CHAPTER II
REVIEW OF METAL COMPLEXES

The present survey briefly covers the work reported on oxomolybdenum(V),
dioxomolybdenum(VI), dioxouranium(VI), ruthenium(III) and niobium(V)
complexes during the last two decades.

a. Oxomolybdenum(V) and dioxomolybdenum(VI) complexes

The enthusiasm shown in the coordination chemistry of molybdenum
enhanced after the discovery of these elements in a number of redox enzymes.
The chemistry of Mo is dominated by the complexes containing metal-oxo
group, although in the last 20 years it was discovered that S\(^{2-}\) and other ligands,
such as selenide (Se\(^{2-}\)), peroxide (O\(_2\)\(^{2-}\)), imide (NR\(^2-\)), nitride (N\(^3-\)), alkylcarbide
(RC\(^3-\)), hydrazide (R\(_2\)NN\(^2-\)) and hydroxylamide (R\(_2\)NO\(^-\)) were able to undergo
chemistry related to that of the oxo ligand. Various reviews on Mo coordination
chemistry appeared in different journals (Mitchell, 1966; Steifel, 1977; Syamal
and Maurya, 1989; Abramenko and Sergienko, 2009; Sergienko et al., 2009)
reveal the importance of these elements in various fields.

Monomeric molybdenum(V) complexes with tridentate ONO chelating
ligands derived from the condensation reaction between various salicylaldehydes
and 2-amino phenol have been reported. The coordination around the molybdenum
was described as distorted octahedral, the equatorial positions occupied by the
two oxygen atoms of the tridentate ligand and the two isothiocyanate group and
the apical positions by the terminal oxygen and nitrogen atom (Kim and Koo, 1992).

The reaction between the oxomolybdenum(V) complex
Et\(_4\)N[MoO\(_4\)(H\(_2\)O)] and triphenylphosphine oxide (L = OPPh\(_3\)) produces the
mononuclear complex [MoO\textsubscript{3}L\textsubscript{2}] and the dinuclear complex 1 [Mo\textsubscript{2}O\textsubscript{4}I\textsubscript{2}L\textsubscript{3}], the crystal structure of which has been studied by X-ray. Each metal centre is bound to a terminal and two bridging oxygen atoms; the Mo\textsubscript{2}O\textsubscript{2} central fragment appears slightly disymmetric with a short Mo-Mo distance [2.557(1) Å], in agreement with a single metal-metal bond. The whole structure is strongly asymmetric, with the three phosphorus ligands bound to a first molybdenum atom with a distorted octahedral MoO\textsubscript{6} coordination and the two iodo ligands bound to a second molybdenum atom which has a cis-MoO\textsubscript{2}I\textsubscript{2} square-pyramidal coordination. Extended Hückel calculations on the model [Mo\textsubscript{2}O\textsubscript{4}I\textsubscript{2}L\textsubscript{3}] (L = OPH\textsubscript{3}), the structure of which was derived from the averaged structure of 1, have been performed to understand the structure and bonding in this unsymmetrical dimer (Rabe et al., 1993).

Salunke et al. (1994) have reported a series of dinuclear complexes of the type [(MoO\textsubscript{2}Cl\textsubscript{2}(H\textsubscript{2}O))\textsubscript{2}(LH\textsubscript{2})] (where LH\textsubscript{2} = dimethylene bis-2-benzimidazole, tetramethylene bis-2-benzimidazole or hexamethylene bis-2-benzimidazole) and [Mo\textsubscript{2}O\textsubscript{3}Cl\textsubscript{4}(LH\textsubscript{2})\textsubscript{2}] (where LH\textsubscript{2} = tetramethylene bis-5-nitro-2-benzimidazole). The dinuclear complexes did not absorb in the visible region, possibly due to the presence of a Mo\textsubscript{2}O\textsubscript{4}\textsuperscript{2+} core, which was also indicated by their diamagnetic behaviour.

Perera et al. (1995) reported the air oxidation of the tricarbonylmolybdenum(II) complex [MoCl\textsubscript{2}(CO)\textsubscript{a}(PPh\textsubscript{2}ClOH\textsubscript{15}=NI-I)] (2) gave the binuclear oxygen- bridged oxomolybdenum(V) complex [{Mo(=O)Cl\textsubscript{2}(O=PPh\textsubscript{2}C\textsubscript{10}H\textsubscript{15}=NH)}\textsubscript{20} ] (4), containing bidentate imino-phosphine oxide ligands. Crystals of 4 are orthorhombic, space group P2\textsubscript{1}-212- with a = 13.885(2), b = 18.308(4), c = 18.439(5)/, Z = 4, R = 0.0395 for 3531 observed reflections with I>2.0tr (/). Each molybdenum atom is in a distorted octahedral coordination linked by a bent Mo-O-Mo bridge with an angle of 158.2(3) °, and Mo(=O) groups are c/s to each other.
Synthesis, characterization and thermal decomposition studies of several Mo(V) complexes with ONS ligands derived from salicylaldehyde and S-methyl isothiosemicarbazone (Szécsényi et al., 1997) and hydrazone ligands derived by the condensation of morpholine N-thiohydrazide with salicylaldehyde and 2-hydroxyacetophenone have been reported (Dey and Chakraborty, 1999).

New oxomolybdenum(V) porphyrin complexes, [MoO(tmp)(C₆H₅SO₃)] 1, [MoO(tpp)(C₆H₅SO₃)] 2, [MoO(tpp)(HSO₄)] 3, [{MoO(tpp)}₂(MU·SO₄)] 4, and [MoO(tpp)(NO₃)] 5, were synthesized and characterized by UV-vis, IR, FAB-MS, and ESR measurements. The structures of the complexes, 1, 4, and 5, were determined by X-ray crystallographic analysis. The oxidation number of the central molybdenum ion of these complexes was confirmed to be 5+ by ESR measurements. In the dinuclear complex 4, a sulfate ion bridges two molybdenum porphyrins. The dinuclear complex 4 exhibited spin coupling between the two molybdenum nuclei (Okubo et al. 1999).

Harikumaran and Prabhakaran have synthesized and characterized series of oxomolybdenum(V) and dioxomolybdenum(VI) complexes of Schiff bases derived from 4-aminoantipyrine (Harikumaran and Prabhakaran, 1998) and isonicotinoylhydrazide (Prabhakaran and Harikumaran, 2000) with various aldehydes such as salicylaldehyde, 2-hydroxy-1-naphthaldehyde, furan-2-aldehyde, 4-dimethylamino benzaldehyde, 2-hydroxyacetophenone or p-chlorobenzaldehyde. The ligands were monoanionic tridentate or neutral bidentate. They were characterized by elemental analysis, magnetic moments, molar conductance, IR, EPR and UV-Vis spectral data. Harikumaran et al. have also reported the synthesis and characterization of a number of oxomolybdenum(V) and dioxomolybdenum(VI) complexes with this class of Schiff base ligands (Sheela et al., 2007; Harikumaran and Pramila, 2008; Harikumaran and Siji, 2009). Harikumaran and Thankamani (2009, 2010a, 2010b, 2011) have reported the synthesis and single crystal X-ray diffraction studies of
oxomolybdenum(V) and dioxomolybdenum(VI) complexes of hydrazones derived from isonicotinoylhydrazide. Some of these complexes were tested for their possible anti cancer and antimicrobial activities.

Ligands such as azo dyes with ONO donor site were also used for the preparation of oxomolybdenum(V) and dioxomolybdenum(VI) complexes. Synthesis and characterization of these complexes with azo ligands derived from 4-aminoantipyrrine have been reported (Harikumaran and Prabhakaran, 2000; Harikumaran and Siji, 2008). In all complexes, the ligands act as monovalent tridentate ONO chelating agents. The complexes were found to be monomeric with distorted octahedral geometry.

Recently Harikumaran and Anju (2012) have reported the synthesis of some novel oxomolybdenum(V) and dioxomolybdenum(VI) complexes with an azo dye methoxyphenolazoantipyrrine (HL) derived from 4-aminoantipyrrine and 2-methoxyphenol. The complexes have been characterized by elemental analyses, molar conductance, magnetic susceptibility data, IR, UV-Vis, $^1$H NMR, EPR and FAB mass spectral studies. Structural and morphological characterization of the complexes [MoO(HL)XCl$_2$] and [MoO$_2$(HL)XCl] before and after gamma ray irradiation, was performed by X-ray diffraction and scanning electron microscopy (SEM). The ligand and the complexes were screened for their possible antimicrobial activities.

Oxomolybdenum(V) and dioxomolybdenum(VI) complexes with neutral bidentate ligands having NO (Sali and Harikumaran, 2007; Harikumaran and Nisha, 2007a; Harikumaran and Sheela, 2008) and NS (Harikumaran and Nisha, 2007b) coordinating sites have been reported. All of them have been characterized by elemental analysis, magnetic susceptibility data, molar conductance, IR, EPR, UV-Vis and $^1$H NMR spectra. CV profile of the complexes showed a quasi-reversible peak, which can be attributed to the
Mo(V)/Mo(IV) redox system. The EPR spectrum was characterized by only a single line with unresolved parallel and perpendicular components. The EPR parameters indicated that the complexes were monomeric with molybdenum in the pentavalent state.

