CHAPTER 1

BRIEF REVIEW OF VO,
Co AND Ni PORPHYRINS
CHAPTER – 1

1.1. INTRODUCTION

In this chapter a brief review of the VO, Co and Ni porphyrins with special reference to substituted TPP systems are presented. Emphasis is given to the studies of Electron Paramagnetic Resonance(EPR) and Cyclic voltammetry(CV).

1.2. VANADYL PORPHYRIN

Reports on EPR of VOTPP and its oxidised products are available in the literature. Selyutin et al. observed that VOTPP on oxidation with Br2/SbCl3/SnCl4/TiCl4 formed pre-oxidised complexes. The biradical/triplet state generated by SbCl3 could not be observed even in the glass state. The pre-oxidised complexes could also be observed only at low temperature. The reason for not observing these complexes was attributed to thermodynamic instability of the complexes. The EPR data of the two pre-oxidised complexes at liquid nitrogen temperature were reported as \( g_0 = 1.977, g_\perp = 1.973, A = 141 \times 10^{-4} \text{ cm}^{-1}, B = 39 \times 10^{-4} \text{ cm}^{-1} \) for \([V^{4+}\text{OSbCl}_4\text{Cl}(\text{TPP})]\) while \( g_0 = 1.977, A = 140 \times 10^{-4} \text{ cm}^{-1} \) for \([V^{4+}\text{OSbCl}_4\text{Cl}^- (\text{TPP})] \text{ SbCl}_5\). The EPR data for the dication were \( g_0 = 1.973, g_\perp = 1.980, A = 144 \times 10^{-4} \text{ cm}^{-1}, B = 44 \times 10^{-4} \text{ cm}^{-1} \) for \([\text{VOTPP}^{2+}]\text{2Br}_2; g_0 = 1.973, g_\perp = 1.980, A = 144 \times 10^{-4} \text{ cm}^{-1}, B = 44 \times 10^{-4} \text{ cm}^{-1} \) for \([V^{4+}\text{OSbCl}_4\text{Cl}^- (\text{TPP}^{2+})]\text{2Cl}^{-}\) and \( g_0 = 1.973, g_\perp = 1.962, A = 147 \times 10^{-4} \text{ cm}^{-1}, B = 41 \times 10^{-4} \text{ cm}^{-1} \) for \([V^{4+}\text{OTiCl}_3\text{Cl}^- (\text{TPP}^{2+})]\text{2Cl}^{-}\). The smaller value of the hyperfine coupling constant
was attributed to the compression along N-V-N bonding due to the additional bonding of [SbCl₄]⁻ or [TiCl₃]⁻ with the oxygen of the vanadyl with Cl⁻.

Hoshino et al.³ irradiated the VOTPP in TCE (1, 1', 2, 2' - tetra chloroethane) with γ-radiation and generated the triplet state at 77K. EPR spectra corresponding to Δmₛ=±1 transitions could not be observed due to very intense background signal from VOTPP. Only the half – field signals with coupling constant of 90G were observed. On the basis of the visible spectrum i.e. broad band around 615nm and 850nm the species was assigned to VOTPP⁺. The D value was estimated as D ≤ 0.024 while the distance of the vanadium atom was estimated to be 0.5Å out of the porphyrin plane. It was also suggested that VOTPP⁺ to be in ²A₂u state.

Oxidation potentials of VOTPP are well documented in the literature⁴⁻⁶. Electro-reductions of substituted VOTPP systems are also available in the literature but very little information on the electro-oxidation are available.

Kadish et al.⁶ reported the electrochemistry of [VO(TpyP)]²⁻, VO[T(p-SO₃Na)PP] and VO[T(p-Et₂N)PP] in DMF.

VO(DMF)[T(pyP)] exhibited two reversible processes at E₁/₂ = − 0.82 and −1.27V. Besides these potentials no other oxidation or reduction were observed in DMF between −2.0V and +1.4V.

