CHAPTER 5

ELECTRON PARAMAGNETIC RESONANCE (EPR) OF SOME
SUBSTITUTED VANADYL MESO-TETRAPHENYL
PORPHYRINS OXIDIZED WITH SbCl₅

5.1. INTRODUCTION

Electron paramagnetic resonance (EPR) is a technique which is extensively used by chemists and other scientists to monitor the paramagnetic properties of the system they study. The basic theories of the EPR are well documented in the literature. In porphyrin chemistry EPR has been used extensively and exhaustive literatures are available. In view of this we simply present here a very brief and selective discussion on paramagnetic resonance theory.

In a metalloporphyrin one or more unpaired electrons may exist on the central metal atom. Also one or more unpaired electrons may be generated on the π-ligand system or on the central metal atom or in both. Such unpaired electrons will give EPR spectra and will give rise to EPR spectra. The features of EPR spectra are dependent on the number of unpaired electrons and its environment.
5.2. SOME BASIC PRINCIPLES OF EPR\textsuperscript{1-7}

5.2.1. Resonance Condition, g-value and symmetry

An unpaired electron is associated with a spin angular momentum giving rise to a magnetic moment $\mu$, which is given by

$$\mu = g\beta S. \quad \text{(4.2.1)}$$

Where $g$ is the electron g factor and is dimensionless. $B$ is the electronic Bohr magneton ($=e\hbar/2mc$, where $e=-e$, charge on the electron and $m$ = mass of the electron).

If we subject such a system to an external magnetic field $B$, the interaction between the electron magnetic moment and the external magnetic field is given by the Hamiltonian

$$H = -\mu.B \quad \text{(4.2.2)}$$

From equations (4.2.1) and (4.2.2), we get

$$H = g\beta B.S \quad \text{(4.2.3)}$$

If the applied magnetic field is in the Z-direction, then

$$H = g\beta BzSz \quad \text{(4.2.4)}$$

Since $Sz = \pm 1/2$, we can have two allowed orientations of spins ($Mz =\pm 1/2$) parallel or antiparallel to $Hz$, Replacing the Hamiltonian $H$ by $E$ (Energy), then equation (4.2.4) can be written as

$$E = (\pm 1/2) g\beta Bz \quad \text{(4.2.5)}$$

Since

$$\Delta E = h\gamma \quad \text{(4.2.5)}$$
We get

\[ H\gamma = g\beta_e B_z \] ..............................................(4.2.7)

gives the resonance condition. The frequency of electromagnetic radiation required to induce transitions between the two spin states is given by

\[ \gamma = (g\beta_e/h) B_z \] ................................................(4.2.8)

For a magnetic field of 3500G, the absorption frequency lies in the X-band (3 cm) microwave region. The selection rule for an EPR transition is \( \Delta M_s = \pm 1 \), with the irradiation oscillating magnetic field being perpendicular to the external magnetic field.

One can determine the g-value, from the experimental EPR spectrum. It's value is mainly dependent on the spin and the orbital angular momentum of the unpaired electron. For a spherically symmetric system in (S-state), the orbital angular momentum is zero and the g-value is more or less equal to free-spin value \( g = 2.0023 \). For an organic free radical, the electrons are delocalized, and have very little angular momentum resulting in a small derivation from the free electron g-value. The picture is different in the case of transition metals. In a transition metal complex the orbital angular momentum of the metal electron(s) is quenched fully or partially by the ligand atoms or by other
neighboring ions. This leads to a deviation from the free spin $g$-value.

This derivation is correlated to the spin-orbit interactions. In solid state $g$-value depends on the symmetry i.e. the orientation of the magnetic field to the symmetry axes of the electric field about the ion. This leads to the anisotropy in $g$-values. One can observe EPR signals at two $g$-values for a polycrystalline sample if the ligand field has an axial symmetry. For such system two types of absorptions are exhibited in the spectrum. A major absorption is observed if the external magnetic field is perpendicular to the symmetry axis (considering the symmetry axis as $Z$ axis, then $g_x = g_y = g_z$) and minor absorption is observed if the applied field is parallel to the symmetry axis. Most of the metalloporphyrins have axial symmetry and we observe two $g$-values. If the symmetry changes, we may observe more $g$-values. This is what we observe in the case of orthorhombic, where three different $g$-values are exhibited. On the other hand the situation is different in solution. The molecules are in rapid tumbling motion and averages out to a single $g$-value. It is also to be noted that the $g$-value depends on the oxidation state of the metal ion.
5.2.3. ZERO FIELD SPLITTING AND FINE STRUCTURE

