APPENDIX – A\textsuperscript{1,2}

CYCLIC VOLTAMMETRY OF METALLOPORPHYRINS

Let us consider one -electron oxidation of a molecule R

\[ R \xrightarrow{-e} R^- \xrightarrow{+e} R \text{ } (1) \]

During the forward triangular sweep (triangular wave) a peak is obtained at a potential \( E_a \) corresponding to the process \( R \rightarrow R^+ \). In the reverse sweep the species \( R^+ \) is reduced back to \( R \) at a peak potential \( E_c \). Thus, we obtain half - wave potential corresponding to this redox couple.

\[ E_{1/2} = \frac{E_a + E_c}{2} \text{ } (2) \]

For a reversible process, the peak – to – peak difference is given by

\[ E = E_a - E_c = \frac{0.059V}{n} \text{ } (3) \]

at 25°C.

If the peak currents are \( i_{pa} \) and \( i_{pc} \) corresponding to \( E_a \) and \( E_c \) respectively, then for a one -electron reversible process,

\[ \frac{i_{pa}}{i_{pc}} = 1 \text{ } (4) \]

For a metalloporphyrin having \( D_{4h} \) or \( C_{4h} \) symmetry, the two highest occupied MO (HOMO) \( a_{1u} \) and \( a_{2u} \) are nearly degenerate. During oxidations, electrons are
removed from the HOMO levels. Removal of electrons may be either from the metal or from the porphyrin ring or may be from both. In a metalloporphyrin, the central metal ions such as Zn, Cu etc. are quite inactive to the redox process while metal ions such as Fe, Co, Mn, Ni etc. are electro active and redox process may occur in the metal center as well as in the ligand. This can be understood by considering HOMO levels of the metal as well as the ligand. Thus, it can be represented as

\[ \begin{align*}
&\text{E} \\
&\text{d - energy level (HOMO of the metal ion)} \\
&\pi - \text{energy level (HOMO of the ligand)} \\
&\text{(i)} \\
&\pi - \text{energy level (HOMO of the ligand)} \\
&\text{d - energy level (HOMO of the metal ion)} \\
&\text{(ii)} \\
&\text{d - energy level (HOMO metal)} \\
&\pi - \text{energy level (HOMO ligand)} \\
&\text{(iii)}
\end{align*} \]

Fig. 1. HOMO representative for metallo porphyrin.
System (i) contains electron-active metal center. Therefore, the redox process will occur first in the metal center and then the ligand. System (ii) contains non-electroactive metal center, therefore, redox process will occur in the ligand. System (iii) contains electron active metal center, therefore, redox process will occur in both the metal as well as in the ligand. Thus, this process becomes complicated.

In general one can represent the redox process by the following scheme

System I, considering a bivalent metal.

\[
\begin{align*}
M(\text{II})P & \xrightarrow{e^-} M(\text{III})P^+ \quad E_{1/2}(1) \\
M(\text{II})P & \xrightarrow{e^-} M(\text{III})^+ \xrightarrow{e^-} M(\text{III})^{++} \quad E_{1/2}(2) \quad E_{1/2}(3)
\end{align*}
\]

\[
\begin{align*}
M(\text{II})P & \xrightarrow{\text{red}} M(\text{III})P^- \xrightarrow{\text{red}} M(\text{III})^- \xrightarrow{\text{red}} M(\text{III})^{-+} \\
E_{1/2}(1) & \quad E_{1/2}(2) \quad E_{1/2}(3)
\end{align*}
\]

\[
\Delta_{\text{ox}} = E_{1/2}^{\text{ox}}(2) - E_{1/2}^{\text{ox}}(1)
\]

\[
\Delta_{\text{red}} = E_{1/2}^{\text{red}}(1) - E_{1/2}^{\text{red}}(2)
\]

For ring oxidation and reduction a constancy of \( \Delta_{\text{ox}} \) and \( \Delta_{\text{red}} \) are observed. \( \Delta_{\text{ox}} \approx 0.3eV \) and \( \Delta_{\text{red}} \approx 0.5eV \).

