GENERAL INTRODUCTION

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GENERAL INTRODUCTION

SECTION A : HISTORICAL REVIEW

In the modern era coordination chemistry forms an integral part of several interdisciplinary researches. In a brief period of about four decades of growth in chemistry, no field has received as much attention as the study of coordination compounds. Over recent years there has been considerable progress in our understanding on the reactivity of the coordinated ligands with transition and non-transition metal ions. New types of complexes displaying remarkable properties are being continuously turning up. It should soon be possible to "tailor make" any type of individual metal complex to suit any purpose with the help of suitable complexing agents.

Studies of the coordination complexes are interesting not only for the sake of fundamental knowledge but also for their practical utility. Metal complexes are successfully employed in the processes for separating the rare earth elements, in chemical technology of gold, nickel, cobalt and copper, in electroplating\(^1\), mordant dyeing, tanning, water
softening\textsuperscript{2,3} and in other fields of technology. With the industrial and technological advances, metal pollution in the atmosphere has been progressively increasing. Controlled removal of atmospheric pollutants can be achieved by the use of appropriate complexing agents.\textsuperscript{4} Metal complexes have been successfully used in the treatment of many diseases such as rheumatoid arthritis, malaria, tuberculosis\textsuperscript{5}, tumor\textsuperscript{6} and cancer.

For over a century, chemists have been studying the interaction of transition metal ions with other species. A mystery which intrigued chemistry of nineteenth century was how any two stable compounds each capable of independent existence like ammonia and copper (II) or cobalt (III) chlorides could react with each other to form new products as $\text{CuCl}_2.4\text{NH}_3$ or $\text{CoCl}_3.6\text{NH}_3$ with entirely different properties. In these compounds it is amazing to understand how four and six ammonia molecules are held to copper (II) and Cobalt (III) chlorides when the plus charges on the metal ions is already used up in forming bonds with the chloride ions. This led the chemists like Tassaert\textsuperscript{7}, Graham\textsuperscript{8}, Berzilius\textsuperscript{9}, Claus\textsuperscript{10}, Blomstrand\textsuperscript{11} and Jorgensen\textsuperscript{12} to study the formation and structure of transition metal complexes. However the explanation suggested by them
were not satisfactory because these were based on the then available valence theories. Later Alfred Werner\textsuperscript{13}, who was trained as an organic chemist, suggested that every metal ion has two kinds of valences, the primary and secondary and latter are directed in space in a fixed manner. The metal and the fixed number of groups attached to it by these secondary valences constitute a "Coordination complex". Very little was known about the origin of chemical bonds and the basis of molecular shapes at that time. Werner's idea of valence polyhedra crystallised from analysis of relatively simple chemical facts. It was a creative flash of rare beauty, probably triggered by the tetrahedral carbon of organic chemistry. Werner was an experimentalist and a synthetic chemist of rare ability and went on translating his predictions into practice. He predicted and experimentally proved that optical activity is not a special feature of carbon compounds but is a general property of unsymmetrical polyhedral binding. The earliest attempt to interpret the coordination link was that of Sidgwick\textsuperscript{14,15} who suggested the donation of a pair of electron from each group (so called ligand) gives rise to secondary valency, while the primary valencies are simple ionic bonds.
After the advent of quantum mechanics, directed valence and valence polyhedra appeared as natural consequences of the shape, number and energy of wave functions. Four distinct approaches are now available for the bonding in coordination complexes. These are outlined as follows:

**Valence bond theory:**

The present form of the valence bond treatment is largely due to L. Pauling. This treatment has made a major contribution to chemical theory, particularly in explaining the stereochemistry of complexes in terms of hybrid orbitals. The theory is however, somewhat inflexible and cannot be used as a basis for quantitative discussion of some of the interesting physical properties of complexes, such as electronic spectra.

**Crystal Field Theory:**

The crystal field theory developed by H.A. Bethe and J.H. Van Vleck considers the electrostatic interactions of the ligands taken as negative point charges equally spaced along the x, y and z axis, with the d orbitals of the metal ion. The theory concentrates on the interaction of the negatively charged or negative ends of
the dipolar molecules such as H₂O or NH₃ with the d-orbitals of the metal ion. The interaction between the electrons of the central metal ion and those of the ligands is entirely repulsive. The total binding energy is calculated by considering:

(a) energy of attraction between positive charge and negative charges.

(b) repulsive energies between the negative charges of the ligands.

In an octahedral complex, as the ligands approach the central metal ion to form a complex compound, the octahedral field of the ligands raises the five degenerate orbitals to split into two sets in accordance with the following crystal field splitting (Fig.1).

![Diagram of five fold degenerate orbitals in an Octahedral complex](image)

**Fig.1**
Five fold degenerate orbitals in an Octahedral complex
In principle, the magnitude of the orbital splitting, \( \Delta \), depends on
(i) charge on the ligands
(ii) the internuclear distance
(iii) the electron distribution in the d-orbitals.

The main achievement of this theory is that it can offer a possible explanation of the electronic spectra of the complexes. It explains distortions from regular geometries, and magnetic and kinetic behaviour. A number of experimental evidences, however, do suggest that the metal ligand interactions are not purely electrostatic as predicted in the above theory but some kind of orbital overlap is also present. The crystal field theory has no room for the \( \pi \) bonding and can not be expected to give an accurate estimate of orbital splitting.

**Ligand Field Theory**

This theory was developed essentially for the interpretation of spectroscopic data though it has actually clarified our understanding of chemical bonding in polyatomic molecules of comparatively high symmetry. \( 21, 22, 23 \)

The approach in the ligand field theory is essentially the same as the pure crystal field
approach, but with covalent character taken into account whenever necessary.

