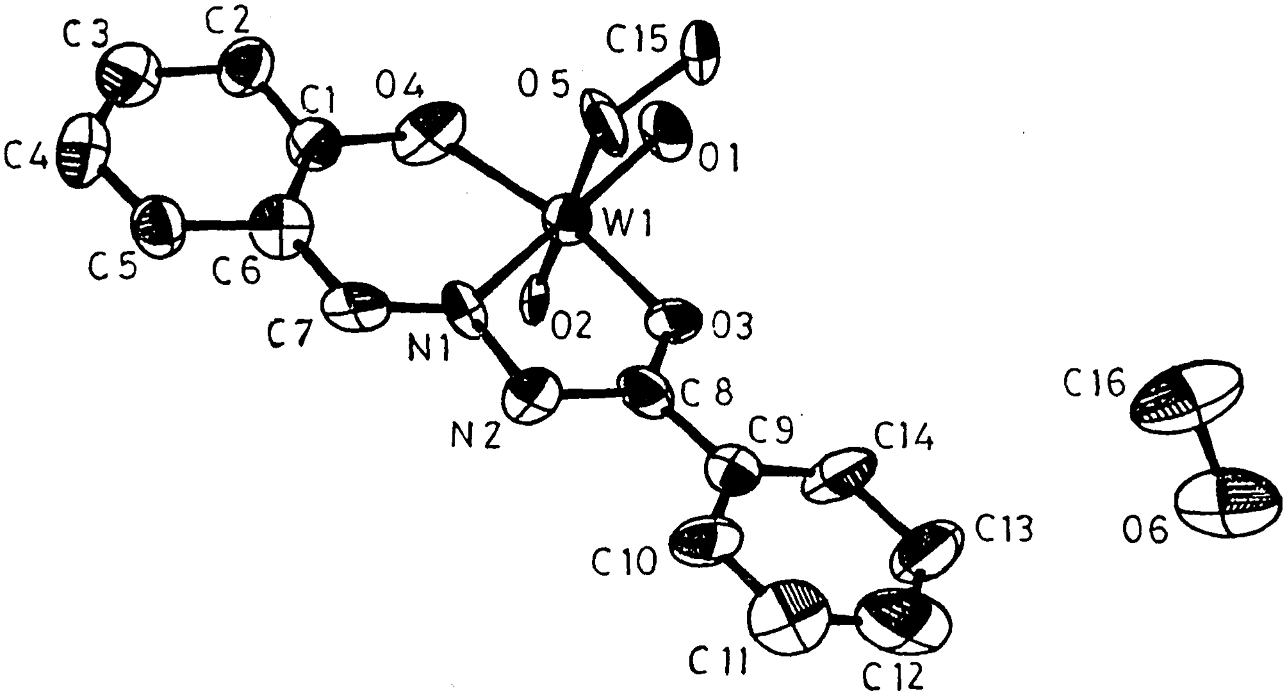

FIG. 5·9 : ORTEP DIAGRAM OF $[WO_2(o\text{-}OC_6H_4CH{=}NN{=}C(O)C_6H_5)(MeOH)]$. MeOH ALONG WITH THE CRYSTALLOGRAPHIC NUMBERING ELLIPSOIDS ARE DRAWN WITH 50% PROBABILITY.

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CHAPTER 6

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SYNTHESIS AND SPECTRAL PROPERTIES OF DIOXOTUNGSTEN(VI) COMPLEXES OF BINUCLEATING ONO⁀ONO DONOR SCHIFF BASES

6.1 INTRODUCTION

Although there has been considerable interest in the coordination compounds of Schiff bases with molybdenum ion[1-4], comparatively very little is known about the coordination compounds of Schiff bases with the analogous tungsten.[5-11]

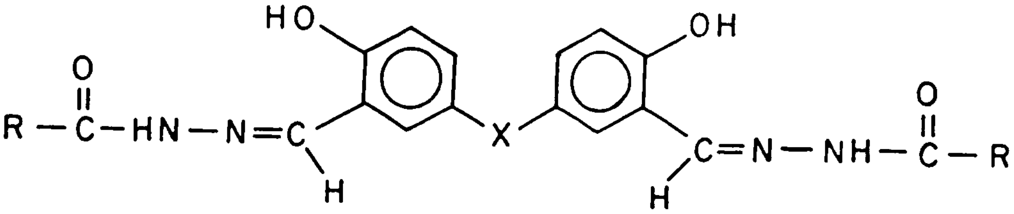
Yamanouchi et. al.[5] have studied the reaction of WO_2Cl_2 with various N-aryl salicylaldimines and observed that the two chlorine atoms remained intact in the complexes suggesting the lone pair (neutral) coordination of the Schiff bases. They have also synthesized oxotungsten(VI) complexes with bi-, tri- and tetradentate Schiff bases obtained from salicylaldehyde and various amines.[6] The following type of complexes have been isolated. (1) $WOCl_3$(bidentate) (2) $WOCl_2$(tridentate) (3) WO_2(tridentate).L (L being DMF, pyridine etc.).

Rice et.al.[7] have synthesized tungsten(V)- and (VI) -oxo complexes and studied by IR and EPR spectroscopy and by electrometry. Cyclic voltammograms of both tungsten(V) and (VI) complexes show reduction peaks that are considerably more negative than those of the corresponding molybdenum complexes and the reductions are less reversible.

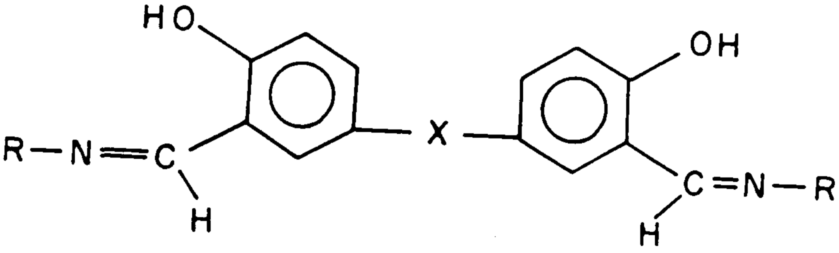
Syamal and Maurya[8] have prepared dioxotungsten(VI) complexes of the type WO_2L (where LH_2 = Schiff base derived from *o*-aminophenol and salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde or 3-ethoxysalicylaldehyde) by the reaction of Schiff base with sodium tungstate at pH 6 in aqueous medium. The reaction of WO_2L with monodentate ligand X (X = DMF, DMSO or pyridine) leads to the formation of the complexes of the type $WO_2L.X$. The NN-donor bidentate ligands (BB) (BB = 2,2′-dipyridyl or o-phenanthroline) react with WO_2L in methanol-DMF solution and the complexes of the type $[WO_2L(BB)]$ are formed.

Recently Yu and Holm[11] have reported a rather simple reproducible preparation of $WO_2(acac)_2$ and its reaction with the Schiff bases H_2(sal-OAP) and H_2(sal-ATP) [H_2(sal-OAP) = 2-(salicylideneamino phenolate(2-) and H_2(sal-ATP) = 2-(salicylidene amino) benzene thiolate(2-)].

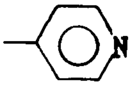
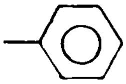
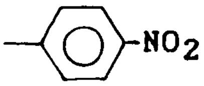
In chapters 2, 3 and 4 we have reported some binuclear dioxomolybdenum(VI) complexes with tetraanionic hexadentate Schiff base ligands and have shown that these complexes extend two labile binding sites within the molecule.[12] Such studies are important to understand the binding and displacement of various substrate molecules. This chapter deals with the binuclear dioxotungsten(VI) complexes of flexibly-bridged hexadentate ligands (structures I and II). Only few reports have appeared in the literature dealing with such dioxotungsten(VI) complexes of Schiff base ligands and those are mainly concerned with mononuclear complexes.[5-11,13]

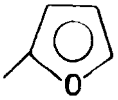
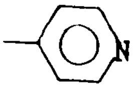
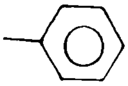
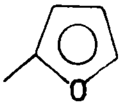


(I)



(II)

	Ligand	**X**	**R**	**Abbreviations.**
1	I	CH_2		$\mathrm{CH_2(H_2sal\text{-}INH)_2}$
2	I	CH_2		$\mathrm{CH_2(H_2sal\text{-}BZH)_2}$
3	I	CH_2		$\mathrm{CH_2(H_2sal\text{-}NO_2BZH)_2}$

4	I	CH_2		$CH_2(H_2sal\text{-}FAH)_2$
5	I	S-S		$S_2(H_2sal\text{-}INH)_2$
6	I	S-S		$S_2(H_2sal\text{-}BZH)_2$
7	I	S-S		$S_2(H_2sal\text{-}FAH)_2$
8	II	CH_2	*o*-C_6H_4OH	$CH_2(H_2sal\text{-}OAP)_2$
9	II	CH_2	CH_2CH_2OH	$CH_2(H_2sal\text{-}EA)_2$
10	II	S-S	*o*-C_6H_4OH	$S_2(H_2sal\text{-}OAP)_2$
11	II	S-S	CH_2CH_2OH	$S_2(H_2sal\text{-}EA)_2$

6.2 EXPERIMENTAL

WO_2Cl_2 (Alfa) was used as received. Salicylaldehyde and acetylacetone (S.D. Fine Chemicals) were distilled under reduced pressure prior to use. Other reagents and solvents were of analytical grade. 5,5′-Methylene bis(salicylaldehyde)[14], 5,5′-dithio bis(salicylaldehyde)[15] and $[WO_2(acac)_2]$[11] (Hacac = acetyl acetone) were synthesized by the method described in literature. The Schiff bases **2, 3, 6, 8, 9, 10** and **11** were prepared by the methods described in the previous chapters.[12a,12c]

The carbon, hydrogen and nitrogen contents were estimated by the microanalytical section of this laboratory. The electrical conductance measurements were carried out in 10^{-3} M solution of the complexes in DMF using a Biochem model DC 808 digital conductivity bridge calibrated with potassium chloride solution. The IR spectra were recorded in nujol mulls on a Perkin-Elmer model 1620 FT-IR spectrophotometer. The electronic spectra were obtained in DMF on a Shimadzu model UV-2101PC UV-VIS scanning spectrophotometer. The ^1H NMR spectra were scanned in DMSO-d6 on a Bruker WH-200 spectrometer and chemical shift (δ in ppm) are reported relative to DMSO-d6 (2.40 ppm). All the cyclic voltammograms (CV) were recorded in dry DMF at ambient temperature (25 ± 1°) under nitrogen using 0.1M tert-butylammonium fluoroborate as a supporting electrolyte. Other instrumental details are given in chapter 3.[12a]

(1) Preparation of 5,5′-methylene bis(salicylideneamino isonicotinoyl hydrazine) [$CH_2(H_2sal\text{-}INH)_2$]

A solution of isonicotinoylhydrazine (0.274 g, 0.002 mol) in methanol (10 ml) was added to a hot solution of 5,5′- methylene bis(salicylaldehyde) (0.256 g, 0.001 mol) in methanol (10 ml) and the reaction mixture was refluxed for 2h on a water bath. After reducing the solvent to 10 ml, the solution was cooled to 10° overnight. The separated pale yellow solid product was filtered, washed with methanol and dried under reduced pressure at ambient temperature. Yield 0.420 g (85%); m.p. 194°.