Also, \( \delta = E_{1/2}(1) - E_{1/2}(2) \) is constant for a variety of metallo porphyrins (i.e. \( 2.20 \pm 0.15V \)), where the redox processes involve the ligand only. It is observed that \( \Delta_{\text{ox}} \) or \( \Delta_{\text{red}} \) of the metal is independent and is explained in terms of HOMO \( (a_{1u} \text{ and } a_{2u}) \) or LUMO \( (e_{g}) \) \( \pi \)-molecular orbitals of the porphyrin ligand and metal central
orbitals. There is negligible mixing between the metal orbitals and the porphyrin $\pi$-orbitals. Thus, the metal ion exerts an inductive Coulombic effect on the $\pi$-orbitals of the ligand through $\sigma$ frame work. It effects only the absolute values of $\pi$ energy levels but not the relative values i.e. the difference in the energies between HOMO and LUMO. Using PPP $\pi$ electron energies, the value of $\Delta_{\text{ox}}$, $\Delta_{\text{red}}$ and $\delta$ have been estimated which agree reasonably well with the corresponding experimental data. However, when metal–centered redox process occur, this correlation fails.

**APPENDIX – B3-6**

**B.1. SPIN HAMILTONIAN:** The spin Hamiltonian for a metalloporphyrin having an unpaired electron on the central metal atom is presented here.

**Liquid/Solution state:** In solution/liquid media the spin Hamiltonian is simple and is given by

$$\mathcal{H}_{\text{iso}} = g \beta_e H_z S_z + a_M \hat{I}_M \hat{S} + \hat{S} \cdot \sum_i a_i \hat{I}_i$$

where $g = \text{isotopic g-value}$

- $a_M = \text{Hyperfine Coupling of the metal atom}$
- $a_i = \text{Hyperfine coupling of the ligand}$
- $\hat{I}_M = \text{nuclear spin of the metal atom}$
- $\hat{I}_i = \text{nuclear spin of the ligand atoms}$

and $\hat{S} = \text{unpaired electron spin of the metal atom}$
Solid state (frozen solutions/glass state/single crystal)

The spin Hamiltonian is given by

\[ \mathcal{H} = \beta_e [g_{\text{eff}} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{\text{eff}} S_z + A_{\perp} (S_x I_x + S_y I_y) \]  

(2)

Neglecting the nuclear quadrupole interaction for a nucleus of spin \( I > 1 \).

It is to be noted that \( \hat{S} \) is a fictitious spin operator containing both orbital angular momentum (\( \hat{L} \)) and spin angular momentum (\( \hat{S} \)). For a metal atom with unpaired electrons in the \( d \)-orbital, the effect of the spin-orbit coupling is included as a perturbation term (\( \lambda \hat{L} \hat{S} \)) while the interaction such as \( \hat{L} \cdot \hat{H} \) and \( \hat{L} \cdot \hat{I} \) are considered as second-order corrections to the \( g \)- and \( A \)-values. Consider a \( d^9 \) system (having an unpaired electron) in a square-planar ligand field and assuming that each of the four nitrogens of the ligand has available 2s, 2pz, 2py, and 2px orbitals with 3d orbitals of the metal atom. Assigning \( x \) and \( y \) axes along M-N bonds, then the antibonding molecular orbitals are

\[ B_{1g} = |x^2 - y^2> = \alpha d_x^2 \cdot y^2 + (\alpha'/2)(-\sigma_x^a + \sigma_y^b - \sigma_x^c - \sigma_y^d) \]  

(3)

\[ B_{2g} = |xy> = \beta_1 d_{xy} - (\beta'/2)(p_y^b + p_x^b - p_y^c - p_x^d) \]  

(4)

\[ A_{1g} = \alpha_1 |3z^2 - r^2> = \alpha_1 d_{3z^2 - r^2} - \alpha'/2 (\sigma_x^a + \sigma_y^b - \sigma_x^c - \sigma_y^d) \]  

(5)

\[ \begin{align*}
|xy> &= \beta_{1xy} - \beta'/\sqrt{2} (p_z^{(1)} - p_z^{(3)}) \\
E_g &= |yz> = \beta_{1yz} - \beta'/\sqrt{2} (p_z^{(2)} - p_z^{(4)})
\end{align*} \]  

(6)
where \( \sigma^{(i)} = np^{(i)} \pm (1-x^2)^{1/2} S^{(i)} \) for \( 0 \leq n \leq 1 \)  

(7)

Bonding orbitals are constructed by replacing the unprimed by primed and the primed by minus the unprimed coefficients in the antibonding orbitals.

