Chapter 3

Experimental Technique and Data of Spectroscopic (Infrared, Ultraviolet, visible) Magnetic Moment and Conductometric Studies on the Complexes
In this chapter the experimental techniques and their results of the analytical and spectroscopic studies are described. The purpose of these experiments is to elucidate the nature of the metal ligand bonding in the complexes. In addition to this, there results also indicate the possible special configuration for the various complexes.
Infrared Absorption Spectra

Infrared spectra of these complexes were recorded with the help of Jasco FT/IR-5300. Diffraction Grating Double Beam infrared spectrophotometer in the range of 4000-400 cm\(^{-1}\) at CDRI, Lucknow and analytical department of Banaras Hindu University, Varanasi (U.P.), India. These measurements were made in Nujal mull or in KBr Pellets.

Mull Technique

The sample was finally powdered in a polished agate mortar so that the particle size was reduced to less than the minimum wavelength of radiation they were to transmit. A drop of mulling agent nujal was added. Excess of nujol was avoided as it caused unnecessary dilution of the sample. After the sample had been completely suspended and adjusted to a viscosity so as to allow even flow. It was then transferred to a windo slate (NaBr) at a demountable cell. The plate was then covered by a second plate, which forced the mull to spread as thin film. The plates were assembled and the specimen was ready for taking the spectrum. In the reference the cell was assembled that it was clear and free of opaque granules. The mulling agent nujol was taken for purity suitable for spectroscopic works. Nujol which is a mixture of high molecular weight liquid paraffinic hydrocarbon absorb at 3.3-3.5µ, 6.55 and 7.28µ.
Pellet Technique

In this technique small amount of final grind solid sample is intimately mixed with about 100 times its weight of powdered potassium bromide. The final grind mixture is then passed under very high pressure in a press (at least 25,000 p.s.i) to form a small pellet (about 1-2mm, thick and 1 cm in diameter). The resulting pellet is transparent in I.R. radiation and is run as such.

Since potassium bromide does not absorb in the region 2.5-15μ, a complete spectra of the complex was obtained.

The major I.R. bonds are given in the discussion chapter at suitable places of this thesis.

The Ultra violet and visible absorption spectra

The UV and visible spectra of Fe(II) Fe(III) Co(II) and Ni(II) complexes of 4-amino-3-ethyle-5-mercapto-5-triazole and 4-amino-3-hydrozino-5-mercapto-1,2,4-triazole were recorded with Carl Zeiss (Jenna) model. The spectra were recorded in DMF for solution spectra standard rectangular absorption quartz all of 10mm. light path were used, the test cell were match against the blank cell over the entire wavelength range in all experiment. In the subsequent measurements, the cells were oriented in the same way as they were placed when measurements were made with blank cells.
The result and spectra of interest are given in discussion chapter at suitable places of this thesis.

**Magnetic measurements**

Magnetic properties in chemical substances arises from the spins of elections and nucleus. But the matter of interest of chemists are only the magnetic effects exerted by electrons. The magnetic effects of electrons may be determined by followed two ways:

(a) From classical Bohr’s theory, an electron is traveling in a close path around the nucleus. Such an electron will produce a magnetic movement just like an electric correct traveling in a loop of wire. The magnetic moment produced in this way is called orbital moment.

(b) Each electron in effect, is a magnet in it self from per wave mechanical view point (ie. Classical Bohr theory) electron is regarded as a small sphere of negative charge which is spinning at its axis and the spinning of charge (I,e. electron) produces a magnetic moment which is called spin magnetic moment or spin moment of the electron.

A combination of there two moments viz. the inherent spin moment and the orbital moment gives rise to magnetic moment found for certain individual atoms, ions or molecules.

The magnetic moments of atoms, ions and molecules are usually expressed in units called Bohr magnet ions. (B.M.)
1 B.M. = \( \frac{e h}{4\lambda m_e} = 9.27 \times 10^{-27} \text{ erg/gauss} \)

where, \( h = \) Plank’s constant
\( e = \) Electric charge in ems units
\( C = \) Velocity of light
\( M = \) Mass of electron

The magnetic measurements on all solid complexes have been made at room temperature on the Gouy balance. A long Gouy tube was suspended from one solid of an analytical balance by a fine silk-thread so as to hang vertically in a magnetic field. The tube was filled with the finally powdered sample to be investigated up to a length of about 5cm. The specimen tube lay between the pole of an electromagnet which produce field of about 9000 gauss with an approximately 1.8 cm pole gap. The magnet and suspension were kept in closed room to avoid any air damping.