Preparation of new model complexes, $\text{Tp}^*\text{MoX(pterin-R-dithiolene)}$ ($\text{Tp}^*=$tris(3,5,-dimethylpyrazolyl)borate), $X=\text{O, S;} R=\text{aryl}$, for the molybdenum cofactor have been reported. The complexes were characterized by electrospray ionization mass spectrometry, electrochemistry, infrared spectroscopy, electron paramagnetic resonance and magnetic circular dichroism. Cyclic voltammetry reveals that the $\text{Mo(5+/4+)}$ reduction potential is intermediate between that for dithiolenes with electron-withdrawing substituents and simple dithiolates chelates (Burgmayer et al., 2007). An oxo-molybdenum(V) model complex that possesses both thiolate and ene-1, 2, dithiolate donors provided by heteroscorpionate ligand (2-dimethylethanethiol)bis(3,5-dimethylpyrazolyl)methane has also been reported (Kirk and Peariso, 2004).

Synthesis, characterization and electrochemical behavior of oxo-bridged (arylimido)[$\text{tris}(3,5\text{-dimethylpyrazolyl})\text{borato}$]molybdenum(V) complexes have been reported (Topaloglu-Sozuer et al., 2005). Cyclic voltammetric studies of the new compounds revealed a reversible one-electron oxidation process that was little affected by the nature of the substituent on the aryl group, whereas it was greatly affected by replacement of the imido ligand with an oxo ligand.

Kahrovic et al. (2006) have prepared and investigated the molecular structure of dinuclear Mo(V) Schiff base complexes derived from alkylamines and salicylaldehydes. The structure was found to be composed of a di-$\mu$-oxo-$\mu$-acetato-bis [(N-butylsalicylaldeniminato-NO oxomolybdenum(V))] anion, butylammonium cation and two solvent molecules, benzene and acetic acid. The Mo atoms of the binuclear complex [with Mo-Mo bond of 2.5675(5) Å] exhibited the octahedral geometry.
coordinated by a terminal Mo-O_{terminal} [1.681(4) Å], a double Mo-O_{bridging}, Mo-O_{acetato} with bridging function [2.325(3) and 2.353(3) Å], Mo-O_{phenolic} [2.050(3)] Å and azomethine nitrogen from a Schiff base [2.1929(4) Å].

Vrdoljak et al. (2007) have reported Mononuclear oxomolybdenum(V) complexes with thiosemicarbazonato ligands as condensation products of aldehydes (salicylaldehyde, 2-hydroxynaphthaldehyde) with thiosemicarbazides (H$_2$NNHC:SNHR; R = H, CH$_3$, C$_6$H$_5$) were prepared. The [MoOCl$_2$HL] complexes (HL = thiosemicarbazonato ligand) were characterized by chemical analysis, IR spectroscopy, thermogravimetry and two of them, [MoOCl$_2$\{C$_6$H$_4$(O)CH:NNHC:SNHC$_6$H$_5$\}] and [MoOCl$_2$\{C$_{10}$H$_6$(O)CH:NNHC:SNHC$_6$H$_5$\}] CH$_3$CN, by single-crystal X-ray structural analysis. In both complexes the MoO$^{3+}$core is coordinated by a monobasic tridentate ONS thiosemicarbazonato ligand and two chloro ligands. The coordination around the molybdenum atom is a distorted octahedron.

Synthesis and crystal structure of hexanuclear (Cindric et al., 2000a) and octanuclear oxomolybdenum(V) complexes (Modec et al., 2000) have been reported. Oxomolybdenum(V) complexes with a tridentate heteroscorpionate ligand that act as effective models for the one-electron reduced active site of SO have been reported (Peariso et al., 2003). Oxomolybdenum complexes having catalytic and technological applications (Adam et al., 2003.; Douvas et al., 2006) have also been reported. Synthesis, structure and reactions of another series of 1, 2-dicyanoethylenedithiolate coordinated dimeric Mo(V) complexes relevant to the chemistry of Mo(V) dithiolate coordinated Mo-cofactor in molybdenum enzymes were described by Pal et al. (2007).

Awval et al. (2007) have obtained a series of binuclear oxomolybdenum(V) O, O'-ditolyl dithiophosphate complexes, Mo$_2$O$_3$[S$_2$P(OR)$_2$]$_4$ (R = o-, m-, p-C$_6$H$_4$Me) by reacting an aqueous solution of the ammonium salt of O,O'-
ditolyldithiophosphoric acid with an acidic solution of sodium molybdate with constant stirring. These complexes were characterized by elemental analysis and IR, $^1$H and $^{31}$P NMR spectroscopy and X-ray crystallography.

Triply-bridged oxomolybdenum(V) dinuclear complexes with a series of dithiocarbamate ligands [Mo$_2$O$_3$(OC$_2$H$_4$S)(RR'dtc)$_2$](RR'dtc$^-=$dithiocarbamate) have been investigated (Unoura et al., 1999).

The first $\mu$-oxomolybdenum(V) pyridine-2-selenolato complex [Mo$_2$O$_3$(PySe)$_4$] and its pyridine-2-thionato analogues [Mo$_2$O$_3$(PyS)$_4$], [Mo$_2$O$_3$(4-CF$_3$-PymS)$_4$] were synthesized by the reactions of the [MoO$_2$Cl$_2$(DME)] precursor with the corresponding heterocyclic bidentate (N, X) ligands, X = S, Se, where PyS, PySe and 4-CF$_3$-PymS being anions of pyridine-2-thione, pyridine-2-selenolato and 4-trifluoromethyl-2-pyrimidinethiol respectively (Ma et al., 2007).

Soria et al., 2008 have reported the synthesis of mono and binuclear complexes of oxomolybdenum(V) with 2, 2'-bipyrimidine (bpym), MoOCl$_3$(bpym), Mo$_2$O$_3$Cl$_4$(bpym)$_2$, Mo$_2$O$_4$Cl$_2$(bpym)$_2$ and Mo$_2$O$_2$Cl$_6$(\(\mu\)-bpym). They were characterized by EPR, electronic, infrared and Raman spectroscopy, thermal analysis and theoretical calculations.

New molybdenum complexes were prepared by the reaction of [Mo$^{VI}$O$_2$(acac)$_2$] or (NH$_4$)$_2$[Mo$^{V}$OCl$_3$] with different $N$-substituted pyridoxal thiosemicarbazone ligands ($H_2L^1$ = pyridoxal 4-phenylthiosemicarbazone; $H_2L^2$ = pyridoxal 4-methylthiosemicarbazone, $H_2L^3$ = pyridoxal thiosemi carbazone). The investigation of monomeric [MoO$_2$L$^1$(CH$_3$OH)] or polymeric [MoO$_2$L$^{1-3}$] molybdenum(VI) complexes revealed that molybdenum is coordinated with a tridentate doubly-deprotonated ligand. In the oxomolybdenum(V) complexes [MoOCl$_2$(HL$^{1-3}$)] the pyridoxal thiosemicarbazonato ligands are tridentate mono-deprotonated. Crystal and molecular structures of molybdenum(VI) [MoO$_2$L$^1$(CH$_3$OH)]·CH$_3$OH, and
molybdenum(V) complexes \([\text{MoOCl}_2(\text{HL}^1)]\cdot\text{C}_2\text{H}_5\text{OH}\), as well as of the pyridoxal thiosemicarbazone ligand methanol solvate \(\text{H}_2\text{L}^3\cdot\text{MeOH}\), were determined by the single crystal X-ray diffraction method (Vrdoljak \textit{et al.}, 2009).

Six mononuclear Mo(V) Schiff base complexes were prepared by the reaction of \(\text{MoCl}_5\) with Schiff bases, namely \(\text{HL}^1–\text{HL}^3\) and \(\text{HL}^4–\text{HL}^6\), such as 5-hydroxy-3-methyl-1(2-chloro)phenyl-1H-pyrazolone-4-carbaldehyde(I), 5-hydroxy-3-methyl-1(3-chloro)phenyl-1H-pyrazolone-4-carbaldehyde (II), and 5-hydroxy-3-methyl-1(3-sulfoamido)phenyl-1H-pyrazolone-4-carbaldehyde (III) with ethanolamine and propanolamine, respectively, in aqueous ethanolic medium. The resulting complexes have been characterized by elemental analyses, molar conductance, FT-IR, \(^1\text{H}-\text{NMR},\) electronic, electron spin resonance (ESR) spectra, magnetic susceptibility, and thermal study. The molar conductivity data show them to be non-electrolytes. IR and \(^1\text{H}-\text{NMR}\) spectral data suggest that the ligand is a dibasic bidentate with ON donor toward metal ion. Electronic, magnetic, and ESR spectral data suggest that the oxomolybdenum(V) complexes have distorted octahedral geometry (Thaker and Barvalia, 2010).

Oxomolybdenum chemistry is of great interest since such units are found in the active sites of a majority of molybdoenzymes. This review describes synthesis, structure and applications of oxomolybdenum complexes particularly \(\text{cis-MoO}_2(\text{L})(\text{D})\) where L stands for a dianionic tridentate ONO ligand and D for a donor solvent molecule/monodentate ligand. The ligand moieties are derived from Schiff base, hydrazide Schiff base and other related tridentate ligands \(\text{L(H)}_2\). The coordination geometry around the Mo center in these complexes can be best described as a distorted octahedron in which the ONO-tridentate ligand occupies meridional position with two anionic oxygen donors mutually trans and are cis to the oxygen centers of the cis-dioxo
group. Mostly the applications of cis-MoO2-(ONO) type complexes seen in literature are oxo transfer reactions like epoxidation, sulfoxidation and phosphine oxidation reactions (Chakravarthy and Chand, 2012).