For a system having a total spin $S>1/2$ i.e. having more than one unpaired electron, we often see some $2S$ features in the spectra especially in the oriented system. This structure is known as fine structure. This fine structure is due to the interaction of the individual magnetic moments (due to spin) with the magnetic fields generated by other electrons. This interaction exists even in the absence of the external magnetic field. This phenomenon is called the zero field splitting. Thus, the fine structure reflects a splitting of the $(2S+1)$ levels in the absence of the external magnetic field. Obviously, zero field splitting lead $\Delta M_s = 1$ transitions to occur at different values of the applied field for a particular microwave frequency. The EPR spectrum of $\Delta M_s = 1$ transitions is sometimes anisotropic and one can determine the zero field splitting from its analysis. Zero field splitting observed for transition metal ions if there are some distortions in the cubic symmetry. The effect of zero field splitting for $\Delta M_s = 1$ and $\Delta M_s = 3/2$ is shown below (fig.5.2.1). From the EPR measurements of the zero field splitting one can also approximately calculate the average distance between two unpaired electrons of a triplet state (organic triplet state molecule).
Fig. 5.2.1. Effect of zero field splitting, Energy levels
A triplet state (ii) a quartet state for of an axially symmetric system
Arrow (→) indicates $\Delta M_s = 1$ and dotted line (· · · · · · →) indicates $\Delta M_s = 2$
5.3. HYPERFINE INTERACTION

One of the main objectives of the EPR measurements is to obtain the hyperfine splittings, and to analyze and interpret it. The hyperfine interactions originate from the interaction between the magnetic moment of the unpaired electron spin and the magnetic moment of the nuclei present in the system. There are two types of such interaction viz. (a) Fermi contact interaction and (b) Dipolar interaction.

(a) FERMI CONTACT INTERACTION

This interaction occurs due to the non vanishing electron spin density on the surface of the nucleus or in the S-orbital of the atom. This is so because p, d, f orbitals have nodes at the nucleus. In the case of the organic \( \pi \)-radical the hyperfine interaction of occurs due to \( \sigma - \pi \) spin polarization mechanism. Similarly, a contact interaction occurs involving a transition metal ion. In both cases some electron spin density should exist in the S-orbital of the atom. This spin polarization mechanism is explained elsewhere in the literature. However, the better explanation may be given if we invoke Realistic quantum mechanics. The hyperfine coupling constants are observed to be much large for transition metal ions than those for organic free radicals.
(b) THE DIPOLAR INTERACTION

This interaction is similar to the classical dipolar interaction between two bar magnets. In solution this interaction averages out to zero due to rapid tumbling motions of the molecules. We normally observed this interaction only in the solid state. Therefore, it depends on the orientation of both the magnetic moments i.e., Electrons spin moment and the nuclear magnetic moment with respect to the applied magnetic moment. Thus, it is anisotropic. This interaction becomes more complicated in the case of transition metal ion due to spin-orbit coupling which is also dependent on the symmetry of the molecule.

5.4. LINE SHAPE AND RELAXATION

To obtain information out of EPR spectra one has to study the line shape /line widths. Shape of the EPR lines depends greatly on the spin relaxation time. We observe EPR observe EPR absorption line due to population difference between the two spin states (large population in the lower energy spin state) at thermal equilibrium. This condition is maintained by spin relaxation. Therefore, it is obvious that the spin states have finite life time. Thus, the line widths of an EPR spectrum are inversely proportional to the relaxation line. In this case the relaxation
undergo without emission of radiation. The relaxation process through two mechanisms via spin-lattice relaxation and spin-spin relaxation. Spin-lattice relaxation involves spin-orbit coupling. Strong spin-orbit coupling results in a short spin-lattice relaxation time ($T_1$) giving broad lines or sometimes too broad for detection (say at room temperature). On lowering the temperature (liquid nitrogen, liquid helium) the spin lattice relaxation time ($T_1$) increases and we observe EPR spectra. Obviously, at lower temperature the lower energy spin state population increases and we observe better EPR spectra. One observes sharper EPR spectra for free radicals even at room temperature. This is because in free radicals, the spin-orbit coupling is negligible and gives rise to longer spin-lattice relaxation time. Thus, free radicals exhibit narrower line widths.