(2) Preparation of 5,5′-methylene bis(salicylideneamino furoylhydrazine) [$CH_2(H_2sal\text{-}FAH)_2$]

The ligand [$CH_2(H_2sal\text{-}FAH)_2$] was prepared by condensing 5,5′-methylene bis(salicylaldehyde) (0.256g, 0.001 mol) with furoylhydrazine (0.252 g, 0.001 mol) in 20 ml methanol. After refluxing on a water bath for 5h, the solution was concentrated to 10 ml and cooled. The separated yellow solid product was filtered, washed with hot methanol and finally recrystallized from methanol. Yield 0.430 g (91%); m.p. 298°.

(3) Preparation of 5,5′-dithio bis(salicylideneamino isonicotinoyl hydrazine) [$S_2(H_2sal\text{-}INH)_2$]

Isonicotinoylhydrazine (0.274 g, 0.002 mol) dissolved in methanol (10 ml) and 5,5′-dithio bis(salicylaldehyde) (0.306 g, 0.001 mol) dissolved in methanol (10 ml) were mixed and then refluxed for 5h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated yellow solid product was filtered, air dried and recrystallized from methanol. Yield 0.480 g (88%); m.p. 254°.

(4) Preparation of 5,5′-dithio bis(salicylideneamino furoyl hydrazine) [$S_2(H_2sal\text{-}FAH)_2$]

The yellow coloured binucleating Schiff base ligand [$S_2(H_2sal\text{-}FAH)_2$] was prepared by the reaction of furoylhydrazine (0.252 g, 0.002 mol) and 5,5′-dithio bis(salicylaldehyde) (0.306 g, 0.001 mol) in 20 ml methanol according to the procedure described for 3. Yield 0.470 g (90%); m.p. 270°.

(1a) Preparation of $[(WO_2)_2(CH_2\{sal\text{-}INH\}_2)]$

A solution of $[WO_2(acac)_2]$ (0.414 g, 0.001 mol) in methanol (20 ml) was added to a hot solution of the Schiff base $[CH_2(H_2sal\text{-}INH)]$ (0.247 g, 0.0005 mol) in methanol (50 ml) with stirring. The resulting solution was filtered immediately and then refluxed on a water bath for 8h. After cooling the solution to room temperature the separated yellow tungsten complex was filtered, washed with hot methanol and dried at 100° in air. Yield 0.420 g (91%); m.p. >250°.

(2a) Preparation of $[(WO_2)_2(CH_2\{sal\text{-}BZH\}_2)]$

The Schiff base $[CH_2(H_2sal\text{-}BZH)_2]$ (0.248 g, 0.0005 mol) was dissolved in 50 ml methanol by heating on water bath and to this was added $WO_2(acac)_2$ (0.414 g, 0.001 mol)in 20 ml methanol with vigorous shaking. The resulting turbid solution was filtered and the clear filtrate refluxed on water bath for 6h. After concentrating the solution to 10 ml and cooling to 10° overnight, the separated yellow solid product was filtered, washed with hot methanol and dried at 100°in air. Yield 0.400 g (87%); m.p. >250°.

(3a) Preparation of $[(WO_2)_2(CH_2\{sal\text{-}NO_2BZH\}_2)]$

The brown complex $[(WO_2)_2(CH_2\{sal\text{-}NO_2BZH\}_2)]$ was prepared by the reaction of the Schiff base ligand $[CH_2(H_2sal\text{-}NO_2BZH)_2]$ (0.291 g, 0.0005 mol) in 50 ml methanol and $WO_2(acac)_2$ (0.414 g, 0.001 mol) in 20 ml methanol following the above procedure. Yield 0.460 g (91%); m.p. >250°.

(4a) Preparation of $[(WO_2)_2(CH_2\{sal\text{-}FAH\}_2)]$

$WO_2(acac)_2$ (0.414 g, 0.001 mol) in 20 ml methanol was added to a refluxing solution of the ligand $[CH_2(H_2sal\text{-}FAH)_2$ (0.236 g, 0.0005 mol) in methanol(50 ml). The resulting mixture was filtered immediately and the solution refluxed on water bath for 6h. After reducing the solvent to 10 ml, the solution was cooled at room temperature. The separated orange solid product was filtered, washed with hot methanol and dried at 100°. Yield 0.400 g (88%); m.p. >250°.

(5a) Preparation of $[(WO_2)_2(S_2\{sal\text{-}INH\}_2)]$

The yellow coloured complex $[(WO_2)_2(S_2\{sal\text{-}INH)_2]$ was prepared following the above procedure by the reaction of the ligand $[S_2(H_2sal\text{-}INH)_2]$ (0.272 g, 0.0005 mol) in 50 ml of methanol and $WO_2(acac)_2$ (0.414 g, 0.001 mol) in 20 ml methanol. Yield 0.450 g (92%); m.p. >250°.

(6a) Preparation of $[(WO_2)_2(S_2\{sal\text{-}BZH\}_2)]$

To a refluxing solution of the ligand $[S_2(H_2sal\text{-}BZH)_2]$ (0.271 g, 0.0005 mol) in 50 ml of methanol $WO_2(acac)_2$ (0.414 g, 0.001 mol) was added in 20 ml methanol. The resulting turbid solution was filtered while hot and again refluxed for 6h. After reducing the solvent to 10 ml, the solution was filtered, washed with hot methanol and dried at 100°. Yield 0.450 g (93%);

m.p. >250°.

(8a) Preparation of [$(WO_2)_2(CH_2\{sal\text{-}OAP\}_2)$]

$WO_2(acac)_2$ (0.414 g, 0.001 mol) in 20 ml methanol was added to refluxing solution of the ligand [$CH_2(H_2sal\text{-}OAP)_2$] (0.218 g, 0.0005 mol) in 25 ml methanol. The resulting solution was filtered and the filtrate was again refluxed on water bath for 6h. After reducing the volume of the solvent, the mixture was cooled at 0° overnight. The separated brown tungsten complex was filtered, washed with hot methanol and dried at 100°. Yield 0.380 g (90%);m.p. >250°.

(9a) Preparation of [$(WO_2)_2(CH_2\{sal\text{-}EA\}_2)$]

The yellow coloured complex [$(WO_2)_2(CH_2\{sal\text{-}EA\}_2)$] was prepared according to the above mentioned procedure by the reaction of the ligand [$CH_2(H_2sal\text{-}EA)_2$] (0.171 g, 0.0005 mol) in 25 ml methanol and $WO_2(acac)_2$ (0.414 g, 0.001 mol) in 20 ml methanol. Yield 0.350 g (91%); m.p. >250°.

(10a) Preparation of [$(WO_2)_2(S_2\{sal\text{-}OAP\}_2)$]

To a refluxing solution of the ligand [$S_2(H_2sal\text{-}OAP)_2$] (0.244 g, 0.0005 mol) in 25 ml of methanol $WO_2(acac)_2$ (0.414 g, 0.001 mol) was added in 20 ml methanol. The refluxing solution was filtered while hot and again refluxed for 6h. After reducing the solvent to 10 ml, the solution was cooled at 0° overnight. The separated brown solid was filtered, washed with hot methanol and dried at 100°. Yield 0.400 g (91%); m.p. >250°.

(11a) Preparation of [$(WO_2)_2(S_2\{sal-EA\}_2)$]

The yellow coloured complex [$(WO_2)_2(S_2\{sal-EA\}_2)$] was prepared following the above mentioned procedure by the reaction of [$S_2(H_2sal-EA)_2$] (0.186 g, 0.0005 mol) in 25 ml methanol and $WO_2(acac)_2$ (0.414 g, 0.001 mol) in 20 ml methanol. Yield 0.360 g (88%); m.p. >250°.

The analytical and other physico-chemical data of the tungsten complexes are presented in Table 6.1.

6.3 RESULTS AND DISCUSSION

The binucleating tetraanionic Schiff base ligands **2, 3, 6, 8, 9, 10** and **11** have already been reported in literature. Other ligands **1, 4, 5** and **7** can be prepared easily following the same method. The elemental analyses and spectral data are consistent with their structures I and II.

The Schiff bases I and II react with methanolic solution of [$WO_2(acac)_2$] in 1:2 molar ratio to form complexes of the type [$(WO_2)_2L$] (LH_4 = Schiff base I and II) as shown by equation (1):

$$2\ [WO_2(acac)_2] + LH_4 \longrightarrow [(WO_2)_2L] + 4\ acacH \quad (1)$$

The analytical data support the formation of five coordinated binuclear complexes [$(WO_2)_2L$]. This is further supported by the thermal analysis data which show no weight loss of the complexes up to 250° . If [$(WO_2)_2L.2\ MeOH$] type complexes were formed, thermograms of the complexes would have shown weight loss corresponding to the loss of two methanol molecules within 250° range as such coordinated monodentate ligands are known to undergo dissociation on heating due to weak coordination and their labile nature.[16] The high decomposition temperature of the complexes also indicates their good thermal stability.

All the complexes are diamagnetic as expected for $5d^{0}$ tungsten(VI) ion. They are yellow-orange in colour, insoluble in most organic solvents but soluble in coordinating solvents like pyridine, DMF and DMSO. The complexes have been found to be non-electrolytes (Λ_M = 2.6 - 9.8 ohm^{-1} cm^{2} mol^{-1}) in DMF.

IR Spectral studies

A partial listing of the IR spectra of the ligands and their complexes is given in Table 6.2. The binucleating hexadentate tetraanionic Schiff base ligand $[CH_2(H_2sal\text{-}FAH)_2]$ exhibits two bands due to ν(C=O) and ν(NH) at 1657 and 3210 cm^{-1}, respectively suggest the existence of the ligand in the keto form. The band due to ν(C=N) is observed at 1622 cm^{-1}. In the IR spectra of the Schiff bases **1**, **5** and **7** a similar pattern of bands is observed. These Schiff bases show ν(C=O) and ν(NH) stretches in the regions 1649-1683 and 3201-3257 cm^{-1}, respectively and ν(C=N) at ~1610 cm^{-1}. The IR spectra of the rest of the Schiff bases are described in chapters 2 and 3.

In the binuclear tungsten(VI) complex $[(WO_2)_2(CH_2\{sal\text{-}FAH\}_2)]$ the bands due to ν(C=O) and ν(NH), respectively are absent, suggesting the enolization of the ligand followed by coordination of the enolic oxygen to the tungsten atom after proton replacement. The band due to intramolecularly hydrogen bonded phenolic OH at 2800 cm^{-1} is absent suggesting the coordination of phenolic oxygen after deprotonation. The band due to azomethine group, ν(C=N) shifts to a lower frequency and appears at 1615 cm^{-1} indicating the coordination of the azomethine nitrogen atom.[11]

Similarly in the complexes obtained from Schiff bases 8-11, the bands due to alcoholic and phenolic OH which are observed at 3200 and 2700 cm^{-1}, respectively are absent indicating the coordination of both the alcoholic and phenolic protons after proton replacement. A strong band at 1630-1645 cm^{-1} shifts to a lower frequency by 2-16 cm^{-1}, indicating the participation of azomethine nitrogen atom in coordination.[16] Thus, the IR spectral data very well indicate the ONO donor behaviour of the each Schiff base unit bridged by $-CH_2-$ or -S-S- groups.

