RESULTS AND DISCUSSION

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RESULTS AND DISCUSSION

This chapter outlines in detail, the discussion relating to the use of various physico-chemical techniques of the complexes in establishing their structures and geometries and for the sake of convenience is divided into four sections. Section(A) consists of the discussion pertaining to the analytical and molar conductance data of complexes, Section(B) contains the discussion on the infra red spectral measurements, while Section (C) and (D) deal with the electronic and magnetic studies and 'H NMR spectral data respectively.

Section(A) - Analytical and molar conductance data

An idea regarding the molecular formulae of the complexes is obtained by the estimation of percentages of C, H, N microanalytically and metal by standard methods and the true molecular stoichiometry is ascertained by the measurements on their molar conductance as outlined below:

(i) Complexes of amine ligands

The analytical data of the eighteen complexes of different oxozirconium(IV), oxovanadium(IV) and dioxouranium(VI) salts with diethylenetriamine (L₁)
triethylenetetramine (L\textsubscript{2}) and tetraethylenepentamine (L\textsubscript{3}) correspond to 1:1 stoichiometry and may be represented as MX\textsubscript{2}.L where M = ZrO\textsuperscript{2+}, VO\textsuperscript{2+}, UO\textsubscript{2}\textsuperscript{2+}, X = Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, \(\frac{1}{2}\)SO\textsubscript{4}\textsuperscript{2-} and L = L\textsubscript{1}, L\textsubscript{2} or L\textsubscript{3}. Molar conductance values of these complexes in water and DMF fall in the range 1.47-2.49 mhos thereby suggesting that these anions are coordinated to the central oxometal ions. It thus appears that the ligands(L) are only bidentate in nature and the true molecular formulae of the complexes are represented thus as [MLX\textsubscript{2}].

(ii) Complexes of macrocyclic ligands

Twelve complexes derived from two macrocyclic ligands and different oxometal salts have been prepared. The analytical data of these correspond to 1:1 stoichiometry and their molar conductances fall in the range 47.10-58.50 mhos suggesting that in all the complexes the anions are not coordinated and the complexes possess the general formulae M(L)X\textsubscript{2} where M=ZrO\textsuperscript{2+}, VO\textsuperscript{2+}, UO\textsubscript{2}\textsuperscript{2+}, L = mac-1 = 1,4,8,11-tetraaza 2,3,9,10-dibenzocyclooctetradeca 5, 7, 12, 14 - tetraene (C\textsubscript{22}H\textsubscript{24}N\textsubscript{4}) or mac-II = 1,4,7,10-tetraaza 2,5,8,9-dibenzocyclooctadeca 10,13-diene (C\textsubscript{19}H\textsubscript{24}N\textsubscript{6}). Both the ligands coordinate through their azomethine and NH groups conferring coordination numbers of five and six.
to zirconyl, vanadyl and uranyl ions respectively.

As shown above, the analytical and molar conductance data have helped in the assignment of true molecular stoichiometry to the prepared complexes. The conclusive evidence regarding the site of coordination of ligands has been obtained by the discussion on the infrared data as given in the following section.

(B) **Infra red spectral measurements**

A molecule is an assemblage of various atoms, possessing different kinds of molecular vibrations, the amplitude of which in free molecule is almost insignificant. However, if the same molecule is exposed to infrared radiation and if it absorbs a part of it, the amplitude of these vibrations is considerably increased. Moreover these absorptions occur at a particular wave length and this gives rise to an infrared spectrum. The infra red studies are thus very important as these help in studying the different vibrational modes of a molecule, which in turn helps in establishing the site of coordination of the ligand.

Whenever a ligand is coordinated to a metal, the vibrational modes associated with different groups in the ligand molecule are altered measurably due to
the fact that one additional atom (the metal atom) has been introduced in the normal vibrating system of the ligand. These changes which occur if accurately located help in deciding the site of coordination of ligand.

The infra red spectra of all the complexes have been recorded in the range 4000-650 cm\(^{-1}\) in KBr medium, while for locating the absorptions associated with oxometal ions, the spectra have also been located in the region 4000-200 cm\(^{-1}\).

The coordination of a ligand to metal is known to cause, the following type of changes in the spectra\(^1\):

(i) During the formation of a metal-ligand coordinate bond, the electrons are either drained away or shifted towards the metal ion, causing the bond order to decrease or increase. This in turn is responsible for shifting the infra red frequency to higher or lower field.

(ii) The process of coordination causes a significant decrease in the total electron density of the system, thereby lowering the symmetry of the molecule. This change can manifest itself in three ways:—
(a) Decrease in the absorption bonds of coordinated ligand.

(b) Appearance of several new bands absent from the spectra of the free ligands and

(c) Splitting of some single peaks into several components.

As in most of the complexes being studied in the present work, a number of groups are coordinated, the absolute and accurate analysis of the spectra has not been possible as coupling or overlapping of different bands occurs. But by making a critical examination of the spectra of free and coordinated ligand, the band positions have been assigned and these have been used to indicate the site of coordination. The discussion is presented under following heads:

A. Absorption due to ligands.
B. Absorption due to anions
C. Absorption due to oxoions and
D. Absorption due to water molecule

A. Absorption due to ligands

The two ligands used in the present investigation are chelating amines and macrocyclic schiffs bases, and the following series of vibrations
help in establishing coordination.