Dioxomolybdenum(VI) complexes with the MoO$_2^{2+}$ core have been readily synthesized by ligand exchange reaction of MoO$_2$(acac)$_2$ with different ligands such as Schiff bases prepared by the condensation of appropriate amines with substituted salicylaldehydes (Rao et al., 1995b; Kathale et al., 2001; Gupta et al., 2009), polydentatedioxime based Schiff bases (Mohanty et al., 1990), hydrazones derived from various acid hydrazides (R. Maurya et al., 2003; Vrdoljak et al., 2011a). These reactions proceed in THF, MeOH or EtOH, sometimes with an amine, such as triethylamine to assist the ionization of the incoming ligands. Materials like MoO$_2$X$_2$ (X=Cl, Br), MoO$_2$X$_2$L$_2$ (L=DMF, DMSO, H$_2$O) (Arnáiz et al., 2000, 2002, 2004), MoO$_3$ (Arnáiz et al., 1994; Harikumaran and Thankamani, 2009), Molybdates (Wong et al., 1998; Drake et al., 2007), [MoO$_2$(butanediolato)$_2$] (Zhai et al., 1992) have also been used in the preparation of complexes with the MoO$_2^{2+}$ core. Dioxomolybdenum(VI) complexes prepared by the oxidation of oxo Mo(IV) complexes were also reported (Laughlin and Young, 1996; Sugimoto, 2011).

Several new cis-dioxomolybdenum(VI) coordination complexes have been synthesized incorporating dibasic tridentate Schiff base ligands derived from 5-substituted salicylaldehydes and o-aminophenol,2-aminoethanol or anthranilic acid (Topich, 1981).

The cis-dioxomolybdenum complexes MoO$_2$(L) (L = HPD, APAC, AAC, ACEN and APS) have been synthesized and characterized. The epoxidation of olefins has been studied using these molybdenum complexes as catalysts and tert-butylhydroperoxide (TBHP) as oxidant. The studies suggest that these complexes, except [MoO$_2$(APAC)], did not demetallate during the
reaction (Agarwal and shrivastava, 1988).

Synthesis, characterization, and structural aspects of a new class of dioxomolybdenum(VI) complexes with biologically active benzothiazolines, 2-(2-pyridyl) benzothiazoline, 2-(2-thienyl) benzothiazoline, 2-(2-furyl) benzothiazoline, 2-(3-indolyl) benzothiazoline, glyoxal benzothiazoline, biaacetyl-benzothiazoline, benzil benzothiazoline and terphthaldehyde benzothiazoline have been reported. Two benzothiazolines and their corresponding metal complexes were screened for their antifungicidal and antibacterial activity on several fungi and bacteria and found to be quite active in this respect. They have also been evaluated and experimented in male mice (Kanoongo et al., 1990).

Dioxomolybdenum (VI)-tridentate Schiff base complexes, [MoO₂{nap-(R)-btol}(py)], (1), [{MoO₂{nap-(R)-btol}]₂(4,4′-bpy)] (2), and [MoO₂{nap-(R)-btol}]·CH₂Cl₂(3)(H₂nap-(R)-btol=(R)-2-[(2-hydroxy-1-naphthyl)methylidene]neamino]butanol, py = pyridine, 4,4′-bpy = bipyridine) were prepared and their structures determined by the X-ray method. In 1–3, the geometry around molybdenum is a distorted octahedron with one oxide ligand and the Schiff base ligand in the equatorial position. The oxide ligand occupies the axial position and the nitrogen atom of pyridine or 4, 4′-bipyridine coordinates at the sixth site of the molybdenum center for 1 or 2 respectively. In 3, the axial oxide ligand of one molecule coordinates to the sixth site of the molybdenum atom in an adjacent molecule to give an infinite linear MoO...MoO... chain.1 contains only one of the four possible isomers, while 2 and 3 are composed of two isomers. The ¹H NMR spectra suggest rapid isomerization between the isomers in CD₂Cl₂ even at low temperatures. The isomers would proceed via a five-coordinate intermediate where rotations of the cis-MoO₂ moiety takes place have been reported by Nakajimaa et al. (1998).

Synthesis of variety of cis-MoO₂⁵⁺ epoxidation catalysts bearing chiral
ligands, such as (4'R)-2-(4'-ethyl-3',4'-dihydroxazol-2'-yl)phenolato, (4'S)-2-
(4'-isopropyl-3',4'-dihydroxazol-2'-yl)phenolato (Gómez et al., 2001),
bis(oxazoline) (Kühn et al., 2001) and cis-diol (Brito et al., 2008) have been
reported.

Number of binuclear dioxo complexes with ligands such as tetrade nate
Schiff bases derived from sulpha drugs and 4-benzoyl-3-methyl-1-phenyl-2-
pyrazolin-5-one (R. Maurya et al., 2004) have been reported. Mononuclear
complexes with tetrade nate ligands having amide groups obtained by the
condensation of methylsalicylate and 1, 2-diaminoethane, 1,2-diaminopropane
or 1,3-diaminopropane were prepared by M. Maurya and Singh (2004).

The ligands 5-chloro-1,3-dihydro-3-[2-(phenyl)-ethylidene]-2H-indol-2-
one-hydrazinecarbo-thioamide (L1H) and 5-chloro-1,3-dihydro-3-[2-(phenyl)-
ethylidene]-2H-indol-2-one-hydrazine-carboxamide (L2H) and their dioxo
complexes have been tested in vitro against a number of microorganisms in
order to assess their antimicrobial properties (Garg et al., 2006). Dio xo Mo(VI)
complexes with Schiff bases derived from 2-hydroxychloroacetophenone and
4-amino-5-mercapto-3-methyl-1,2,4-triazole having moderate activity against
_E. coli_ and _P. aeruginosa_ have been reported (Badwaik and Aswar, 2007).
Antimicrobial and antifertility studies of dio xo molybdenum(VI) unsymmetrical
imine complexes were reported. The antifertility screening data indicated the
antiandroge nic nature of the complexes (R. Singh et al., 2004).

Six dio xo molybdenum(VI) complexes of Schiff-bases derivatives of
_trans-_1,2-diaminocyclohexane and R-salicylaldehyde as well as 2-hydroxyp
aphthaldehyde have been synthesised and characterized by IR, UV-Vis and
NMR-spectroscopic methods. The catalytic activities of the complexes in the
reaction of epoxidation of cyclohexene and 1-octene with tert-butyl
hydroperoxide (TBHP) as oxidant have been studied (Ambroziak et al., 2004).
Polymer complexes of the composition MoO$_2$X$_2$ and dioxomolybdenum species bound to the active sites of silica have been reported to be efficient catalysts for a variety of catalytic reactions (Jarupatrakorn et al., 2005; M. Maurya et al., 2005).

Antimicrobial and antifertility studies of dioxomolybdenum(VI) unsymmetrical imine complexes were reported. The antifertility screening data indicated the antiandrogenic nature of the complexes (R. Singh et al., 2004). Complexes with salen-type ligand functionalised with two pyrrole derivative pendant arms have also been reported (Bruno et al., 2007).

Majority of mononuclear molybdenum containing enzymes have the general function of catalyzing a net oxygen atom transfer (OAT) to or from a physiological donor/acceptor with the metal cycling between the +6 and +4 oxidation states. It initiated the development of models for the active sites of oxo-transfer molybdoenzymes. Complexes with bulky ligands like bis(4-tert-butylphenyl)-2-pyridylnmethanol, diphenyl-2-pyridylmethanethiol, bis-(4-tert-butylphenyl)-2-pyridylmethanethiol (Schultz et al., 1993), hydrotiris(3, 5-dimethyl-pyrazol-1-yl)borate (Sengar et al., 2007) have been prepared to study oxygen atom transfer reactions. Synthesis of a series of dioxoMo(VI) complexes of the “soft” tripodal ligand, sodium tris(mercaptoimidazolyl)borate (NaTm$^\text{Me}$), as potential oxygen atom transfer (OAT) models for sulfite oxidase have been reported (Tran and Carrano, 2007a).

Mixed ligand complexes of dioxomolybdenum(VI) with 2-hydroxybenzaldehyde 4-phenyl-S-methylthiosemicarbazone (H$_2$L) were prepared with the formula [MoO$_2$(L)D] (D = H$_2$O, methyl, n-butyl, and n-undecyl alcohol, DMF, DMSO, pyridine, 4-picoline, and 3,5-lutidine). The compounds were characterized by elemental analysis, IR and $^1$H NMR spectroscopy. The thermal decomposition of the compounds were investigated.
by using TGA, DTG, and DTA methods in air, and the thermal behavior depending on the second ligand molecule was discussed. A single crystal of the DMF coordinated complex was studied by X-ray diffractometry (Kurt et al., 2007).