Ligand field theory uses all the parameters of interelectronic interactions as variables rather than taking them equal to the values found for the free ions. The important parameters are: the spin orbit coupling constant, $\lambda$, and the interelectronic repulsion parameters - Slater integrals, $F_n$, and the two Racah parameters $B$ and $C$.

The spin-orbit coupling constant $\lambda$, which in the transition metal complexes is about 70-85% of the corresponding values of the free metal ion, plays an important role in determining the magnetic properties and temperature dependence of magnetic moments of many ions in their complexes.

The Racah parameters $B$ and $C$ are measures of the energy separation of the various Russell-Saunders state of an atom. The energy differences between states of the same spin multiplicity are, in general, multiples of $B$ only, whereas the differences between states of different multiplicity are expressed as sums of multiples of both $B$ and $C$.

The usefulness of the ligand field theory in the interpretation of spectra of transition metal
complexes has been one of its greatest advantages over the valence bond treatment. It also provides for a more detailed understanding of the main features of the magnetic susceptibilities of transition-metal complexes.

**Molecular Orbital Theory**

A big development in ligand field theory was the recognition of the importance of covalent bonding and the reformation of the theory in terms of the molecular orbital approach. There are good reasons to believe that the electrons in a purely electrostatic theory are considered to be isolated; ligands in fact become delocalized to a greater or lesser extent on to the metal, and those on the metal become delocalised on to the ligands. In the molecular orbital approach we allow for this by combining the orbitals of the ligands with the 3d, 4s, and 4p orbitals of the metal.

In a regular octahedral complex, the six orbitals of the ligands may be represented as one that is totally symmetric and combines with 4s orbital of the metal; three that have a single node and combine with p orbitals; and two more that interact with the 3dx^2-y^2 and 3dz^2 orbitals. The 3dxy, 3dxz, and 3dyz orbitals do not combine with any of the ligand orbitals and take no part in the bonding.
Whenever a pair of orbitals, one on the ligands and one on the metal, combine together, we get two new orbitals, one more and one less in energy than either of the original orbitals. The energy level diagram of an octahedral complex involving only sigma bonding can be shown in Fig.2.

![Energy level diagram of an octahedral complex involving only sigma bonding](image)

*Fig. 2*

Molecular orbital energy level diagram involving only sigma bonding
The complex contains twelve electrons from the ligands and \( n \) from the metal ion, \( n \) being determined by the nature of the metal and its oxidation state. The former fill the bonding orbitals, leaving just \( n \) to be distributed between the \( t_{2g} \) and \( eg \) orbitals of the complex. It is observed that the \( t_{2g} \) orbitals are unaffected by sigma bonding while the \( eg \) orbitals combine with the corresponding separating ligand orbitals to give double degenerate bonding and antibonding molecular orbitals. This follows from the theory that a molecular orbital formed from two component orbitals includes a larger contribution from that component which is closer in energy to it.

Hence the molecular orbital theory could well be adapted to rationalize the new information that has accumulated in the past decade or so.

Thus the combined applications of theoretical studies and experimental methods provide the basis for the deep understanding of structure and bonding of transition metal complexes.
SECTION B

B. SURVEY OF LITERATURE

The present investigations are concerned with the studies on the synthetic and structural aspects of some simple polyamine and macrocyclic schiffs base complexes of oxozirconium (IV), oxovanadium (IV) and dioxouranium (VI) complexes and the reported literature shows that a comparatively little amount of work has been reported on such complexes. Therefore an attempt is being made to describe the work already reported on such complexes which is relevant to the present investigation in the following pages.

Of many oxometal species studied, the above three ions namely oxozirconium (IV), oxovanadium (IV) and dioxouranium (VI) are by far the most stable and most well studied. Zirconyl and uranyl ions are expected to be diamagnetic with $d^6$ configuration while $\text{VO}^{2+}$ has a $d^1$ configuration with one unpaired electron. These studies have usually utilised nitrogen & oxygen ligands and it is further observed that the donor properties of nitrogen are very strong and the tendency to coordinate with amine nitrogen and the Schiffs base azomethine group is a characteristic of oxometal ions.
(i) **Simple ligand complexes**

The complexes formed with chelating amines are the ones most thoroughly studied. Amongst these the maximum coordinating abilities are displayed by ethylene or propylenediamine and some tertiary amines & their derivatives. The complexes are relatively stable as coordination results in the formation of five membered rings. These also present a variety of structures and a brief review of these is presented in following pages.

Oxozirconium (IV) complexes of type $\text{ZrOX}_2\text{L}_n$ [$L = \text{Pyridine, } \alpha\text{-picoline, 2-aminopyridine 2,4, -lutidine or quinoline, } n = 4 \text{ and } x = \text{Cl}^-, \text{Br}^-, \text{I}^- \text{ or } \text{ClO}_4^-].$ These compounds are monomeric, non electrolytes in nitrobenzenes except for perchlorate derivatives which behave as 1:2 electrolyte$^{26-28}$.

Synthesis of some oxozirconium (IV) complexes at thiocarbohydrazone of general formula $\text{ZrO(HL)}_2$ is reported by treating $\text{ZrOCl}_2$ with the ligand $\text{H}_2\text{L}$ in anhydrous methanol, where $\text{H}_2\text{L}=\text{SC(NHN(CH}_3\text{)}_2\text{OH}_5\text{R)}_2$ $\text{R} = \text{H, CH}_3, \text{Cl, OMe.}$ These complexes are assigned five coordinate trigonal bipyramidal geometries.$^{29}$
ZrOL and ZrOCl\textsubscript{3} L\textsubscript{3} type complexes of oxo zirconium (IV) with salicylaldehyde - o aminophenol and glyoxal-o-aminophenol have been reported\textsuperscript{30,31}.