Mercury tetra this cyanato cobalt(II)’ \( (g = 16.44 \times 10^{-6} \text{ c.g.s unit at } 20^\circ\text{c}) \) was used as the magnetic susceptibility calibrates. The tube constant was checked from time to time to ensure satisfactory working of the apparatus. The weight of the sample in the presence and absence of a field are taken by turning on end of the field of electromagnet respectively.

If a substance with permanent moment ‘\( \mu \)’ is placed in magnetic field with a molecular magnet free to orient themselves, they will be subjected to two opposite effects.
(a) The magnet field of a strength $H$ which tend to align all molecular magnets in the same directions.

(b) The thermal effect of the vibration, rotation and translation motion, which tends to make the direction of the molecular magnet entirely random. It can be shown-

$$\chi_m = \frac{N\mu^2}{3kT}$$

Where $N = \text{Avagadvo's Number}$

$\mu = \text{Magnetic moment}$

From this expression it follows that:

$$\mu = \sqrt[3]{\frac{3kT}{N}} \chi_m.$$  

In practice we were interested in magnetic moment of a particular atom in a compound, rather than that of a molecule as a whole. Hence we replace $\chi_m$ by the susceptibility of atom $\chi_A$ with which we are concerned. Therefore, to most be added, a correction of magnetic susceptibility for all the atoms present in the molecule including that of paramagnetic atom itself, although the last correction is often ignored.

Numerically, the permanent magnetic moment of a substance is expressed in Bohr magnetones having the magnitude 5564 Gauss cm per gram mole and being given by the expression.

$$\mu = \frac{eh}{4\pi m c}$$

where, $h = \text{Plank's constant}$
e = electronic charge

c = velocity of light

m = mass of electron

It has been pointed out that both the spin and the orbital motion of an electron are sources of magnetic moment. The total magnetic moment of a substance is then made up of two components, so-called spin and orbital contributions. Both these contributions are due to the presence of unpaired electrons but in many intense there unpaired electron are in effect the outermost once in the species under consideration and are not screened by other electrons. In such cases the spin contribution may be neglected. The most common example embrace ions of the transition metals. On the other hand when the unpaired electrons, well within the ions and are screened by other electrons, as is true among ions derived from the inner transition metals. The orbital contribution can not be neglected and must be combined with spin contribution to give the total moment for many cases, the permanent moment is given by the expression:

$$\mu = \sqrt{4S(S+1)+L(L+1)}$$

Where “S” is the resultant spin angular moment for those cases where orbital contribution is small and can be neglected, the magnetic moment then becomes:

$$\mu = \sqrt{4S(S+1)} = 2\sqrt{S(S+1)}$$
In the terms of unpaired electron (n) above equation takes the form: \( \mu = \sqrt{n(n+2)} B.M. \).

Hence the expected magnetic moment for one unpaired electron would be 1.73 B.M., for two unpaired electron 2.83 B.M. for three unpaired electron 3.88 B.M. as so. on, to values of 4.90, 5.92 and 6.93 for 4, 5 and 6 unpaired respectively.

The magnetic moment of material may be calculated if the number of unpaired electron is known or conversely the observed magnetic moment may be used to find out the number of unpaired electrons in the substance concerned.

So, useful information is obtained by proper interpretation of measured values by magnetic moment are not measured directly. Instead of one measures the magnetic susceptibility of a material for which it is possible to calculate the magnetic moment of paramagnetic ion or atom with the help of expression (13) given later.

**Magnetic susceptibility is defined as**

If a substance is placed in a magnetic field of magnitude H Gausses, the total magnetic flux with in the substance is given by the relation:

\[
\vec{B} = H + 4\pi \vec{I}
\]  
(1)

"I" is called intensity of magnetism. The ratio B/M called the magnetic permability of material is given by the relation

\[
\frac{B}{H} = \frac{H}{H} + 4\pi \frac{I}{H}
\]  
(2)
\[
\frac{B}{H} = 1 + 4\pi \chi
\]  \hspace{1cm} (3)

Where \( \chi \) is called magnetic susceptibility per unit volume or simply the volume susceptibility.