The \( A_{1g} \) level do not contribute even in the second order correction. \( B_{1g} \) represents in-plane \( \sigma \) bonding, \( B_{2g} \) represent in a plane \( \sigma \) - bonding while \( E_g \) represents out-of-plane \( \pi \) bonding. The orbitals \( \sigma_x, \sigma_y \) etc. are sp\(^2\) hybridised \( \sigma \) lone pairs of the nitrogen atoms, that are bonded to the metal atom. On normalizing equation (3), we get

\[
\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1
\]

(8)

where \( S \) is the overlap integral between the metal and the ligand orbitals. The coefficients \( \alpha, \alpha' \) can be evaluated using the EPR data as follows:

\[
g_{ii} = 2.0023 - 8p [\alpha\beta_1 - \alpha' (1-\beta_1^2)S T(n)/2]
\]

(9)

\[
g_{\perp} = 2.0023 - 2\mu [\alpha\beta - \alpha'\beta S - (\alpha (1-\beta^2)^{1/2} T(n)v^2] 
\]

(10)

\[
A_{ii} = p[ - \alpha^2 (4/7 + k_0) + (g_{\perp} - 2) + 3/7 (g_{ii} - 2) + \text{terms containing } T(n)]
\]

(11)

\[
A_{\perp} = p[ - \alpha^2 (2/7 - k_0) + 11/14 (g_{\perp} - 2) + \text{terms containing } T(n)]
\]

(12)

where \( \rho = \lambda_0\alpha\beta_1/(E_{xy} - E_x^2 - E_y^2) \)

(13)

\[
\mu = \lambda_0\alpha\beta/(E_{xx} - E_x^2 - E_y^2)
\]

(14)

\[
p = 2.0023g_{ii}\beta_N<\mathbf{r}^3> 
\]

(15)

\[
\approx 2\gamma\beta_0\beta_N<d_x^2 \cdot d_y^2> 
\]

(15)
\( \lambda_o \) is the spin-spin coupling constant for the free metal ion which is given by the integral

\[
<3d | \lambda(r) | 3d>
\]

and \( k_o \) is the Fermi - contact interaction for the free ion.

The term \( T(n) \) is given by

\[
T(n) = n - (1-x^2)^{1/2} R^8 (Z_p Z_o)^{5/2} (Z_s - S_p)/(Z_s + Z_p)^5 a_o
\]

Where \( Z_s \) and \( Z_p \) are the effective nuclear charges on the s and p orbitals respectively and \( a_o \) is the Bohr radius. The values of effective charges from the literature\(^7\) are

<table>
<thead>
<tr>
<th></th>
<th>For Nitrogen</th>
<th>For Oxygen</th>
<th>For Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Z_{2s} )</td>
<td>4.50</td>
<td>5.25</td>
<td></td>
</tr>
<tr>
<td>( Z_{2p} )</td>
<td>3.54</td>
<td>4.06</td>
<td></td>
</tr>
</tbody>
</table>

For Vanadium

\( Z_{3d} = 7.22 \)

Using the above values the overlap integrals for nitrogen and oxygen are calculated.

Considering ligand – to – metal distance \( R = 3.62a_o \) and \( n=(2/3)^{1/2} \)

The overlap integrals

\( S_{\text{nitrogen}} = 0.093 \)

\( S_{\text{oxygen}} = 0.076 \)

And \( T(n) \) values are

\( T(n)_{\text{nitrogen}} = 0.333 \)

\( T(n)_{\text{oxygen}} = 0.220 \)
Generally the orbital excitation energies (for copper complex)

$$\Delta E_{xy} \approx 15,000 \text{cm}^{-1}$$

$$\Delta E_{xz} \approx 25,000 \text{cm}^{-1}$$

and knowing $g_n, g_\perp, A_n$ and $A_{\perp}$ one can calculate $\alpha_2, \beta_1$ and $\beta_1'$. An approximate expression for $\alpha^2$ is written as

$$\alpha^2 = -\frac{A}{P} + (g_n - 2) + \frac{3}{7}(g_\perp - 2) + 0.04$$

If $\alpha^2 = 1$, then the band will be ionic. If the overlap integral is vanishingly small and $\alpha^2 = 0.5$, then band will be completely covalent. Thus, smaller the value of $\alpha^2$ more is the covalent character.

**B.2. Superhyperfine structure:** In metalloporphyrin the interaction of the metal unpaired electron with the four N nuclei give rise to superhyperfine structure. The Hamiltonian is expressed as

$$\mathcal{H}_{\text{suphyp}} = \hat{S} \sum_{n=1}^{4} A_n \hat{l}_n$$

(17)

For D$_{4h}$ symmetry

$$\mathcal{H}_{\text{suphyp}} = A_{N_{\parallel}} S_z^N + A_{N_{\perp}} (S_x^N + S_y^N)$$

(18)

Where $I_x^N$, $I_y^N$ and $I_z^N$ are the nuclear spin components of the nitrogen atom along the three coordinates. In most cases the superhyperfine tensors are found to be isotropic i.e. $A_{N_{\parallel}} = A_{N_{\perp}}$. However, $A_{N_{\parallel}}$ and $A_{N_{\perp}}$ can express as
The equations are expressed in terms of 2s and 2p orbitals of nitrogen.