(i) Absorption due to chelating amines

The amine complexes in which the predominant donor is a \( \text{NH}_2 \) group, which have been studied in the present investigation are chelating tri, tetra and pentamines, in all of which the stearic reasons suggest the coordination through the two terminal \( \text{NH}_2 \) groups. This conclusion has been drawn from the study of the most characteristic vibrational frequency in the infrared spectra associated with the \( \text{NH}_2 \) groups which has given information regarding the real position of the amine group in the complex. The different vibrational modes of amine group if taken headwise are:

(a) \( \text{NH stretching frequency} \)

The fact that all the three amines used in the investigation contain primary aminogroups can be identified by the presence of two absorption bands in the stretching region 3500-3200 cm\(^{-1}\), caused due to asymmetric and symmetric vibrations of the \( \text{NH}_2 \) group, was first noted by coblentz\(^2\) and was established conclusively by Bell\(^3\)-6. The secondary amines show only one absorption band in this region while tertiary amines show none. This \( \text{NH}_2 \) stretch is known to show a
lowering in the frequency in the event of coordination, due to the drainage of electrons from the nitrogen atom which consequently weakens the NH bond order. It is further found that the negative shift in the frequency indicates coordination and its magnitude depends upon the strength of coordinate bond formed.\textsuperscript{7-13}

In some of these complexes being reported, these vibrations are observed in the form of a doublet while in most, these are so broad that it has not been possible to see the two components. The reason probably appears, that all these amines contain NH groups as well which are not coordinated and the merging of these coordinated and non coordinated groups together, gives a broad band in the region 3360-3250 cm\textsuperscript{-1}.\textsuperscript{14,15}

(b) \textbf{NH deformation frequency}

NH deformation bands appear in the region 1650-1590 cm\textsuperscript{-1} and are found to be of strong to medium intensity. These bands have a tendency to be masked by some other vibrations occurring in that region viz. aromatic ring vibrations and azomethine vibration. On the formation of complexes these vibrations are shifted to positive wave numbers and are expected any where in the region 1600-1620 cm\textsuperscript{-1} indicating coordination.\textsuperscript{12}
(c) NH wagging & twisting vibrations

In the aliphatic diamines, the bands due to above vibrations lie in the region 1125 to 1040 cm\(^{-1}\). On coordination these vibrations also shift to lower wave numbers theoretically\(^1\) but in the polyamine complexes where coordinated and uncoordinated groups are present, band at both positions original & shifted are observed and hence no definite information regarding coordination can be drawn from their positions.

(d) NH rocking vibrations

These vibrations occur at still lower frequency around 800 cm\(^{-1}\) and in some of the present complexes these have been observed and included in table-1.

(e) CH\(_2\) angle vibration in polyamines

These vibrations are of four types: Scissoring, Wagging, twisting and rocking. The scissoring vibrations occur in present complexes at 1450 cm\(^{-1}\), the absorption due to wagging modes occurs in the region 1340-1260 cm\(^{-1}\) in the form of two bands one of which is weak and other of medium intensity.
(f) **CN stretching vibration**

These vibrations lie in the range 1220-1020 cm\(^{-1}\) and their position depends upon the electron density at the carbon atom\(^{14}\). In these complexes the CN stretching frequency appears to have undergone a large negative shift indicating that the nitrogen is coordinated.\(^{15}\)

(ii) **Absorption due to macrocyclic ligands**

The two macrocycles used in the investigation contain amino, phenyl, azomethine, methyl and methylene groups as a part of their structural frame work and all these groups are affected directly on coordination. The findings on their vibrational spectra are thus discussed separately under following subheadings:

(a) **Absorption due to amino groups**

The ligand mac-II contains NH as well as NH\(_2\) groups and its structure drawn on page shows that NH groups are potential sites for coordination while the NH\(_2\) groups present on the 4-position of the ring are free. In the spectra of its complexes thus all the characteristic vibrations of these groups are expected and observed, but due to the overlapping between
coordinated and uncoordinated bands broadening occurs as discussed before. The NH stretch is thus observed as a broad band around 3380-3280 cm\(^{-1}\), NH deformation occurs around 1600, but it is coupled with azomethine stretch and in case of NH wagging and twisting vibration no regular pattern is observed. However the negative shift of former indicates coordination through the NH group of the macrocycle.

