SECTION - I

CHEMISTRY OF DIOXO-BRIDGED
MANGANESE (III, IV) COMPLEXES
CHAPTER -1
INTRODUCTION TO MIXED-VALENCE CHEMISTRY
AND A SURVEY OF THE LITERATURE ON
MANGANESE (III, IV) COMPLEXES
1.1 General introduction to mixed-valence compounds:

Compounds containing a given element in more than one formal oxidation state have been known for a long time. They usually have intense colours as exemplified by Prussian Blue which has been in use as an ink and dye-stuff for a few hundred years\(^1\). Werner proposed\(^2\) variable valency for the brightly coloured complexes prepared in the early 19\(^{th}\) century. The development of crystal field theory and new physical techniques have provided deeper insight into the electronic structure of the mixed-valence compounds. Consequently, around 1967, several review articles have appeared which emphasised the optical properties and developed a scheme of classification based on electronic delocalisation\(^3\). These reviews as well as the earlier results on controlled valency semi-conductors\(^4\) which illustrated the correlation between structure and physical properties have stimulated much theoretical and experimental investigation. It is now recognised that mixed-valency plays an important role in several areas of science ranging from minerology to biology. Many of these various aspects are discussed in a recent volume on the subject edited by D.B.Brown\(^5\). Mixed-valency involving copper centers is believed to be of crucial importance in the recently discovered high temperature ceramic superconductors\(^6\). The next three sub-sections contain a brief review of the present theoretical understanding with reference to certain well studied mixed-valence systems.

1.2 Classification of mixed-valence compounds:

The mixed-valence complexes were classified by Robin and Day\(^3e\) on the basis of the strength and symmetry of the ligand fields about metal ions and their relationship to \(\alpha\), the valence delocalisation coefficient appropriate to a particular system, into three groups.
Class I: The different valence sites have quite different symmetry and ligand field strength, so that the energy difference is large and \( \alpha \) approaches zero. An example would be the spinel, \( \text{Co}_3\text{O}_4 \), in which the Co(III) ions are in octahedral ligand fields with low-spin configurations while the Co(II) ion is in tetrahedral ligand field with high-spin configuration. The two sites are so different that the properties of this compound can be thought of as a superposition of both the ions taken separately. The intervalence transition \( \text{Co(II)} \rightarrow \text{Co(III)} \rightarrow \text{Co(II)} \) has such a high energy that it does not contribute to the colour of this black compound. Another example is \( \text{Cu(en)}_2\text{(CuBr}_2\text{)}_2 \) containing Cu(I) and Cu(II) ions having different geometry.

Class II: The compounds belonging to this class are characterised by an absorption band in the visible region of the spectrum (14-27kK) which is absent in the constituent ions taken separately. The two A and B sites in this class of compounds are crystallographically distinguishable. For example they may both be octahedral, but with small differences in bond length or angle. Then the valence bond configuration \( \text{A(IV)} \rightarrow \text{B(III)} \) has an energy not too much greater than \( \text{A(III)} \rightarrow \text{B(IV)} \). In simple terms, the energy of the transition can be written as

\[
\hbar \nu = E_A + E_B + E_{\text{mad}} \quad \ldots 1.
\]

where \( E_A \) and \( E_B \) are the changes in internal energy at sites A and B respectively, on transferring an electron from A to B and \( E_{\text{mad}} \) is the Madelung energy expended in moving the optical electron from A to B in the electrostatic field of all the other electrons in the molecule.

If the compound is a discrete dimer electron transfer takes place within
the molecule, but if it is a solid, bulk charge migration may be detected as semiconductivity. The properties of one of the most famous class II compounds, Prussian Blue, have been fully characterised and described. Another set of examples are the compounds containing octahedral SbX$_6^{3-}$ and SbX$_6^{2-}$ ions, where X is a halogen. Depending on the cation they are either blue or red, colours which are not found in any other Sb compounds. The compounds are diamagnetic. Both the far i.r and Mössbauer spectra show separate peaks characteristic of Sb (III) and Sb (V).