Magnetic and spectroscopic studies of oxozirconium complexes of Schiffs bases derived from aminophenol and salicylaldehyde indicate seven coordinated complexes, which are diamagnetic in nature confirming the quadrivalence of Zirconium\textsuperscript{32-34}.

A few complexes of type Zr(OH)\textsubscript{2}LCH\textsubscript{3}OH and Zr(OH)\textsubscript{2}(LH)\textsubscript{2} where LH = Schiffs base derived from o-aminophenol and 2-hydroxy-1-naphthaldehyde are also reported\textsuperscript{35}.

A new series of five or seven coordinate complexes of oxozirconium (IV) of type ZrO(pico)\textsubscript{2}X\textsubscript{2} (X=Cl, Br, NO\textsubscript{3} or NCS) and ZrO(pico)\textsubscript{4}X\textsubscript{2} (X=ClO\textsubscript{4} or F) where pico = 2-methylpyridine-N-oxide have been prepared. In all these complexes pico is bonded through ionic oxygen and stearic hindrance is introduced in the complex formation by the presence of 2-methyl substituent in pico\textsuperscript{36}.

I.R. and thermal studies of oxozirconium (IV) complexes of 2-Acetyl pyridine-N-oxide (L) of general formula ZrOX\textsubscript{2}.2L where X = Cl\textsuperscript{-}, Br\textsuperscript{-}, I\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, NCS\textsuperscript{-} are
reported showing that ligand L is monodentate and coordinates through its N-oxide fraction.\textsuperscript{37}

Selbin & Holmes have prepared a long series of Vanadyl complexes such as Vodip\textsubscript{2}\textsuperscript{2+}, Vophen\textsubscript{2}\textsuperscript{2+} etc. while Clark has reported VCl\textsubscript{4}dip & VCl\textsubscript{3}phen. These isolated complexes are mostly five coordinated and assume square pyramidal geometry.\textsuperscript{38-42}

Bhattacharya has prepared the adduct of quinoline-N-oxide oxovanadium (IV) which may be five coordinated square pyramidal species having either Cis or trans Configuration.\textsuperscript{43}

Ethylenediamine oxovanadium (IV) complexes in water have been reported and dark brown [Vo(en)\textsubscript{3}]F\textsubscript{4}\textsuperscript{+} has been prepared by adding VF\textsubscript{4} to diamine at low temp.\textsuperscript{44-45} V\textsubscript{2}O\textsubscript{5} reacts with HF and diamine or 2,2'-dipyridyl to give HVOF\textsubscript{4}.Am.\textsuperscript{46}

The N-heterocycles usually being less basic than most of the amines are more useful as nitrogen donors. Thus some oxovanadium (IV) complexes of substituted benzimidazoles are reported. The study of these complexes shows that aromaticity enhances the chelating ability of the heterocyclic ligand. A distorted octahedral structure has been suggested.\textsuperscript{47-48}
Imidazole complexing with oxovanadium(IV) has been studied by ESR and proton and ENDOR spectra and the study indicates that four imidazole ligands are bound to \( \text{VO}^{2+} \).\(^{49}\)

Infrared & thermal properties of some oxozirconium(IV) & oxovanadium(IV) chelates of 2,2' - bipyridylmono-N-oxide of type \( \text{MOX}_2\text{Bipy NO.2H}_2\text{O} \) (Bipy N-oxide = 2,2'-bipyridine N-oxide, \( \text{X} = \text{Cl,Br,SCN} \) & \( \text{NO}_3 \) & \( \text{MO} = \text{ZrO}^{2+} \) & \( \text{VO}^{2+} \)) were prepared & characterised by elemental analysis, molar conductance & i.r. methods. Bipy NO acts as a bidentate O,N-chelating agent.\(^{50}\)

Some cationic mixed ligand complexes of oxovanadium (IV) containing a s-carboxylate and neutral bidentate nitrogen base of formula \([\text{VOAL}]\text{ClO}_4\) (A=2,2'-bipyridyl or O-phenanthroline & HL=\( \beta \)-diketone, acetyl acetone, benzoylacetonate are characterised.\(^{51}\)

\( \text{VOSO}_4 \) and \( \text{VOCl}_3 \) react with imidazoles, substituted imidazoles, piperidine and piperizine derivatives to yield \([\text{VO(IM)}_3\text{H}_2\text{O}]\text{SO}_4\), \( \text{VOL(H}_2\text{O})\text{SO}_4 \), \( \text{L=1-Me or VinIm} \). These were characterised by elemental analysis, IR and electronic spectra and assigned octahedral and square pyramidal structures.\(^{52}\) Some other imidazole, benzimidazole and substituted
benzimidazole complexes have also been reported.\textsuperscript{53}

Complexes of VOCl\textsubscript{2} with organic ligands having formulae VOCl\textsubscript{2}L\textsubscript{2}\textsuperscript{+}, VOCl\textsubscript{2}L\textsubscript{2}\textsuperscript{2+}, VOCl\textsubscript{2}LL\textsubscript{2} where L=THF, L'=1,2-dimethoxyethane, L\textsuperscript{2} = L\textsubscript{1} = Pyridine, picoline were prepared and characterised.\textsuperscript{54}

Complexes of oxovanadium (IV) histidine-glycol-water system were studied using ESR spectral measurements and the dominant species was found to be VO(H\textsubscript{2}O)\textsubscript{5}\textsuperscript{2+}, VO(HL)\textsuperscript{2+}, VO(H\textsubscript{2}O)L\textsubscript{2} + VOL\textsubscript{2} where HL is the mono dentate ligand coordinating through carbonyl oxygen and aminonitrogen ligand.\textsuperscript{55}

