Chapter 5

Studies on Complexes of Isonicotinic acid hydrazide with VO$_2$(I) and VO(IV) ions
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This chapter deals with the studies on the complexes of VO$_2$(I) and VO(IV) with Isonicotanic acid hydrazide (INTAH). The microanalytical data, magnetic and chemical properties, molar conductivity, infrared spectra, UV and visible spectra of complexes are described have in and reasonable conclusion have been drawn regarding structure and bonding of the complexes.
Interpretation of analytical, conductometric and magnetic moment data of VO$_2$(I) and VO(IV) complexes

The analytical data VO$_2$(I) and VO(IV) complexes with Isonicotanic acid hydrazide (INTAH) have been given in chapter II of this thesis which indicate following stoiochiometries:

(i) VOSO$_4$.2H$_2$O.2(INTAH)
(ii) VOSO$_4$.H$_2$O.2(INTAH)(DPTU)
(iii) VOSO$_4$.H$_2$O.2(INTAH)(TU)
(iv) VOSO$_4$.H$_2$O.2(INTAH) (Py)
(v) VO$_2$.Cl.H$_2$O.2(INTAH) and
(vi) VO$_2$.Cl.2 (INTAH).(DPTU)

All VO$_2$(I) and VO(IV) complexes are either insoluble or partial soluble in methanol, hexanol, ethanol, carbon tetrachloride, petroleum ether but fairly soluble in DMF. VOSO$_4$.2H$_2$O.2(INTAH) is green. VOSO$_4$.H$_2$O.2(INTAH) (DPTU) is light yellow, VOSO$_4$.2H$_2$O.2(INTAH) (TU) is blue, VOSO$_4$.H$_2$O.2(INTAH) (Py) is gray, VO$_2$.Cl.H$_2$O.2(INTAH) is black and VO$_2$.Cl.2(INTAH) (DPTU) is deep blue in colour. The conductivity data (shown in table III, chapter III) shows that all VO$_2$(I) and VO(IV) complexes are non-electrolytic in nature. It is further supported by their qualitative analysis. When these oxy and dioxy complexes were shaken with concentrated aqueous Na$_2$CO$_3$ solution and resulting
Na$_2$CO$_3$ extract is listed for sulphate and chloride ions then negative tests indicate the absence of sulphate and chloride ions in corresponding complexes. Thus, sulphate and chloride are present inside the coordination sphere and involved in coordination covalent bonding with vanadium atom in all oxy and dioxy vanadium complexes.

The magnetic moment measurement data of oxovanadium and dioxovanadium complexes are given in table III, chapter III of this thesis. All dioxo vanadium complexes was found to be in between 1.68 to 1.72 BM which is lower then expected for d$^1$ system. In d$^1$ system containing VO(IV) complexes, orbital contribution is almost quenched and the spin orbital coupling constant is positive. It supports the present magnetic moment values.$^{1-5}$

This value is well with in the range of oxovanadium(IV) complexes having symmetry lower than octahedral. This value also suggests that there is no significant anti ferromagnetic interaction between the pairs of oxovanadium(IV) ions in the complexes in solid state. Regarding the lower $\mu_{\text{eff}}$ values then spin only in present case, the explanation given by Zelentsov$^6$ may be extend to case and most probably suggested due to partial metal-metal bonding arising from overlapping of d orbitals in neighbouring vanadium atom. Moreover, the magnetic behaviour of the complexes are very near to Ca Ti (SO$_4$)$_2$.2H$_2$O which posses d$^1$ configuration and octahedral symmetry.
Octahedral configuration has been found for all dioxivanadium complexes having d<sup>2</sup>sp<sup>3</sup> hybridization. But distorted octahedral configuration has been found for all oxovanadium (IV) complexes having d<sup>2</sup>sp<sup>3</sup> hybridization.

So, all oxovanadium(IV) and dioxovanadium(I) complexes formulated as:

(i) [VO(INTAH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(SO<sub>4</sub>)]
(ii) [VO(INTAH)<sub>2</sub>(DPTU)(H<sub>2</sub>O)(SO<sub>4</sub>)]
(iii) [VO(INTAH)<sub>2</sub>(TU)(H<sub>2</sub>O)(SO<sub>4</sub>)]
(iv) [VO(INTAH)<sub>2</sub>(Py)(H<sub>2</sub>O)(SO<sub>4</sub>)]
(v) [VO(INTAH)<sub>2</sub>(H<sub>2</sub>O)Cl] and
(vi) [VO<sub>2</sub>(INTAH)<sub>2</sub>(DPTU)Cl]
The above geometry of complexes has been supported by infrared and electronic spectral data described at suitable places of this chapter.