(b) **Absorption due to aromatic rings**

In both macrocycles as well as their complexes, atleast two aromatic rings are present and consequently absorptions in the region 1600-600 cm\(^{-1}\) which are due to phenyl group are expected in the spectra. As the donors are the nitrogen atoms of the azomethine or NH groups present on the ring, the process of coordination is expected to tighten the aromatic ring and to shift the various vibrations associated with these to higher wave numbers as has been observed for other similar complexes\(^{16-17}\). The important vibrations expected in the various ranges are as follows :-

**Region 1600-1390 cm\(^{-1}\)**

A total of four or five bands of measurable intensities attributable to > C=C < and ring stretches
are observed in free ligands around 1610, 1570, 1540, 1470 and 1400 cm\(^{-1}\). Either all or some of these bands are observed in the spectra of complexes around 1620, 1590, 1550 & 1440 cm\(^{-1}\). Out of these the 1620 cm\(^{-1}\) vibration can not be treated as a pure vibration as it couples with azomethine stretch in both the ligands and with NH deformation vibration also in mac-II. The band as 1590 cm\(^{-1}\) of the free ligand is often not observed in the complexes while the band at 1540 cm\(^{-1}\) shifts to 1570±10 cm\(^{-1}\) in complexes due to coordination.\(^{18}\) The same process splits the 1450 cm\(^{-1}\) band due to in plane-deformation of CH group conjugated to aromatic system and the two separate components are observed at 1480±10 cm\(^{-1}\) and 1440±10 cm\(^{-1}\) in some complexes. The position of these bands of complexes show positive shift which is an outcome of the tightening of the aromatic ring on coordination.\(^{19,20}\)

**Region 1370-1000 cm\(^{-1}\)**

In agreement with the reported data, the bands in this region are due to C-H-in-plane deformation and ring breathing and are expected to show positive shift on coordination. These shifts are compatible with the suggestion that complex formation leads to an increased localisation to electrons in the
ligands and there is a possibility of an increase in the electron density in the pi system of ligand. Thus the C-H band system of the ligand at 1150 & 1125 cm\(^{-1}\) exhibits a positive shift of the order of 50 cm\(^{-1}\) on complexation and is observed at 1175 cm\(^{-1}\), in the form of a single broad band. The bands due to in-plane ring breathing are seen at 1040±10 cm\(^{-1}\) in free ligand at 1060±10 cm\(^{-1}\) in complexes and the positive shift is due to coordination.\(^{21}\)

**Region 1000-600 cm\(^{-1}\)**

A number of bands of variable intensity in this region are due to >C=N-C\(=\) and C-H-out-of-plane deformation centered around 930-850 cm\(^{-1}\). In free compounds the former occurs at 920 cm\(^{-1}\) while latter at 858, 825 and 780 cm\(^{-1}\) are due to one, two or four adjacent hydrogen atoms in the ring. The 858 cm\(^{-1}\) band of free ligand may be identified in complexes at 870 cm\(^{-1}\) showing positive shift while the one of 825 cm\(^{-1}\) undergoes splitting yielding one band at lower side 800±20 cm\(^{-1}\) and another around 740±10 cm\(^{-1}\). The band at 930±10 cm\(^{-1}\) is either observed unshifted in complexes or shows almost negligible shift and is not of any significance.
(c) Absorption due to azomethine groups

The schiffs bases are formed whenever a carbonyl group is condensed with an amine and contain at least one azomethine $\text{C}=\text{N}$- group in their structure and act as very good donors. In the present investigation both the macrocycles contain azomethine groups, the nitrogen of which is involved in coordination and this fact has been established by the study of its infra red frequency which occurs anywhere in the range $1660-1600 \text{ cm}^{-1}$ in free schiffs bases.$^{22-24}$

The effect of coordination on this vibration has been found to result in either negative or positive shift and the two situations depend upon the presence or absence of pi bonding and also upon the extent of conjugation in the system. Normally in the involvement of azomethine nitrogen in coordination, the drain of electrons from this group towards the metal occurs and this process increases the bond order and frequency.$^{25-30}$ On the other hand in a large number of reported complexes, the complexing through nitrogen shifts the frequency to higher wave number as well due to various reasons.$^{31}$ In the two macrocyclic schiffs bases in the present study (mac-I & mac-II), the $\text{C}=\text{N}$- group is derived from aromatic system and is conjugated. It is thus expected that the interaction of
the pi electrons of the azomethine group with the pi electron system of the aromatic ring containing >N-H or another azomethine group as the adjacent donors will tend to reduce the bond order of the >C=N- group causing a shift in the stretching frequency towards the lower side. It is thus seen that in free ligands the frequency is observed at 1660±10 cm\(^{-1}\) which shifts to 1620±10 cm\(^{-1}\) in complexes of ligand mac-II as an outcome of coordination. \(^{32-37}\)