Mn (III, IV) μ-dioxo-bridged complexes also form good examples of this class of compounds. Both the ions are of octahedral geometry but differ in bond lengths and also show an interivalence absorption band which gives a green colour to the complexes.

Class III: Polynuclear mixed-valence anions, cations and neutral species whose structures do not contain crystallographically distinguishable sites where the oxidation sites might be localised are classified as class III-A compounds. They differ from class II systems where the distinction between A and B sites is lost completely so that $E_A = -E_B$ and $E_{\text{mad}}$ is zero. The excitation energies are dependent on ligand field splittings and molecular orbital resonance integrals, just as they are in an ordinary polynuclear complex having metal-metal bonds. An example of this class would be Nb$_6$Cl$_{12}^{2+}$ ion. Class III-B systems are metals and as such show an absorption edge, usually in the i.r and are opaque with a metallic sheen in the visible region. These show differences of two units in the oxidation states of the ions exemplified by Pd and Pt compounds. The non-stoichiometric tungsten bronzes $^{11}$ Na$_x$WO$_{3.5}$ ($x = 0.4$ to $0.9$) and the
'molecular metals' of the type \(K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O\) (KCP)\(^{12}\) are important members of this class. The bronzes are metallic, their specific conductivities proportional to \(x\) and their optical and magnetic properties are typical of metals. These are known to be three-dimensional lattices. In KCP the Br ions are non-stoichiometrically distributed in channels between the chains of square Pt(CN)\(_4\) groups stacked plane to plane. The partial oxidation leaves the \(d_z^2\) band incompletely occupied leading to metallic conductivity along the Pt chains.

**Theoretical description of mixed-valence compounds:** A summary of the theoretical treatment with special reference to the PKS model\(^{13}\) for binuclear systems is given in this section. The two possible states of the binuclear system A-B can be written as,

\[ \psi_a = \psi_A(M) \psi_B(N) \]  
\[ \psi_b = \psi_A(M-n) \psi_B(N+n) \]

where \(M\) and \(N\) are the oxidation states of site A and B respectively. \(\psi_b\) differs from \(\psi_a\) in that \(n\) electrons have been transferred from B to A. The electronic Hamiltonian, \(\hat{H}_e = \hat{H}_A + \hat{H}_B + \hat{V}\), in which \(\hat{V}\) is the interaction term, will mix the two mixed-valence states to give

\[ \psi_1 = C_a \psi_a + C_b \psi_b \]  
\[ \psi_2 = C_b \psi_a - C_a \psi_b \]

with energies

\[ W_1 = 1/2 \left[ E_1 - \sqrt{E_1^2 + 4V^2} \right] \]  
\[ W_2 = 1/2 \left[ E_1 + \sqrt{E_1^2 + 4V^2} \right] \]

where, \(E_1 = H_{bb} - H_{aa}\). The important quantity here is the ratio of the energy difference between the two sites to the interaction energy, viz., \(R = E_1/V_{ab}\). The coefficients in \(\psi_1\) and \(\psi_2\) can be written as,
The valence delocalisation coefficient is defined as \( \alpha^2 = \frac{C}{\langle a \rangle^2} \).

Piepho, Krausz and Schatz (PKS) have shown that inclusion of vibronic coupling gives a more complete picture of mixed-valence delocalisation.

### 1.3.1 Basic assumptions of the PKS model:

1. Overlap between the orbitals on the two centres, A and B, is negligible.

2. A single antisymmetric mode is involved in coupling the two centres. This mode is assumed to be a combination of the totally symmetric normal modes of the two sites with identical force constants.

3. The electronic ground states for A and B belong to non-degenerate representations.

4. The energy of interaction between the two centres is small compared to electronic binding energies, i.e., the influence of excited state potential surfaces can be neglected.

### 1.3.2 Results of the PKS model for the static case:

The parameters in the model are the dimensionless quantities \( \lambda, \epsilon \), and \( \delta \). The quantities \( \epsilon \) and \( \delta \) are related to the previously defined \( V_{ab} \) and \( E_1 \):

\[
\epsilon = \frac{V_{ab}}{\hbar \nu} \quad \text{and} \quad \delta = \frac{1}{2} \frac{E_1}{\hbar \nu}.
\]

\( \lambda \) is the linear force constant which is responsible for displacing the potential surface for the two centres from their equilibrium value along
the antisymmetric coupling mode, \( q \), having frequency, \( \nu \).