Spin-spin relaxation occurs due to the intermolecular interactions. A particular molecule having an unpaired electron will have spin moment which will be affected by the local field generated by the neighboring spins. These local fields produce fluctuation in the actual external magnetic applied ($B_0$). Therefore, this particular spin will experience a field equal to $B_0 + B_{local}$. Further, it also induces transitions within the system. Obviously, spin-spin relaxation is concentration dependant. Thus, spin-spin
relaxation time ($T_2$) decreases with increase in concentration and vice versa. Therefore, for a strong paramagnetic sample, sharper EPR lines will be obtained on dilution.

Besides, these two processes mentioned above there are other factors that contribute to the EPR line shape.

Normally, one encounters of line shapes via, Lorentzian and Gaussian. In solution spectra one commonly encounters Lorentzian line shape, which is given by

$$f(w) = \frac{1}{(1/T_2)\sqrt{1/4(1/T_2)^2/w_0-w)^2}}$$

where $w_0$ is the angular frequency corresponding to the centre of the line and $w$ is the angular frequency of normal additional field $B_1$.

In solid spectra one generally observe Gaussian line shape which is given by

$$f(w) = T_2(w_0-w)^2\exp[-1/2T_2(w_0-w)^2]$$

5.5. SPIN HAMILTONIAN

One can write the spin Hamiltonian for Hydrogen atom easily as

$$H = g\beta BS_z - g_N\beta_NB_l + a.S.I$$

The third term in the equation (4.5.1) tells that it is isotropic hyperfine coupling, but does not indicate anything about the mechanism of the coupling. Therefore, one has to formulate
proper spin Hamiltonian and obtain the values of these parameters from the experimental EPR spectra and fit them into the spin Hamiltonian. In transition metal ions, spin-orbit coupling complicates the EPR spectra. In the spin Hamiltonian terms like $S_B$, $L_B$, $S_I S_I$, $L_I$, $S_L$ and $S_1 S_2$ occur. (where $S$ = electron spin, $I$ = nuclear spin, $B$ = external magnetic field, $L$ = orbital angular momentum and $S_1$ and $S_2$ are the spins of electrons 1 and 2 respectively). To interpret the EPR spectra in terms of these interactions is quite different and not straightforward. The effect of the spin-orbit coupling is included in the $g$-values ($g_x = g_y = g_z$) and the hyperfine coupling $A_x$, $A_y$, $A_z$. These values can be obtained from the experimental EPR spectra and then fit into the spin Hamiltonian. One can compute the spin Hamiltonian parameters by proper choice of wave function. It is to be noted that the Hamiltonian has to be defined with respect to the co-ordinates of $g$ tensor and $A$ tensor in which they are diagonal.

5.6. METALLOPORPHYRINS WITH PARAMAGNETIC METAL ATOM UNPAIRED ELECTRON ON THE LIGAND

In general there are two types of porphyrin ligands: (i) OEP-type (OEP = octa ethyl porphyrin) and (ii) TPP type (TPP = meso tetraphenyl porphyrin)$^{8-13}$. 

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(i) OEP type: The porphyrin ligands which do not have any substituents in the meso positions. Typical examples are octaethyl porphyrin, Etio porphyrin, proto porphyrin and many other naturally occurring porphyrins.

(ii) TPP type: The porphyrin ligands which have alky or aryl substituents into meso positions. Typical example is mesotetraphenyl porphyrin. etc.

In a metalloporphyrin having $D_{4h}$ symmetry, the highest occupied pi molecular orbits are very close lying, with symmetry labels $a_{1u}$ and $a_{2u}$. The energy difference between these two molecular orbitals is of the order of 0.5eV or less. Therefore, their relative ordering is quite sensitive to the central metal ion. However, it has been normally observed that for metalloporphyrin radical cations belonging to OEP type the HOMO (Highest occupied molecular orbital) have $a_{1u}$ ground state. On the other hand that of the TPP type has $a_{2u}$ ground state. It is to be noted that these generalization is not rigid and in some case the ground state of the pi radical changes from $a_{1u}$ to $a_{2u}$ on changing the axial ligand. On the whole the above generalization holds fairly well for a large number of metalloporphyrin.
5.7. EPR OF SOME SUBSTITUTED VANADYL meso-TETRAPHENYL PORPHYRINS OXIDIZED WITH SbCl₅

5.7.1. RESULTS

(i) VO[T(ο-NO₂)PP]

Oxidation of VO[T(ο-NO₂)PP] with SbCl₅ follows exactly in the same manner to that of the VOTPP oxidation. Addition of 1.8ml of 0.1M SbCl₅ to 0.2ml of 10⁻³M VO[T(ο-NO₂)PP] gives rise to the spectrum(fig.5.7.1(i)). Further addition of SbCl₅ leads to triplet state.