In case of mac-I, in which the azomethine group is derived from o-phenylenediamine and acetylacetone, this band appears to split in two strong peaks at 1685±20 cm\(^{-1}\) and at 1620±20 cm\(^{-1}\). The former is assigned as the actual azomethine stretching frequency, while the lower band may be attributed to >C=N-stretch coupled with aromatic >C=C< stretch. This type of splitting has been observed and reported for those schiffs bases which contain more than two adjacent donor groups near the nitrogen\(^{38,39}\). In the present ligand in fact four adjacent donor groups are present all of which donate to oxometal ion and hence this type of splitting is expected. The increase in frequency is attributed to coordination through the acyclic nitrogen atoms as discussed below.
During complexation the unshared pair of electrons on the azomethine nitrogen atoms are attracted towards the metal ion as a result of which \( \pi, \pi^* \) conjugation of aromatic ring is broken down and a partial positive charge develops on the ring. This positive charge hinders the usual pi-pi conjugation of the group and the electronic structure analogous to \(-\text{CH}=\text{N}^+-\text{R}^-\) are formed which tend to increase the frequency of absorption. This increase is also due to change in hybridisation of the nitrogen atom, which also increases the pi character of the \( sp^2 \) hybridised orbital of the lone pair of electrons on the nitrogen atom. This results in the strengthening of the \( \text{C}=\text{N}^- \) bond due to increase in both sigma overlap and electronic interaction, on the other hand the change in hybridisation of nitrogen atom causes a change in the spatial orientation of orbitals which reduces the possibility of pi-pi overlap and leads to the weakening of \( \text{C}=\text{N}^- \) bond. Thus the observed shifts towards the positive side suggest that the change in sigma overlap and the electrostatic interaction is the predominant factor.

\( \text{C}=\text{N}^- \text{C}< \) deformation vibration

Two bands appearing in the spectra of free schiffs bases around 920±20 and 850±10 cm\(^{-1}\) are due to
above mentioned vibrational modes. In complexes both these bands appear at almost the same position as in the free ligands, although coordination has occurred through the nitrogen atom of the azomethine group. The absence of any significant shift is due to the following factors,

a) effect of bonded atom on $\text{N}^\equiv\text{N}^-$ group tends to shift the frequency to higher side. 

b) decrease in the $\pi$-bond character tends to lower the frequency.

Since the two factors operate simultaneously and oppose each other to almost equal extent, little shift is observed in frequency.

(B) Absorption due to anions

The various anions used in the investigation are chloride, nitrate and sulphate ions and the conductance measurements show that in the complexes of chelating amines these are coordinated, while in complexes of macrocyclic ligands, these are not coordinated. The vibrational spectra of complexes clearly indicates this and therefore confirms the mode of attachment of anions to acceptor ion. The i.r. spectra of these anions is discussed below:
(i) Absorptions due to chloride ions

Several evidences indicating the presence of coordinated and uncoordinated ions are reported in literature and the i.r. spectra can to some extent, though not conclusively differentiate between the two situations. In the i.r. spectra of many metal chlorides, three vibrations $\nu_1$, $\nu_2$ and $\nu_3$ are seen at 350, 420 and 510 cm$^{-1}$ corresponding to uninegative chloride ion.\textsuperscript{45-47} In the complex no.20,22,26,28 these are not coordinated as suggested by their molar conductances and precipitation of two equivalents of AgCl with AgNO$_3$. In the i.r. some weak bands are seen at 350, 425 & 515 cm$^{-1}$ confirming the presence of free chloride ions.

In the complex no.2,4,8,10,14 & 16 these ions are shown to be coordinated on the basis of conductivity measurements. As the i.r. spectra of these complexes have been recorded upto 650 cm$^{-1}$ the various vibrational modes could not be located and coordination has been suggested only on the basis of conductivity data.

(ii) Absorptions due to nitrate ions

X-ray analysis shows the nitrate ion may be coordinated to a metal as a unidentate symmetrical and asymmetrical bidentate and bridged bidentate ligand and
it is somewhat difficult to differentiate between these structures on the basis of vibrational spectra as the symmetry of one structure differs very little from other.

In the present complexes no. 19, 24, 25 & 30 the nitrate ion is found to be ionic and the two bands corresponding to asymmetric and symmetric nitro stretches are observed around 1380±20 and 820±10 cm⁻¹ respectively with almost no shift while in complex no. 1, 6, 7, 12, 13 & 18 these are coordinated and observed at lower wave numbers around 1340±20 and 800±20 cm⁻¹ corresponding to coordination.

(iii) Absorption due to sulphate ions

The free sulphate ion belongs to the point group Td, and of the four fundamentals only \( \nu_3 \) and \( \nu_4 \) are infra red active. If the ion is coordinated to metal the symmetry is lowered and splitting of degenerate modes along with the appearance of new bands corresponding to Raman active bands, occurs. The lowering of symmetry is however, different for uni and bidentate ions as shown:
Free ion (Td)  Unidentate ($C_3v$)  Bidentate ($C_2v$)  Bridged bidentate ($C_2v$)

It has been found that if the ion is not coordinated $\nu_1$ & $\nu_4$ do not split and occur at 1120 and 650 cm$^{-1}$ while $\nu_2$ does not appear and if $\nu_1$ is observed it is very weak. However in the event of coordination both $\nu_1$ & $\nu_2$ appear with medium intensity and $\nu_3$ & $\nu_4$ each split into two bands and the expected frequencies are at 1230, 1089, 995 & 960 cm$^{-1}$.

(C) Absorption due to oxometal ions

The oxometal salts of Zr, V & U have been used to prepare complexes with different ligands and the infra red spectra has helped in locating M=O stretching frequency of various oxometal ions used in the investigation.