The IR spectra of $[(WO_2)_2L]$ also exhibit a new sharp band at 956 - 966 cm^{-1} due to the νsym $(O = W = O)$ mode of the *cis* WO_2 structure. In addition, a broad band at 800 - 853 cm^{-1} is assigned due to the $W \cdots O \longrightarrow W$ interaction. As the complexes under study are five coordinated, presence of such $W=O\longrightarrow W$ interaction band suggests an oligomeric structure (structure II) for $[(WO_2)_2L]$ similar to that suggested for $[(MoO_2)_2L]$ (where LH_4 = Schiff base).[12] Thus in oligomeric structure each W(VI) ion achieves a pseudooctahedral structure *via* oxo-bridging of the WO_2 moiety. Such oxo-bridged oligomeric type structure has been extensively reported for dioxomolybdenum(VI) complexes of dibasic tridentate ligands.[4]

Electronic Spectral Studies

The electronic spectral data of the ligands and complexes are given in Table 6.2. The Schiff bases **1-7** show electronic spectral bands at 37735 - 38810 (ϵ = 24400 - 43618), 34130 - 34480 (ϵ = 29570 - 82230), 32898 - 33557(ϵ = 26731 - 87894) and 29070 - 29806 cm-1 (ϵ = 15690 - 56710). These bands may be assigned to $\phi \rightarrow \phi^*, \pi \rightarrow \pi_1^*, \pi \rightarrow \pi_2^*$ and $n \rightarrow \pi^*$ transitions, respectively.[17] However, the ligand **3a** exhibit only three electronic spectral bands at 39215 (ϵ = 24400), 36490(ϵ = 27500), 29070(ϵ = 18700) which are due to $\phi \rightarrow \phi^*, \pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. These bands are still present in the metal complexes but with slight shifting in band positions. No systematic trend in shifting has been noticed in the ligand bands. In addition, all the complexes show a new band at 24813 - 25510 cm^{-1} (ϵ = 19827 - 34859) which is assigned to the ligand to metal charge transfer transition between the highest occupied ligand molecular orbital and the lowest empty *d*-orbital of tungsten.

^{1}H NMR Spectral Studies

The ^{1}H NMR spectra of the Schiff bases and their metal complexes are summarized in Table 6.3. The presence of a signal due to NH proton at 10.90 ppm in the ligand [$CH_2(H_2$sal-FAH$)_2$] indicates that the ligand is in the keto form. The phenolic OH proton signal is observed at 12.10 ppm which is confirmed by D_2O exchange studies. A sharp singlet due to azomethine proton is observed at 8.60 ppm. The presence of a singlet due to bridging methylene group at 3.85 ppm suggests that the Schiff base units are held by the methylene group. A similar pattern of signals is observed in the ligands 1, 5 and 7. These Schiff bases exhibit a signal at 10.82 - 11.55 ppm region due to the NH proton which indicate that the ligands also are in their keto form. The signal due to phenolic protons and azomethine protons are observed at 12.00 - 12.30 and 8.60 - 8.70 ppm, respectively.

In the ^{1}H NMR spectrum of the complex [$(WO_2)_2(CH_2$\{sal-FAH\}$_2)$], the band at 10.90 ppm due to NH proton is absent, suggesting the enolization followed by coordination of enolic oxygen after proton replacement. The signal due to phenolic proton also disappears on complexation. The sharp singlet due to azomethine proton at 8.60 ppm shifts downfield indicating the coordination of lone pair of electrons present on the nitrogen atom.[18] A similar pattern of resonances is observed in rest of the complexes derived from the hydrazone ligands.

In the case of ligands **8** and **10** resonances due to the phenolic protons of the salicylaldehyde residue are observed at 13.50 and 14.85 ppm as a singlet and an additional signal at 9.56- 9.71 ppm due to the phenolic proton of the *o*-aminophenol residue. The absence of hydroxyl resonances in the spectra of the complexes (**8a-12a**) indicates the coordination of the phenolic oxygen atoms to tungsten after proton replacement. The sharp singlet due to the azomethine proton shifts downfield, suggesting the coordination of the azomethine nitrogen to the tungsten atom. The spectra of Schiff bases **9** and **11** in DMSO show the alcoholic proton signal at 4.26 and 4.70 ppm respectively which is confirmed by D_2O exchange studies. The absence of this signal in the complexes suggests deprotonation as a result of complex formation.

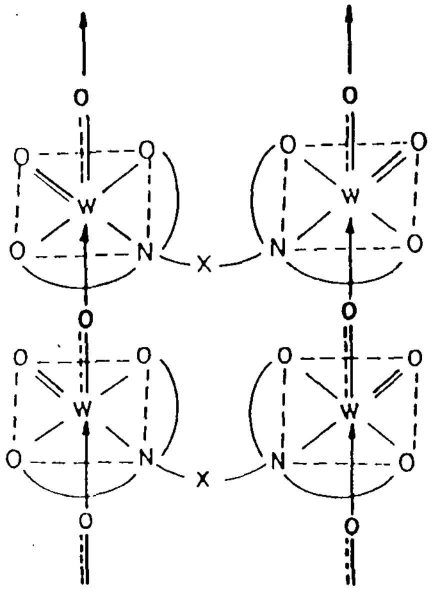
The presence of a singlet due to $-CH_2-$ protons attached to two Schiff base units in the ligands as well as in complexes at nearly the same positions, is in agreement with the two Schiff base units still attached by the methylene group. Other resonances due to aromatic protons are also observed in the same region as in the respective Schiff bases. Thus the NMR results agree well with the conclusion drawn from the IR data.

Electrochemical Studies

The cyclic voltammograms of $[(WO_2)_2(CH_2\{sal\text{-}BZH\}_2)]$ **(2a)** $[(WO_2)_2(CH_2\{sal\text{-}NO_2BZH\}_2)]$ **(3a)** and $[(WO_2)_2(S_2\{sal\text{-}BZH\}_2)]$ **(6a)**, recorded in dry DMF, are reproduced in Fig.6.7. The sharp reductive peak potential with an E_{pc} value of -1.0 to -1.1 V for all these complexes indicate a kinetically facile reduction of W(VI) complexes to W(IV). Very similar reduction potential values of **2a** (-1.1) and **6a** (-1.0 V) indicate that the bridging methylene ($-CH_2-$) or dithio(-S-S-) group has very little effect on the thermodynamic stability of these complexes. Similar conclusion has been drawn in case of dioxomolybdenum(VI) complexes of the same ligands **2** and **3** (ref.3). To see the effect of scan rate on the shape of the reductive and oxidative peaks and on the reduction of W(VI) to W(IV), we have also recorded the voltammograms of these complexes at three scan rates (e.g., 100, 500 and 1000 mV/sec). The oxidative peak in all the voltammograms is very weak. But, within the complex, the reductive peak potential becomes more negative with the increment of scan rate which is indicative of the quasireversible behaviour of the complexes. Such irreversible to quasireversible behaviour of similar mononuclear dioxotungsten(VI)[7] and various mononuclear and binuclear dioxomolybdenum(VI) complexes have also been reported.[12c]

6.4 CONCLUSION

The spectroscopic data indicate the formation of the complexes of the type $(WO_2)_2L$ (where LH_4 = binucleating hexadentate tetraanionic Schiff bases) in which tungsten atom achieves a pseudo - octahedral structure *via* $W \overset{-}{=} O \longrightarrow W$ bridging. In coordinating solvents the oligomeric bridges are broken to form complexes of the type $(WO_2)_2L(D)_2$ as in the case of their molybdenum analogues. The cyclic voltammetric measurements indicate irreversible to quasireversible reduction of the tungsten(VI) complexes to tungsten(IV) with a cathodic reduction potential of -1.0 to -1.15 V *vs*. SCE at the scan rate of 500 mv/s.



X = CH_2 or S_2

(II)

Table 6.1. Physicochemical and analytical data of the new Schiff bases and complexes.

Sl no.	Compound^a/ Stoichiometry	Colour	M.p. (°)	Found(Calcd.)%			Λ_M^b
				C	H	N	
1	$CH_2(H_2\text{sal-INH})_2$ $C_{27}H_{22}N_6O_4$	Pale yellow	194	65.2 (65.6)	4.1 (4.5)	16.8 (17.0)	
4	$CH_2(H_2\text{sal-FAH})_2$ $C_{25}H_{20}N_4O_6$	Yellow	298	63.2 (63.6)	4.1 (4.3)	11.6 (11.9)	
5	$S_2(H_2\text{sal-INH})_2$ $C_{26}H_{20}N_6O_4S_2$	Yellow	254	57.1 (57.3)	3.5 (3.7)	15.2 (15.4)	
7	$S_2(H_2\text{sal-FAH})_2$ $C_{24}H_{18}N_4O_6S_2$	Yellow	270	54.9 (55.1)	3.3 (3.5)	10.5 (10.7)	
1a	$[(WO_2)_2(CH_2\{\text{sal-INH}\}_2)]$ $C_{27}H_{18}N_6O_8W_2$	Yellow	>250	35.5 (35.2)	2.2 (2.0)	8.8 (9.1)	5.6
2a	$[(WO_2)_2(CH_2\{\text{sal-BZH}\}_2)]$ $C_{29}H_{20}N_4O_8W_2$	Yellow	>250	37.6 (37.9)	2.3 (2.2)	6.3 (6.1)	2.9
3a	$[(WO_2)_2(CH_2\{\text{sal-}NO_2\text{BZH}\}_2)]$ $C_{29}H_{18}N_6O_{12}W_2$	Brown	>250	34.4 (34.5)	2.0 (1.8)	8.5 (8.3)	2.6
4a	$[(WO_2)_2(CH_2\{\text{sal-FAH}\}_2)]$ $C_{25}H_{18}N_4O_{10}W_2$	Orange	>250	33.6 (33.4)	1.6 (1.8)	6.5 (6.2)	9.8
5a	$[(WO_2)_2(S_2\{\text{sal-INH}\}_2)]$ $C_{26}H_{16}N_6O_8S_2W_2$	Yellow	>250	32.5 (32.1)	1.8 (1.7)	8.3 (8.6)	6.6
6a	$[(WO_2)_2(S_2\{\text{sal-BZH}\}_2)]$ $C_{28}H_{18}N_4O_8S_2W_2$	Brown	>250	34.5 (34.7)	1.8 (1.7)	5.9 (5.8)	3.5
8a	$[(WO_2)_2(CH_2\{\text{sal-OAP}\}_2)]$ $C_{27}H_{18}N_2O_8W_2$	Brown	>250	37.2 (37.4)	2.4 (2.1)	2.9 (3.2)	4.5
9a	$[(WO_2)_2(CH_2\{\text{sal-EA}\}_2)]$ $C_{19}H_{18}N_2O_8W_2$	Yellow	>250	29.1 (29.6)	2.3 (2.3)	3.1 (3.6)	5.0
10a	$[(WO_2)_2(S_2\{\text{sal-OAP}\}_2)]$ $C_{26}H_{16}N_2O_8S_2W_2$	Brown	>250	34.4 (34.1)	1.7 (1.8)	3.6 (3.1)	6.6
11a	$[(WO_2)_2(S_2\{\text{sal-EA}\}_2)]$ $C_{18}H_{16}N_2O_8S_2W_2$	Yellow	>250	26.2 (26.4)	1.9 (2.0)	3.2 (3.4)	6.9