Oxovanadium(IV) complexes with dibenzo methylene and their pyridine adducts were synthesised having formulae such as VOL\textsubscript{2}, VOL\textsubscript{2}L', where HL = dibenzoemethane & L'=pyridine, 3-or 4-methyl pyridine, 3-or 4-aminopyridine. The complexes were characterised and VOL\textsubscript{2} possesses square pyramidal and VOL\textsubscript{2}L' octahedral geometry.\textsuperscript{56}

Some other oxovanadium(IV) complexes of type [VO\textsubscript{2}(NAPP)\textsubscript{3}]X(1) and [VO(HNAPP)I\textsubscript{2}]II where HNAPP = 1-Phenyl-2,3-dimethyl-4-(2'-hydroxy naphthylazo)-5-pyrazolone, X=Cl\textsuperscript{-}, Br\textsuperscript{-} & NO\textsubscript{3}\textsuperscript{-} were prepared which showed normal magnetic behaviour and the IR spectral
evidences suggest an univalent tridentate nature of the ligand in I and a neutral tridentate nature in II.  

Magnetic, spectral and thermal investigations of some oxovanadium (IV) chelates of 2-ethoxy-carbonyl-
amino pyridine-N-oxide(L) of type VOX₂.L, where X = Cl⁻, Br⁻, I⁻, NO₃⁻, NCS⁻ & ClO₄⁻ are reported. Except for perchlorate in all the complexes, there is no metal-
metal interaction between X atoms at 30°C and the ligand is bonded through h oxygen atoms of carbonyl group & N-oxide fraction forming a seven membered ring.  

A review containing 103 references concerning the chemistry of a variety of oxovanadium(IV) complexes by X-Ray, I.R., thermodynamic and solution studies is presented and the lack of unambiguous assignments for the electronic energy transitions occurring in VO²⁺ is pointed out.  

Low symmetry oxovanadium (IV) complexes with mixed chelates arising out of the combination of bidentate Schiffs bases and 2,2'-bipyridine or O-
phenanthroline were prepared and all the complexes were deeply coloured, non electrolytes & paramagnetic in nature with μ\text{eff} values equal to 1.73 B.M.
α-nitrosodiphenylamine (HL) in ethanol was added to an aqueous solution of VOSO₄, maintained at a pH of 4-4.5 by the addition of NH₄OH to precipitate VO₂⁺. Similarly VO₂⁺ type of complexes where HR = β-nitro-α-naphthylamine, α-amino-β-naphthol-4-sulphonic acid have also been reported.⁶¹

Bis, N-N'-disubstituted dithiocarbamato oxovanadium (IV) complexes with N-substituted methyl, ethyl and isopropyl groups have been prepared and characterised. Molecular weight studies in tetramethylene sulphone show the monomeric nature of complexes and these are assigned tetragonal pyramidal structure. The open coordination position of which situated trans to oxygen atom can accept a sixth ligand such as pyridine and dimethylsulphoxide to give a pseudo octahedral structures.⁶²

High symmetry VO⁴⁺ complexes have been prepared and their electronic spectra have been examined at both room temperature and 77°C which become more revealing at 4°C. These include VOF₅³⁻, VO₄(H₂O)²⁻, VOCl₄²⁻, VOCl₃SO₄(H₂O)³⁻, VO(NCS)₅³⁻ and VO(NCS)₄(H₂O)²⁻. The band assignments have been made on much firmer and broader experimental ground than previously possible.⁶³
The results of IR and Raman spectral studies of some peroxosulphato Zr(IV) complexes of type Zr$_2$(O$_2$)$_3$SO$_4$.10H$_2$O support the molecular structure proposed originally on the basis of chemical studies. The thermal studies indicate that four water molecules are coordinated to Zr atom and compounds are diamagnetic.$^{64}$

Water coordination, nucleophilic tendencies of anions and steric hindrance were found to be the factors affecting the coordination of pyridine-N-oxide (LH) or Vanadyl ion. The low steric interaction of pyridine-1-oxide and 4-methyl-pyridine-1-oxide (L') combined with the low nucleophilic tendency of tetrafluoroborate anion resulted in the formation [VOL$_5$(BF$_4$)$_2$], [VOL$_4$(BF$_4$)$_2$]H$_2$O, [VOL'$_5$(BF$_4$)$_2$]. The high steric interaction of 2-methyl-pyridine-1-oxide[L''] combined with the high nucleophilic tendency of sulphate gave the complex [VO(L'')$_2$.SO$_4$].2H$_2$O.$^{65}$

The coordination chemistry of dioxo uranium (VI) cation is of interest because of the existence of a strong multiple uranium oxygen covalent bond persisting in various chemical environments. This can be employed as an internal probe to understand more about the nature of metal-ligand bonds in the complexes of this ion.$^{66}$
Majumdar & Bhattacharya isolated and characterised various complexes of dioxouranium (VI) with neutral unidentate ligands from different physiochemical studies and concluded that $\text{UO}_2^{2+}$ ion behaves as a special type of electrophile because of the large number of vacant d & f - orbitals, which are easily acceptable for bond formation.$^{67}$

The complexes of type $[\text{UO}_2X_2(\text{HMPA})_2] \ X = \text{Cl, Br, NO}_3$, NCS and HMPA = hexamethyl phosphobromide and $[\text{UO}_2(\text{NCS})_2(\text{HMPA})_3]$ have been characterised.$^{68}$ It has been found that the stretching frequency and the molar magnetic susceptibility of the $\text{UO}_2^{2+}$ ion depend upon the donor ability of the anionic ligand towards the uranyl ion.