**Interpretation of infrared spectra of Isonicotanic acid (INTAH) and their VO$_2$(I) and VO(IV) complexes**

The infrared spectrum of ligand and complexes were recorded by means of Perkin Elemer 621 spectrophotometer using KBr pellets as described in chapter III of this thesis. The spectra run in the range of 4000-200 cm$^{-1}$ and calibration were made by means of polystyrene film.
Infrared spectra of Isonicotanic Acid Hydrazide (INTAH)

The infrared spectrum of Isonicotanic acid hydrazide (INTAH) has been shown in Fig. IV.2 and interpretation has been done in chapter IV of this thesis.

Interpretation of Infrared spectra of Isonicotanic acid hydrazide with oxovanadium and dioxivanadium complexes

The infrared spectra of ligand INTAH, [VO(INTAH)₂(H₂O)₂(SO₄)], [VO(INTAH)₂(DPTU)(H₂O)(SO₄)], [VO(INTAH)₂(TU)(H₂O)(SO₄)], [VO₂(INTAH)₂(H₂O).Cl] and [VO₂(INTAH)₂(DPTU)Cl] have been shown in figure IV.2, V.1, V.2, V.3, V.4, V.5 and V.6 respectively and their major infrared spectral band in cm⁻¹ have been given in table V.1.

A big hump centred at region of 3500-3350, 3600-3350 and 3500-3400 cm⁻¹ in the IR-specta of [VO₂(INTAH)₂(H₂O)₂(SO₄)], [VO₂(INTAH)₂(TU)(H₂O)(SO₄)], [VO₂(INTAH)₂(Py)(H₂O)SO₄], [VO₂₂[INTAH)₂(H₂O).Cl] and a medium broad band at 3650 cm⁻¹ for [VO₂₂(INTAH)₂(DPTU)(H₂O)(SO₄)] respectively. No such bands are present in the IR spectra of ligand and other vanadium complexes. This indicates VO(IV) & VO₂(I).
Table V.1
IR spectral data of interested Isonicotinic acid hydrazide and their oxovanadium(IV) and dioxovanadium(I) complexes

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<th>[VO(INTAH)(_2) (H(_2)O)Cl]</th>
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<th>[VO(INTAH)(_2) (TU) (H(_2)O)SO(_4)]</th>
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IR spectrum of [VO(NTAH)(H₂O)₂SO₄]
IR spectrum of [VO(NTA),\(\text{H}_2\text{O}\)\(\text{SO}_4\)]

Wave Number (in cm\(^{-1}\))

Transmittance (%)
Fig. V. 3

IR spectrum of $[\text{VO(NTAH)}_2(TU)(\text{H}_2\text{O})\text{SO}_4]$
Fig. V. 5

IR spectrum of $[\text{VO}_2(\text{INTAH})_2(\text{H}_2\text{O})\text{Cl}]$
Fig. V. 6

IR spectrum of $[\text{VO}_2(\text{INTAH})_3(\text{DPTU})\text{Cl}]$
The presence of coordinated hydrogen bonded water molecules in all concerning complexes. This observation is further supported by a strong band at 1605 cm\(^{-1}\) and weak band in the region of 850-855 cm\(^{-1}\) and a big sharp band at 530 cm\(^{-1}\) in all aqua vanadium complexes. Which may be assigned at \(\delta H_2O\), \(\pi H_2O\) and \(\sigma H_2O\) mode of vibrations respectively. The observation indicates the presence of coordinated water molecules in concerning aqua complexes. No considerable loss in weight has been observed on heating these complexes upto 120°C. It indicates that the aqua molecules are present inside the coordinating sphere of concerning complexes as monodentate hydrogen bonded ligand. This assignments are good agreement with previous literature for aqua complexes.\(^{7-18}\) The infrared spectra of ligand contains medium band at 3400, 3310 and 3210 cm\(^{-1}\) which are assigned at \(\nu NH_2\), \(\nu asy-NH\) and \(\nu sym.NH\) in respectively. These bands are red shifted (~30~90 cm\(^{-1}\)) after complexation with reduction in splitting in all oxovanadium (IV) and dioxovanadium(I) complexes. It shows the evolvement of N-atom of ligand in coordination to vanadium atom in all these complexes.