The band due to the V=O stretch is observed
in the range 970-950 cm\(^{-1}\) in the oxo vanadium complexes belonging to symmetry \(C_4\nu\), while in oxovanadium salts in uncoordinated state a band is seen at 1012 cm\(^{-1}\) which on sublimation disappears and reappears again on exposure to moist air. The negative shift on coordination takes place because of lowering of symmetry.\(^{49-54}\) In the present complexes a strong band at 930±15 cm\(^{-1}\) is observed in the spectra which is assigned to the coordinated \(\text{V}=\text{O}\) stretch. A large negative shift in its frequency depends upon a greater amount of \(\pi^* - d\pi\) donation from oxygen to vanadium.

A strong band at 960±10 assigned to be due to \(\text{Zr}=\text{O}\) stretch by analogy with other reported oxozirconium complexes, is observed clearly in the present complexes and its presence corresponds to axial oxygen atom attached to Zr ion.\(^{55,56}\)

The spectra of present dioxouranium(VI) complexes are characterised by the presence of medium intensity bands in the range 920-950 cm\(^{-1}\) and 855-840 cm\(^{-1}\) due to \(\text{U} = \text{O}\) asymmetric (\(\nu_3\)) and \(\text{U} = \text{O}\) symmetric (\(\nu_1\)) mode of vibration and confirm the presence of linear \(\text{UO}_2\) moiety in complexes\(^{57-65}\).

Occurrence of a weak band at 945 cm\(^{-1}\) as observed in some complexes may be due to \(\nu(0\rightarrow\text{U} = \text{O})\) from
solid state interactions between the complex and potassium bromide as reported for related uranyl(VI) complexes\textsuperscript{56,66}

(D) \textbf{Absorption due to water molecules}

The literature indicates that water molecules present with in a complex may either be lattice water or coordinated water in nature. The infra red spectroscopy can make out a sharp distinction between the two situations as discussed below.

In free water molecule a medium vibration appears around 3500 cm\textsuperscript{-1} which corresponds to OH stretch. On coordination, the electrons are drained from oxygen atoms towards the metal and this decreases the bond order and shifts the stretching frequency to lower region, while if the water molecules are not coordinated, almost negligible change in the frequency is observed.

In case of present investigation, only complex no.1,3,7,9,13,18 show a broad band around 3500 ± 10 cm\textsuperscript{-1} which is the OH stretch. As there is no shift in its position when compared to free molecule, it is suggested that water molecules are present as lattice water only.
(C) **Magnetic and Spectral measurements**

The magnetic and electronic spectral properties of the complexes depend upon the number and spin states of 'd' electrons present in the orbitals of central metal ions. Depending upon which oxo metal has been used, this section has been divided into three parts:

(i) **Oxozirconium(IV) complexes**

(a) **Magnetic measurements**: The zirconium metal possessing the configuration $4d^25s^2$ may form complexes with a variety of coordination numbers as $5, 6, 7 \& 8$ depending upon the nature and crystal field strength of ligands. The hydrolysed ion is the one which is referred to as "Zirconyl" or oxozirconium(IV) ion and is written as $\text{ZrO}^{2+}$, but there is a little evidence of the existence of such an ion either in crystalline state or solution.\(^6\) The most common oxidation state is $4^+$, which corresponds to $d^6$ system, and the most common coordination number for this state is 5. The zirconyl (IV) ion is diagrammatically shown to be formed as:
It is thus clear that all such complexes since these contain no unpaired electrons possess almost zero magnetic moments.

(b) **Electronic spectra**

The splitting pattern of the orbitals in a square pyramidal complex is given in the following figure and this has been derived from a molecular orbital diagram similar to a square planar arrangement and depends upon the $C_4V$ symmetry.\(^{68}\)

\[ b_1 = dx^2 - y^2 \]
\[ a_1 = dz^2 \]
\[ e = dxz, dyz \]
\[ b_2 = dxy \]

Since there are no unpaired electrons in the vacant 'd' orbitals, electronic spectra is essentially composed of charge transfer bands and there are no d-d transitions.
(ii) Dioxouranium(VI) complexes

Discovered by Klaproth Uranium metal with atomic number 92 has ground state electronic configuration \([\text{Rn}] \text{6d}^1 \text{5f}^3 \text{7s}^2\). \(\text{UO}_2^{2+}\) ion is the stabellest species and is known to behave as a very good Lewis acids towards suitable donors. The compounds are known to exist in various oxidation states viz +3 to +6 out of which +6 is most stable and the 'Uranyl', dioxouranium(VI) or \(\text{UO}_2^{2+}\) ion is derived from this. Diagramatically, its bonding is shown to occur in the following manner:

![Image of bonding diagram]

The appropriate 'd' & 'f' orbitals can be combined to give molecular orbitals of required symmetry resulting
in two sigma and two pi bonds. In case of $\text{UO}_2^{2+}$ complexes the successive electrons are fed into the non bonding orbitals$^{69}$. These are diamagnetic due to the absence of unpaired electrons and correspond to d$^0$ system.