Seena and Prathapachandra Kurup (2007) had prepared two dinuclear complexes, [(MoO$_2$L$_1^1$)$_2$] and [(MoO$_2$L$_2^2$)$_2$] by the reaction of [MoO$_2$(acac)$_2$] with 2-hydroxy-acetophenone N(4)-cyclohexyl (H$_2$L$_1^1$) and N(4)-phenyl (H$_2$L$_2^2$) thiosemicarbazones in alcoholic medium and two mononuclear dioxomolybdenum(VI) complexes, [MoO$_2$L$_1^1$py] and [MoO$_2$L$_2^2$py] by the reaction of the above dinuclear complexes with pyridine in alcoholic medium. In all complexes, molybdenum was coordinated by two terminal oxo-oxygen atoms, O($t$), oxygen, nitrogen and sulfur atoms from the principal ligand and by an oxygen atom (from the second unit in the dinuclear complex) or by a nitrogen atom (from pyridine in mononuclear complexes). All complexes had been spectroscopically characterized. The molecular structures of three complexes had been determined by the single crystal X-ray diffraction method.

Presence of the hydrogen bonding near a metal center can influence the properties of the complex. Here, we describe changes in redox and spectral properties in discrete dioxo-molybdenum centers coordinated by a single thiolato ligand that can support an intra-ligand hydrogen bond. We have utilized thiophenolato ligands that can harbor hydrogen bonding between the thiophenolato sulfur with an amide functionality creating either a five- or a six-membered ring. Methylation of the amide functionality removes the NH...S hydrogen bonding thus providing a basis for understanding the effect of hydrogen bonding. These thiophenolato ligands have been used in synthesizing dioxo-MoVI complexes. The complexes have been characterized by NMR, infrared, and UV-visible spectroscopy. Spectroscopic data clearly indicate the presence of hydrogen bonding in both, and stronger in, where hydrogen
bonding stabilizes a five-membered ring. All complexes exhibit a Mo(VI)/Mo(V) redox couple and redox potentials are modulated by the nature of H-bonding. Compound with the electron-releasing N(Me)COMe group has the highest reduction potential and is more difficult to reduce (Sengar et al., 2008).

Synthesis and X-ray crystal structure of cis-dioxomolybdenum(VI) complexes with amino acid functionalized Schiff bases were reported by Mancka and Plass (2007) and Cindric et al. (2009). The new cis-dioxomolybdenum(VI) complexes were found to be efficient catalysts for the peroxidic oxidation of sulfides, but did not show any activity towards the oxidation of bromide.

New molybdenum complexes were prepared by the reaction of \([\text{Mo}^\text{VI}O_2(\text{acac})_2]\) or \((\text{NH}_4)_2[\text{Mo}^\text{V}O\text{Cl}_5]\) with different \(N\)-substituted pyridoxal thiosemicarbazone ligands \((\text{H}_2\text{L}^1 = \text{pyridoxal 4-phenylthiosemicarbazone}; \ \text{H}_2\text{L}^2 = \text{pyridoxal 4-methylthiosemicarbazone}, \ \text{H}_2\text{L}^3 = \text{pyridoxal thiosemi carbazone})\). The investigation of monomeric \([\text{MoO}_2\text{L}^1(\text{CH}_3\text{OH})]\) or polymeric \([\text{MoO}_2\text{L}^{1-3}]\) molybdenum(VI) complexes revealed that molybdenum is coordinated with a tridentate doubly-deprotonated ligand. In the oxomolybdenum(V) complexes \([\text{MoOCl}_2(\text{HL}^{1-3})]\) the pyridoxal thiosemicarbazonato ligands are tridentate mono-deprotonated. Crystal and molecular structures of molybdenum(VI) \([\text{MoO}_2\text{L}^1(\text{CH}_3\text{OH})]\cdot\text{CH}_3\text{OH}, \ \text{and molybdenum(V) complexes [MoOCl}_2(\text{HL}^1)]\cdot\text{C}_2\text{H}_5\text{OH}, \ as well as of the pyridoxal thiosemicarbazone ligand methanol solvate \(\text{H}_2\text{L}^3\cdot\text{MeOH}, \ were determined by the single crystal X-ray diffraction method (Vrdoljak et al., 2009).

Ligands with two or three different donor atoms are usually used for the preparation of dioxomolybdenum(VI) complexes. Several dioxomolybdenum(VI)
complexes of the type cis-[MoO₂LX] (where X = H₂O, pyridine, THF, C₂H₅OH, Imz, Cl, NCS, NO₃, ClO₄) bearing tridentate ONO ligands formed by the condensation of various acid hydrazides with substituted salicylaldehydes, acetophenone and p-hydroxy benzoylhydrazone have been reported in the literature (Liu et al., 1994; Ivanović et al., 1996, Harikumaran and Thankamani, 2010b). The ligands were dibasic or monobasic tridentate and the complexes possess a cis-MoO₂ structure.

Vrdoljak et al. (2010, 2011b) reported the synthesis, characterization and molecular structure of zigzag chain, square tetra nuclear and polyoxometalate cis-dioxo Mo(VI) complexes using aroylhydrazone ligands, 2-hydroxy-1-naphthaldehyde (H₂NIH), 3-methoxy-2-hydroxybenzaldehyde (H₂VIH) and salicylaldehyde isonicotinoylhydrazone (H₂SIH). Synthesis, characterization and molecular structure of monomeric tridentate ONO Schiff base complexes, [MoO₂(O−C₆H₄CH≡NN−COCH₂N(CH₃)₂)CH₃OH] (Wang et al., 1994) and Mo⁶O₂ (2−O−C₁₀H₆−C=N−C₆H₄−o−S)(CH₃−SO−CH₃) (Hahn et al., 1995) have been reported. X-ray structure analysis revealed that the complexes possess the usual cis-MoO₂²⁺ core and had distorted octahedral coordination geometry. Rao et al. (1995a) reported the synthesis and characterization of some 8-coordinate cis-dioxomolybdenum(VI) complexes of Schiff bases derived from 4-aminoantipyrine and 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one, 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one and 4-benzyol-3-methyl-1-phenyl-2-pyrazolin-5-one.

Neutral dioxomolybdenum(VI) complexes of dibasic 2-hydroxy-1-naphthaldehyde S-ethyl-4-H/phenyl-thiosemicarbazones (H: L¹, C₆H₅: L²) have been synthesized. The complexes, [MoO₂L¹(ROH)] (1a–d) and [MoO₂L²(ROH)] (2a–d) (R: CH₃, C₂H₅, C₃H₇, C₄H₉) were characterized by elemental analysis, electronic, IR and ¹H NMR spectra. X-ray crystal studies indicated a distorted octahedral geometry for [MoO₂(L¹)(C₂H₅OH)] (1b) (Duman et al., 2010).
b. dioxouranium(V) complexes

The syntheses of several new coordination complexes of nickel(II), cobalt(II), manganese(II), copper(II), zinc(II), dioxouranium(VI) and dioxomolybdenum(VI) with new Schiff bases derived from 2-benzothiazolecarbohydrazide and salicylaldehyde or 2-hydroxy-1-naphthaldehyde are described. These complexes have been characterised by elemental analyses, electrical conductance, magnetic susceptibility, molecular weight, i.r. and electronic spectra (Syamal and Maurya, 1986).

Dioxouranium(VI) complexes of the types UO$_2$LSO$_4$ and UO$_2$L$_2$SO$_4$ (where L=SH, ASH) have been prepared from reaction of uranyl sulphate with salicylhydrazine (SH) and acetone salicylhydrazone (ASH) and characterized by conventional chemical and physical measurements. Infrared and Raman spectra indicate that mono- and bis-complexes contain six-and seven-coordinate uranium atom respectively with all the ligand atoms arranged in an equatorial plane around the linear uranyl group (Lal, 1987).

Some thorium(IV) and dioxouranium(VI) complexes with pentamethylene sulphoxide (PMSO) of the general composition [ThX$_4$(PMSO)$_n$] (X = Cl, Br, NO$_3$, or NCS, n = 2; X = I, n = 4; X = ClO$_4$, n = 6) and [UO$_2$X$_2$(PMSO)$_n$] (X = Cl, Br, I, NO$_3$, NCS or CH$_3$COO, n = 2; X = ClO$_4$, n = 4) were synthesized and characterized by IR, conductivity, molecular weight and analytical techniques. In all the complexes the PMSO is coordinated to the metal ion via its oxygen donor atom (Agarwal and Prakash, 1991).

Keeping in view the chemotherapeutic value of the sulfa-drugs, two scruff base ligands viz vanillin-sulfanilamide (VSAH) and oorder-vanillin-sulfamerazine (VSmrzH) and their bipositive, tripositive tetrapositive and uranyl metal complexes have been synthesized and characterized by elemental
analysis, IR spectra, thermal analysis, magnetic susceptibility measurements, diffuse reflectance spectra and $^1$H NMR spectra and molar conductance measurements (Maurya and Pratibha Patel, 1999).

