CHAPTER 4

CYCLIC VOLTAMMETRIC STUDIES OF SOME MANGANESE, CADMIUM AND COPPER Porphyrins

4.1. INTRODUCTION

In Manganese porphyrins the central metal atoms as well as the ligand are electro active. Therefore, redox processes may occur in both the ligand as well as in the metal. Therefore, such systems give some interesting situation to study. Further, many workers have reported the catalytic activities of manganese porphyrins in alkane oxidations.

On the other hand cadmium and copper porphyrins do not have electro active metal center. Therefore, oxidation occurs in the ligand system. However, these oxidations depend on the central metal atom as well as the substitution in the ligand system. Further, redox processes will reflect the type of bonding that exists between the metal and the ligand\textsuperscript{1-9}.

4.2. RESULTS OF MANGANESE Porphyrins

Voltammograms of manganese porphyrins that are recorded are presented (fig.4.2.1, 4.2.2, 4.2.3 and 4.2.4). The results are summarized in the table 4.1. In all four manganese porphyrins three redox couples are observed.
**Mn[T(2,5-(OCH₃)₂)PP]** gives oxidation potentials 0.798V, 0.964V and 1.460V with their corresponding reduction potentials 0.5997V, 0.727V and 1.289V. Their ΔE values are 0.198V, 0.217V and 0.171V. Also $E_{1/2}$ values are 0.6989V, 0.8455V and 1.3745V.

**Mn[T(p-OH)PP]**: The oxidation potentials are 0.7255V, 1.1872V, and 1.2891V and their corresponding reduction potentials are 0.5675V, 0.8841V, and 1.1381V. ΔE values are 0.158V, 0.303V and 0.151V. Also $E_{1/2}$ Values are 0.6465V, 1.0357V, and 1.2136V.

**Mn[T(o-NO₂)PP]**: The oxidation potentials are 0.6493V, 0.9240V and 1.1988V and their corresponding reduction potentials are 0.5789V, 0.8404V, and 1.1188V. ΔE values are 0.0704V, 0.0836V and 0.08V. $E_{1/2}$ values are 0.6141V, 0.8822V and 1.1588V.

**Mn[TpyP]**: Oxidation potentials are 0.8521V, 1.2024V and 1.4902V with their corresponding reduction potentials 0.6408V and 1.5402V. ΔE values are 0.2113V and 0.050V and $E_{1/2}$ values are 0.7465 and 1.5152V.
4.3. DISCUSSION OF CYCLIC VOLTAMMETRY OF MANGANESE PORPHYRINS

The oxidation potential 0.798V of Mn[T(2,5-(OCH$_3$)$_2$)PP] is attributed to the oxidation of Mn(II)$\rightarrow$Mn(III), while 0.964V and 1.460V are the first and the second ligand oxidations respectively. Irrespective of the large $\Delta E$ values, they exhibit reversibility (Fig.4.3.1, 4.3.2, 4.3.3 and 4.3.4)

For Mn[T(p-OH)PP], the oxidation potential 0.7255 V is attributed to Mn(II)$\rightarrow$Mn(III) oxidation while 1.1872V and 1.2891V are the first and second ligand oxidations and are reversible. Another oxidation is observed at the potential 1.2891V without its counterpart reduction peak. This oxidation seems to be occurring at the ligand but not reversible. This could be due to polymerization at the electrode surface$^{12}$. It is also possible that due to polymerization oxidations potentials are observed to be at lower potentials compared to that of Mn[T(2,5-(OCH$_3$)$_2$)PP].

In Mn[T(o-NO$_2$)PP] the metal oxidation (Mn(II)$\rightarrow$Mn(III)) occurs at 0.6493V while the ligand oxidations occur at 0.9240V and 1.1988V. We expected the oxidation potentials are to be shifted higher because $-\text{NO}_2$ is electron withdrawing group. Instead the potentials are shifted lower compared to Mn[T(2,5-}
(OCH₃)₂PP. On a possible reason could be due to ruffling in the porphyrin ligand structure¹⁰⁻¹³.

In the voltammogram of Mn[Tpyp], three oxidations are observed with only two reduction peaks. The metal oxidation is observed at 0.8521V. Their E₁/₂ values are 0.050V and 0.746V. Only one redox couple for the ligand is observed. The oxidation potentials, are higher than that of Mn[T(o-NO₂)PP]. To understand these changes we need to investigate structural changes (porphyrin ligand ruffling) which are beyond the scope of this thesis.