This is further supported by the red shifting of bands present in the region of 1610, 785 which are assigned as \(\delta NH\) and \(\tau NH\) mode of vibration respectively.

These observation of good agreement with the work done on IR spectra of various worker.\(^{19-29}\)
(iii) A very strong band centred at 1680 cm\(^{-1}\) in the spectrum of ligand is assigned to \(\nu\)\,CO mode of vibrations.\(^{30-31}\) This band is observed either at identical or slightly blue shifting (\(~5\,cm\)^{-1}\) after complexation with oxovanadium (IV) and dioxovanadium(I) ions. Suggesting the absence of bonding through carbonyl group in complex formation.

(iv) A strong band at 1640 cm\(^{-1}\) and very strong band at 1560 cm\(^{-1}\) in the IR spectrum of ligand are assigned as amide band (I) & (II) respectively. These bands are almost all identical in all complexes with reduced intensity. The reduction of intensity may due to electronic hinderance arises after complexation through nitrogen atoms to metal atoms.\(^{32-33}\)

(v) A new band observed at 1615 cm\(^{-1}\) only in the IR spectrum of [VO(INTAH)\(_2\)(Py)(H\(_2\)O)(SO\(_4\))] which may be assigned as \(\nu\)\,P\,Py mode of vibrations.\(^{34}\) The pyridine is used as a secondary ligand in [VO(INTAH)\(_2\)(Py)(H\(_2\)O)(SO\(_4\))]\(_{\text{II}}\). It is further supported by the IR spectral bands observed at 625 and 425 cm\(^{-1}\) which may be assigned as \(\nu\,V\,-P\,y\) mode of vibrations.\(^{35}\)

A very strong band observed at 1010 cm\(^{-1}\) in the IR spectral non ligand band which is assigned at \(\nu\,V\,=\,O\) mode of vibrations in all VO\(_2\)(I) VO(IV) complexes.

(vi) Hydrazino mode of vibrations\(^{36}\) are observed at 1420 cm\(^{-1}\) in the IR spectrum of ligand (INTAH). This is red shifted towards lower frequencies (\(~5-10\,cm\)^{-1}\) in all VO\(_2\)(I) and VO(IV) complexes. Suggesting the tautness of one of the hydrazino nitrogen in bonding with VO\(_2\)(I) and VO(IV) ions.
A medium band at 1515 and 1470 cm\(^{-1}\) are observed only in the IR spectra of [VO(INTAH)\(_2\)(TU)(H\(_2\)O)(SO\(_4\))] and [VO(INTAH)\(_2\)(DPTU)(H\(_2\)O)(SO\(_4\))] respectively. These bands are assigned due to IR vibrational mode of thiourea and diphenyl thiourea present as a mixed secondary ligands.\(^{37-38}\)

(vii) The bands observed at 1119 \(\pm\) 1, 1072-1065, 1005 and 640 cm\(^{-1}\) in the IR spectra of [VO(INTAH)\(_2\)(H\(_2\)O)(SO\(_4\))] , [VO(INTAH)\(_2\)(DPTU)(H\(_2\)O)(SO\(_4\))] , [VO(INTAH)\(_2\)(TU)(H\(_2\)O)SO\(_4\)] and [VO(INTAH)\(_2\)(Py)(H\(_2\)O)(SO\(_4\))] . These spectral bands are absent in ligand and other dioxovanadium(I) complexes. These are assigned due to sulphato mode of vibrations. Since sulphate plays four type of coordinating behavior such as ionic unidentate, bidentate and bidentate bridging. All these linkage shows different characteristic vibrational bands. Which are mentioned in chapter IV of this thesis. On comparising with their characteristic vibrational modes, our reported [VO(INTAH)\(_2\)(H\(_2\)O)(SO\(_4\))] , [VO(INTAH)\(_2\)(DPTU)(H\(_2\)O)(SO\(_4\))] , [VO(INTAH)\(_2\)(TU)(H\(_2\)O)(SO\(_4\))] and [VO(INTAH)\(_2\)(Py)(H\(_2\)O)(SO\(_4\))] complexes show sulphate as a unidentate ligand present inside the coordinating sphere in these complexes.\(^{39-44}\)