The potential surfaces are given as (Figure 1),

\[
\frac{W_a}{\nu} = \lambda q + \frac{1}{2}q^2 \quad \ldots 9.
\]

\[
\frac{W_b}{\nu} = -\lambda q + \frac{1}{2}q^2 \quad \ldots 10.
\]

**Figure 1:** Potential surfaces for static case
with energies
\[ W_{1,2} = \frac{q^2}{2} \pm \sqrt{\varepsilon^2 + (\lambda q + \delta)^2} \]...11.

and
\[ \frac{C_b}{C_a} = \frac{\varepsilon - \lambda q - \delta - \sqrt{\varepsilon^2 + (\lambda q + \delta)^2}}{\varepsilon + \lambda q + \delta - \sqrt{\varepsilon^2 + (\lambda q + \delta)^2}} \]...12.

When \( \varepsilon = 0, \lambda = 0 \), the potential surfaces are centered at \( q = 0 \) and displaced from each other by \( 2\delta \), and \( \Psi_a \) and \( \Psi_b \) are not mixed. When \( \varepsilon \neq 0, \lambda \neq 0 \), \( \Psi_a \) and \( \Psi_b \) are mixed and are dependent on \( q \). The \( q \)-dependence vanishes when either \( \lambda = 0 \) \( (\psi_{1,2} = \frac{1}{\sqrt{2}}(\Psi_a \pm \Psi_b)) \) or \( \varepsilon = 0 \) \( (\psi_{1,2} = \Psi_b^\dagger \Psi_a) \).

When \( \delta = 0 \), the barrier height (activation energy for thermal electron transfer) is given by
\[ \frac{E_{\text{th}}}{h\nu} = \frac{1}{2} \lambda^2 - |\varepsilon| + \frac{\varepsilon^2}{2\lambda^2}, |\varepsilon| \leq \lambda^2 \]...13.

when \( E_{\text{th}} \) is large, \( \lambda^2 \) is large, \( \varepsilon/\lambda^2 \ll 1 \), we have localised (class I) system.
when \( E_{\text{th}} \) + zero, \( |\varepsilon|/\lambda^2 \geq 1 \) it corresponds to class III.

In the static case the vibronic wave function can be written as Born-Oppenheimer products.
\[ \psi_n^{(1)}(r, q) = \psi_1(r) \chi_{1,n}(q); \psi_n^{(2)} = \psi_2(r) \chi_{2,n}(q), n = 1,2, \ldots \ldots \]...14.

The nuclei are confined to individual potential surfaces, and the intervalence transfer absorption can be thought of as a Frank-Condon transition from the minimum of one surface to an excited vibrational level of the other potential surface.

1.3.3 Results of the PKS model for the dynamic case:-
Born-Oppenheimer approximation is no longer valid when \( \lambda \) and \( \varepsilon \) are both non-zero. The deviations are expected to be especially large when \( \lambda \sim \varepsilon \).
The nuclei will be moving on both potential surfaces and the vibronic wave function will have to be written as a linear combination of Born-Oppenheimer products.

\[
\psi_n(r,q) = \psi_a(r)\chi_a(q) + \psi_b(r)\chi_b(q)
\]

...15.

where

\[
\chi_{a,b}(q) = \frac{1}{\sqrt{\pi}} \left\{ \sum_{k=0}^{\infty} \left( \begin{array}{cc} r_n, k, r' & n, k \end{array} \right) \chi_k(q) \right\},
\]

...16.

\(\chi_k(q)\) are harmonic oscillator wave functions. The vibronic energies and the coefficients \(r\) and \(r'\) have to be determined by numerical diagonalisation of a suitably truncated matrix of the Hamiltonian including nuclear kinetic energy, \(\hat{H} = \hat{H}_e + \hat{T}_n(q)\). Typical vibronic energy level diagram for the symmetrical case (\(\delta = 0\)) is shown in Figure 2.