4.4. CONCLUSIONS ON THE CYCLIC VOLTAMMETRY STUDIES OF MANGANESE PORPHYRINS

From the CV studies of the above mentioned Manganese, porphyrins we confirm the following observations;

i) In all four manganese porphyrins, Mn(II)→Mn(III) oxidation occurs although at slightly different potentials depending on the ligand.

ii) Variation in the oxidation potential is attributed mainly to the nature of substitutions in the phenyl ring and the ruffling of the ligand structure.

iii) In the case of Mn[T(p-OH)PP] polymerization at the surface of the electrode is observed.
4.5. RESULTS OF CYCLIC VOLTAMMETRY STUDIES OF CADMIUM AND COPPER PORPHYRINS

Cd[T(2,5-(OCH3)2)PP] give two redox couples at $E_{1/2}$ values 1.0486V and 1.2216V. Oxidation potentials are 1.0852V and 1.279V with their corresponding reduction potentials at 1.0120V and 1.1642 respectively. The $\Delta E$ values are 0.0732V and 0.1149V (fig. 4.5.1 and Table.4.2).

The voltammogram of Cd[T(o-NO2)PP] show two oxidations at 0.7149V and 1.5324V with their corresponding reductions at 0.6027V and 0.9972V respectively. $\Delta E$ values are 0.1122V and 0.5352V and $E_{1/2}$ values are 0.6588V and 1.2648V respectively (fig.4.5.2 and Table.4.2).

Cu[T(2,5-(OCH3)2)PP] voltammogram give two oxidations at 0.638V and 0.910V with their corresponding reductions at 0.5346V and 0.8098V respectively. The $\Delta E$ values are 0.1034V and 0.1002V and $E_{1/2}$ values are 0.863V and 0.8599V (fig.4.5.3 and Table.4.2).

Cu[T(o-NO2)PP] produces voltammogram consists of two oxidations at 0.7702V and 1.2145V with their corresponding
reduction at 0.6607V and 1.0332V respectively. The $\Delta E$ values are 0.1095V and 0.1813V and $E_{1/2}$ values are 0.7154V and 1.1238 (fig. 4.5.4 and Table.4.2)

4.6 DISCUSSION OF CYCLIC VOLTAMMETRY OF CADMIUM AND COPPER PORPHYRINS

For cadmium porphyrins two ligand oxidations are observed with their potentials higher than that of Cd(II)TPP. On the contrary Cd[T(o-NO$_2$ )PP] exhibits lower oxidation potentials. This is quite surprising and we do not know why? Perhaps due to distortion in the ligand structure.

In the voltammogram of Cu[T(2,5-(OCH$_3$)$_2$ )PP], the oxidation potentials are lower than that of Cu(II)TPP. This is as expected and is due to the electron donating group (-OCH$_3$). On the other hand the first oxidation potential of Cu[T(o-NO$_2$ )PP] is lower than that of Cu(II)TPP while the second oxidation potential is slightly higher (Table.4.2). This is due to the electron withdrawing group (-NO$_2$) and the structural conformation of the porphyrin ligand$^{10-13}$.

4.7. CONCLUSIONS ON THE CYCLIC VOLTAMMETRY STUDIES OF CADMIUM AND COPPER PORPHYRINS

From the electrochemical studies of cadmium and copper porphyrins we observe the following;
i) No redox processes occur at the metal center. The redox processes occur at the ligand.

ii) Cu[T(2,5-(OCH₃)₂ )PP] shows lowering in the oxidation potentials due to electron donating group(-OCH₃). On the other hand Cu[T(o-NO₂ )PP] show increase in the oxidation potentials due to the electron with drawing group(-NO₂).

iii) Variations in the oxidation potentials may also be dependent on the ligand structural ruffling.
Table 4.1  Cyclic voltammetric data for manganese porphyrins at room temperature