Table 6.2. IR and electronic spectral data (cm-1)

	IR			Electronic spectra
Compoundsa	√-CH=N	√O=M=O	√M=O-->M	(ϵ)b
1	1625			34,130(40,100), 33,557(36,800), 29,412(31,718)
$1a^c$	1615	956	809	
2	1625			38,910(35,980), 34,480(63,175), 33,110(62,710) 29,850(42,445)
2a	1615	964	853	30,395(31,786), 29,240(30,317), 25,510(19,827)
3	1605			39,215(24,400), 36,490(27,500), 29,070(18,700)
3a	1595	962	783	37,593(58,818), 29,411(51,898), 24,813(34,272)
4	1625			34,246(82,232), 32,896(87,894), 29,761(56,710)
4a	1622	958,908	850	30,030(62,090), 29,070(60,734), 25,445(34,859)
5^c	1632			
$5a^c$	1610	956	810	
6	1607			37,735(25,691), 35,335(29,574), 29,850(15,691)
6a	1589	966	822	37,593(86,280), 34,843(85,426), 30,581(54,878) 25,316(24,390)
7	1609			33,783(76,052), 32,362(69,680), 29,411(38,605)
8	1631			35,090(35,350), 27,860(48,330)
$8a^c$	1615	941	853	
9	1634			37,170(2663), 30,860(9695), 23,810(1413)
9a	1612	943	870	37,593(22,174), 31,152(8922)

10	1633			34,720(18,867), 28,090(18,773)
10a[c]	1615	943	859	
11	1645			37,590(11,539), 31,060(6157)
11a	1643	943	820	37,735(21,913), 31,948(6172)

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[a] For abbreviations see Table 6.1.

[b] ϵ in l mol^{-1} cm^{-1}.

[c] Electronic spectra could not be recorded

Table 6.3. ^{1}H NMR data of the ligands and complexes[a]

Compound	-CH=N	Aromatic protons	$-CH_2$	-NH	-OH
1	8.65(s, 2H)	6.85 - 8.75(m, 10H)	3.85(s, 2H)	10.82(s, 2H)	12.20(s, 2H)
1a	9.00(s, 2H)	7.00 - 8.80(m, 10H)	3.90(s, 2H)		
2	8.60(s, 2H)	6.80 - 7.95(m, 16H)	3.85(s, 2H)	11.05(s, 2H)	12.00(s, 2H)
2a	8.90(s, 2H)	6.95 - 8.00(m, 16H)	3.95(s, 2H)		
4	8.60(s, 2H)	6.60 - 7.30(m. 12H)	3.85(s, 2H)	10.90(s, 2H)	12.10(s, 2H
4a	8.80(s, 2H)	6.65 - 7.90(m, 12H)	3.95(s, 2H)		
5	8.60(s, 2H)	6.95 - 7.95(m, 16H)		11.55(s, 2H)	12.17(s, 2H)
5a	9.00(s, 2H)	7.00 - 8.00(m, 16H)			
6	8.70(s, 2H)	6.95 - 8.75(m, 14H)		11.35(s, 2H)	12.30(s, 2H)
6a	9.00(s, 2H)	7.00 - 8.80(m, 14H)			
7	8.60(s, 2H)	6.65 - 7.90(m, 12H)		11.40(b, 2H)	12.15(b, 2H)
8	8.90(s, 2H)	6.88 - 7.45(m, 14H)	3.88(s, 2H)		13.61(s, 2H)
8a	9.25(s, 2H)	6.90 - 7.75(m, 14H)	4.05(s, 2H)		
9[b]	8.47(s, 2H)	6.80 - 7.26(m, 6H)			4.26(b, 2H)
9a	8.64(s, 2H)	6.86 - 7.44(m, 6H)			
10	8.80(s, 2H)	6.72 - 7.77(m, 14H)	3.80(s, 2H)		14.15(s, 2H)
10a	9.25(s, 2H)	6.85 - 8.10(m, 6H)	3.85(s, 2H)		
11[b]	8.35(s, 2H)	6.60 - 7.20(m, 6H)			4.70(b, 2H)
11a	8.65(s, 2H)	6.95 - 7.85(m, 6H)			

[a] Letters given in parentheses indicate the type of signal. s = singlet, m = multiplet b = broad.

[b] Alcoholic OH resonance.

Table 6.4. Cyclic voltammetric data of the complexes 2a, 3a and 6a.[a]

Compound	E_{pc} (V)	E_{pa} (V)	I_{pc} (μA)	I_{pa} (μA)	Scan rate (mV/s)
1a	−1.10	−0.60	0.0056	0.0144	500
	−1.15	−0.50	0.0064	0.0122	1000
	−1.00	−0.60	0.0056	0.0096	100
3a	−1.10	−0.50	0.0184	0.0248	500
	−1.11	−0.50	0.020	0.0208	1000
	−1.00	−0.60	0.0152	0.0240	100
6a	−1.00	−0.50	0.0048	0.0056	500
	−1.10	−0.30	0.0104	0.0064	1000
	−1.00	−0.60	0.0072	0.0032	100

[a] For abbreviations see Table 6.1.