The electronic spectra of simple and macrocyclic complexes of uranyl ion do not show any d-d bonds, but latter do show some bands in the region 36000-38000 cm$^{-1}$ which are due to $\pi - \pi^*$ transitions which occur due to the formation of azomethine linkages as reported by some other workers.$^{70}$

The uranyl complexes however show two bands at 25,000 and 22,000 cm$^{-1}$ which may be assigned due to O=U=O linkage in $\text{UO}_2^+$ moiety.$^{71}$

(iii) Oxovanadium (IV) complexes

Vanadium, with an atomic number of 23, possesses the electronic configuration $[\text{Ar}] 4s^2 3d^3$ and shows all the oxidation states from +1 to +5. Compounds of oxovanadium(IV) possess one unpaired electron and the magnetic moment of these compounds are found to be close to 1.79 B.M.$^{72,73}$ The normal magnetic moment expected for vanadyl (IV) complexes when the orbital contribution is completely quenched by the low
symmetry field is 1.5-1.73 B.M. These values do not alter much either with temperature or field strength. Complexes of VO$^{2+}$ using all the three chelating polyamines and the two macrocyclic ligands have been prepared and their magnetic moments are observed to be 1.70-1.89 B.M. The above values correspond to one unpaired electron as the coordination number is five and the geometry is square pyramidal. The oxygen atom of VO$^{2+}$ ion projects outside the square coordination plane formed by four donor atoms around the metal ion. The formation of these is diagrammatically shown as -

\[ \text{V atom} \]
\[ \text{Ground state} \]
\[ \text{V}^{4+} \text{ ion} \]
\[ \text{VO}^{2+} \text{ in square pyramidal geometry} \]

\[ d\sigma p^3 \]

The unpaired electron in the 'd' orbital responsible for paramagnetism, belongs to a 'd' system and hence gives rise to a $2D$ term. In an octahedral
field the splitting pattern is shown to be -

\[ 2_{T_{2g}} \rightarrow 2_{E_g} \]

The bands corresponding to the single transition \( 2_{T_{2g}} \rightarrow 2_{E_g} \) are observed in the spectra at room temperature in the region \( 8000 \text{ cm}^{-1} - 25,000 \text{ cm}^{-1} \). In the five coordinate complexes, which possess \( C_{4v} \) symmetry corresponding to square pyramidal shape, the transitions are proposed to be as follows:

\[
\begin{align*}
2_{T_{2g}} & \rightarrow 2_{E_g} \\
& \rightarrow 2a_1(dz^2) \\
& \rightarrow 2b_1(dx^2-y^2) \\
& \rightarrow 2e(dxz, dyz) \\
& \rightarrow 2b_2(dxy)
\end{align*}
\]

\[ 2_{B_2} \rightarrow 2\varepsilon(I) \]

\[ \text{dxy} \rightarrow \text{dxz, dyz} \]

\[ (12,000-13,000 \text{ cm}^{-1}) \]
\[ ^{2}B_{2} \rightarrow ^{2}B_{1} \text{(II)} \, dxy \rightarrow dx^2 - y^2 \]
\[ (15,000-16,000 \text{ cm}^{-1}) \]

\[ ^{2}B_{2} \rightarrow ^{2}A_{1} \text{ (III)} \, dxy \rightarrow dz^2 \]
\[ (22,000-22,500 \text{ cm}^{-1}) \]

The following one electron energy level sequence is responsible for the above transitions.\(^76\)

\[ b_2 > e^{*} < b_1^{*} < a_1 \]

The other possible geometry due to the pentacoordination is trigonal bipyramidal, having an effective symmetry \( C_{2v} \) and the sequence of energy level in this case is

\[ a_2 < b_1 < b_2 < a_1 < a_1 \]
\[ (dzy) \, (dxz) \, (dyz) \, (dx^2-y^2) \, (dz^2) \]

Kuska & Young have also proposed the following energy level order to account for the electronic spectrum of molecule having symmetry \( C_{2v} \)\(^77-79\).

\[ a_2 < b_1 \cong b_2 < a_1 < a_1 \]
\[ (dxy) \, (dxz) \, (dyz) \, (dx^2-y^2) \, (dz^2) \]

Stronger field strengths can inter change the position of \( dxz \) and \( dyz \). The symmetry group \( C_{2v} \)
completely removes the d orbital degeneracy. Thus four d-d transitions are possible although all are not spin allowed and are found to appear in the range 11,000-19,000 cm\(^{-1}\).

Electronic spectra of VO\(^{2+}\) ion indicates that in this ion there is considerable \(\pi\pi\)-bonding between vanadium & oxygen and thus the basicity of oxygen is weakened by \(\pi\pi\)-bonding. This fact varies with the donor strength of ligand and in turn affects band III\(^{80}\).

In the present investigation, in the vanadyl complexes the bands in the range 12.00-15.00 KK, 14.50-19.00 KK and 21.00-30.00 KK are observed. The \(\nu_3\) band which is observed at 22.00 KK is due to charge transfer transition between \(dz^2\) orbitals of vanadium and \(2px\) or \(2py\) orbitals of oxygen atom. The \(\nu_2\) & \(\nu_1\) bands are assigned to be due to transition \(^2B_2\rightarrow^2E_1\) and \(^2B_2\rightarrow^2B_1\) respectively and these spectra confirm the square pyramidal structure for complexes.