Figure 2: Vibronic energy level diagram for (\(\delta = 0\)) symmetrical case. The long vertical arrow shows the strongest single intervalence transition at low temperature. Tunneling transitions occur primarily between successive low-lying vibronic levels, the short vertical arrow showing the one from the ground vibronic state (Ref. 13b).
Optical transitions in mixed-valence systems:

Two types of optical transitions are predicted by the vibronic model - the well known IVTA and the lesser known tunneling transition in the ground vibronic manifold (See Figure 2). The latter transition which is predicted to occur in the far i.r. region has not been observed so far. The band contours for the IVTA can be calculated once the parameters \( \lambda, \epsilon \) and \( \delta \) are known. In actual practice, comparison of calculated and experimental band contours is complicated by the possible presence of low symmetry splittings and spin-orbit coupling effects. Many features of the IVTA have been analysed since long using the Hush formulae\(^{14} \) which do not require detailed knowledge of the wave functions. The vibronic model predicts that these formulae are valid only in the strongly localised situations.

The occurrence of two maxima against one in a plot of \( P_n(q) \) versus \( q \) distinguishes a localised system from a delocalised one. Analogous to \( \alpha^2 \), a delocalisation coefficient \( \beta_d(n) \) can be defined as the coefficient of the cross term in \( P_n(r) \)

\[
\beta_d^2(n) = \left[ \sum_k \left( r_{nk}^2 - r_{nk}'^2 \right) \right] \frac{\epsilon^2}{\lambda^2 + \delta^2} = 4\alpha_d^2
\]

in the localised limit.

The criterion for localised and delocalised cases can be defined by calculating the nuclear and electronic probability distributions \( P_n(q) \) and \( P_n(r) \),

\[
P_n(q) = \int |\psi_n(q)|^2 dq = \sum_k \sum_{nk'} |\chi_k(q)|^2 (r_{nk} r_{nk}' + r_{nk}' r_{nk})
\]

\[
P_n(r) = \int |\psi_n(r)|^2 dq = \frac{1}{2} (\psi_a^2 + \psi_b^2 - 2\psi_a \psi_b \rho_{nk} r_{nk} r_{nk}' + \psi_a \psi_b \rho_{nk} r_{nk} r_{nk}' r_{nk})
\]

\[
\text{...17.}
\]

\[
\text{...18.}
\]
where $\varepsilon$ is the molar extinction coefficient and $R$ is the distance between the two centres (in Å).

The PKS model also makes definite predictions regarding the resonance Raman effect, but the RR transitions have not so far been explored in detail experimentally.

### 1.3.5 Improved models:

In addition to the approximations listed in 1.3.1, the PKS model has the serious drawback that it is essentially a two-site model. Experiments on the Creutz-Taube ion $[\text{(NH}_3)_5\text{Ru (pz) Ru (NH}_3)_5]^+$, have shown that the bridging ligand interacts strongly with the two Ru centres. A three-site model which explicitly includes the bridging species has been proposed recently. It was shown that in the strongly coupled case the totally symmetric vibrational mode has to be included in the vibronic coupling problem. A ligand field model which includes spin-orbit coupling and low-symmetry components have also been put forward to explain the electronic properties of the Creutz-Taube ion. This again has the drawback that orbitals on the bridging species are excluded from the treatment. It appears that the ligand field model will be suitable for treating the electronic structure, while the inclusion of all the coupled vibrations will be necessary.
to account for the IVTA band profiles.

1.4 Study of two model complexes:

Two well studied mixed-valence systems are discussed here in order to illustrate the several experimental methods as well as to highlight the potential difficulties in characterising a system as localised or delocalised.