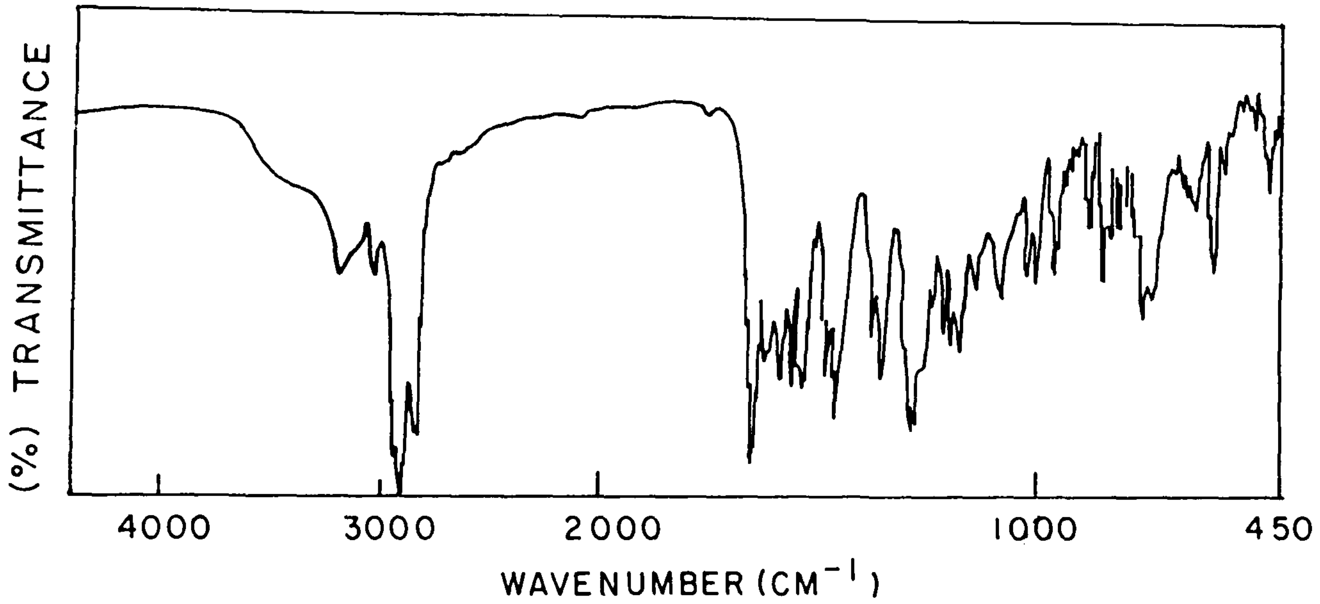

FIG. 6.1 : IR SPECTRUM OF [$CH_2(H_2Sal-FAH)_2$] IN NUJOL

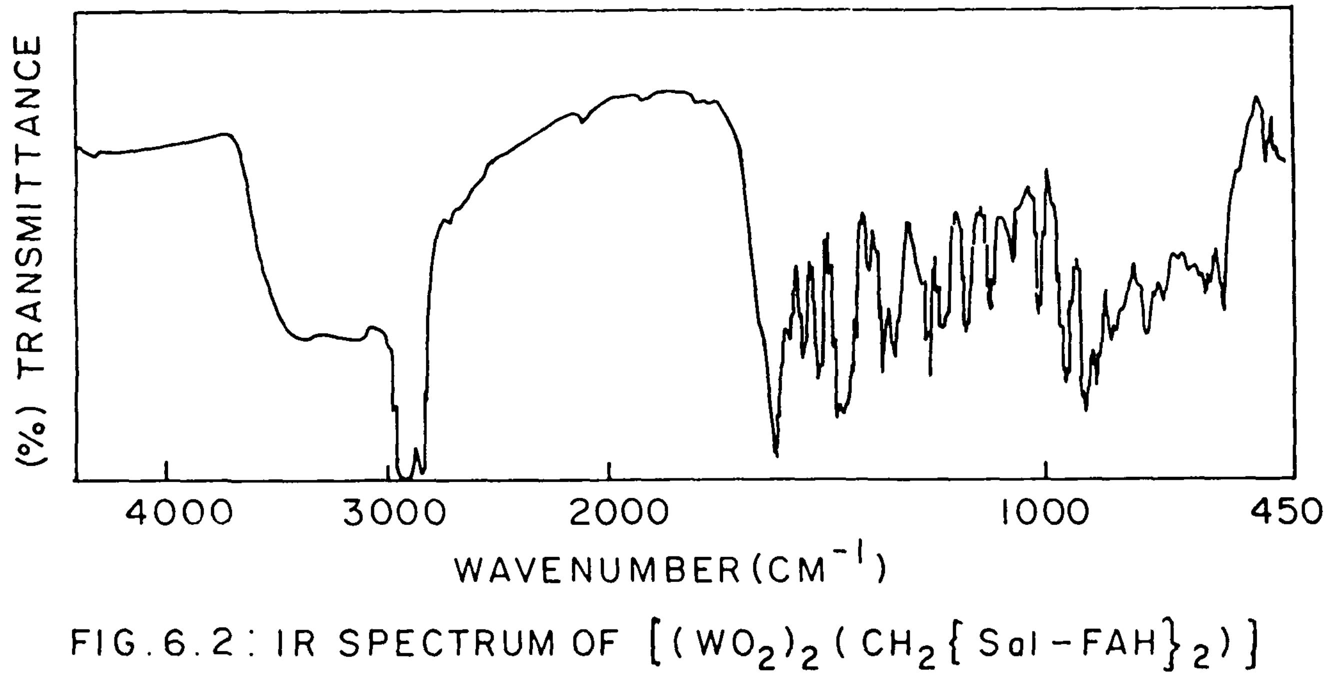

FIG. 6.2 : IR SPECTRUM OF $[(WO_2)_2(CH_2\{Sal-FAH\}_2)]$

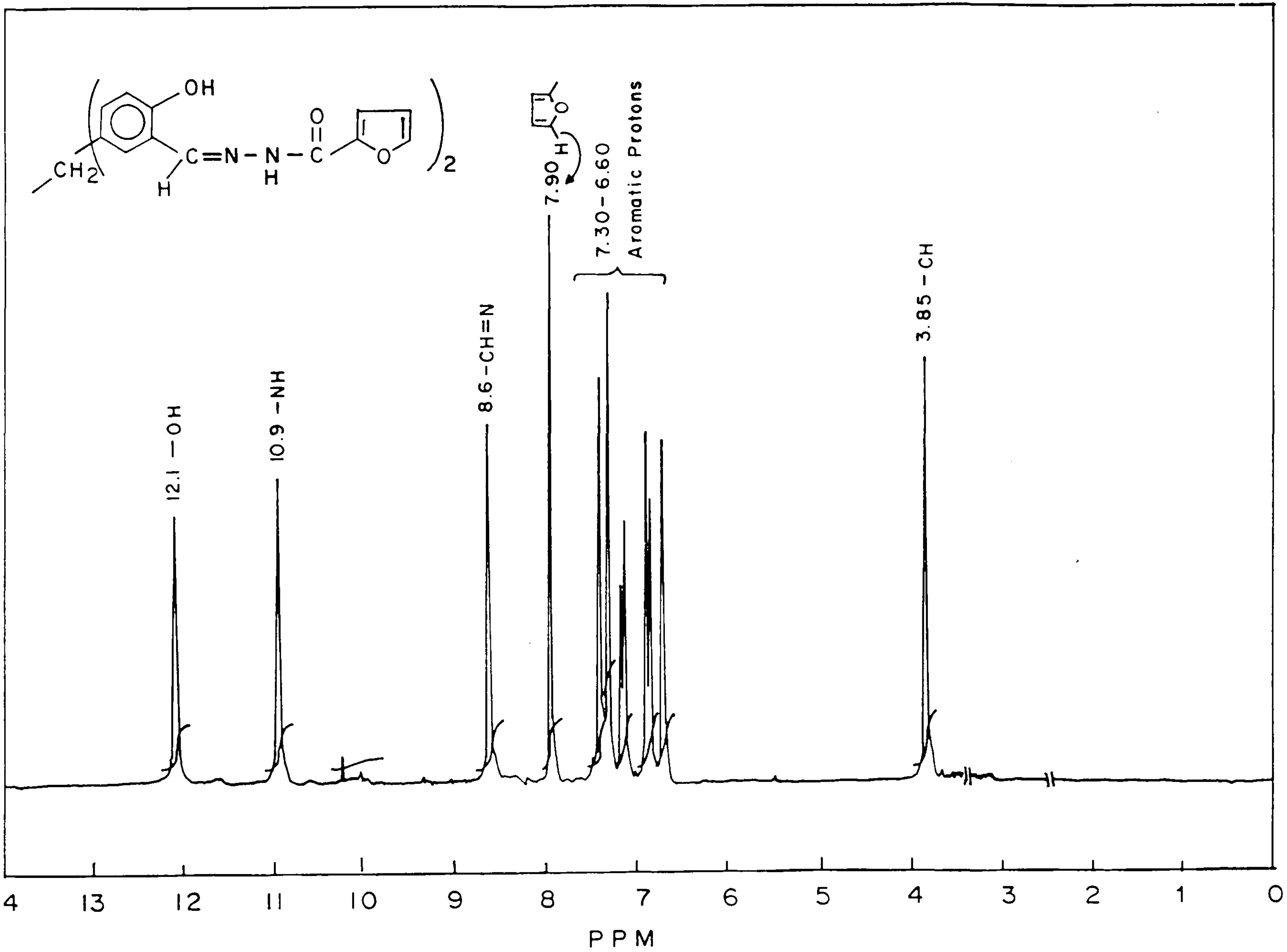

FIG. 6.3: ^1H NMR SPECTRUM OF $[CH_2(H_2\ Sal\text{-}FAH)_2]$ IN DMSO-d_6.

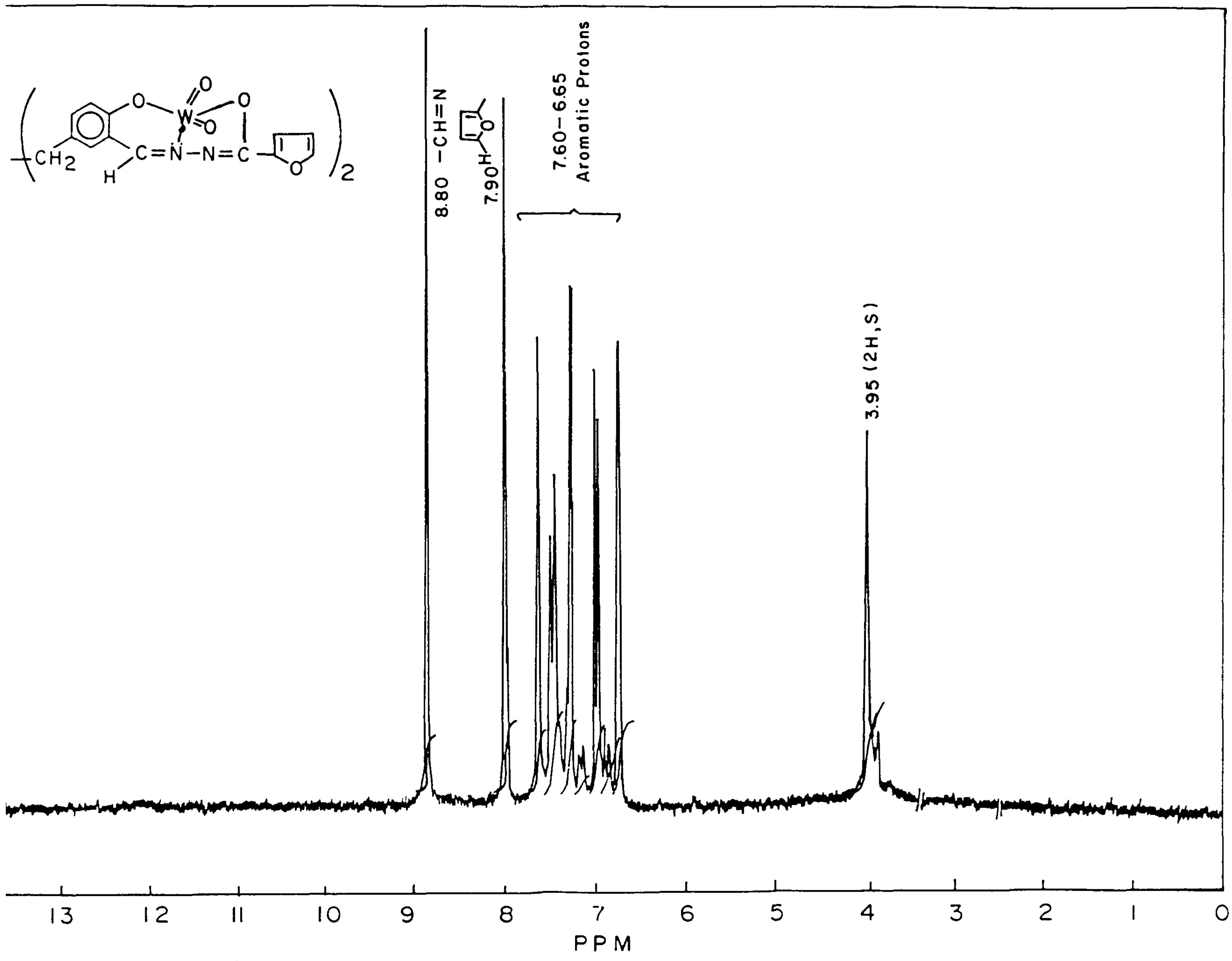

FIG.6.4 : ^{1}H NMR SPECTRUM OF $[(WO_2)_2(CH_2\{Sal-FAH\}_2)]$ IN DMSO-d_6.

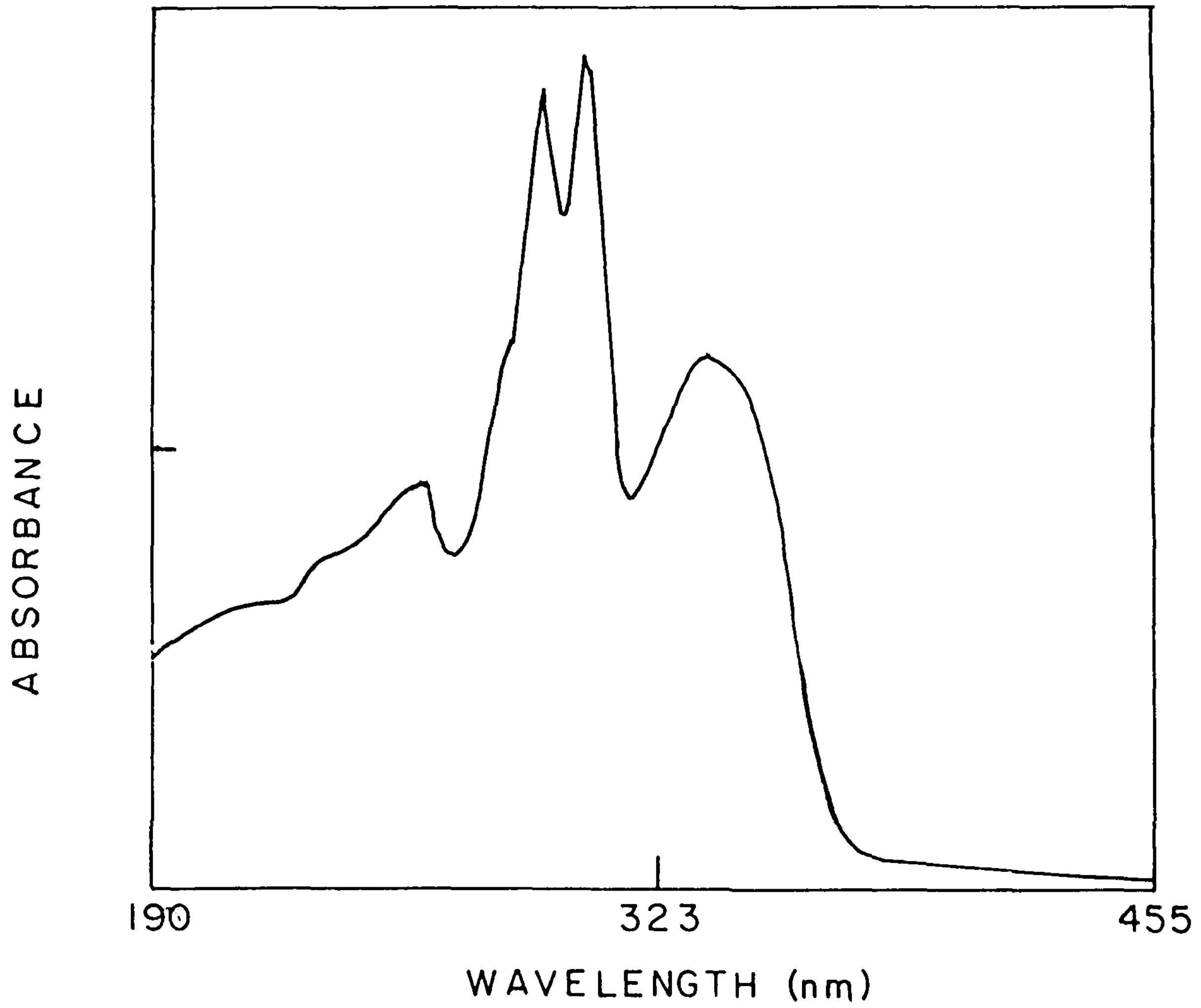

FIG. 6.5: UV-VISIBLE SPECTRUM OF $[(CH_2(H_2Sal-FAH)_2]$ IN DMF.