It is generally more convenient to discuss magnetic susceptibility on a weight basis than on a volume basis and the following relation used.

\[
\chi_g = \frac{\chi}{d}
\]  \hspace{1cm} (4)

where \( \chi_g \) is called gram susceptibility or specific susceptibility and \( d \) is density in gram cm\(^{-3}\). So the equation (3) becomes:

\[
\frac{B}{H} = 1 + 4\pi d \chi_g
\]  \hspace{1cm} (5)

for discussion of chemical problems molar susceptibility

\[
\chi_m = \chi_g M
\]

where \( M \) is molecular weight

In there classical studies Pierre curie showed that paramagnetic susceptibility varies inversely as temperature and often follow or closely approximate to the behaviour required by the simple equation,

\[
\chi_m = \frac{C}{T}
\]  \hspace{1cm} (6)

Where ‘\( T \)’ is absolute temperature and ‘\( C \)’ is constant which is characteristic of the substance and known as curie constant.
Latter work of Onnes and Perrier showed that for many paramagnetic substances, a more exact relationship as observed.

\[ \chi_m = \frac{C}{T} + \theta \]

Where \( \chi_m \) = molar susceptibility and \( \theta \) = Curie-Weiss constant. Applying straightforward statistical treatment, it can be shown that molar susceptibility and magnetic moment are related by the equation stated earlier.

\[ \chi_m = \frac{N\mu^2}{3kT} \] \hspace{1cm} (8)

where, \( N \) is Avagadro’s number and \( k \) is the Boltzmann constant obviously by comparison of equation (7) & (8) we obtained:

\[ C = \frac{N\mu^2}{3k} \]

or

\[ \mu^2 = \frac{3kC}{N} \] \hspace{1cm} (9)

and at any given temperature

\[ \mu^2 = \frac{3k}{N} \chi_m T \] \hspace{1cm} (10)

So the magnetic moment of paramagnetic ion atoms or molecule is given by:

\[ \mu = \sqrt{\frac{3k\chi_m T}{N}} \] \hspace{1cm} (11)

which on evaluating \( \sqrt{\frac{3k}{N}} \) numerically becomes
\[ \mu = 2.84 \sqrt{\chi_m T} \]  \hspace{1cm} (12)

In practice, most transition metal compounds, are magnetically dilute, that the atom with a permanent magnetic moment is surrounded by other atoms without any permanent moment. This prevent any possibility of interaction between neighbouring magnetic atoms, but as all atoms with paired electron are slight diamagnetic (i.e. tend to move away from a magnetic field), it is necessary to correct experimentally determined susceptibility for the combined effect of the diamagnetism of all the atoms in the compound. This correction is comparatively small but may sometimes amount to about a quarter of the total so that it can not always be ignored.

Replacement of \( \chi_m \) in equation (12) by corrected susceptibility \( X_m \) gives the effective magnetic moment of the paramagnetic atom, ion or molecules.

\[ \mu_{\text{eff}} = 2.84 \sqrt{\chi_m T} \]  \hspace{1cm} (13)

Many different methods have been used to measure the magnetic property of material in solid, liquid and gaseous state of the most of the methods applied. Goug, faraday Quincke and NMR methods are most useful. It consists essentially of suspending a uniform rod of a specimen in non-homogenous magnetic field and measuring by conventional weighting technique for the force exerted on it. The more paramagnetic body is more strongly drawn towards the more intense part of the field. The specimen is weighted with and without the magnetic field in
the same position. The difference between the two weighting gives
the apparent mass or increase in weight ‘m’ and the relation for
calculation of $\delta V$ of specimen is $\delta H$. then the force. $\delta F$ exerted is
given by-

$$\delta F = (k_1 - k_2)V \frac{\delta H}{\delta l}$$

(14)

Where $k_1$ and $k_2$ are the susceptibilities per unit volume of
the specimen and the displaced medium respectively. Integration
over the whole length of the specimen from $H = H_1$ at zero length
to $H = H_0$ at length $I$ gives

$$F = \frac{(k_1 - k_2)V(H_i^2 - H_o^2)}{2I}$$

(15)