La(III), Ce(III), Th(IV) and UO$_2$(VI) chelates with 3-phenyl-4-arylazo-5-pyrazolones have been synthesized and were characterized by several analytical tools such as elemental analyses, IR, NMR, TG and molar conductance techniques. The data obtained show that all of the prepared complexes contain water and/or alcohol molecules in their coordination sphere and the ligands form 1:1 and 1:2 complexes which are in good agreement with the proposed formulae. The NMR data of the prepared ligands show the existence of the ketonic structure rather than the enolic form. The TG data revealed no crystal water outside the coordination sphere. The azopyrazolone ligands act as neutral bidentate ligands bonded to the metal ions through the oxygen atom of the carbonyl group and the $\alpha$ nitrogen of the arylazo group. All solid chelates prepared behave as non-electrolytes in DMF solution. The coordination numbers of the prepared chelates are ranging from 6 to 12 for 1:1 and from 7 to 12 for 1:2 chelate (Abdel-Latif, 2001).

The polydentate ligands, N,N' - ethylene - bis-(2-aminobenzamide) [EBAB], N,N' - propylene-bis-(2-aminobenzamide) [PBAB], N,N' - (o-phenylene)-bis-(2-aminobenzamide) [PhBAB], N,N' - ethylene-bis-(3-carboxypropenamide) [EBCP], N,N' - propylene-bis-(3-carboxypropenamide) [PBCP] and 1 -(2'-hydroxyphenyl)- 3-phenyl 1,3-propane-dione [HPPPD] react with uranyl acetate to form crystalline complexes with different coordination environments. The geometries of the complexes have been confirmed with the help of the spectroscopic methods, conductance measurements and thermal studies. The neutral tetradeutate ligands (EBAB, PBAB and PhBAB) form eight coordinate hexagonal bipyramidal complexes, while anionic tetradeutate
ligands (EBCP and PBCP) and tridentate ligand (HPPPD) form seven coordinate pentagonal bipyramidal complexes (Swamy and Bhaskar, 1999).

Dioxouranium(VI) complexes with four ligands which were obtained by the condensation of acetoacetanilide with benzoyl-, salicyloyl- and isonicotinoylhydrazines and semicarbazide hydrochloride, have been synthesized and characterized on the basis of elemental analyses, molar conductance and magnetic measurements as well as electronic and IR spectral studies. The hydrazones and semicarbazone act as neutral bidentate ligands bonding through the anilide carbonyl oxygen and azomethine nitrogen atoms and the nitrate and the acetate anions coordinate in a monodentate fashion (Jayasree and Aravindakshan, 1999).

Gatto et al., 2004 reported dioxouranium(VI) complexes with 2,6-acetylpyridinebenzoylhydrazones and semicarbazones. The neutral compounds contain doubly deprotonated ligands and possess uranium atoms with distorted pentagonal bipyramidal coordination spheres. The equatorial coordination spheres of the metal atoms can be extended by the addition of a monodentate ligand such as pyridine or DMSO. The uranium atoms in the resulting complexes have hexagonal-bipyramidal coordination environments with the oxo ligands in axial positions. X-ray diffraction studies on [UO$_2$(L$_1$)(DMSO)], [UO$_2$(L$_2$)], [UO$_2$(L$_3$)(DMSO)] and [UO$_2$(L$_3$)] show relatively short U-O bonds to the benzoic oxygen atoms between 2.273(6) and 2.368(5) Å. This suggests a preference of these donor sites of the ligands over their imino and amine functionalities (U-N bond lengths: 2.502(7)-2.671(7) Å). The addition of a sixth ligand to the equatorial coordination sphere results in a lengthening of the metal-pyridine bonds.

Four acyl dipyridoxal hydrozones ligands, H$_4$PL$^n$, have been prepared by condensing the ester of the diacids, hydrazine hydrate and pyridoxal
hydrochloride in 1:2:2 molar ratio. The UO$_2^{\text{VI}}$ complexes of these ligands have been synthesized and characterized by various analytical and spectroscopic methods including X-ray crystallography. The ligands and UO$_2^{\text{VI}}$ complexes have been tested for cytotoxicity. The solid-state structure of [(UO$_2$)$_4$(PL$_1^1$)$_2$(H$_2$O)$_4$]$\cdot$12H$_2$O has been found to be a cyclic tetramer and this may or may not represent the structure of the bulk sample. The structures of bulk 1–4 have been proposed to be polymeric (Yang et al., 2005).

The synthesis of thorium(IV) and dioxouranium(VI) coordination compounds of 4[N-(2’-hydroxy-1’-naphthaldene) amino] antipyrine thio semi carbazone (HNAAPTS) with the general composition ThX$_n$(HNAAPTS) (X = Cl, Br, I, NCS or ClO$_4$; n = 2; X= NO$_3$, n = 1) and UO$_2$X$_2.n$(HNAAPTS) (X = Br, I, NCS or ClO$_4$, n = 2, X = NO$_3$ or CH$_3$COO, n = 1). All the coordination compounds were characterized by analytical, molar mass, molar conductance and infrared studies. The infrared spectral studies reveal that the ligand HNAAPTS is coordinated in neutral tridentate (N,N,S) fashion. The coordination number of Th(IV) in these coordination compounds varies from 6, 8, 10 or 11; while for U(VI) the coordination number are 8, 9 or 10. Thermal stabilities of these complexes were investigated through thermogravimetric analysis (Agarwal et al., 2005).

The reactions of dioxouranium(VI) acetate with several semicarbazones derived from 4-aminoantipyrine in the presence of diphenyl sulfoxide (DPSO) led to the formation of complexes. The complexes were characterised by means of elemental analyses, conductivity measurements, molecular weight, magnetic moments and infrared studies. The coordination number 10 is proposed for these complexes. Thermal properties of the representative complexes are also reported (Agarwal and Prasad, 2006).
The mononuclear complex of the second-generation quinolone antibacterial agent ciprofloxacin with UO$_2^{2+}$ has been prepared and characterized with physicochemical and spectroscopic techniques. In this complex, ciprofloxacin acts as a bidentate deprotonated ligand bound to the metal through the pyridone oxygen and one carboxylate oxygen. The central U(VI) atom is six-coordinate and a slightly distorted octahedral geometry is proposed. The lowest energy model structure of the complex has been determined with molecular modelling calculations. The biological activity of the complex has been evaluated by examining its ability to bind to calf-thymus DNA (Psomas et al., 2007).

Some dioxouranium(VI) bis-complexes of ligands (LH); benzoylhydrazine (BH), salicyloylhydrazine (SalH), nicotinoylhydrazine (NH) and their Schiff bases with acetone (LH); isopropylenebenzoylhydrazine (IPBH), isopropylensalicyloylhydrazine (IPSalH), isopropylenicotinoylhydrazine (IPNH) in their both keto and enol forms have been prepared. Magnetic moment, electronic and infra-red spectral data, conductance and elemental analyses help describing the possible stereochemistry of the prepared complexes (Chowdhury et al., 2008).

Reactions of salicyl- and 3,5-dichlorosalicylaldehyde-S-propyl-thiosemicarbazones with salicyl- and 3,5-dichlorosalicylaldehyde in the presence of UO$_2$(CH$_3$COO)$_2$ in different alcohols yielded stable solid complexes corresponding to the general formula [UO$_2$(L)ROH] (R: propyl-, butyl-, pentyl-, and octyl-). The complexes were characterized by means of elemental analysis, IR and $^1$H NMR spectroscopies. The thermal stabilities of the alcohol solvated complexes were investigated in air and nitrogen atm., and determined their decomposition phases. In the crystal structure of the [UO$_2$(L)(C$_4$H$_9$OH)], the U(VI) centre is seven-coordinated in a distorted pentagonal bipyramidal geometry involving O,O,N,N atoms of two phenolic
and two imine groups and one oxygen atom of alcohol molecule in basal plane and two O atoms of dioxo group in apical positions (Sahin et al., 2009).

A series of homo binuclear complexes have been synthesized in template method from ethylenediamine/orthophenylene diamine, benzil monohydrazone and acetyl monoxime and characterized on the basis of elemental analysis, thermal analysis, molar conductivity, magnetic moment, electronic, infrared, $^1$H-NMR studies. The results indicate that the VO(IV) ion is penta co-ordinated yielding paramagnetic complexes; UO$_2$(VI), ZrO(IV) ions are hexa co-ordinated where as Th(IV) ion is octa co-ordinated yielding diamagnetic complexes of above composition (Mohapatra et al., 2012).

N-[(Diphenylamino)methyl]acetamidewas synthesized using Mannich reaction and its complexes of cerium(IV), thorium(IV) and dioxouranium(VI) were prepared and characterized by elemental analysis and various spectral studies. The bidendate chelation of ligand, bonding through carbonyl oxygen and azomethine nitrogen is suggested. Based on spectral and magnetic studies, hexa coordinate geometry is assigned for all the complexes. The complexes were screened for their antibacterial, antifungal and anticancer activities. They show positive results (Muruganandam et al., 2013).

c. Ruthenium(III) complexes

The $g$-tensor theory of low-spin $d^5$ configuration in octahedral fields having axial (tetragonal or trigonal) and rhombic distortions is summarised. Illustrations taken from literature concern the following ruthenium(III) species: Ru(H$_2$O)$_6^{3+}$ (trigonal), Ru(bpy)$_3^{3+}$ (trigonal), the Creutz-Taube cation (axial + rhombic) and RuCl$_2$(HL) (L) (axial + rhombic: HL = isonitrosoketone). The rationalisation of distorttion parameters in terms of bonding is considered (Bhattacharya and Chakravorty, 1985).
Stable ruthenium(III) carbonyl chelates of Schiff bases with axial ligands chloro, imidazole, and 2-methylimidazole are synthesized by interacting the methanolic solutions of their corresponding Ru(III) chloro complexes with carbon monoxide. The Schiff bases used are bis(salicylaldehyde) ethylenediimine (salen), bis(salicylaldehyde) o-phenylenediimine (saloph), bis(salicylaldehyde) diethylenetriimine (saldien), bis(picolinaldehyde) ethylenediimine (picen), bis(picolinaldehyde) o-phenylenediimine (picoph), and bis(picolinaldehyde) diethylenetriimine (picdien). These complexes are characterized by elemental analysis and IR, UV-visible, differential-pulse polarography, conductivity, magnetic susceptibility, and EPR techniques. (Taqui Khan et al., 1990).