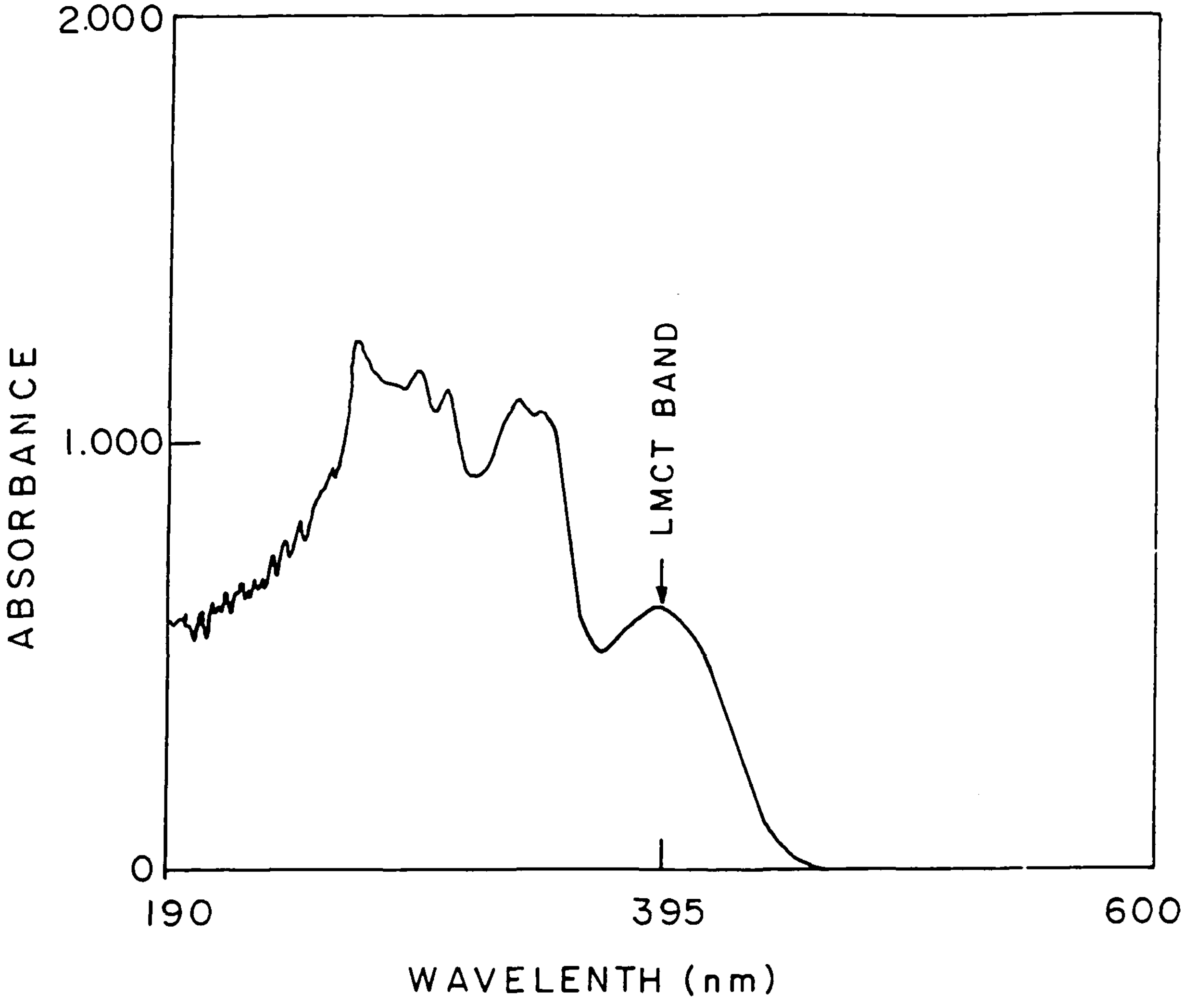

FIG. 6.6 : UV-VISIBLE SPECTRUM OF $[(WO_2)_2(CH_2\{Sal-FAH\}_2)]$ IN DMF.

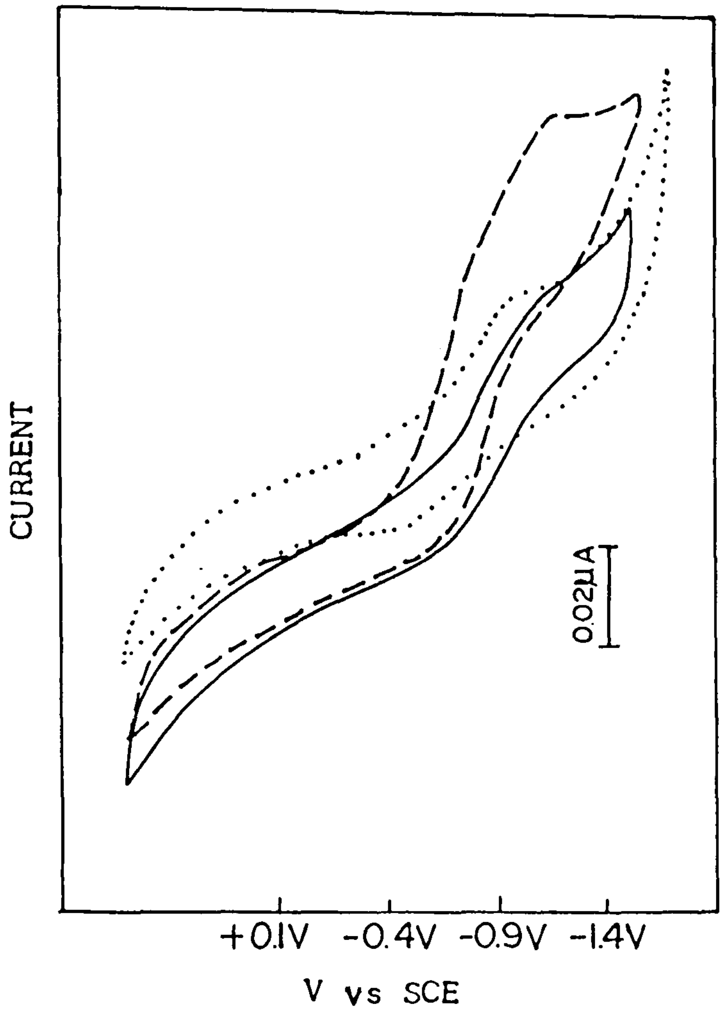

Fig. 6.7: Cyclic voltammograms for 2a (—), 3a (---), and 6a (···) in DMF at scan rate 500 mV/s.

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CHAPTER 7

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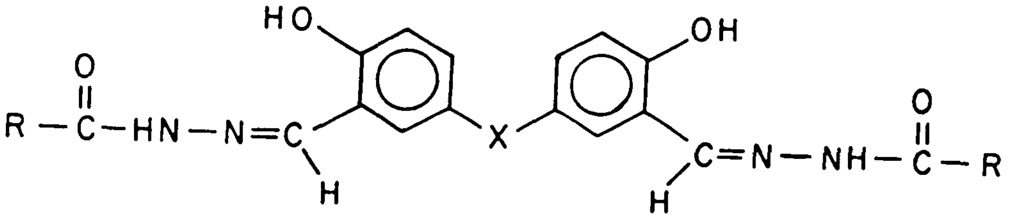
SYNTHESIS AND CHARACTERIZATION OF SOME BINUCLEAR ORGANO OXO-PEROXO COMPLEXES OF TUNGSTEN(VI) AND MOLYBDENUM(VI) AND THEIR CONVERSION TO THE CORRESPONDING DIOXO TUNGSTEN(VI) AND MOLYBDENUM(VI) COMPLEXES USING TRIPHENYLPHOSPHINE.

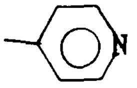
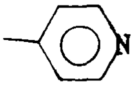
7.1 INTRODUCTION

Peroxo complexes of molybdenum and tungsten are well known to oxidize triphenylphosphine and triphenylarsine through transfer of an oxygen.[1-8] In such oxidation reactions, only oxidized products have been isolated and characterized and no effort has been paid to isolate metal complex and characterize after such reaction.

Recently Yang et.al.[9] have synthesized and characterized the $[W(O)(O_2)(TPP)]$ (TPP = tetraphenylporphyrinato) complex by the reaction of H_2O_2 with W(V) porphyrin complexes. Maurya has prepared dioxomolybdenum(VI) and dioxotungsten(VI) complexes of N-isonicotinamidosalicylaldimine from oxo-peroxo complexes in a single-step process by reacting oxo-peroxo complex with PPh_3.[10] Isolation of dioxotungsten(VI) complexes *via* oxo-peroxo complexes is of great importance as precursor involved to such complexes is tungstic acid. The most useful precursor $[WO_2(acac)_2]$ known so far for the synthesis of dioxotungsten(VI) complexes, requires expensive starting material WO_2Cl_2 and rigorous reaction conditions.[11,12] Other precursors such as WO_2Cl_2 and Na_2WO_4 have very limited success.[13] Thus the development and feasibility of a new method to prepare dioxotungsten(VI) complexes is desirable. In this chapter we report the preparation of oxo-peroxo complexes with following binucleating ligands and their single-step conversion to dioxo complexes. We have also prepared oxo-peroxo complexes of molybdenum and converted them to the corresponding dioxo complexes to test the feasibility of this method in case of molybdenum.