1.4.1 Creutz-Taube ion:-

The Creutz-Taube complex $^{19}_5\mu^+ \text{- pyrazine - bis (pentaammine ruthenium)}^{5+}$ ion, provided a suitable starting point for theoretical analysis of binuclear mixed-valence complexes, since the two coupled Ru centres are identical and only a single bridging ligand is involved. The electronic spectra showed $^{19(a)}$ a band at 17.7 kK for the metal to ligand charge transfer and an intense broad band around 6.4 kK ($\varepsilon = 5500 \text{ cm}^{-1} \text{ m}^{-1}$) characteristic of IVTA. The electron transfer was expected to be rapid, $k_{th} > 10^9 \text{ sec}^{-1}$. However, n.m.r studies $^{19}$ gave $k_{th} > 10^7 \text{ sec}^{-1}$. Mössbauer measurements $^{20}$ made on $p$ - toluenesulfonate salts at 4K and interpreted in terms of class II behaviour were later found to be in error $^{16}$. ESCA spectra $^{21}$ exhibited one $3d_{5/2} \text{Ru (II)}$ peak and $3d_{3/2}$ and $3d_{5/2} \text{Ru(III)}$ peaks, expected for class II ion; but this behaviour was later $^{22}$ shown to be compatible with that of a class III ion as well. The resonance Raman spectrum $^{23}$ was found to be very similar to the fully reduced ion, with the exception of a band at 1070 cm$^{-1}$ which was attributed to pz bound to Ru(III) thus indicating a class II system. Powder e.s.r. studies $^{24}$ implicating a localised electronic structure were contradicted by single crystal studies $^{25}$ consistent with valence delocalisation. A crystal structure $^{26}$ of mixed halide salt gave results consistent with both descriptions.
Recently Fürholz et al. have made a comprehensive restudy of the Creutz-Taube complex involving single crystal, optical, resonance Raman, x-ray crystallographic, Mössbauer and e.s.r. techniques. The main conclusions from the above work are (i) there is more than one transition under the IVTA band envelope, (ii) the system is not localised on the Mössbauer time scale, however, the isomer shift is close to that of Ru (III, III), (iii) in the chloride salt the two Ru centres are crystallographically equivalent, while for the tosylate the centres are significantly different; the structure of (II, III) closely resembles that of (II, II), (iv) e.s.r. shows considerable rhombic splitting implying strong interaction between the metal centres and the pyrazine bridge, (v) Raman and e.s.r. studies do not establish ground state symmetry, and (vi) the experiments do not "allow one to decide whether the odd electron is trapped on one Ru or delocalised equally over both".

Prussian Blue: Another widely studied complex is Prussian Blue which was studied first in 18th century. The several studies carried out for the assignment of oxidation states of this complex have been reviewed by Sharpe. The structure of this complex was derived from x-ray powder data. Powder neutron diffraction studies have put an upper limit of about 5% for the spin delocalisation in the electronic ground state. Single crystal x-ray work confirmed the cubic polymeric structure with 25% of Fe(II) sites being vacant leading to an inherent structural disorder.

Robin has assigned an inter-valence band at 14.1 kK whose intensity
suggested a value of valence delocalisation coefficient $\alpha = 0.1$ consistent with estimated $^{31} \alpha = 0.11$ from the perturbation model. Magnetic moment measured between 10 and 300 K corresponded to $\mu_{\text{eff}} = 5.98 \text{BM/Fe(III)}$ high-spin and a diamagnetic low-spin Fe(II) atom. Mössbauer spectra showed separate transitions from the Fe(II) and Fe(III) sites. It was necessary to resort to selective isotopic substitutions to resolve the overlapping signals. A ferromagnetic transition is assumed below 5.5 K where the exchange pathway lies through N-C-Fe-C-N.

In summary one can conclude that Prussian Blue contains trapped valences at Fe(II) and Fe(III) sites.

Mn(III), Mn(IV) and dinuclear mixed-valence complexes.

Complexes with heteroaromatic ligands:- The first proposed complex of a binuclear cation was $(\text{Mn}_2\text{O}_2\text{bpy}_4)^{3+}$ by Nyholm and Turco in 1960. They have determined the oxidation state by reacting the complex with oxalic acid in the presence of silver sulphate and also by potentiometry. They also determined the magnetic moment to be 1.7 BM at 25°C. Stoufer et al., in 1972, determined the crystal structure of the perchlorate salt. The monoclinic greenish black crystal contains two manganese centres with different metal-ligand bond distances - the one with shorter distance is considered to be Mn(IV) ($d^3$) and the other Mn(III) ($d^4$ high-spin). The difference in the average bond length is 0.138 Å.