<table>
<thead>
<tr>
<th>System/</th>
<th>Scan Rate (V/s)</th>
<th>Epa(1) V</th>
<th>Epa(2) V</th>
<th>Epa(3) V</th>
<th>Epc(1) V</th>
<th>Epc(2) V</th>
<th>Epc(3) V</th>
<th>ΔE(1) V</th>
<th>ΔE(2) V</th>
<th>ΔE(3) V</th>
<th>E_{1/2}(1) V</th>
<th>E_{1/2}(2) V</th>
<th>E_{1/2} (3) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn[T(2,5- (OCH₃)₂)PP]</td>
<td>0.1</td>
<td>0.798</td>
<td>0.964</td>
<td>1.460</td>
<td>0.5997</td>
<td>0.727</td>
<td>1.289</td>
<td>0.1983</td>
<td>0.217</td>
<td>0.1710</td>
<td>0.6989</td>
<td>0.8455</td>
<td>1.3745</td>
</tr>
<tr>
<td>Mn[T(p-OH)PP]</td>
<td>0.03</td>
<td>0.7255</td>
<td>1.1872</td>
<td>1.2891</td>
<td>0.5675</td>
<td>0.8841</td>
<td>1.1381</td>
<td>0.1580</td>
<td>0.3031</td>
<td>0.1510</td>
<td>0.6465</td>
<td>1.0357</td>
<td>1.2136</td>
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<tr>
<td>Mn[T(o-NO₂)PP]</td>
<td>0.04</td>
<td>0.6493</td>
<td>0.9240</td>
<td>1.1988</td>
<td>0.5789</td>
<td>0.8404</td>
<td>1.1188</td>
<td>0.0704</td>
<td>0.0836</td>
<td>0.080</td>
<td>0.6141</td>
<td>0.8822</td>
<td>1.1588</td>
</tr>
<tr>
<td>Mn[TPyPP]</td>
<td>0.01</td>
<td>0.8521</td>
<td>1.2024</td>
<td>1.4902</td>
<td>0.6408</td>
<td></td>
<td></td>
<td>1.5402</td>
<td>0.2113</td>
<td></td>
<td>0.7465</td>
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<td>1.5152</td>
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</table>
Fig. 4.2.1. Cyclic voltammogram of Mn[T(2,5-(OCH₃)₂)PP] in CH₂Cl₂ containing 0.1M TBAP at room temperature. Scan rate 0.1V/s.
Fig. 4.2.2. Cyclic voltammogram of Mn[T(p-OH)PP] in CH2Cl2 containing 0.1M TBAP

at room temperature. Scan rate 0.03 V/s.
Fig. 4.2.4. Cyclic voltammogram of Mn[TpyPP] in CH₂Cl₂ containing 0.1M TBAP at room temperature. Scan rate 0.01 V/s.
Figure 4.3.1. UV-visible absorption spectrum of Mn[(2,5-(OCH₃)₃C₆H₃)₄PPi] in CH₂Cl₂, oxidized with (---) SbCl₅ at room temperature and (---) reduced with diethylamine.
Figure 4.3.2. UV-visible absorption spectrum of Mn[T(p-OH)PP]in CH\textsubscript{2}Cl\textsubscript{2} oxidized with\(\_\_\_)\text{SbCl}_5\) at room temperature, (\(\_\_\_\_\_\))\ldots and (\_\_\_) reduced with diethyl amine.
Figure 4.3.3: UV-visible absorption spectrum of Mn[T(\(\sigma\)-NO\(_2\))PP] in CH\(_2\)Cl\(_2\) oxidized with \(\text{___}\)SbCl\(_5\) at room temperature, (\(\ldots\)), (\(\ldots\)) and (\(\ldots\)) reduced with diethyl amine.
Figure 4.3.4. UV-visible absorption spectrum of Mn[tpyP] in CH₂Cl₂ oxidized with (-----) SbCl₅ at room temperature, (-----), ...... and (-----) reduced with diethyl amine
<table>
<thead>
<tr>
<th>System/Scan Rate (V/s)</th>
<th>Cd[T(2,5- (OCH3)2)PP]</th>
<th>Cd[T(4-NO2)PP]</th>
<th>Cd[Tl(2,5- (OCH3)2)PP]</th>
<th>Cd[Tl(4-NO2)PP]</th>
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<tr>
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<td>Epa(1)</td>
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<td>V</td>
<td>V</td>
<td>V</td>
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<td></td>
<td>1.012</td>
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<td></td>
<td>1.2791</td>
<td>1.3324</td>
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<td></td>
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<td>1.2216</td>
<td>1.2216</td>
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**Table 4.2** Cyclic voltammetric data for Cadmium and Copper porphyrins at room temperature

Solvent: Dichloromethane
Supporting electrolyte: TBAP
Concentration: 10^{-3}M
Reference electrode: Ag/AgCl
Fig.4.5.1. Cyclic voltammogram of Cd[T(2,5-(OCH₃)₂)PP] in CH₂Cl₂ containing 0.1M TBAP at room temperature Scan rate 0.06V/s
Fig. 4.5.2. Cyclic voltammogram of Cd[T(o-NO₂)PP] in CH₂Cl₂ containing 0.1M TBAP at room temperature. Scan rate 0.05 V/s.
Fig. 4.3. Cyclic voltammogram of Cu(T2,5-(OCH3)2)PP in CH2Cl2 containing 0.1 M TBAP at room temperature. Scan rate 0.02 V/s.
Fig. 4.5.4. Cyclic voltammogram of Cu[T(\(\sigma\)-NO\(_2\))PP] in CH\(_2\)Cl\(_2\) containing 0.1 M TBAP at room temperature. Scan rate 0.05 V/s.
REFERENCES