(I)

	X	R	Abbreviation
1	CH_2		$CH_2(H_2sal\text{-}INH)_2$
2	S-S		$S_2(H_2sal\text{-}INH)_2$

7.2 EXPERIMENTAL

Molybdenum trioxide, tungstic acid and hydrogen peroxide were procured from Loba chemie, Bombay and were of analytical grade. The Schiff bases 1 and 2 used for the present study were prepared by the literature method.[14]

Mo and W were determined gravimetrically after decomposing the complexes with con. HNO_3.[15] Carbon, hydrogen and nitrogen analyses were carried out by microanalytical section of National Chemical laboratory. ^1H NMR spectra were scanned on a Bruker WH-200 instrument in DMSO-d_6 and chemical Shifts (δ ppm) are reported relative to DMSO-d_6 (2.40 ppm). IR spectra were recorded as nujol mulls on a Perkin-Elmer model 1620 FT-IR spectrophotometer.

(1a) Preparation of $[\{WO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$

Peroxotungstic acid was prepared by stirring $WO_3.H_2O$ (1 g, 0.004 mol) in H_2O_2 (30%, 50 ml) for 15h.[1] The resulting solution was added to the ligand $CH_2(H_2sal\text{-}INH)_2$ (0.988 g, 0.002 mol) in hot ethanol (50 ml). The mixture was then cooled in an ice-bath while stirring. After 2h the orange-yellow precipitate was filtered off, washed with ethanol-water (3:2 v/v), followed by petroleum ether. Yield 0.830 g (40%); m.p. >250°.

(1b) Preparation of $[\{MoO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$

The orange-yellow coloured complex $[\{MoO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ was prepared following the above mentioned procedure **(1a)** using peroxomolybdic acid (0.004 mol) and the ligand $CH_2(H_2sal\text{-}INH)_2$ (0.988 g, 0.002 mol) in 50 ml ethanol. Yield 0.609 g (35%);m.p. >250°.

(2a) Preparation of $[\{WO(O_2)\}_2(S_2\{sal\text{-}INH\}_2)(H_2O)_2]$

Peroxotungstic acid (0.004 mol) was added to a hot solution of the ligand $S_2(H_2sal\text{-}INH)_2$ (1.088g, 0.002 mol) in 50 ml ethanol. The resulting mixture was cooled in an ice-bath while stirring. After 2h, the separated yellow precipitate was filtered off, washed with ethanol-water (3:2 v/v), followed by petroleum ether. Yield 0.876 g (40%);m.p. >250°.

(2b) Preparation of $[\{MoO(O_2)\}_2(S_2\{sal\text{-}INH\}_2)(H_2O)_2]$

The yellow coloured complex $[\{MoO(O_2)\}_2(S_2\{sal\text{-}INH\}_2)(H_2O)_2]$ was prepared following the above mentioned procedure **(2a)** using peroxomolybdic acid (0.004 mol) and the ligand $S_2(H_2sal\text{-}INH)_2$ (1.088 g, 0.002 mol). Yield 0.736 g (40%);m.p. >250°.

Preparation of the complexes of the type and $[(MO_2)_2(L)]$ (where M = W or Mo) using PPh_3.

A mixture of the complex $[\{WO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ (0.495 g, 0.0005 mol) and PPh_3 (0.262 g, 0.001 mol) in methanol (50 ml) was refluxed on an oil bath for 48 h. After cooling the reaction mixture to ambient temperature, the yellow complex separated was filtered off, washed with methanol and dried in *vacuo*. Yield (80%); m.p. >250°.

The other complexes of the type $[(MO_2)_2L]$ were prepared in 80-85% yield following the same procedure. The elemental analyses data of all the oxo-peroxo and dioxo complexes are presented in Table 7.1.

Attempted reactions of 1a and 1b with cyclohexene, styrene trans-stilbene and cyclohexanol.

Trans-stilbene (0.02 mol), TBHP (0.002 mol), the catalyst $[\{WO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ **(1a)** or $[\{MoO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ **(1b)** (0.002 mmol) and benzene (20 ml) were heated at 70° for 12h. The hydroperoxide was decomposed, the contents were then extracted with ether and the product was identified. This was nothing but *trans*-stilbene. The complexes also failed to give epoxides of cyclohexene and styrene. However, the oxidation of cyclohexanol to cyclohexanone using the above procedure was observed and confirmed both by GC and TLC.

7.3 RESULTS AND DISCUSSION

Agitation of WO_3 or MoO_3 in excess of 30% aqueous H_2O_2 generates *insitu* peroxotungstic acid or peroxomolybdic acid. These peroxo species readily react with alcoholic solution of the Schiff base ligand H_4L to give the corresponding binuclear oxo-peroxo complexes which on crystallization from 95% alcohol have the general formula $[\{MO(O_2)\}_2L(H_2O)_2]$ (M = Mo or W). These oxo-peroxo complexes exhibit three IR active vibrational modes namely, the O-O stretching (ν_1) at ~880 cm^{-1}, the symmetric M-O stretch (ν_2) at ~670 cm^{-1} and the antisymmetric M-O stretch (ν_3) at ~560 cm^{-1} (Table 7.2).[1-8] There is a decrease in ν_1 upon passing from molybdenum complexes to the corresponding tungsten complexes. In addition the oxo-peroxo complexes exhibit ν(M=O) at *ca.*960 cm^{-1}. These oxo-peroxo complexes readily undergo oxygen transfer reaction with PPh_3 in anhydrous methanol to give the corresponding dioxo complexes of formula $[(MO_2)_2L]$. The formation of a representative dioxotungsten(VI) complex may be presented by equation (1).

$$[\{WO(O_2)\}_2L(H_2O)_2] + 2\ PPh_3 \longrightarrow [(WO_2)_2L] + 2\ OPPh_3 + 2\ H_2O \qquad (1)$$

The presence of a sharp band at *ca.*950 cm^{-1} due to ν(O=M=O) stretch and one broad band at *ca.* 810 cm^{-1} due to weakened ν(M=O) as a result of M$\cdots$O⟶M interaction and the absence of bands due to metal-peroxo group in the IR spectra clearly indicate the formation of the $[MO_2]^{2+}$ complexes. We did not observe methanol coordination in the binuclear dioxo complexes (**1c**, **1d**, **2c** and **2d**) obtained by reaction (1) as reported in the case of mononuclear dioxo complexes.[10]

IR Spectral Studies

IR spectral data are shown in Table 7.2. The Schiff base ligand $CH_2(H_2sal\text{-}INH)_2$ shows IR bands at 3257, 2800, 1672, 1625 and 1540 cm^{-1} due to ν(NH), ν(OH) (intramolecularly hydrogen bonded) ν(C=O), ν(C=N) and ν(C-O) (phenolic) modes, respectively. A similar pattern of IR bands is also observed in the ligand

$S_2(H_2sal\text{-}INH)_2$.

The ν(NH) and ν(C=O) disappear in the spectra of the complex $[\{WO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ and $[\{MoO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ indicating the destruction of the carbonyl moiety as a result of enolization and subsequent coordination of the enolic oxygen after proton replacement. A new band appearing at 1282 cm^{-1} is assigned to the ν(C-O) (enolic) mode.[16] The shift of the ν(C-O) (phenolic) stretch to higher frequency by 12 cm^{-1} and the ν(C=N) stretch to lower frequency by 12 cm^{-1} in the complexes indicate the coordination of the phenolic oxygen and the azomethine nitrogen atoms to the metal ion.[17] In the other binuclear metal complexes a similar pattern is observed.

As reported in literature, the oxo-peroxo complexes exhibit a decrease in ν_1 mode which is predominantly (O-O) stretching from the molybdenum complex to the corresponding tungsten complex. In the complex $[\{WO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ ν_1 mode appears at 881 cm^{-1} whereas in $[\{MoO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ ν_1 mode appears at 913 cm^{-1}. A broad band which appears at *ca*.3400 cm^{-1} suggests the coordination of water molecule. In the rest of the binuclear oxo-peroxo complexes, a similar pattern is observed.

In the dioxotungsten(VI) complex $[(WO_2)_2(CH_2\{sal\text{-}INH\}_2)]$ obtained by the reaction of the oxo-peroxo complex $[\{WO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ a sharp band is observed at 951

cm^{-1} due to ν(O=W=O) stretch and a broad band is observed at 807 cm^{-1} due to weakened ν(W=O) as a result of $W \overset{\cdots}{=} O \longrightarrow W$ interaction. This suggests an oligomeric (pseudo-octahedral) structure for the complex which is in agreement with the structure proposed for the same complex obtained from the reaction of $WO_2(acac)_2$ and the ligand.[14] A similar pattern of bands is observed in the other dioxo complexes suggesting an oligomeric structure for all the complexes. The formation of $OPPh_3$ is evident by the presence of an IR band at 1190 cm^{-1} due to ν(P=O) mode.[18] Thus, the IR data suggest a single step conversion of the oxo-peroxo complexes to the corresponding dioxo complexes by the reaction with PPh_3.

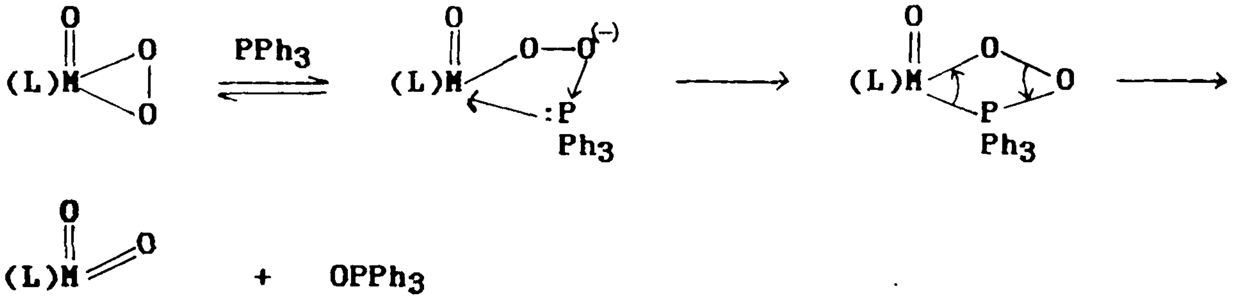
^1H NMR Studies

The ^1H NMR spectra of the ligands and their dioxotungsten(VI) and dioxomolybdenum(VI) complexes are presented in Table 7.3. The ligand $CH_2(H_2sal\text{-}INH)_2$ exhibits two resonances at 10.82 and 12.20 ppm (singlet, 2H each) due to NH and phenolic protons , respectively indicating the existence of the ligand in the keto form. The ^1H NMR spectral details of the binucleating ligands are described in chapter 6.

In the complex $[(WO_2)_2(CH_2\{sal\text{-}INH\}_2)]$, both NH and phenolic resonances are absent suggesting the coordination of the enolic oxygen (due to enolization of the ketonic group) and the phenolic oxygen atoms to the metal after proton replacement. The sharp singlet due to azomethine proton shifts downfield and appears at 8.00 ppm due to the coordination of lone pair of electrons present on the nitrogen atom. A similar pattern of signals is observed in the complexes **1d**, **2c** and **2d**. Thus, the NMR data suggests the ONO⁀ONO donor behaviour of the Schiff bases. We have not attempted to record NMR spectra of the peroxo complexes as these complexes are expected to give similar spectra.