The first term within the square brackets is the isotropic part of the hyperfine coupling arising from the spin density at 2s – orbital of the nitrogen atom. The second term is the dipolar coupling arising out of the spin density in the px and py orbitals of the ligand atom. The sp² hybridised orbitals of the nitrogen is given by

\[ \psi = \gamma |2s\rangle + (1 - \gamma^2)^{1/2} |p_\sigma\rangle \]  

The value of \( \gamma^2 \) can be obtained from the magnitude of \( A^N_u \) and \( A^N_\perp \). Thus, one can obtain \( \alpha \) and \( \alpha' \) of the equation (3).

The magnitude of d-d transitions can be obtained from the optical spectra.

The coefficient \( \beta, \beta_1 \) and \( \beta_1' \) are also obtained in the similar way (using the EPR data).

**APPENDIX – C**

**TRIPLET STATE**: A metalloporphyrins containing an unpaired electron on the metal atom on oxidation another unpaired electron is generated in the ligand. Thus, a triplet state (\( S=1 \)) is generated in the molecule. A spin Hamiltonian for such a system can be written as

\[ \mathcal{H} = \beta [S_1.g_1.H + S_2.g_2.H] + S.A.I + S_1.D.S_2 + JS_1.S_2 \]  

------------------------ (1)
where the indexes 1 and 2 represents unpaired electron on the metal atom and the unpaired \( \pi \)-electron on the ligand respectively. The hyperfine coupling between the ligand \( \pi \)-electron and the metal atom nucleus is neglected. Also, the value of \( J \) is larger then the microwave frequency (X-band). Thus, an approximate Hamiltonian can be written as

\[
\mathcal{H} = \beta g SH + S AI + SDS \quad \text{---------------------------------------- (2)}
\]

Here we consider the contribution to the zero-field splitting (ZFS) in only from the dipolar coupling.

For an axially symmetric system

\[
\mathcal{H} = \beta g SH + D_\perp (S_x^2 + S_y^2) + D_\parallel S_z^2 \quad \text{---------------------------------------- (3)}
\]

In terms of \( D \) and \( E \)

\[
\mathcal{H} = \beta g SH + D[(S_x^2 - 1/2 S(S + 1) + E(S_x^2 - S_y^2)] \quad \text{---------------------------------------- (4)}
\]

where \( D = 3/2 D_n \)

\( D \) and \( g \) terms are expressed in the same principle axis system with the four-fold symmetry axis as the \( Z \)-axis. Considering the interelectron axis is in the plane of the porphyrin ring and expressing the ZFS tensor along the interelectron axis \( (z') \):

\[
D_{xx'} = D_{yy'} = -D_{zz'}/2 \]

\[
\begin{align*}
D_{xx'} = D_{yy'} = -D_{zz'}/2 \\
\{ & \\
D_n = D_{x'x'} = D_{y'y'} = -D_{zz'}/2
\end{align*}
\]
\[ D_{2x}(\text{in MHz}) = 1.298 \times 10^4 g^2/R^3 \]  

where \( R \) is expressed in Å and 
\[ g^2 = g_u^2 + 0.5g_\perp^2 \]

**C.1. Basis functions (triplet state)**

As there are two unpaired spins, we have the following basis functions:

\[
\begin{align*}
|T_{+1}\rangle &= \alpha(1)\alpha(2) \\
|T_{0}\rangle &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\
|T_{-1}\rangle &= \beta(1)\beta(2)
\end{align*}
\]

Antisymmetric (singlet state, \( S = 0 \))

\[
|S\rangle = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]
\]

Re-writing the triplet functions along x, y and z axes

\[
\begin{align*}
|T_x\rangle &= \frac{1}{\sqrt{2}}[\beta(1)\beta(2) - \alpha(1)\alpha(2)] = \frac{1}{\sqrt{2}} |T_{-1} - T_{+1}\rangle \\
|T_y\rangle &= \frac{1}{\sqrt{2}}[\beta(1)\beta(2) + \alpha(1)\alpha(2)] = \frac{1}{\sqrt{2}} |T_{+1} + T_{-1}\rangle \\
|T_z\rangle &= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = \frac{1}{\sqrt{2}} |T_0\rangle
\end{align*}
\]

The following computer program were obtained from Prof. J. Subramanian, Department of Chemistry, Pondicherry University, Pondicherry, INDIA (i) ZFS and (ii) powder and the spectrum were printed using MSExcel
REFERENCES