(D) **Nuclear Magnetic resonance spectroscopy**

In principle when a substance is placed in a magnetic field of certain strength, it gives a spectrum in the same way as in infra red or ultraviolet
spectrum. Varying the magnetic field strength shows that at some value of field strength, the energy needed to flip the proton matches with the energy of radiation and at this point the absorption of radiation occurs and a signal is observed. This is called the 'H NMR spectrum.

In the present investigation, due to the insoluble nature of complexes in CDCl₃ & DMSO, their 'H NMR spectra could not be recorded, but the same had been done for ligands mac-I & mac-II and helped in assigning their structure.

The spectrum of ligand mac-I which is derived from o-phenylenediamine and acetylacetone shows two singlets centered at δ1.70 & δ2.40 and one multiplet in the region δ6.70-δ7.10 and their integral ratios are 12:4:8 respectively. This shows that former singlet at δ1.70 is due to four methyl group protons and the other singlet at δ2.40 is due to the methylene protons and the multiplet is due to the presence of two disubstituted benzene rings. On the basis of these results, the structure is proposed to be
The ligand mac-2 shows five different types of signals in the $^1$H NMR spectrum. A singlet corresponding to six protons is observed at $\delta 1.10$ due to the presence of two methyl groups. Another singlet corresponding to two protons is observed at $\delta 1.40$ which is due to $-CH_2$ protons of acetyl acetone part of the ligand. The two $CH_2$ group protons corresponding to the ethylenediamine part of the macrocycle are observed at $\delta 2.20$-$\delta 2.50$. This splitting of the signal into a doublet is a result of neighbouring $-NH$ protons. This shows that the condensation between ethylenediamine and 1-chloro 2,4-dinitro benzene has taken place. The NH protons are observed as a triplet at $\delta 3.70$-$\delta 3.90$ corresponding to two protons and the splitting is due to neighbouring $CH_2$ protons. In addition, a singlet is observed at $\delta 3.60$ which corresponds to four protons of
two terminal -NH₂ groups of the ligand. The fact that these signals are due to NH₂ & NH protons is confirmed by the observation that these disappear on 'D₂O' shake as these exchange with deuterium. The structure of the macrocycle is thus drawn.

[Diagram of the macrocycle]
### Table 1: I.R. frequencies in cm\(^{-1}\) of complexes of amino ligands.

<table>
<thead>
<tr>
<th>Complex No.</th>
<th>NH stretch</th>
<th>NH deformation</th>
<th>NH wagging</th>
<th>NH Twist</th>
<th>NH Rocking</th>
<th>CN stretch</th>
<th>M-O stretch</th>
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<tbody>
<tr>
<td>1.</td>
<td>3380br</td>
<td>1580vbr</td>
<td>1380vs</td>
<td>-</td>
<td>820wbr</td>
<td>1080w</td>
<td>960m</td>
</tr>
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<td>2.</td>
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<td>1370s</td>
<td>890m</td>
<td>-</td>
<td>1070brm</td>
<td>955m</td>
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<tr>
<td>3.</td>
<td>3240vbrm</td>
<td>1650mbr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1040br</td>
<td>915s</td>
</tr>
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<td>4.</td>
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<td>1612vs</td>
<td>1380s</td>
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<td>1020m</td>
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</tr>
<tr>
<td>5.</td>
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<td>1620mbr</td>
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</tr>
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<td>6.</td>
<td>3360mbr</td>
<td>1620mbr</td>
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<td>820m</td>
<td>1030wbr</td>
<td>930m</td>
</tr>
<tr>
<td>7.</td>
<td>3320sbr</td>
<td>1580wbr</td>
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<td>950s</td>
</tr>
<tr>
<td>8.</td>
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<td>1600vsbr</td>
<td>-</td>
<td>880w</td>
<td>820w</td>
<td>1100vs</td>
<td>940s</td>
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<tr>
<td>9.</td>
<td>3310wbr</td>
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<td>1370s</td>
<td>890w</td>
<td>-</td>
<td>1060m</td>
<td>920w</td>
</tr>
<tr>
<td>10.</td>
<td>3320vs, 3160vs</td>
<td>1610vs</td>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>11.</td>
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<td>1630brm</td>
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<td>900w</td>
<td>850s</td>
<td>1070m</td>
<td>920m</td>
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<td>12.</td>
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<td>1380sbr</td>
<td>890s</td>
<td>820m</td>
<td>1080wbr</td>
<td>930m, 840m</td>
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<tr>
<td>13.</td>
<td>3420sbr</td>
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<td>-</td>
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<tr>
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<td>1630m</td>
<td>1390m</td>
<td>890w</td>
<td>820m</td>
<td>1060m</td>
<td>915m</td>
</tr>
<tr>
<td>16.</td>
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<td>1620m</td>
<td>1380m</td>
<td>900w</td>
<td>850w</td>
<td>1070m</td>
<td>925m</td>
</tr>
<tr>
<td>17.</td>
<td>3300mbr</td>
<td>1630mbr</td>
<td>-</td>
<td>910mbr</td>
<td>850s</td>
<td>1020m</td>
<td>930m</td>
</tr>
<tr>
<td>18.</td>
<td>3360mbr</td>
<td>1600wbr</td>
<td>1380s</td>
<td>920s</td>
<td>860s</td>
<td>1030wbr</td>
<td>920m</td>
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Table - 1 (contd.)
Table II: I.R. frequencies in cm\(^{-1}\) of complexes of Ligand in mac-I