Synthesis and characterization of ruthenium(III) complexes with azo dyes derived from 4-aminoantipyrine have been reported (Harikumaran and George, 2004; Harikumaran and Mariamma, 2007). All of them have been characterized by elemental analysis, magnetic susceptibility data, molar conductance, IR, EPR, UV-Vis and $^1$H NMR spectra. Recently Harikumaran and Anju, 2012) have reported the synthesis and characterization of Ru$^{III}$ complexes with an azo dye methoxyphenolazoantipyrine( HL) derived from 4-aminoantipyrine and 2-methoxyphenol are reported. The complexes have been characterized by elemental analyses, molar conductance, magnetic susceptibility data, IR, UV-Vis, EPR and FAB mass spectral studies. The physico-chemical studies and spectral data indicate that HL acts as a bidentate chelating ligand. The effect of gamma ray irradiation on the thermal behaviour and the surface morphology of a selected complex [RuCl$_3$(PPh$_3$)(HL)] was studied.

Three ruthenium(III) complexes containing 1H-1,2,4-triazole (Htrz), viz., (H$_2$trz)[cis-RuCl$_4$(Htrz)$_2$], 1, (H$_2$trz)[trans-RuCl$_4$(Htrz)$_2$], 2, and (Ph$_3$PCH$_2$Ph)[trans-RuCl$_4$(Htrz)$_2$], 3, have been synthesized by reaction between RuCl$_3$ and excess of the triazole in 2.38M HCl (1 and 2), while 3 was
obtained by metathesis of 2 and [Ph$_3$PCH$_2$Ph]Cl in water. The products were characterized by IR, UV-vis, electrospray mass spectrometry, cyclic voltammetry, and X-ray crystallography (1 and 3). X-ray diffraction study revealed cis and trans arrangements of the triazole ligands in 1 and 3, correspondingly, and unprecedented monodentate coordination of the triazole through N$_2$ and stabilization of its 4H tautomeric form, which is the disfavored one for the free triazole. The cytotoxicity of 1 and 2 has been assayed in three human carcinoma cell lines SW 480, HT 29 (colon carcinoma), and SK-BR-3 (mammary carcinoma). Both compounds exhibit antiproliferative activity in vitro (Vladimir et al., 2003).

Ru$^{III}$ complexes of the type [RuX(L)$_2$(E)] (X = Cl or Br; L = novel bidentate Schiff base ligand; E = PPh$_3$ or AsPh$_3$) have been prepared by reacting [RuX$_3$(E)$_3$] or [RuBr$_3$(PPh$_3$)$_2$(MeOH)] with two novel bidentate Schiff base ligands derived from 4-[(1-methyl-1-mesitylcyclobutane-3-yl)-2-aminothiazole, in a 1:2 molar ratio in benzene, and characterised by analytical, spectral (IR, electronic, $^1$H, $^{13}$C- NMR, and EPR) and electrochemical data. An octahedral structure has been tentatively proposed for all the new complexes. The new Ru$^{III}$ complexes are effective catalysts for the oxidation of alcohols to carbonyl compounds but are unable to oxidise alkenes in the presence of N-methylmorpholine-N-oxide (NMO) as co-oxidant (Daniel Thangadurai and Son-Ki Ihm, 2004).

Schiff-base complexes of ruthenium have been synthesized using Schiff-base ligands derived by condensation of either 1,2-phenylenediamine with aldehydes (salicyldehyde, 2-pyridinecarboxaldehyde) or acetylacetone with amines (2-aminophenol, 2-aminomethylpyridine). All complexes were characterized by analytical, spectroscopic, conductance, magnetic moment and electrochemical studies. At room temperature, complexes catalyze the oxidation of both saturated and unsaturated hydrocarbons using tert-butylhydroperoxide
(t-BuOOH). A mechanism involving formation of and transfer from a reactive high valency Ru(V)-oxo species as the catalytic intermediate is proposed for the processes (Chatterjee and Mitra, 2004).

A novel complex \([\text{Li}_3\{\mu-(\text{H}_2\text{O})_6\}(\text{H}_2\text{O})_6]\cdot[\text{RuCl}_6]\) has been synthesized and was characterized by single-crystal X-ray diffraction. The compound consists of a cation, which contains three lithium ions linked by six bridged water molecules, and an anion, which contains a ruthenium(III) ion. The whole complex can be described as a three dimensional structure linked by hydrogen bonds between cation and anion. The magnetic properties of the complex have been investigated. The IR, UV-vis and EPR spectra are studied (Bai et al., 2004).

Reaction of N-(aryl)picolinamide with ruthenium trichloride or \([\text{Ru(DMSO)}_4\text{Cl}_2]\) in refluxing 2-methoxyethanol in the presence of a base (\(\text{NEt}_3\)) affords tris complexes of the type \([\text{Ru(L}-\text{R})_3]\). The structure of the \([\text{Ru(L}–\text{OCH}_3)_3]\) complex has been determined by X-ray crystallography. In these complexes the amide ligands are coordinated to the metal center as monoanionic bidentate N, N-donors. All the \([\text{Ru(L}–\text{R})_3]\) complexes are one-electron paramagnetic and show rhombic ESR spectra at 77 K. They also show intense LMCT transitions in the visible region. Cyclic voltammetry on all the complexes shows a ruthenium(III)/ruthenium(IV) oxidation within the range of 0.89 to 1.21 V vs. SCE and a ruthenium(III)/ruthenium(II) reduction within the range of -0.22 to -0.41 V vs. SCE. Representative one-electron oxidized and reduced complexes have also been generated in solution and characterized spectroscopically as well as electrochemically (Das et al., 2004).

The synthesis and characterization of several hexa-coordinated ruthenium(III) complexes of the type \([\text{RuX}_2(\text{EPh}_3)(L)]\) (\(E 5 \text{P or As; } X 5 \text{Cl or Br; } L 5 \text{monobasic tridentate ligand derived by the condensation of o-}

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phenylene diamine or ethylene diamine with salicylaldehyde or o-hydroxyacetophenone) are reported. Elemental analyses, IR, electronic, EPR, and cyclic voltammetric data of the complexes are discussed. An octahedral geometry has been tentatively proposed for all the complexes. The new complexes were found to be effective catalysts for the oxidation of benzyl alcohol and cyclohexanol to benzaldehyde and cyclohexanone, respectively, using N-methylmorpholine-N-oxide as a co-oxidant (Karvembu et al., 2005).

A series of octahedral Ru(III), Rh(III) and Ir(III) complexes have been prepared with tetradeinate Schiff bases derived by condensing isatin with 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,2-diaminobenzene and 1,3-diaminobenzene. The obtained complexes were characterized on the basis of their elemental analyses, magnetic moment, conductance, IR, electronic, $^1$HNMR and FAB mass spectra, as well as thermal analyses. (Sharma et al., 2006).

The Schiff base octaazamacrocyclic ligands derived from primary diamines and 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione, and their binuclear complexes $[M_2LCl_4]Cl_2$ [$M = Cr(III), Fe(III), Co(III)$ or Ru(III)] and $[Mn_2L(AcO)_4](AcO)_2$ were synthesized by template condensation reactions. The overall geometry and stereochemistry of these complexes were elucidated by elemental analyses, magnetic susceptibilities, electronic spectra, infrared spectra, molar conductance measurements, $^1$H NMR, and thermogravimetric analysis (Sharma and Srivastava, 2006a).

The Schiff base octaazamacrocyclic ligands derived from primary diamines and 3,6-dimethyl/diphenyl-4,5-diazaocta-3,5-diene-2,7-dione, and their binuclear complexes $[M_2LCl_4]Cl_2$ [$M = Cr(III), Fe(III), Co(III)$, or Ru(III)] and $[Mn_2L(AcO)_4](AcO)_2$ were synthesized by template condensation reactions. Attempts to synthesize the corresponding metal-free macrocyclic
ligands did not prove successful. The overall geometry and stereochemistry of these complexes were elucidated by elemental analyses, magnetic susceptibilities, electronic spectra, infrared spectra, molar conductance measurements, $^1$H NMR, and thermogravimetric analysis. All the trivalent metal ion complexes appear to be 1:2 electrolytes. An octahedral geometry is proposed for all the complexes (Sharma and Srivastava, 2006b).