This complex and the phenanthroline analogue have been prepared and studied in detail by Cooper et al. in 1977. They have characte-
rised them by i.r., electronic spectra and electrochemistry. A 680 cm$^{-1}$ band observed in i.r was attributed to MnO$_2$Mn bridge in the dimer. The three shoulders at 19.0, 18.0 and 14.6 kK observed in electronic spectra were assigned to high-spin Mn(III) ion and the band in near-i.r. around 12.1 kK to IVTA. The solution studies have shown that the original green solution of the dimer turned red on acidification and was found reversible upon addition of sodium acetate solution. At lower pH, the IVTA band disappeared and reappeared only on making the solution pH 4.5. They have also measured solution magnetic moments by n.m.r and found consistent with the value for a single electron. The electrochemical studies in acetonitrile revealed that these dimers participate in one-electron oxidation processes. By using Hush’s formulae$^{14}$ they have calculated the electron delocalisation coefficient $\alpha^2$ as 0.01 which implied that the electron spends 99% of the time on the Mn(III) atom. They have compared with selected data$^{37}$ of (III, IV) dimers and showed that the extent of delocalisation in these dimers is high due to the short metal-metal distance (2.7 Å). It is quite evident in comparison$^{38}$ with $\alpha^2 = 0.0026$ for $\text{[(NH}_3)_5 \text{Ru}(\text{pz}) \text{RuCl(bpy)}_2{\text{]}^{4+}}$ where the metal-metal distance is approximately 7 Å. A thermal activation energy of 8.6 kcal m$^{-1}$ was calculated from which a maximum thermal electron transfer rate of $10^6$ s$^{-1}$ was estimated assuming no activation entropy and a transmission coefficient of unity.

Single crystal e.s.r. studies of (Mn$\text{O}_2\text{bpy}_4\text{ClO}_4$)$_3$ complex were reported by Inoue$^{39}$ in 1978. He observed weak signals at $g = 4$
attributable to excited states and at $g = 2$ for ground state. The hyperfine splitting in the ground doublet state showed at least 16 lines with 70-100G spacings. Hence the odd electron in Mn(III, IV) was said to be mostly localised on one of the manganese atoms and unequally distributed between both the manganese in the dimer. In the same year Morrison et al. reported the formation of Mn (III, IV) complexes with bpy, phen, 4,4'-dmbp, 4,4'-dpbp, 4,7-dpp and terpy by electrochemical oxidation of Mn(II)L$_2$ complexes in acetonitrile. Except terpy, all other complexes were oxidised quantitatively. They have suggested that the oxidation of Mn (II) complexes and the subsequent dimerisation of the product species require release of four protons to yield the Mn (III, IV) dimers as follows:

$$2(MnL_3)^{2+} + 2H_2O \rightarrow (Mn_2O_2L_4)^{3+} + 4H^+ + 3e^- + 2L \quad \ldots\ldots 23.$$  

The redox potentials for bpy complexes were found to be more than phen complexes. They have also reported e.s.r. spectra with 6 lines attributing them to broadening due to super-exchange between the two metal centres. They have also prepared mononuclear Mn(II), Mn(III) and Mn (IV) complexes of bpyO$_2$ and terpyO$_3$ electrochemically in acetonitrile. These complexes were found stabilised against dimerisation unlike in the case of bpy and phen ligands.