New dioxouranium (VI) complexes with dibasic tridentate ligand of the type $[\text{UO}_2(\text{H}_2\text{L})_2X_2] \ X = \text{Cl, I, NCS, NO}_5, \text{ClO}_4, \frac{1}{2}\text{SO}_4$ were synthesised. The ligand coordinated through either as a neutral molecule or an uninegative ion.$^{69}$

Few dioxouranium (VI) complexes with Schiffs bases derived from di and tridentate ONO donor ligands are reported.$^{70-73}$ Salicylaldehyde semicarbazone acts as singly negatively charged bidentate anion and two
such anions coordinate to the metal ion through the hydroxyl oxygen and nitrogen of the $\text{C=N}$-group yielding a neutral chelate.\textsuperscript{74}

A few uranyl complexes with some N & S donor ligands have also been reported and characterised by analytical and spectral data. The ligand coordinates through imino and amino nitrogens to uranyl acetate and uranyl chloride.\textsuperscript{75}

Uranyl chelates of some aromatic amine oxides were isolated and the chelate of uranyl (VI) with 2-ethoxy carbonylamino pyridine-N-oxide is also reported. The ligand has four potential donor sites as tertiary amine, N-oxygen, iminonitrogen and carbonyl oxygen and the ligand behaves as bidentate coordinating through N-oxygen and carbonyl oxygen forming a seven membered chelate ring.\textsuperscript{76,77}

Some ternary complexes of UO$_2^{2+}$ with some oxygen & nitrogen donor ligands have been investigated.\textsuperscript{78-81} The studies of ternary complexes of UO$_2^{2+}$ with 8-quinolinol (8-HQ), O-aminophenol (OA) revealed the involvement of tertiary nitrogen in coordination.\textsuperscript{82} Jain et al prepared some complexes with aromatic heterocyclic ligands such as pyrazole as well.\textsuperscript{83,84}
Some complexes of dioxouranium (VI) with 2,2'-dithioaniline have been synthesised and the ligand is found to behave as tridentate and the complexes were assigned an octahedral structure.\(^{85}\)

(ii) **Macro cyclic Complexes**

Those Schiffs base ligands which consist of closed ring structures consisting of at least a nine membered structural frame work out of which not less than two members behave as donors are called macrocyclic ligands. These structures are very important as they are essential part of many biological systems. Most of these are generally prepared by Schiffs base condensation reactions between dialdehyde/diketone with primary amines.

Such condensation reactions are usually done in presence of a metal which acts as a template in directing the steric course of these reactions.\(^{86-90}\) The macrocyclic ligands contain the imine or azomethine linkages through which the coordination to central metal atom takes place.

The great importance of these ligands which is due to their exceptional thermodynamic and kinetic stabilities and tendency to stabilise unusual oxidation
states, is evident from the extensive literature which has accumulated on the subject in the last two decades. Most of the reported work is concerned with complexes of transition metals, while comparatively little work has been done on corresponding complexes of oxometal ions. Therefore an attempt is made to describe the work already reported on such complexes relevant to the present investigation.

Some asymmetrical bis bidentate ligands were obtained by condensing \(4,4'-(4,4'\text{-biphenylenediazo})\text{disalicylaldehyde}\) with \(O-, m-\) & \(p\)-chloroaniline. The polychelates of \(\text{VO(II)}\), and \(\text{UO}_2(\text{II})\) with these ligands were prepared and characterised.

Binuclear macrocyclic Schiff bases derived from thiophene-2,5-dithiocarboxaldehyde with \(\alpha, \omega\), \(-\text{alkane diamines were complexed with some oxometal ions. The x-ray crystallography shows that the oxo ions are strongly coordinated by a pair of imino N-atoms and by water molecules.}\)

Three types of novel polymeric ligands in which \(6,8,15,17\text{-tetramethyldibenzo-5,9,14,18\text{-tetrazacyclotetradecane was present as an integral part of the}\)
polymeric back bone were prepared. Among these the ligand which contained a triethylene glycol bi (phenylene) group was found to be an excellent extractant for Cu(II).  

Some new acyclic and cyclic Schiff bases containing either two similar or two dissimilar compartments in close proximity capable of linking two metal ions in identical or different environment have been obtained using the reaction of 4-chloro-2,6-diformylphenol and \( \text{NH}_2(\text{CH}_2)_2.\text{NH}(\text{CH}_2)_2\text{NH}_2 \) and their mono & binuclear \( \text{UO}_2^{++} \) (VI), Ni(II) & Cu(II) complexes have also been reported along with their physicochemical properties.  

The preparation, characterisation and geometrical features of coordinated \([\text{VOCl}_2(\text{SB})]_3\) \([\text{VOCl}(\text{SB})_2]\) where \(\text{SBH}\) = a monobasic Schiff base are described. The isolated products are non electrolytic, crystalline & monomeric solids, in which the magnetic susceptibility measurements show trigonal bipyramidal and octahedral structures.  