(ii) VO[T(2,5-(οCH₃)₂)PP]

Addition of 2.6ml of 0.1M SbCl₅ to 0.2ml of 10⁻³M VO[T(2,5-(οCH₃)₂)PP] give the spectrum(fig.5.7.1(ii)A). Further addition of SbCl₅ leads to triplet (fig.5.7.1(ii)B). This leads to a triplet state.

(iii) VO[TpyP]

Addition of 1.2ml of 0.1M SbCl₅ to 0.2ml of 10⁻³M VO[TpyP] exhibits the spectrum(fig.5.7.1(iii)A). Further addition of SbCl₅ yield the spectrum (fig.5.7.1(iii)B).

(iv) VO[T(p-OH)PP]

Oxidation of VO[T(p-OH)PP] with SbCl₅ gives rise to the spectrum(fig.5.7.1(iv)A). Further addition of SbCl₅ give rise to spectrum (fig.5.7.1(iv)B) and the spectrum (fig.5.7.1(iv)C). EPR
parameters are summarizing in the table 5.1. The formation of mono cations is further supplemented by IR spectra\textsuperscript{18-19}. In all cases an additional band at 1275 cm\textsuperscript{-1} are observed (fig.5.7.(v)). Further, during the oxidation with SbCl\textsubscript{5}, demetallation does not take place. This is checked by taking UV-Vis spectra after quenching the solutions containing mono cations and the SbCl\textsubscript{5} with diethyl amine. (fig.5.7.(vi) A, B, C, and D).

5.7.2 DISCUSSION

Except for the VO[T(p-OH)PP] other three vanadyl porphyrins undergo oxidation with SbCl\textsubscript{5} in the same manner to that of VOTPP oxidation\textsuperscript{14-17}. In case of VO[T(o-NO\textsubscript{2})PP] it clearly undergoes oxidation quite similar to that of the oxidation of VOTPP. Oxidation steps can be represented as

\[\text{VO}[T(o-\text{NO}_2)\text{PP}] \rightarrow \text{VO}[\text{SbCl}_4\text{Cl-T(o-NO}_2)\text{PP}]{\text{SbCl}_5}\]

\[\text{I}\]

\[\text{VO}[T(o-\text{NO}_2)\text{PP}^+]\text{Cl}^-\]

\[\text{II}\]

The pre oxidized form I is observable at room temperature. Further, it forms triplet state (II) on further addition of SbCl\textsubscript{5} and its
spectrum is observable at a higher modulation. The EPR parameters are obtained using the simulation program.

In the case of VO[T(p-OH)PP] formation of solids (precipitates) on further addition of SbCl₅ is observed. This is due to polymerization which is also observed by some earlier workers. This is also evident from the CV study. The cations of these vanadyl porphyrins give two g-values indicating that the ligand field possesses an axial symmetry.

5.7.3. CONCLUSION

From the EPR study of the oxidation of VO[T(2,5-(OCH₃)₂)PP], VO[T(p-OH)PP], VO[T(o-NO₂ )PP], and VO[TpyP] with SbCl₅ following observations are made:

i) Except VO[T(p-OH)PP] all three vanadyl porphyrins undergo oxidation with SbCl₅ generating radical cations in the same process to that of the oxidation of VOTPP.

ii) The pre-oxidized species are also observable at room temperature. The triplet state spectra are observable at higher modulation even at room temperature.

iii) The inter-electronic distances ranging between 3.629Å – 3.601Å are observed which points to a₂u ground state.

iv) VO[T(p-OH)PP] polymerizes on oxidation.
### Table 5.1: ESR spectrum at Room Temperature