(viii) The far infrared spectra in the range of 700-200 cm\(^{-1}\) of all Vanedyl(IV) and dioxovanadium(I) complexes contains some new bands. A new weak band observed at the region of 435 cm\(^{-1}\) in [VO\(_2\)(INTAH)\(_2\)(H\(_2\)O)Cl] and [VO\(_2\)(INTAH)\(_2\)(DPTU)Cl] which may be assigned due to \(\nu\) V-Cl mode of vibrations.\(^{45}\)

The new band at 440 cm\(^{-1}\) in all VO(IV) and VO\(_2\)(I) complexes are assigned due to \(\nu\) V-N-N mode of vibrations.\(^{46}\) New
band at 520 cm\(^{-1}\) in the IR spectra of all complexes are assigned due to \(\nu\) \(V \leftarrow OH\)\(_2\) mode of vibrations.\(^{47}\)

Thus on the basis of normal coordinating analysis of \([Mx_2y_2zw]\) type of complexes tentative distored octahedral arrangement may be assigned for VO(IV) complexes and regular octahedral arrangement for VO\(_2\)(I) complexes.

**Interpretation of UV and visible spectral data of ligand (INTAH) and VO\(_2\)(I) and VO(IV) complexes**

UV and visible spectra of Isonicotanic acid hydrazide (INTAH), \([\text{VO}(\text{INTAH})_2(\text{H}_2\text{O})_2(\text{SO}_4)]\), \([\text{VO}(\text{INTAH})_2(\text{DPTU})(\text{H}_2\text{O})\) (\text{SO}_4)]\), \([\text{VO}(\text{INTAH})_2(\text{TU})(\text{H}_2\text{O})(\text{SO}_4)]\), \([\text{VO}(\text{INTAH})_2(\text{Py})(\text{H}_2\text{O})(\text{SO}_4)]\), \([\text{VO}(\text{INTAH})_2(\text{H}_2\text{O})\text{Cl}]\) and \([\text{VO}_2(\text{INTAH})_2(\text{DPTU})\text{Cl}]\) have been shown in fig. IV. 11, V. 7, V.8, V.9, V.10, V.11 and V.12 respectively and spectral data have been given table V.2. The comparison of UV and visible spectra of ligand and dioxovanadium (I) and oxovanadium(IV) complexes indicates the following:

There is a strong absorption band at 350 nm (28571 cm\(^{-1}\)) in the ultraviolet spectrum of isonicotanic acid hydrazide (INTAH) which is assigned due to \(n \rightarrow \pi^*\) or C.T. spectral bands. This band of ligand is red shifted (~5 to 10nm) in all oxo and dioxo complexes indicating the involvement of ligand in complexation through N atom of ligand (INTAH). The VO(IV) exhibit d-d-transition around 445-443 nm (22472-22573 cm\(^{-1}\)), 560 562 nm.
Fig. V. 7
UV and visible spectrum of [VO(INTAH)$_2$(H$_2$O)$_2$(SO$_4$)]
Fig. V. 8
UV and visible spectrum of [VO(INTAH)$_2$(DPTU)(H$_2$O)(SO$_4$)]
Fig. V. 9
UV and visible spectrum of [VO(INTAH)₂(TU)(H₂O)(SO₄)]
Fig. V. 10
UV and visible spectrum of [VO(INTAH)₂(Py)(H₂O)(SO₄)]
Fig. V.11
UV and visible spectra of [VO$_2$(NTHAH)$_5$(H$_2$O)Cl]
Fig. V. 12
UV and visible spectrum of [VO₂(INTAH)₂(DPTU)Cl]
Table V.2

Electronic spectral data of Isonicotanic acid hydrazide and their oxovanadium(IV) and dioxovanadium(I)