The synthesis & characterisation of dioxouranium (VI) and oxovanadium (II) complexes using a hexadentate schiffs base ligand with the VO(IV) and
UO(IV) units occupying the outer \((O_2 O_2)\) compartment of potentially binuclear ligand have also been reported.\(^{100}\)

A review of some oxygen, nitrogen and sulphur donor macrocycles discussing the effect of metal ion, ligands, percentage of water content of solution, acidity and reaction time on template condensation containing seventeen references is described and in following pages some relevant references are also outlined.\(^{101}\)

Complexes of the macrocyclic ligand tetrabenco\((b,f,j,n)\)-115, 9,13-tetraazacyclohexadecine (TAAB) with \(\text{UO}_2\)(II), \(\text{VO}(\text{II}), \text{TiO}(\text{II})\) and \(\text{ZrO}(\text{II})\) ions, in which the ligand has been obtained by self condensation of four moles of \(\text{o-aminobenzaldehyde}\) were prepared & characterised using various physicochemical methods.\(^{102}\)

Complexes of some transition metal oxoions with schiffs bases derived from acetylacetone and aromatic diamines include squarepyramidal \([\text{(VO)}_2 L_2]\) in which the base is shown to be tetridentate which coordinate through both its nitrogen & oxygen atoms,\(^{103,104}\) while some similar vanadyl complexes having formulae \(\text{VOL}_2\) where \(\text{HL}=[4-\text{Octyloxy-N-(2-hydroxy-4-helptyloxy benzyldene)aniline}]\) were prepared &
characterised by I.R. and ESR Spectra.\textsuperscript{105}

Complexes of bivalent metal and oxometal ions with some mixed nitrogen and oxygen donor macrocycles as 9-ane N\textsubscript{2}O (1-Oxa-4-diazacyclononane), 12-ane N\textsubscript{3}O (1-Oxa-4,7,10-triazacyclodecane), 12-an\textsubscript{e} (1,4)N\textsubscript{2}O\textsubscript{2} (1,4-dioxo-7,10-diazocylo dodecane), 13-ane N\textsubscript{3}O (1-oxa, 4,7,11-triazacyclotridecane), HEEN [1-oxa-4,7, diaza heptane], ODEN (4-oxa-1,4-diazaheptane) and 12-are N\textsubscript{4} (1,4,7,10-tetraazacyclododecane)] have been prepared. The effect of steric hindrance on the solvation of free ligand and its macrocyclic properties is also discussed.\textsuperscript{106}

Template condensation of RC' (CO)NHNH\textsubscript{2} with acetylacetone and its consequent complexes with oxouranium (VI) and oxovanadium (IV) were prepared & characterised by i,r, electronic and magnetic measurements. The macrocycle acts as a tetradentate ligand coordinating through its azomethine nitrogen atoms & pyridyl nitrogen or carbonyl oxygen.\textsuperscript{107}

From the literature survey given above it is seen that although some work has been done on aliphatic, aromatic heterocyclic compounds, no systematic data are available. The present work thus aims at the preparation & characterisation of some
osocirconium (IV), oxovanadium (IV) and dioxoauranium (VI) complexes with some nitrogen donor ligands such as di, tri & tetramines and two macrocyclic ligands in order to understand and explore the structures of the synthesised complexes.
SECTION C:

PRINCIPLES UNDERLYING THE PHYSICO-CHEMICAL METHODS USED FOR CHARACTERISATION OF COMPLEXES

The characterisation of a coordination complex normally involves the identification as well as structural determinations and may be done by using various physico-chemical methods. The routine methods such as elemental analysis, conductance, and magnetic susceptibility help in deciding the true molecular formulae of the complexes; while the use of sophisticated spectroscopic methods such as infrared, electronic spectra and nuclear magnetic resonance help to establish the coordination of the various ligands to metal and also the geometry of the complex respectively. The detailed use and interpretation of these data in the characterisation of the complexes is described in chapter III while this chapter gives an idea of the principles underlying these methods.

1. Elemental Analysis:

The molecular formula of the prepared coordination compounds can be deduced from elemental analysis. The percentage of carbon, hydrogen and nitrogen have been estimated microanalytically at
Central Drug Research Institute, Lucknow - The metal content was estimated in the laboratory by following methods.

**Estimation of Zr as ZrO$_2$** - About 0.1 g of compound was decomposed several times by treatment with 5-10 ml of conc. HNO$_3$, which was later removed by evaporating with two ml. Conc. H$_2$SO$_4$ till dense white fumes of SO$_3$ appeared. The resulting semi-solid was treated with 20% HCl solution, and metal was precipitated with 10% aqueous solution of mandelic acid and diluted to 100 ml. The temperature of solution was raised to 85°C and maintained for twenty minutes. The precipitate obtained was filtered, washed with a mixed solution containing 2% HCl (5 ml) and 5% mandelic acid (5 ml), ignited on a silica crucible, and weighed as ZrO$_2$.

**Estimation of U as U$_3$O$_8$**: The parent complex was decomposed several times with HNO$_3$ and H$_2$SO$_4$ and the residue obtained after the removal of HNO$_3$ was dissolved in 100 ml of distilled water. To this 1-2% acetic acid and 5% solution of ammonium acetate was added and resulting solution was treated with 4% oxine solution till precipitation was completed. The precipitate was digested on a water bath filtered, dried, ignited and weighed as U$_3$O$_8$.
Estimation of V as \( \text{Ag}_3\text{VO}_4 \):

0.1 g of the decomposed complex was taken in 100 ml water and excess acid neutralised with an aqueous solution of sodium hydroxide. To this 3.0 g of ammonium acetate and 0.5 ml of conc. \( \text{HNO}_3 \) and an excess of \( \text{AgNO}_3 \) (10%) was added. A precipitate of silver vanadate was obtained which was filtered in a weighed sintered crucible, washed with hot water, dried at 110°C and weighed as \( \text{Ag}_3\text{VO}_4 \).

(2) Conductivity Measurements:

The use of conductivity measurements in both organic and inorganic solvents as an aid for determining the structure of coordination complexes has been made since the time of Alfred Werner\textsuperscript{108}.