<table>
<thead>
<tr>
<th>Metalloporphyrin</th>
<th>Inter electron distance R(Å)</th>
<th>Unoxidized g value</th>
<th>Oxidized g value</th>
<th>Oxidized A(G) Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VO[T(2,5- (OCH₃)₂)PP]</td>
<td>3.629</td>
<td>1.984</td>
<td>1.932</td>
<td>1.971</td>
</tr>
<tr>
<td>VO[T(p-OH)PP]</td>
<td>3.621</td>
<td>1.999</td>
<td>1.920</td>
<td>1.989</td>
</tr>
<tr>
<td>VO[T(o-NO₂PP]</td>
<td>3.612</td>
<td>1.975</td>
<td>1.928</td>
<td>1.969</td>
</tr>
<tr>
<td>VO[TpyP]</td>
<td>3.601</td>
<td>1.987</td>
<td>1.911</td>
<td>1.963</td>
</tr>
</tbody>
</table>
Fig. 5.7.1 (i) Room temperature X-band EPR spectra of VO [T(o-NO₂)PP] in Dichloromethane oxidized with SbCl₅

Experimental conditions:
- Modulation Frequency = 100 KHz
- Microwave power = 2 mW
- Microwave frequency = 9.33 GHz. Scan Hme 8 min, scan range 1600G
- Modulation amplitude = 0.5 x 10G
Fig. 5.7.1 (ii) Room temperature X-band EPR spectra of VO [T(2,5 - (OCH₃)₂)PP] in Dichloromethane oxidize with SbCl₅

Experimental conditions:

- Modulation Frequency = 100 KHz
- Microwave power = 2 mW
- Fig (A) Microwave frequency = 9.31 GHz. Scan Hme 8 min, scan range 1600G
- Modulation amplitude = 1.6 x 10G
- Fig (B) Microwave frequency = 9.33 GHz. Scan Hme 8 min, scan range 1600G
- Modulation amplitude = 1.8 x 10G
Fig. 5.7.1 (iii) Room temperature X - band EPR spectra of VO [TPyP] in Dichloromethane oxidized with SbCl₅

Experimental conditions:

- **Fig (A)**
  - Modulation Frequency = 100 KHz
  - Microwave power = 2 mW
  - Microwave frequency = 9.38 GHz. Scan Hme 8 min, scan range 1600G
  - Modulation amplitude = 0.5 x 10G

- **Fig (B)**
  - Modulation Frequency = 100 KHz
  - Microwave power = 2 mW
  - Microwave frequency = 9.4 GHz. Scan Hme 8 min, scan range 1600G
  - Modulation amplitude = 0.9 x 10G
Fig. 5.7.1 (iv) Room temperature X-band EPR spectra of VO [T(p-OH)PP] in Dichloromethane oxidized with SbCl₅

Experimental conditions:

- Modulation Frequency = 100 KHz
- Microwave power = 2 mW

Fig (A)  
- Microwave frequency = 9.31 GHz. Scan Hme 8 min, scan range 1600G  
- Modulation amplitude = 0.8 x 10G

Fig (B)  
- Microwave frequency = 9.33 GHz. Scan Hme 8 min, scan range 1600G  
- Modulation amplitude = 1.6 x 10G

Fig (C)  
- Microwave frequency = 9.4 GHz. Scan Hme 8 min, scan range 1600G  
- Modulation amplitude = 2 x 10G
fig. 5.7.(c) Infrared spectrum of VO(1,2,5-(OCH₃)₃PP) in CH₂Cl₂, oxidized with SbCl₅ at room temperature.
Figure 5.7.1 (vi) A...UV-visible absorption spectrum of VO[2,5-(OCH₃)₃PP]
in CH₂Cl₂ oxidized with SbCl₅ at room temperature, (...),
and reduced with diethyl amine
Figure 5.7.1 (vi) UV-visible absorption spectrum of VO[T(p-OH)PP]in CH₂Cl₂ oxidized with (---) SbCl₅ at room temperature, (....), ... and (----) reduced with diethyl amine.
Figure 5.7.1 (vi) UV-visible absorption spectrum of VO[T(o-NO$_2$)PP] in CH$_2$Cl$_2$ oxidized with (---) SbCl$_5$ at room temperature, (-----), (-----) and (----) reduced with diethyl amine.
Figure 5.7.1 (vi) D. UV-visible absorption spectrum of VO[TPyP] in CH$_2$Cl$_2$
oxidized with (---)SbCl$_5$ at room temperature, (----),
and (-----) reduced with diethyl amine
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