A series of new mixed ligand hexacoordinated ruthenium(III) Schiff base complexes of the type [RuX$_2$(EPh$_3$)$_2$(LL')] (X=Cl, E=P; X=Cl or Br, E =As and LL' = anion of the Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde with aniline, 4-chloroaniline, 2-methyl aniline and 4-methoxy aniline) are reported. All the complexes have been characterized by analytical and spectral (IR, electronic and EPR) data. The redox behavior of the complexes has also been studied. The complexes exhibit catalytic activity in the oxidation of benzyl alcohol to benzaldehyde in the presence of N-methyl morpholine-N-oxide (NMO). An octahedral structure has been proposed for all of the complexes (Mahalingam et al., 2006).

Five bis-[5-(4'-R-phenylazo)-8-hydroxyquinoline] ruthenium complexes have been prepared and characterized on the basis of elemental analyses, IR, $^1$H NMR, ESR, thermal analysis and magnetic susceptibility measurements. The data show that these complexes exist in trans-isomeric solid form. Two inversion-related ligands and two Ru$^{3+}$ atoms form a cage-like dimer. Both ligands of the dimer are bridged by a pair of inversion-related Ru–N (azodye) bonds. The octahedral coordination geometry of Ru$^{3+}$ is made up of an N of pyridine, the deprotonated quinoline O atom, one of the azodye N atoms, two chlorides and one water (Mubarak et al., 2007).

The reactions of 1 mol equiv. each of [Ru(PPh$_3$)$_3$Cl$_2$] and N-(acetyl)-N'-[(5-R-salicylidene)hydrazines (H$_2$ahsR, R = H, OCH$_3$, Cl, Br and NO$_2$) in
alcoholic media afford simultaneously two types of complexes having the general formulae \([\text{Ru(HahsR)}(\text{PPh}_3)_2\text{Cl}_2]\) and \([\text{Ru(ahsR)}(\text{PPh}_3)_2\text{Cl}]\). The complexes have been characterized by elemental analysis, magnetic, spectroscopic and electrochemical measurements (Raveendran and Pal, 2008).

Four related ruthenium(III) complexes, with the formula mer-[\text{RuCl}_3(\text{dmso})(\text{N-N})] (\text{dmso} = \text{dimethylsulfoxide}; \text{N-N} = 2,20\text{-bipyridine (1), 1,10-phenanthroline (2), dipyrido[3,2-f:20,30-h]quinoxaline (3) and dipyrido[3,2-a:20,30-c]phenazine (4)}), have been reported. Complexes 3 and 4 are newly synthesized and characterized by X-ray diffraction. The hydrolysis process of 1–4 has been studied by UV–vis measurement, and it has been found that the extension of the N-N ligands can increase the stability of the complexes. The binding of these complexes with DNA has been investigated by plasmid cleavage assay, competitive binding with ethidium bromide (EB), DNA melting experiments and viscosity measurements. The DNA binding affinity is increased with the extension of the planar area of the N-N ligands, and complex 4 shows an intercalative mode of interaction with DNA. The in vitro anticancer activities of these compounds are moderate on the five human cancer cell lines screened (Tan et al., 2008).

New six-coordinate ruthenium(III) Schiff-base complexes of general formula \([\text{Ru(X)}(\text{PPh}_3)(\text{L})]\) (where \(X = \text{Cl}/\text{Br} \) and \(L = \text{mononucleating bibasic tetrade} \text{ntate ligand derived by condensing acetoaceta} \text{nilide/acetoacetoludide with } o\text{-aminophenol}/o\text{-aminothiophenol}/o\text{-aminobenzoic acid in } 1:2 \text{ molar ratio in ethanol} \) have been synthesized and characterized by physico-chemical and spectroscopic methods. The new ruthenium(III) complexes possess 2NO/2NS metal binding sites and are catalysts for the oxidation of alcohols using molecular oxygen as co-oxidant and in C–C coupling reactions. These complexes possess good biocidal (antibacterial and antifungal) activity (Arunachalam et al., 2010).
Six different ruthenium(III) complexes of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and o-aminophenol/o-aminothiophenol have been synthesized. The compounds with the general formula \([\text{RuX}(\text{EPh}_3)2(\text{L})]\) (\(X = \text{Cl or Br}; \ E = \text{P or As}; \ L = \text{bifunctional tridentate ONO/ONS donor Schiff base ligand}) were characterized by infrared, electronic, electron paramagnetic resonance spectroscopy and elemental analyses. Spectroscopic investigation reveals coordination of Schiff base ligand through ONO/ONS donor atoms and octahedral geometry around ruthenium metal (Natarajan et al., 2011).

Redox property of complexes has been examined by using cyclic voltammetry. The catalytic oxidation property of ruthenium(III) complexes were also investigated (Priyarega et al., 2011)

The ruthenium(III) complexes \([\text{Ru}(\text{L}_n)^{\text{II}}]\text{ClO}_4\) with 4-\(R\)-2-((2-(pyridin-2-yl)hydrazone)methyl)phenol (HL\(^n\); \(R = \text{H, Cl, Br, Me and OMe}) have been synthesized. Microanalysis, magnetic susceptibility and various spectroscopic (IR, UV–Vis and EPR) measurements have been used for the characterization of these complexes. The molecular structures of all the complexes, except for the complex where \(R = \text{Br})\ have been confirmed by a single crystal X-ray diffraction study. The metal centers in these complex cations are in a distorted octahedral \(\text{N}_4\text{O}_2\) environment formed by the pyridine-N, the imine-N and the phenolate-O donor (L\(^n\))\(^-\) ligands (Nagaraju et al., 2012).

A new Schiff base, 3-(benzothiazol-2-yliminomethyl)-naphthalen-2-ol, has been synthesized and characterized by elemental analysis, Fourier transform infrared spectroscopy (FT-IR), UV–vis, nuclear magnetic resonance, and single-crystal X-ray diffraction. Ruthenium(III) complexes of the Schiff base were synthesized and characterized by analytical and spectroscopic (FT-IR, UV–vis, and electron paramagnetic resonance) data as well as magnetic susceptibility measurements. DNA-binding properties of the ligand and its
ruthenium(III) complexes have been investigated by electronic absorption spectroscopy. The three ruthenium(III) complexes were tested for DNA cleavage. Further in vitro study of the cytotoxicity of the ligand and the complexes on human cervical cancer cell line and human laryngeal epithelial carcinoma cell line were carried out (Sathiyaraj et al., 2013).

d. Niobium(V) complexes

Five niobium(V) complexes with aromatic Schiff bases have been prepared, and characterised by elemental analyses. Infrared spectra of the complexes are discussed. On the grounds of these results, it is proposed that niobium(V) has the coordination number seven in all the complexes and that they have “1:4:2” stereochemistry (Biradar and Kulkarni, 1972).

The reactions of niobium and tantalum pentachlorides and oxotrichlorobis(triphenylphosphine oxide)niobium(V) with N-arylsalicylaldimines, abbreviated as (Sal-R)H, have yielded new niobium(V) and tantalum(V) complexes of the following three types: (1) MCl₃(OR')₂((Sal-R)H); (2) M(NCS)₂(OC₅H₅)₂((Sal-R)H); (3) NbOCl₃((Sal-R)H)₂ (M = Nb, Ta; R' = CH₃, C₂H₅). They are light-yellow to yellow-orange, air-stable crystalline materials and are decomposed rapidly in solutions. On the basis of physical measurements, it is postulated that these complexes assume a six-coordinate structure involving the neutral Schiff base, which is coordinated as a unidentate ligand through an oxygen atom. Possible structures of these complexes are discussed mainly on the basis of pmr and infrared spectra (Yamanouchi and Yamada, 1976).

The preparation and crystal structure of the Nb⁵⁺(Htrencam)·DMSO complex is reported [where H₆trencam is the hexadentate tris(catecholamide) ligand and DMSO is dimethylsulphoxide], revealing a cavitand-like arrangement of the three catecholamide groups with the protonated non-binding
nitrogen atom directed inwards to the niobium atom (Evans et al., 1993).

Reaction of Nb(OEt)$_5$ with 2-mercapto-4-methylphenol (mmpH$_2$) in the presence of triethylamine gave the mononuclear tris complex (Et$_3$NH)[Nb (mmp)$_3$] which was structurally characterized. The coordination geometry around the niobium is between octahedral and trigonal prismatic, with a twist angle of 41.5°. The mercaptophenolate ligands are arranged around the metal in a “propeller” fashion. (Et$_3$NH)[Nb(mmp)$_3$] was characterized by IR, $^1$H NMR and UV-vis spectroscopies, and cyclic voltammetry. A reversible reduction wave found at $-1.03 \text{ V}$ is for reduction to the Nb$^{IV}$ complex (Challen et al., 1997).

The metal complexes of niobium(V) with furoic acid hydrazones have been synthesized in dry chloroform under nitrogen atmosphere and characterized by elemental analysis, molar conductance, electronic, infrared, $^1$H NMR and thermal studies. It is proposed that the complexes exhibit coordination number seven (Goudar and Maravalli, 1998).