The study is based on the fact that as a result of passage of electric current, an electrolyte gets decomposed into its ions. These ions in the solution are responsible for the conductance, the standard unit of which is the specific conductance, i.e., the reciprocal of specific resistance. Since it depends upon the number of ions per unit volume of the solution, it is better to express it in terms of molarity or normality of the solution.
Molar and equivalent conductance are thus the conductance of a solution containing one gram mole or one gram equivalent of a solute and are expressed by the equation.

$$\lambda = \frac{100K}{C}$$

where $\lambda$ is molar or equivalent conductance, $K$ is specific conductance and $C$ is the concentration of the electrolyte in gram moles or gram equivalent per litre respectively.

It is clear from the above equation that the value of $\lambda$ is dependent upon the concentration and at a particular concentration, an electrolyte has fixed value, which varies with dilution. As the electric charges carried by an equivalent number of ions of different electrolytes are equal, the velocity of the ions for the same electrolyte is independent of dilution, it shows that equivalent conductance is dependent only upon the number of ions.

All these properties are also produced in a number of organic solvents and the molar conductance of such solutions depends upon the number of ions. For non-electrolytes the value of $\lambda$ has been found to be less than 0.5 mhos, while for uni-univalent electrolytes
it lies between 27-29 mhos, for uni-bivalent electrolytes about 40-44 mhos and for uni-trivalent electrolytes it comes out to be above 50 mhos. Thus the measurement of molar conductance helps in deciding whether a complex is an electrolyte or not and thus helps in assigning the true molecular formulae. The molar conductances of the present complexes were measured on an Elico conductivity Bridge Type CM82T, using water, DMF and DMSO as solvents.

(III) Magnetic Susceptibility Measurements:

The measurement of the magnetic susceptibility helps in establishing the structure of the coordination complexes as it provides direct information about the bond types and geometries in the complexes, by indicating the number of unpaired electrons. The two important classes of magnetic behaviour associated with the complexes are -

(a) Diamagnetism and
(b) Paramagnetism

(a) In case of the diamagnetic molecules which contain paired electron shells only, on application of a magnetic field a reduction in the density of lines of force occurs. The substance tend to move away from the
applied magnetic field and hence the experimental values of gram or molar susceptibility are very small \( \sim 0.1 \times 10^{-6} \).

Paramagnetic molecules contain unpaired electrons and thus behave like small magnets conferring a definite magnetic moment on the molecule. Such substances when placed in a magnetic field are attracted by it and an increase in the density of lines of force occurs. The gram susceptibility values in this case are large \( \sim 1-100 \times 10^6 \). The values are independent of field strength but are dependent on temperature.

Gram susceptibility is measured directly and is converted into molar susceptibility by multiplying with molecular weight of the complex. The diamagnetic correction which arises from the diamagnetism of the molecule is added to this value. The value of the magnetic moment, \( \mu \text{eff} \) in Bohr Magnetons is then calculated by the equation:

\[
\mu \text{eff} = 2.84 \sqrt{X \mu' M X T}
\]

where \( X \mu' M \) and \( T \) are corrected susceptibility and absolute temperature respectively.
The magnetic measurements were made using Guoy's method. The complexes under investigation were finely powdered and filled in a Gouy tube carefully by tapping, so that no air gaps were left in between. The tube was calibrated with A.F.CuSO₄·5H₂O and Hg[CO(CNS)]₄ and was suspended between the two poles of a strong electromagnet, so that its axis was at right angles to the lines of force. The length of the tube is so adjusted that its lower end is under the influence of the magnetic field and the upper end is out of it.

During the experiment the empty tube is weighed first with and without the field. The substance whose magnetic moment is to be determined is filled in the tube up to the marked level, and is weighed again with and without the field. The gram susceptibility is calculated by using the formula

$$X_g = \frac{1}{\omega} (\alpha v + \beta_f)$$

where $X_g =$ gram susceptibility; $\omega =$ weight of the substance; $\alpha =$ linear coefficient of air, $v =$ volume of the tube, $\beta =$ tube constant and $f =$ change in pull.

(IV) Infrared Spectroscopy:

The inorganic molecules which contain a number of atoms linked by covalent bonds, constitute
the simplest kind of vibrating systems, and absorb the infrared radiations (10,000-100 cm\(^{-1}\)) to obtain enough energy for such vibrations.

In order for a particular vibration to result in the absorption of infrared energy, that vibration must cause a change in the dipole moment of the molecules. A nonlinear molecule containing "n" atoms may have 3n-6 fundamental vibrational modes, which are responsible for the absorption of infrared light.

The two important vibrations for molecules which are affected on coordination are stretching and bending (deformation) modes occurring at certain quantized frequencies. Several other vibrations may also be observed in the form of absorption bands of reduced intensity, because of overtones or hormonics. Bending vibrations are usually weaker and are found to occur at longer wavelength, because they require less energy. On the other hand the stretching vibrations require more energy and as a result occur at shorter wave lengths and are more intense in nature.

The structures of the complexes formed by the amines are interpreted by using a 1:1 model and the important vibrational frequencies are the symmetric and
asymmetric N-H stretchings, symmetric and asymmetric N-H deformations, C-N stretching and M-N stretches. In addition to these C=C and ring stretching modes are also important for aromatic amines. 111

(a) **N-H Stretching Vibration**:

In the region 3570-3333 cm⁻¹, occurs this most characteristic vibration, the position, intensity and the shape of which depends upon the structure of the parent molecule. Thus it is observed as a doublet in primary amines, as a singlet in secondary amines while the tertiary amines do not absorb at all in this region. Coordination almost always causes a negative shift in the position of this band.

(b) **N-H deformation Vibration**:

The deformation vibrations may be observed due to any of the following four modes:

(i) In-plane.
(ii) Out of plane.
(iii) Twisting, and
(iv) Scissoring.