VO(DMF)[T(p-SO₃Na)PP] showed oxidation at E₁/₂ = 1.02V and Eᵢp = 1.45V. The two oxidation processes were observed to be overlapped. At room temperature the controlled-potential oxidation at 1.1V indicate 2.7 electrons transfer while controlled – potential electrolysis at positive of 1.1V yielded much more electrons transfer. At −
63°C higher oxidations were found to be irreversible but involved one electron transfer. Setting the oxidation at higher potential (1.7V) the visible spectrum exhibited the regeneration of the original form. This process was attributed to the catalytic oxidation of DMF. VO(T(p-Et₂N)PP) in DMF exhibited oxidations at \( E_{\text{pa}} = 0.68 \text{V} \) and \( E_{p} = 1.04 \text{V} \) at room temperature. In this case DMF solvent molecule did not show any co-ordination. The first oxidation was reversible but \( E_{\text{pa}} - E_{\text{pc}} \approx 45 + 5 \text{mV} \) which was large for a two electron transfer redox process. The second oxidation involved multi-electron transfer.

It was concluded that the electron - withdrawing substituents such as pyridyl in the meso position leads to easier reduction while making oxidations difficult. The situation was reversed in the case of electron – donating substituents.

1.3. NICKEL Porphyrins

Ni(II) is a d⁸ system with square planar ligand field in Ni(II)P and is diamagnetic. Ligation with a strong axial ligand it assumes a distorted octahedral complex giving rise to paramagnetism⁷.

Wolberg and Manassen⁸ reported the controlled – potential electro-oxidation of Ni(II) tetraphenylporphyrin in benzonitrile at room temperature. Two overlapping voltammetric waves were observed for the oxidation of Ni(II)TPP in benzonitrile. These two peaks were successive one electron transfer steps. The first one was reversible while the second one was irreversible. No EPR signal from the oxidised product was observed at room temperature. On cooling down the oxidised product to liquid nitrogen temperature an axially symmetric EPR signal was observed. The EPR
data were \( g_{||} = 2.116 \) and \( g_{\perp} = 2.295 \). Allowing the solution to attain the room temperature, a symmetric but very weak EPR signal was observed. This signal showed a slight asymmetry cooling again to liquid nitrogen. The EPR data are \( g_{||} = 2.031 \) and \( g_{\perp} = 2.024 \). Thus, two different spectra were observed at liquid nitrogen. The first spectrum was assigned to Ni(III)TPP\(^+\) cation with square – planar d\(^7\) configuration. The second spectrum was assigned to Ni(II)TPP\(^+\) (free – radical). It was proposed that the second oxidation of Ni(III)TPP\(^+\) produced Ni(III)TPP\(^{2+}\) which was rapidly returned to the Ni(III)TPP\(^+\) cation on acquiring an electron. Further, it was proposed that Ni(III)TPP\(^+\) decomposed to Ni(II)TPP via Ni(II)TPP\(^+\) but could not proved it.

Dolphin and Felton et al.\(^9\) reported the electro-oxidation of Ni(II)TPP in CH\(_2\)Cl\(_2\) and simultaneous monitoring of the electronic absorption spectrum indicated that the product was [Ni(II)TPP]\(^-\) and was stable. The electronic absorption spectrum, magnetic circular dichroism spectrum and the EPR spectrum at 300K with \( g=2.0041 \) and peak to peak width of 48.2G characterised the formation of a porphyrin \( \pi \)-cation radical. Further electrolysis of [Ni(II)TPP]\(^-\) at 1.44V yielded \( \pi \)-dication i.e. [Ni(II)TPP]\(^{2+}\) and was identified by optical spectrum.

At liquid nitrogen temperature [Ni(II)TPP]\(^{2+}\) in CH\(_2\)Cl\(_2\) solidified into an orange – red solid. The free radical signal was changed to an EPR spectrum corresponding to the low – spin d\(^7\)Ni(III) complex with \( g_{||} = 2.086 \) and \( g_{\perp} = 2.286 \).
The voltammogram of Ni(II)TPP in CH₂Cl₂ (Ag/AgCl as reference) exhibited two overlapping voltammograms. The two oxidation potentials were 1.20V and 1.29V. Both the redox potentials corresponded to single electron transfer.