Reactivity

The oxo-peroxo complexes were found to be very stable and were not explosive. The complexes readily oxidizes triphenylphosphine to triphenylphosphine oxide. To explore the reactivity of the peroxo complexes we have reacted the complexes **1a** and **1b** with various olefins such as cyclohexene, styrene and *trans*-stilbene. These complexes failed to give epoxides of the olefins. This negative result outline the enhanced stability of the metal peroxide moiety in the presence of tridentate binegative ligands which precludes oxygen transfer reactions. A similar behaviour of various peroxo complexes containing tridentate ligands are reported in literature.[19-21] However, the complexes were found to be useful as catalysts for the conversion of cyclohexanol to cyclohexanone in presence of *tert*-butylhydroperoxide. The formation of *cis*-dioxo group around each metal atom from the binuclear oxoperoxo complex by the reaction with PPh_3 can be easily explained through the following reaction path:



(where M = W or Mo and L = ligand(s) coordinated to M)

7.4 CONCLUSION

The binuclear dioxo complexes of molybdenum(VI) and tungsten(VI) can be easily prepared from the corresponding oxoperoxocomplexes in a single-step using PPh_3. A pentagonal bipyramidal geometry around each metal atom is proposed for these peroxo complexes as reported for $[MoO(O_2)(pydc)(H_2O)]$ (pydc = pyridine-2,6-dicarboxylate(2^-)].[1] However, the Schiff base ligands of hydrazides such as benzoylhydrazide, furoyl hydrazide failed to give oxo-peroxo complexes under similar reaction conditions. This single-step synthesis of dioxo complexes from the corresponding oxo-peroxo complexes is very important specially in the case of dioxotungsten(VI) complexes as the synthesis of such complexes from the precursor $WO_2(acac)_2$ requires expensive chemicals and rigorous reaction conditions.

Other precursors such as WO_2Cl_2 and Na_2WO_4 have very limited success. This synthetic procedure might prove useful for the synthesis of dioxomolybdenum(VI) and dioxotungsten(VI) complexes of a variety of ligands.

Table 7.1. Analytical and physicochemical data of the ligands and complexes.[a]

S. No.	Compound/ Stoichiometry	Colour	Found(Cal.)%		
			C	H	N
(1a)	$[\{WO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ $C_{27}H_{22}N_6O_{12}W_2$	orange-yellow	32.30 (32.75)	2.50 (2.24)	8.30 (8.49)
(1b)	$[\{MoO(O_2)\}_2(CH_2\{sal\text{-}INH\}_2)(H_2O)_2]$ $C_{27}H_{22}N_6O_{12}Mo_2$	orange-yellow	39.50 (39.82)	2.60 (2.72)	10.52 (10.32)
(1c)	$[(WO_2)_2(CH_2\{sal\text{-}INH\}_2)]$ $C_{27}H_{18}N_6O_8W_2$	orange	34.90 (35.16)	1.80 (1.97)	9.00 (9.11)
(1d)	$[(MoO_2)_2(CH_2\{sal\text{-}INH\}_2)]$ $C_{27}H_{18}N_6O_8Mo_2$	greenish-yellow	43.20 (43.45)	2.20 (2.43)	11.15 (11.26)
(2a)	$[\{WO(O_2)\}_2(S_2\{sal\text{-}INH\}_2)(H_2O)_2]$ $C_{26}H_{20}N_6O_{12}S_2W_2$	yellow	30.50 (30.02)	1.32 (1.94)	7.75 (8.08)
(2b)	$[\{MoO(O_2)\}_2(S_2\{sal\text{-}INH\}_2)(H_2O)_2]$ $C_{26}H_{20}N_6O_{12}S_2Mo_2$	yellow	36.50 (36.12)	2.60 (2.33)	9.85 (9.72)
(2c)	$[(WO_2)_2(S_2\{sal\text{-}INH\}_2)]$ $C_{26}H_{16}N_6O_8S_2W_2$	orange	32.00 (32.12)	1.20 (1.66)	8.30 (8.64)
(2d)	$[(MoO_2)_2(S_2\{sal\text{-}INH\}_2)]$ $C_{26}H_{16}N_6O_8S_2Mo_2$	greenish-yellow	38.85 (39.21)	2.00 (2.03)	10.25 (10.55)

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[a] Abbreviations as under structure (I)

Table 7.2. IR spectral data of the tungsten(VI) and molybdenum(VI) Schiff base complexes

Compounds[a]	$\nu(\mathrm{C{=}N})$	$\nu(\mathrm{M{=}O})$	$\nu_1(\mathrm{O{-}O})$	$\nu_3\left(\mathrm{M}\begin{smallmatrix}\diagup\mathrm{O}\\ \vert\\ \diagdown\mathrm{O}\end{smallmatrix}\right)$	$\nu_2\left(\mathrm{M}\begin{smallmatrix}\diagup\mathrm{O}\\ \vert\\ \diagdown\mathrm{O}\end{smallmatrix}\right)$	$\nu(\mathrm{O{=}M{=}O})$	$\nu(\mathrm{M{=}O{\longrightarrow}M})$
(1a)	1613	965	880	678	562		
(1b)	1614	962	908	655	583		
(1c)	1615					951	807
(1d)	1601					942	838
(2a)	1615	968	893	668	585		
(2b)	1610	936	919	675	579		
(2c)	1609					960	813
(2d)	1600					941	843

[a] Abbreviations as in Table.7.1.

Table 7.3. ^1H NMR data of the binucleating ligands and their dioxo complexes.[a]

Sl. No.	-CH=N	Aromatic Protons	-CH$_2$	-NH	-OH
1.	8.65(s, 2H)	6.85-8.75(m, 10H)	3.85(s, 2H)	10.82(s, 2H)	12.20(s, 2H)
1c.	9.00(s, 2H)	7.00-8.80(m, 10H)	3.90(s, 2H)		
1d.	8.95(s, 2H)	6.90-8.75(m, 10H)	3.95(s, 2H)		
2.	8.60(s, 2H)	6.95-7.95(m, 10H)		11.55(s, 2H)	12.17(s, 2H)
2c	9.00(s, 2H)	6.95-7.95(m, 16H)			
2d.	8.95(s, 2H)	6.90-8.30(m, 16H)			

[a] Abbreviations as in Table 7.1.

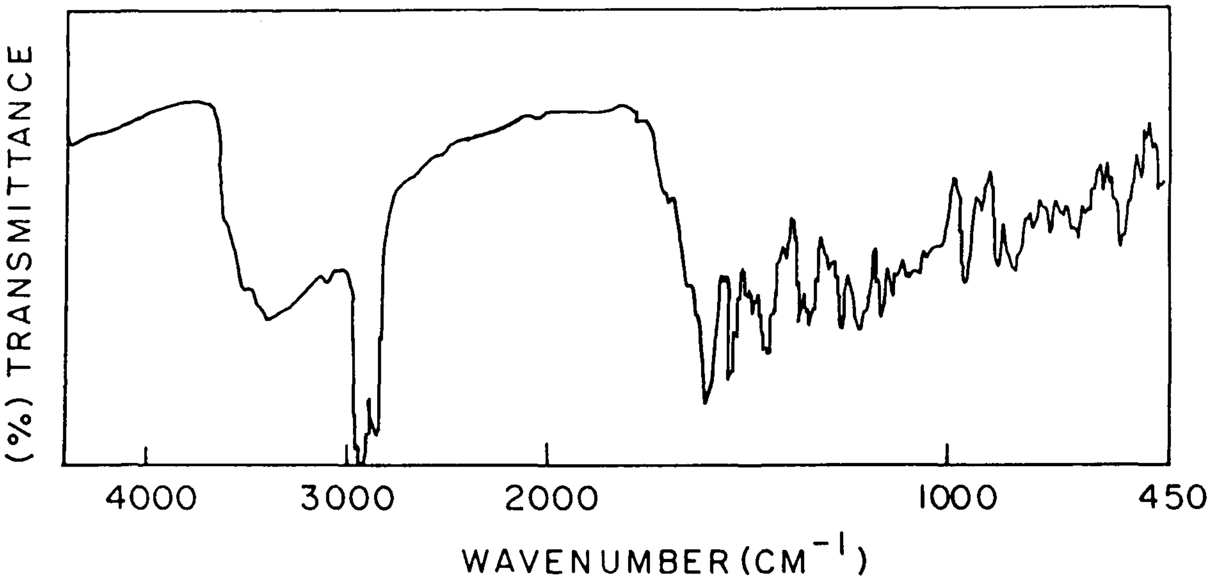

FIG. 7.1 : IR SPECTRUM OF $[\{WO(O_2)\}_2(CH_2\{Sal\text{-}INH\}_2)(H_2O)_2]$ IN NUJOL.

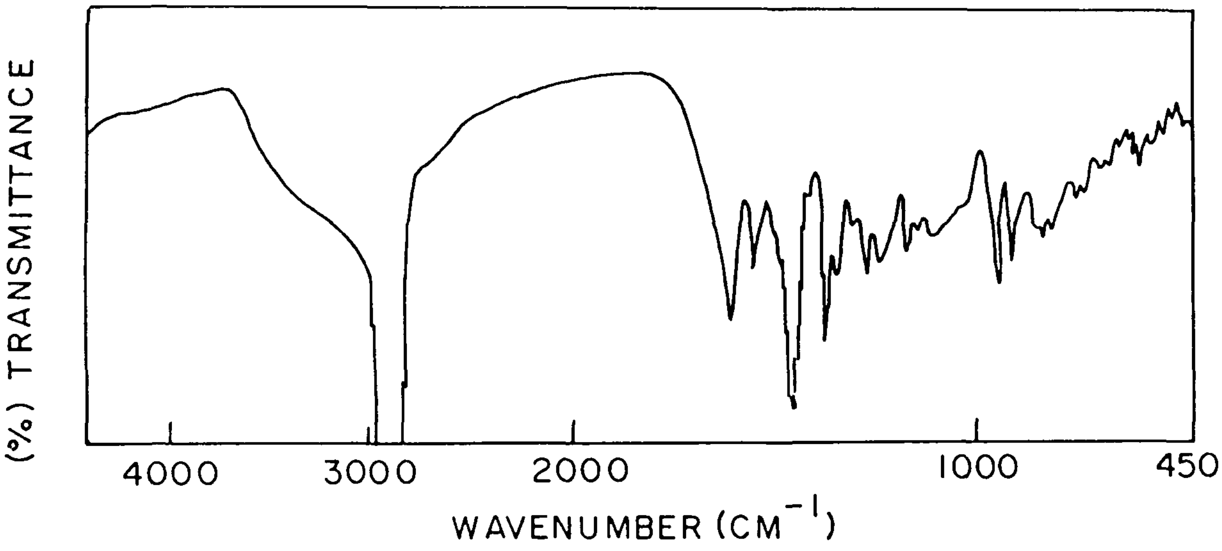

FIG. 7.2: IR SPECTRUM OF $[(WO_2)_2(CH_2\{Sal\text{-}INH\}_2)]$ IN NUJOL

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