The spectra of the primary amines show the symmetric and asymmetric in plane deformation vibrations
in the 851-805 cm\(^{-1}\) and 810-786 cm\(^{-1}\) regions, respectively.\(^{112}\) Sometimes a weak band is observed in the spectra of secondary aliphatic amines in the region 1650-1550 cm\(^{-1}\), whose detection is extremely difficult. The assignment of these bands is also difficult due to complications arising from conjugation effects.\(^{113}\) It is, however, found that on complexation these bands shift to higher or lower wave numbers depending upon the corresponding change in bond order.

(c) **C-N stretching vibration**:

The region 1400-1000 cm\(^{-1}\) is usually the range in which the C-N stretching vibrations have been observed. These are specifically seen between the frequency range of 1340-1250 cm\(^{-1}\) and 1350-1280 cm\(^{-1}\) for primary and secondary aromatic amines respectively.\(^{114}\) In most of the cases these vibrations are coupled with C=C vibrations.\(^{115}\)

It is found that frequencies of these vibrations are significantly lowered on coordination due to the drainage of electrons from the nitrogen atom of the base to the metal.

(d) **Aromatic C-H stretching and Ring vibrations**:

The most prominent and in fact the most important bands in the spectra of aromatic amines are
present in the region 3100-3000 cm\(^{-1}\) and 1600-1300 cm\(^{-1}\) which are the C-H and ring stretching vibrations respectively. The latter absorptions are due to stretching and contractions of all the bonds present in the ring and these usually appear doublets, their nature depending upon the type of substituent present in the ring.

(e) C-H out of plane- deformation:

The out of plane bending vibrations of the aromatic and heteroaromatic rings are coupled with adjacent hydrogens bending in the phase. The position of these absorptions are therefore, characteristic of a particular pattern of the hydrogen atoms in the ring. These bends are comparatively more intense than the previous ones, and appear around 720-960 cm\(^{-1}\) region.

Coordination of the aromatic amine to the metal usually causes a positive shift in the position of these bands.

(f) M-N Stretching Vibration:

The M-N stretching modes provide valuable information about coordination of nitrogen atom of the ligand to the metal ion. These vibrations are affected
by several factors viz.- Oxidation number of the metal, stereochemistry of the Coordination complex, basicity of the donor molecule, and ligand field stabilization energy. M-N absorption bands are always observed in far-infrared region, probably due to relatively heavy mass of the metal and the low bond order of the coordinate bond. 116, 117

The i.r. spectra were recorded on a Perkin Elmer, spectrophotometer model 621 using KBr and Nujol discs. The following notations have been used to denote the intensity of absorption bands throughout the discussion of i.r. spectra.

s = strong, m = medium, w = weak, vw = very week
br = broad, Sbr = strong broad, mbr = medium broad,
wbr = weak broad, Sh = shoulder, db = doublet.

(iv) **Electronic Spectroscopy**:

The complexes of transition metals are usually coloured and they are capable of absorbing radiant energy in the infrared (IR), Ultraviolet (UV) as well as visible regions. Interpretation of IR spectra gives valuable information concerning structure and bonding. The metal ligand vibrations occur generally in the 700 to 200 cm⁻¹ region. Electronic
spectra are used to explain and predict the modern bonding theories, to understand the nature of the electronic structure and bonding in the coordination compounds.

The types of electronic transitions that may be observed with d-block element complexes are:

1. d-d or ligand field spectra arise due to transitions between the split d levels of the central atom. The usual range at which transitions are there is 1000-333 nm.

2. Ligand to metal charge transfer spectra arise due to transition from MO's primarily located on the ligands to non-bonding or antibonding MO's located primarily on the metal atom.

3. Metal-to-ligand charge transfer spectra arise due to transitions which involve electrons being excited from non-bonding or antibonding orbitals located primarily on the metal atom to antibonding orbitals located primarily on the ligands.

4. The intraligand transitions occur due to the electronic transitions which involve electrons being excited from one ligand
orbital into another ligand orbital. These occur in UV region.

There are two selection rules for electronic transitions in complexes. They are:

(A) Transitions between states of different multiplicity $S$, are forbidden; that means the number of unpaired electrons must not be changed. However the transition $S^2 \rightarrow S^1 p^1$ is spin allowed so long as the spins of the two electrons in the $s^1 p^1$ state are $+\frac{1}{2}$ and $-\frac{1}{2}$ (Singlet state) but transition to triplet state is forbidden.

(B) Transitions within a given set of $p$ or $d$ orbitals (i.e., transitions involving only redistribution of electrons in the given Sub-shell) are forbidden if the molecule or ion has a centre of symmetry or the transition between two $g$ states or between two $u$ states are forbidden.\textsuperscript{118}

(V) **Proton Magnetic Resonance Spectroscopic Measurements**

Nuclear magnetic resonance spectroscopy is based on the fact that under, appropriate conditions any compound containing a proton absorbs the electromagnetic radiations in radiofrequency region at a
frequency equal to the frequency emitted by the nuclei of sample. A plot of the frequencies of these absorption against the intensities of magnetic field constitutes a 'HNMR Spectrum.

The 'HNMR Spectra helps in deducing the structure of a compound in the following ways -

(a) The number of 'H NMR signals are generally equal to the number of structurally equivalent protons in a particular compound.

(b) The chemical shifts in the spectra, give information about the types of protons present in the molecule.

(c) The splitting pattern of the peaks i.e., the spin-spin splitting gives an idea about the arrangement of groups containing protons, in the molecule.

(d) The area of the peaks i.e., the integration indicates the number of different types of hydrogens in a molecule.

The 'H NMR spectra of the compounds were recorded at CDRI Lucknow and have been discussed in detail in Chapter III.
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