<table>
<thead>
<tr>
<th>S. N.</th>
<th>Compounds</th>
<th>Bands</th>
<th>Cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Isonicotanic acid hydrazide (INTAH)</td>
<td>350</td>
<td>28571</td>
<td>n → π*/CT Band</td>
</tr>
<tr>
<td>2</td>
<td>[VO(INTAH)₂(H₂O)₂(SO₄)]</td>
<td>345 444 561 796</td>
<td>28986 22523 17825 12563</td>
<td>n → π*/CT Band e₈ → b₁g e₈ → a₁g e₈ → b₂g</td>
</tr>
<tr>
<td>3</td>
<td>[VO(INTAH)₂(DPTU)(H₂O)(SO₄)]</td>
<td>340 443 560 793</td>
<td>29412 22573 17857 12610</td>
<td>n → π*/CT Band e₈ → b₁g e₈ → a₁g e₈ → b₂g</td>
</tr>
<tr>
<td>4</td>
<td>[VO(INTAH)₂(TU)(H₂O)(SO₄)]</td>
<td>345 444 562 793</td>
<td>28986 22523 17794 12610</td>
<td>n → π*/CT Band e₈ → b₁g e₈ → a₁g e₈ → b₂g</td>
</tr>
<tr>
<td>5</td>
<td>[VO(INTAH)₂(Py)(H₂O)(SO₄)]</td>
<td>345 445 562 794</td>
<td>28986 22472 17794 12594</td>
<td>n → π*/CT Band e₈ → b₁g e₈ → a₁g e₈ → b₂g</td>
</tr>
</tbody>
</table>
(17857-17794 cm\(^{-1}\)) and 796-793 nm (12563-12610 cm\(^{-1}\)) which may be assigned as\(^{48}\):

(i) \(d_{xy} \rightarrow d_{z^2}\)

(ii) \(d_{xy} \rightarrow d_{x^2-y^2}\) and 

(iii) \(d_{xy} \rightarrow d_{yz}, d_{zx}\)

It indicates the distorted octahedral geometry with elongation of xy plane. But in the present case the distortion made between axial and equatorial parameter \(D_s\) and \(D_t\) respectively indicates the difference in the bond length. The evaluation of these parameter suggests elongation along axis. So, the energy level scheme proposed by Lever as given below:
The observed transition may be expected as: \(^{49}\)

\[
\begin{align*}
\text{eg} & \rightarrow b_{2g} \ (12500 \ \text{cm}^{-1}) \\
\text{eg} & \rightarrow a_{1g} \ (17600 \ \text{cm}^{-1}) \\
\text{eg} & \rightarrow b_{1g} \ (22300 \ \text{cm}^{-1})
\end{align*}
\]

Moreover, the two bands maxima for vanadyl complexes in the range of 16500-19000 cm\(^{-1}\) and 21000-30000 cm\(^{-1}\) have been assigned in literature according to classification suggested by Selbin.\(^{50}\) These two bands may be charge transfer bands because of their comparatively high intensity. Selbin et al have reported bands for oxovanadium (IV) ion in the spectral region 83000-98600 cm\(^{-1}\) in which are supported to d-d or ligand field bands. The three bands appear in the region 11000-16000, 14500-19000 and 21000-31000 cm\(^{-1}\) Selbin\(^{51}\) suggested after the modification of Ballhusen and Gray’s model for VO(H\(_2\)O)\(_3^{++}\) ion that is in the region 11000-19000 cm\(^{-1}\) arises from expected d-d transition. The third band in the region 25000 cm\(^{-1}\) is charge transfer band which may be also due to partial forbidden of transition for a field bonding level to half filtered non-bonding orbitals. Such band is also observed in the bis (3-phenyl acetyl acetato complex of Cu(II) as a familler shoulder attached to intense charge transfer band at 24000 cm\(^{-1}\).\(^{52}\)

It is also supported by magnetic measurement values discussed in this chapter earlier.

The absence of such type of band for all other dioxovanadium (I) complexes indicates the diamagnetic nature of complexes.

On the basis of above results-discussion and normal coordinate analysis of these complexes following tentative structure have been assigned for all complexes:
Tentative structure \([\text{VO}(\text{INTAH})_2(\text{H}_2\text{O})_2(\text{SO}_4)]\)
Tentative Structure of [VO(INTAH)_2(DPTU)(H_2O)(SO_4)]
Tentative structure of $[\text{VO(INTA\textsubscript{H}})_2\text{TU}(\text{H}_2\text{O})(\text{SO}_4)]$
Tentative structure of $[\text{VO(INTAH)}_2(\text{Py})\{\text{H}_2\text{O}\}{\text{SO}_4}]$
Tentative structure of \([\text{VO}_2(\text{INTAH})_2(\text{H}_2\text{O})\text{Cl}]\)
Tentative Structure of $[\text{VO}_2\text{(INTAH)}_2\text{(DPTU)}\text{Cl}]$
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