Complexes of the type [VO(LH)(H$_2$O)] and [Nb(LH)$_2$Cl$_3$], where LH = a singly deprotonated Schiff base derived from condensation of 3-substituted-4-amino-5-mercapto-1,2,4-triazole with benzoin were synthesized in ethanol or dry chloroform, respectively. A coordination number of five for the oxovanadium(IV) and seven for the niobium(V) complexes have been proposed on the basis of analytical, molar conductance, magnetic, IR and $^1$H NMR spectral data. Kinetic parameters were established by adopting Broido’s method. All of the ligands and their oxovanadium(IV) complexes were screened for their antibacterial, antifungal and antituberculosis activity (Gouda and Shashidhara, 2000).

Niobium(V) complexes [NbCl$_3$L] (where LH$_2$ = thiocarbohydrazones derived from thiocarbohydrazide with salicylaldehyde, 5-CH$_3$, 5-Cl, 5-Br, 3-
OCH$_3$ substituted salicylaldehyde and 2-hydroxy-1-naphthaldehyde have been synthesized and characterized the basis of elemental analyses, conductivity measurements, IR, UV-Vis, $^1$H NMR and thermal studies. The ligands behave as dibasic tetrade Ptate ONNO donors (Chabanur et al., 2001).

Two new diperoxo complexes of niobium using 8-quinolinolate (Q) as the ligand, K[NbOH(O$_2$)$_2$Q]$\cdot$2H$_2$O (1) and K[Nb(O$_2$)$_2$Q$_2$]$\cdot$3H$_2$O (2), have been synthesised and characterised structurally by elemental analysis, IR and NMR ($^1$H, $^{13}$C, $^{93}$Nb) spectroscopy. The $^1$H and $^{13}$C NMR signals of the free ligand undergo shift on complexation (de Oliveira et al., 2001).

Six new dioxobridged binuclear complexes of the type [MO(L)Z]$_2$Z, where M=niobium(V) or tantalum(V), L=N-alkylphenothiazines (NAPs) and Z=tartrate and oxalate for niobium and tantalum respectively, were synthesized. The stoichiometry of the complexes was proposed on the basis of elemental analyses, molar conductance, magnetic and thermal data. The coordination behaviour of the ligands was determined with the help of spectroscopic studies. The fungicidal activity of the complexes was evaluated (Keshavan and Kempe Gowda, 2002).

The preparation and characterization of a series of niobium(V) complexes that incorporate the linear-linked aryloxide trimers 2,6-bis(4,6-dimethylsalicyl)-4-tert-butylphenol [H$_3$(Me-L)] and 2,6-bis(4-methyl-6-tert-butylsalicyl)-4-tert-butylphenol [H$_3$(tBu-L)] are described (Matsuo and Kawaguchi, 2002).

Metal complexes of niobium(V) with 3-substituted-4-amino-5-mercaptopo-1,2,4-triazole Schiff bases have been synthesized in dry chloroform under a nitrogen atmosphere. They were characterized by elemental analysis, molar conductance, electronic, infrared, $^1$H-NMR spectroscopy and thermal studies. Parameters, such as energy of activation ($E_a$), enthalpy ($\Delta H^\#$), entropy
(ΔS#) and Gibbs energy (ΔG#), were computed from the thermal decomposition data. Based on the spectral and thermal studies, a coordination number of seven is proposed (Gudasi et al., 2005).

This review covers the literature about niobium(V) and tantalum(V) complexes containing at least one peroxo ligand in their coordination sphere. In addition to the synthesis aspects, the available structural data as well as several results issued from techniques like IR and Raman spectroscopies, NMR, thermal analyses or mass spectrometry are collected and discussed. This paper also includes a brief description of the applications of these compounds in catalysis and as precursors in materials science (Bayot and Devillers, 2006).

Niobium compounds have been very rarely applied for the polymerization of olefins, notwithstanding their moderate cost, limited toxicity and the large availability of stable oxidation states, which makes them versatile precursors. The catalytic performances in ethylene and norbornene polymerization of the niobium precursors with cyclopentadienyl, diene, amido, amidinate, pyrazolylborate ligands have been compared. The most recent results have been discussed, comparing the reported activities for complexes with phenolate, bis(imino)pyridine and N,N-dialkylcarbamate ligands (Galletti and Pampolini, 2010).

Synthesis, characterization and the anticancer properties of a new watersoluble peroxoniobium complex. The complex was synthesized and characterized by elemental, IR, Raman, thermogravimetric analysis, detailed NMR and mass spectra analysis. The cytotoxic activity of the complex on HL-60 and K562 human leukemia cell lines has been investigated by assessing vital cellular mechanisms. The complex exerts an increased antiproliferative effect primarily on HL60 human leukemia cells, compared to ascorbic acid alone, as well as an inhibitory effect on necrosis caused by ascorbic acid. Its effect on
K562 cells concerns mainly its inhibitory effect upon cell necrosis induced by ascorbic acid alone. Our results support a concentration- and time-dependent enhanced antileukemic effect of the complex, suggesting its significance as a promising tool in the confrontation of leukemia (Thomadaki et al., 2011).

High yields of the ethoxo-α-aminoacidates have been obtained by the reaction of the L-enantiopure α-amino acid (or sarcosine) with a slight molar excess of M(OEt)$_5$ (M = Nb, Ta) in a dichloromethane solution. The new complexes 2-10 have been fully characterized by spectroscopic and analytical methods and by X-ray diffraction for 2 and 7-9. Such X-ray structures are the first ones ever reported for niobium and tantalum coordination compounds containing an α-aminoacidato ligand. (Hayatifar et al., 2013).

**Scope of the present work**

The objective of the present investigation is to synthesis and characterise some novel complexes of oxomolybdenum(V), dioxomolybdenum(VI), dioxouranium(VI), ruthenium(III) and niobium(V) with Schiff bases and azo dyes which are derived from salicylaldehyde, 3-ethoxysalicylaldehyde, 4-chloro-m-cresole, 2-methoxyphenol, 2-naphthol and isoeugenol with 4-aminoantipyrine. The ligands employed are

- 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-ethoxybenzylidene amino)pyrazol-5-one (APES)
- 2,3-dimethyl-1-phenyl-4-(2-hydroxybenzylideneamino)pyrazol-5-one (AAPS)
- 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxyphenylazo)pyrazol-5-one (MPAP)
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- 2,3-dimethyl-1-phenyl-4-(2-hydroxynaphthylazo)pyrazol-5-one (NAAP)
- 2,3-dimethyl-1-phenyl-4-(5-chloro-2-hydroxy-4-methylphenylazo)pyrazol-5-one (CCAP)
- 2,3-dimethyl-1-phenyl-4-(2-hydroxy-3-methoxy-5-prop-1-enylphenylazo)pyrazol-5-one (IEAP)

These ligands have been characterized by elemental analyses, IR, $^1$H NMR, $^{13}$C NMR, UV-Vis and FAB mass spectra.

A total of thirty six such complexes have been synthesized and characterized by elemental analyses, electrical conductance, magnetic measurements, IR, $^1$H NMR, $^{13}$C NMR, UV-Vis, FAB mass and EPR spectral studies. X-ray diffraction (Powder and Single crystal), thermal, SEM, gamma ray irradiation and 3D molecular modeling studies were carried out. The present work is also purported for pursuant antimicrobial and anticancer studies.

As irradiation can affect the physical, chemical and biological properties of metal complexes, knowledge regarding the radiation effects benefits the development of advanced materials in various fields. Therefore the effect of gamma irradiation on thermal properties, X-ray diffraction pattern and surface morphology of some oxomolybdenum(V), dioxomolybdenum(VI) and ruthenium(III) complexes are also incorporated.

The study undertaken in this thesis is presented in nine chapters. Chapter I on introductory, gives a brief account of the field of coordination chemistry. A brief account of the coordination of the metals under study, significance of the ligands and scope of irradiation studies has also been attempted.
Chapter II provides a brief review of literature on the recent works on the oxomolybdenum(V), dioxomolybdenum(VI), dioxouranium(VI), ruthenium(III) and niobium(V) complexes.

The reagents used, analytical procedures adopted, instrumental techniques employed for the study, method of synthesis of the ligands and the procedures adopted for antimicrobial studies are described in Chapter III.

Chapter IV describes the synthesis and characterization of oxomolybdenum(V) and dioxomolybdenum(VI) complexes of APES. The single crystal X-ray structure of APES is also incorporated. Antibacterial studies of APES and its complexes are also recorded herein.

The synthesis and characterization of oxomolybdenum(V) and dioxomolybdenum(VI) complexes of MPAP are presented in Chapter V. Effects of gamma irradiation on X-ray diffraction patterns and surface morphology of one of the oxomolybdenum(V) and dioxomolybdenum(VI) complexes are also described in this chapter.

Chapter VI deals with the synthesis and characterization of the niobium(V) complexes of AAPS and NAAP derived from 4-aminoantipyrine. The single crystal X-ray structures of AAPS and NAAP are also incorporated.

The synthesis and characterization of ruthenium(III) complexes of the azo dye, MPAP are discussed in Chapter VII. Effects of gamma irradiation on thermal properties, X-ray diffraction patterns and surface morphology of one of the ruthenium(III) complexes are also described in this chapter.

Chapter VIII deals with the study of ruthenium(III) complexes of the azodye, CCAP derived from 4-aminoantipyrine. Antimicrobial studies and EPR
studies are also presented therewith.

Chapter IX describes the synthesis and characterization of dioxouranium(VI) complexes of APES and IEAP.

Relevant citations in this work have been referenced towards the end of the thesis.