If $F$ in dyness, is replaced by $wg$ where $w$ is in grames and
$(H_i^2 - H_o^2)$ by $H^2$ then:

$$K_1 = K_2 + \frac{2Igw}{VH^2}$$

(16)

$$Wg = \frac{(k_1 - k_2)VH^2}{2I}$$

$$2IWg = (k_1 - k_2)VH^2$$

$$K_1 = K_2 + \frac{2gIW}{VH^2}$$

but $K = \chi_f = \frac{W}{V}$

where $w$ is the total weight of the specimen

$$\chi = K_2V + \left[2g \cdot \frac{1}{H^2}\right]W$$

(17)
The value of $K_2$ is negligible and the above equation is reduced to:

$$\chi = \frac{2gIw}{WH^2}$$  \hspace{1cm} (18)

where $g$ = acceleration due to gravity

$I$ = length of the specimen in cm.

Thus the magnetic moment value of VO$_2$(I), Fe (II), Mn (II) Cr(III) and VO (IV) complexes were given in table III.1.

**Conductivity measurements**

Conductivity measurements of complexes were done by using Wiss-Werkstatter with in Obb type LBR conductivity meter in DMF. The cell constant was 0.452 and 0.001 molar solution of complexes were used. The data are given in table III.2.
### Table III.1

**Magnetic moment data of the complexes**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>$\mu_{\text{eff}}$ in B.M.</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[VO(INTAH)$_2$(H$_2$O)$_2$(SO$_4$)]</td>
<td>1.69</td>
<td>PM</td>
</tr>
<tr>
<td>2.</td>
<td>[VO(INTAH)$_2$(DPTU)(H$_2$O)(SO$_4$)]</td>
<td>1.70</td>
<td>PM</td>
</tr>
<tr>
<td>3.</td>
<td>[VO(INTAH)$_2$(TU)(H$_2$O)(SO$_4$)]</td>
<td>1.72</td>
<td>PM</td>
</tr>
<tr>
<td>4.</td>
<td>[VO(INTAH)$_2$(PY)(H$_2$O)(SO$_4$)]</td>
<td>1.68</td>
<td>PM</td>
</tr>
<tr>
<td>5.</td>
<td>[VO$_2$(INTAH)$_2$(H$_2$O)Cl]</td>
<td>-</td>
<td>DM</td>
</tr>
<tr>
<td>6.</td>
<td>[VO$_2$(INTAH)$_2$(DPTU)Cl]</td>
<td>-</td>
<td>DM</td>
</tr>
<tr>
<td>7.</td>
<td>[Mn(INTAH)$_2$(H$_2$O)$_2$Cl$_2$]</td>
<td>5.84</td>
<td>PM</td>
</tr>
<tr>
<td>8.</td>
<td>[Mn(INTAH)(DPTU)(H$_2$O)$_2$Cl$_2$]</td>
<td>5.91</td>
<td>PM</td>
</tr>
<tr>
<td>9.</td>
<td>[Mn(INTAH)(TU)(H$_2$O)$_2$Cl$_2$]</td>
<td>5.92</td>
<td>PM</td>
</tr>
<tr>
<td>10.</td>
<td>[MN(INTAH)$_2$(H$_2$O)$_4$]SO$_4$</td>
<td>5.89</td>
<td>PM</td>
</tr>
<tr>
<td>11.</td>
<td>[Mn(INTAH)$_2$(DPTU)$_2$(H$_2$O)$_2$]SO$_4$</td>
<td>5.97</td>
<td>PM</td>
</tr>
<tr>
<td>12.</td>
<td>[Mn(INTAH)$_2$(TU)$_2$(H$_2$O)$_2$]SO$_4$</td>
<td>5.92</td>
<td>PM</td>
</tr>
<tr>
<td>13.</td>
<td><a href="NO$_3$">Cr[INTAH]$_2$(DPTU)$_2$(H$_2$O)$_2$</a>$_3$</td>
<td>3.71</td>
<td>PM</td>
</tr>
<tr>
<td>14.</td>
<td><a href="NO$_3$">Cr[INTAH]$_2$(TU)$_2$(H$_2$O)$_2$</a>$_3$</td>
<td>3.72</td>
<td>PM</td>
</tr>
<tr>
<td>15.</td>
<td>[Cr[INTAH]$_2$(DPTU)$_2$(H$_2$O)$_2$]ac$_3$</td>
<td>3.68</td>
<td>PM</td>
</tr>
<tr>
<td>16.</td>
<td>[Cr[INTAH]$_2$(TU)$_2$(H$_2$O)$_2$]ac$_3$</td>
<td>3.70</td>
<td>PM</td>
</tr>
<tr>
<td>17.</td>
<td>[Fe(INTAH)$_3$(DPTU)$_2$(SO$_4$)]</td>
<td>-</td>
<td>DM</td>
</tr>
<tr>
<td>18.</td>
<td>[Fe(INTAH)$_3$(TU)$_2$(SO$_4$)]</td>
<td>-</td>
<td>DM</td>
</tr>
</tbody>
</table>
Table III.2
Conductometric data of complexes