<table>
<thead>
<tr>
<th>Complex No.</th>
<th>Aromatic &amp; ring vibrations</th>
<th>&gt;C=N-C &lt; and &gt; CH out-of-plane</th>
<th>&gt;C=N-stretch</th>
<th>M-O stretch</th>
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<td>mac-1</td>
<td>1614w(^a), 1580w, 1540s, 1448w, 1400s</td>
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<td>920m, 858w, 825s</td>
<td>1660vs</td>
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<tr>
<td>19</td>
<td>1600w(^a), 1585w, 1472m, 1430m</td>
<td>1180w, 1145w, 1055m</td>
<td>920w, 805s, 710vs</td>
<td>1670vw, 1632m(^a)</td>
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<td>1620m(^a), 1560w, 1500vw, 1470w, 1450s</td>
<td>1170m, 1074m</td>
<td>920m, 880m, 850w, 800m, 725vs</td>
<td>1680w</td>
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<tr>
<td>21</td>
<td>1600w(^a), 1580m, 1535w, 1485m, 1430m</td>
<td>1175w, 1140 w(^b), 1060wbr</td>
<td>930-920mdb, 880-870mdb, 850w, 750vs</td>
<td>1680-1670mdb, 930m(^c)</td>
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<tr>
<td>22</td>
<td>1590w, 1580w, 1530w, 1480w, 1450m</td>
<td>1180w, 1140w</td>
<td>930s, 870s, 800s, 740vs</td>
<td>1675m, 1620m(^a)</td>
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<td>1160m, 1120mb, 1070m</td>
<td>920w(^b), 860w, 790w, 750s</td>
<td>1680-1660mdb, 930m</td>
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<td>24</td>
<td>1590w, 1580m, 1530w, 1465s</td>
<td>1190w, 1130m,</td>
<td>930s, 800w, 805m, 730s</td>
<td>1660m, 1610m(^a)</td>
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</table>

\(a\) = coupled with aromatic/azomethine stretch  
\(b\) = coupled with \(V_1/V_3\) mode of \(SO_4\) ion.  
\(c\&d\) = coupled with ring breathing
<table>
<thead>
<tr>
<th>Complex No.</th>
<th>NH stretch</th>
<th>NH deformation</th>
<th>Aromatic ring vibrations</th>
<th>C=N-stretch</th>
<th>O-stretch</th>
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<tr>
<td>Ligand mac-II</td>
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<td>930w, 850w</td>
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<td>25</td>
<td>3400-3300sbr&lt;sup&gt;b&lt;/sup&gt;db</td>
<td>1620s&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1605w, 1570m, 1530m, 1470w, 1440m, 1160m, 1060m, 930m, 890m, 800wbr, 740m</td>
<td>1628s&lt;sup&gt;a&lt;/sup&gt;</td>
<td>950m</td>
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<tr>
<td>26</td>
<td>3400-3320sbr&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1630m&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1600w, 1580m, 1480w, 1430-1420wdb, 1170s, 1070w, 920wbr, 805w, 740s</td>
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<td>27</td>
<td>3400-3300mdb&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1630s&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>1630vs&lt;sup&gt;a&lt;/sup&gt;</td>
<td>930&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>1620s&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>30</td>
<td>3400-3300sbr&lt;sup&gt;b&lt;/sup&gt;db</td>
<td>1628s&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>1628s&lt;sup&gt;a&lt;/sup&gt;</td>
<td>920wbr&lt;sup&gt;e&lt;/sup&gt;</td>
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</table>

Note: (a) Coupled with aromatic/azomethine stretch or NH deformation
(b) Coupled with $V_1$ and $V_3$ modes of $SO_4^{2-}$ ion
(c) Coupled free and coordinated stretch.
(d&e) Coupled with aromatic stretch.
<table>
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<th>Complexes</th>
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<th>$V_2$</th>
<th>$V_3$</th>
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<tr>
<td>1</td>
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<td>29</td>
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</table>
STRUCTURE OF THE COMPLEXES WITH MACROCYCLIC LIGANDS

MAC-1

MAC-2

\[ M = Zr \text{ or } V; \quad x = \text{NO}_3^-, \text{Cl}^-, \frac{1}{2}\text{SO}_4^{2-} \]

\[ M = U; \quad x = \text{NO}_3^-, \frac{1}{2}\text{SO}_4^{2-} \]
References


60. J. Lecomte and R. Freymann; Bull.Soc.chim. France 8, 622 (1941).


75. J. Selbin; Chem.Rev. 65, 153 (1965).


COMPLEX No. 22

WAVENUMBER (nm)

ABSORBANCE

0 1.0 2.0

200 300 400 500 600 700 800 900
LIGAND-(MAC-1)