Oxidations of Ni(T(p-X)PP) where X = –CH₃, –COOCH₃, –NO₂ in CH₂Cl₂ were reported in the literature\textsuperscript{10}. Ni(T(p-CH₃)PP) showed two oxidations at 1.00V and 1.20V while Ni(T((p-COOCH₃ )PP) showed a single oxidation at 1.17V. The peak current of the later indicated two electron transfer. For Ni(T(p-NO₂)PP) all peaks were found to be shifted anodically. The shift in the first oxidation was found to be more than for the second oxidation. Ni(T(p-X)PP), X= electron - donating or weak electron - withdrawing group exhibited two separate oxidations while for compounds containing X= strong electron - withdrawing group exhibited only a single oxidation. The first oxidation of Ni(T((p-CH₃)TPP) in CH₂Cl₂ yielded a brown coloured solution which corresponds to Ni(II)TPP⁺. Removal of the second electron yielded a green coloured solution. Thus, Kadish and Morrison\textsuperscript{10} proposed the mechanism.

\[ \text{[Ni(II)(p-X)TPP]^+} \rightleftharpoons \text{[Ni(II)(p-X)TPP]^+ + e^-} \]
\[ \text{[Ni(II)(p-X)TPP]^+} \rightleftharpoons \text{[Ni(III)(p-X)TPP]^2+ + e^-} \]

They also pointed out that the metal reaction occurred after the cation radical was formed when X = electron – donating group while the process could be reversed for X = electron - withdrawing group.
Kadish et al.\textsuperscript{11} reported the electron reduction of Ni[(T(p-X)PP)] where X = – Et\textsubscript{2}N and (–Me\textsubscript{2}N)F\textsubscript{4}. Both the Ni(II)P were reduced in two reversible one electron transfer processes. The reduction potentials were presented in a table 1.1 as given below.

**Table 1.1**

Half-Wave Potentials (V vs. SCE) for Electro-reduction of Ni(P) in THF, DMF or Py containing 0.1 M TBAP

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Solvent</th>
<th>1\textsuperscript{st} reduction</th>
<th>2\textsuperscript{nd} reduction</th>
<th>$\Delta E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(T(p-Et\textsubscript{2}N)PP)]</td>
<td>THF</td>
<td>-1.30</td>
<td>-1.77</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>-1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Py</td>
<td>-1.30</td>
<td>-1.81</td>
<td>0.51</td>
</tr>
<tr>
<td>[Ni(T(p-Me\textsubscript{2}N)PP)]</td>
<td>THF</td>
<td>-0.90</td>
<td>-1.39</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>-0.89</td>
<td>-1.46</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Py</td>
<td>-1.08</td>
<td>-1.43</td>
<td>0.35</td>
</tr>
</tbody>
</table>

$\Delta E_{1/2}$ = difference between first and second reduction potential.

The large difference between the two reduction processes in DMF and pyridine were attributed to axial ligation by solvent molecules.

At room temperature both [Ni(T(p-Et\textsubscript{2}N)PP)]$^-$ and [Ni(T(p-Me\textsubscript{2}N)PP)]$^-$ in THF under N\textsubscript{2} atmosphere exhibited isotropic EPR spectra at g = 2.01 and $\Delta H_{pp}$ = 10G.
corresponding to Ni(II) porphyrins $\pi$-anion radicals. At low temperature under the same conditions, both showed anisotropy. The $g$ values were $g_\parallel = 1.99$ or $1.98$, $g_\perp = 2.01$ and $\Delta H_{pp} = 8.0 \text{G} - 11.0 \text{G}$. The spectra were compared with that of the Ni tetraazamacrocycle complex in propylene carbonate and assigned to Ni(I) and Ni(II) $\pi$-anion radical hybrid.

The low temperature EPR spectra changed drastically when N$_2$ atmosphere was changed to CO atmosphere. The spectra became more anisotropic and showed three different $g$ values. $g_1 = 2.10$, $g_2 = 2.01$ and $g_3 = 1.99$ for [Ni(T($p$-Et)$_2$N)PP]$^-$ while $g_1 = 2.16$, $g_2 = 2.06$ and $g_3 = 2.01$ for [Ni(T($p$-Me$_2$N)F,PP)$^-$]. A fifth co-ordination by CO was identified which was represented as

$$\text{Ni(II)(P) + e}^- + \text{CO} \leftrightarrow [\text{Ni(I)(CO)P}].$$

Similar EPR spectra of five co-ordinated non-porphyrin Ni(I) derivatives were reported.

It was shown that some solvent molecules co-ordinated to Ni as the fifth/sixth ligand. THF molecules weakly co-ordinated to the NiP and hence shown very little Ni(I) character. In contrast, solvents like DMF and pyridine strongly co-ordinated to [NiP]$^-$ and exhibited EPR spectra corresponding to Ni(I) complex at low temperature in N$_2$ atmosphere. In DMF the $g$ values were 2.10, 2.01 and 1.93 for [Ni(T($p$-Et$_2$N)PP)] and 2.10, 2.00 and 1.95 for [Ni(T($p$-Me$_2$N)F,PP)]. Similar trends were observed in pyridine. It was also pointed out that the visible absorption bands had to be red shifted for the pyridine or DMF co-ordinated metalloporphyrin and the shift had to be larger for the soret band than the Q band.
1.4. COBALT PORPHYRIN

A brief review on the electrochemistry of CoP (P = TPP and substituted TPP) is presented. More emphasis is given to the oxidation potentials study by cyclic voltammetry.