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>AM (OM⁻¹ Cm⁻¹)</th>
<th>No. of ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[VO(INTAH)₂(H₂O)₂(SO₄)]</td>
<td>7.12</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>[VO(INTAH)₂(DPTU)(H₂O)(SO₄)]</td>
<td>6.69</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>[VO(INTAH)₂(TU)(H₂O)(SO₄)]</td>
<td>11.01</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>[VO(INTAH)₂(PY)(H₂O)(SO₄)]</td>
<td>5.91</td>
<td>-</td>
</tr>
<tr>
<td>5.</td>
<td>[VO₂(INTAH)₂(H₂O)Cl]</td>
<td>7.26</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>[VO₂(INTAH)₂(DPTU)Cl]</td>
<td>10.12</td>
<td>-</td>
</tr>
<tr>
<td>7.</td>
<td>[Mn(INTAH)₂(H₂O)₂Cl₂]</td>
<td>9.63</td>
<td>-</td>
</tr>
<tr>
<td>8.</td>
<td>[Mn(INTAH)(DPTU)(H₂O)₂Cl₂]</td>
<td>7.01</td>
<td>-</td>
</tr>
<tr>
<td>9.</td>
<td>[Mn(INTAH)(TU)(H₂O)₂Cl₂]</td>
<td>10.12</td>
<td>-</td>
</tr>
<tr>
<td>10.</td>
<td>[Mn(INTAH)₂(H₂O)₄]SO₄</td>
<td>32.01</td>
<td>2</td>
</tr>
<tr>
<td>11.</td>
<td>[Mn(INTAH)₂(DPTU)₂(H₂O)₂]SO₄</td>
<td>29.79</td>
<td>2</td>
</tr>
<tr>
<td>12.</td>
<td>[Mn(INTAH)₂(TU)₂(H₂O)₂]SO₄</td>
<td>31.76</td>
<td>2</td>
</tr>
<tr>
<td>13.</td>
<td><a href="NO%E2%82%83">Cr(INTAH)₂(DPTU)₂(H₂O)₂</a>₃</td>
<td>109.13</td>
<td>4</td>
</tr>
<tr>
<td>14.</td>
<td><a href="NO%E2%82%83">Cr(INTAH)₂(TU)₂(H₂O)₂</a>₃</td>
<td>105.41</td>
<td>4</td>
</tr>
<tr>
<td>15.</td>
<td>[Cr(INTAH)₂(DPTU)₂(H₂O)₂]ac₃</td>
<td>10.12</td>
<td>4</td>
</tr>
<tr>
<td>16.</td>
<td>[Cr(INTAH)₂(TU)₂(H₂O)₂]ac₃</td>
<td>7.92</td>
<td>4</td>
</tr>
<tr>
<td>17.</td>
<td>[Fe(INTAH)₃(DPTU)₂(SO₄)]</td>
<td>8.71</td>
<td>-</td>
</tr>
<tr>
<td>18.</td>
<td>[Fe(INTAH)₃(TU)₂(SO₄)]</td>
<td>10.31</td>
<td>-</td>
</tr>
</tbody>
</table>
REFERENCES