Half-wave potentials data (V vs. SCE) of Co(II)TPP were reported in the literature\textsuperscript{12-14}. Three oxidation potentials 0.32V, 1.06V and 1.26V were observed. The first wave was assigned to Co(II) \rightarrow Co(III) oxidation while the other two to π - cation and dication of the ligand. In benzonitrile, oxidation potentials of 0.52V, 1.19V and 1.42V were obtained\textsuperscript{15}. Three one-electron reversible oxidation steps were proposed as

\[
\begin{align*}
0.52V & \quad \text{[Co(II)TPP]} \\
\rightarrow & \quad \text{[Co(III)TPP]}^+ \\
\rightarrow & \quad \text{[Co(III)TPP]}^{2+} \\
\downarrow & \quad 1.42V \\
\rightarrow & \quad \text{[Co(III)TPP]}^{3+}
\end{align*}
\]

The first wave generated an EPR silent [Co(III)TPP]\textsuperscript{+}. This was due to the oxidation of 3d\textsuperscript{7} \rightarrow 3d\textsuperscript{6}. The second wave generated a paramagnetic species [Co(III)TPP]\textsuperscript{2+}, which exhibited a free radical signal. The third oxidation was also on the ligand and generated a diamagnetic dication.

Three reversible successive one-electron transfer oxidations were observed on oxidation of CoTPP in CH\textsubscript{2}Br\textsubscript{2} / TBAP. The oxidation potentials were 0.78V, 0.97V
and 1.15V vs. SCE\textsuperscript{16}. These values were almost identical with the values reported by Kadish et al\textsuperscript{17,18}.

One-electron oxidation of $\sigma$-bonded Cobalt porphyrins was characterised as Co(III) $\pi$-cation radicals and not Co(IV) porphyrins\textsuperscript{20-23}. Migration of the $\sigma$-bonded of the organic ligand from the metal to nitrogen was also reported\textsuperscript{19-24}. The possible electron transfer sites on the first oxidation of $\sigma$-bonded organo Co(III) porphyrins were also indicated\textsuperscript{25}. The possible electron transfer sites were metal, $\pi$-electrons of the porphyrin ligand or $\sigma$-bonded axial organic ligand. The process depended on the solvent systems as well as the nature of the axial ligand. The rate of the R group migration was found to increase with the increased in the electron donor ability of R in the order Ph < Me < Et < Bu. The rate determining step was found to be the one in which the intra-molecular electron transfer was taken place from the R group to the Co(IV) metal of $[\text{Co}(R)(\text{TPP})]^+$. It was observed that d$^5$ Co(IV) character was more if R was strong electron donor. Thus the following scheme was proposed as:
The cyclic voltammograms of [Co(R)(TPP)] where R = Ph / Me in acetonitrile/CHCl₃ (scan rate 100mV/s) at room temperature exhibited two reversible oxidations. The two reversible oxidation potentials were accounted for the slow migration of the σ-bonded axial ligands (i.e. formation of Co(IV) then electron transfer from the R group to the metal atom). On the contrary two anodic peaks without their corresponding cathodic peaks were observed for [(TPP)Co(Et)] and [(TPP)Co(Bu)] systems at room temperature. This was attributed due to very fast migration of the alkyl group. The voltammograms exhibited reversibility at 203K, which were attributed to the slow migration of the alkyl group. The oxidation potentials in neutral solvent such as CH₂Cl₂ were more positive than in solvent like MeCN/CHCl₃. This was due to [(TPP)Co(R)(MeCN)]⁺.
The effect on the oxidation potentials were also observed due to the addition of base(L) such as pyridine. More significant effects were observed in UV-visible spectrum. The effect was also observed in the EPR spectra. The g values were increased as the pKa of the ligand increased. The higher the pKa value, more Co(IV) character was observed. Thus, [(TPP)Co(R)(L)]\(^+\) showed \(d^5\) Co(IV) character.
REFERENCES