At the same time Cooper et al. have examined the e.s.r. spectra of Mn (III, IV) dimers in acetonitrile with a 16 line pattern. They have suggested two inequivalent manganese ions at room temperature with hyperfine splitting values $A_1 = 167 \pm 3$ G and $A_2 = 79 \pm 3$ G. The hyperfine splitting pattern with $|A_1| > |A_2|$ and the small g anisotropy were found consistent with Mn(III) high-spin antiferro-
magnetically coupled to Mn(IV) producing an $s=1/2$ ground state. These dimers are expected to yield 11 lines in the fast exchange limit and up to 36 lines in slow exchange. Hence the 6 line pattern suggested by Morrison et al.\textsuperscript{40} was shown to be consistent with Mn(II) impurity and not Mn (III, IV) dimers. The temperature dependence data of magnetic susceptibility of this $s = (2, 3/2)$ pair was found in good agreement with the isotropic Heisenberg exchange Hamiltonian

$$H = -2J\, s_1 \cdot s_2,$$

yielding $J = -150 \pm 7$ cm$^{-1}$ for the bpy dimer and $J = -134 \pm 5$ cm$^{-1}$ for phen dimer.

Very recently Stebler et al.\textsuperscript{42} have reported crystal and molecular structure of $(\text{Mn}_2\text{O}_2\text{phen}_4)(\text{PF}_6)_3 \cdot \text{CH}_3\text{CN}$. The orthorhombic crystal was found to have crystallographically equivalent manganese ions. Detailed analysis of anisotropic atomic displacement parameters indicated static or dynamic disorder between a Mn(III) - Mn(IV) and a Mn(IV) - Mn (III) ion. Optical absorption band around 12.5 kK, assigned to IVTA, was found to be temperature dependent with an increase in intensity when the temperature was decreased and the band at 14.7 kK was found to be independent. From the magnetic data, based on isotropic Heisenberg operator, exchange coupling constant was calculated as $J = -148$ cm$^{-1}$ in close agreement with Cooper et al.\textsuperscript{9}.

Recently, Pavacik et al.\textsuperscript{43} have reported the formation of a $(\text{Mn}_2\text{Sal}_2\text{bpy})$ where $H_2\text{Sal} =$ salicylic acid. They have treated $(\text{Mn}_2\text{O}_2\text{bpy}_4\text{ClO}_4)_3 \cdot 2H_2O$ with NaHSal (4 equiv.) in acetonitrile solution which led to a rapid precipitation of a brown microcrystalline material which was not identified. However it was found soluble
in dimethylformamide to give a deep red solution. Crystals of (Mn sal₂ bpy) were isolated and structurally characterised. Magnetic moment obtained by Evans method⁴⁴ in dimethylsulfoxide was 3.83 μM consistent for a Mn(IV) ion. The Mn(IV) complex might have formed by the substitution of two sal²⁻ groups for one of the bipyridine groups and both of the oxides. Identification of the initially formed brown crystalline material would make this aspect of its chemistry clearer.

Very recently Ramaraj et al⁴⁵ have reported oxygen evolution by water oxidation with (Mn₂O₂ bpy₄) (ClO₄)₃ complex in heterogeneous medium in the presence of (NH₄)₂ [Ce (NO₃)₆]. They have observed gas bubbles over a period of 4 hrs. The experiment was done in argon atmosphere. The gas evolved was analysed gas-chromatographically. They have carried out c.v. experiments in water and reported that the complexes are stable in water contrary to the observation of Cooper et al⁹.

Complexes with Schiff-bases:-
A number of monomeric Mn(III) Schiff-base complexes are known⁴⁶. Crystal structure of manganese complexes of tetridentate Schiff-bases H₂ salen and H₂ saltm have been reported⁴⁷. It was shown that the Mn(II) complexes react with oxygen irreversibly to yield various oxidation products. A dimer for Mn(saltm)H₂O complex with bridging oxygen atoms (Mn - Mn distance 2.7 Å) is also known⁴⁷. But the x-ray data was not clear as to the two possibilities:

\[ \text{(saltm)Mn}^{III} \text{O} \text{Mn}^{III} \text{ (saltm) or (saltm) Mn} \text{O} \text{Mn (saltm)} \]

However, i.r absorption around 650-600 cm⁻¹ region for MnO₂Mn
ring was reported. The dimer has magnetic moment of $\mu = 2.13$ BM at room temperature consistent with antiferromagnetic coupling of either high-spin Mn(III) or high-spin Mn(IV) atoms. Reaction of oxygen with Mn(salen) yielded a sparingly soluble product $[\text{Mn}_2(\text{salen})_2\text{O}_2]$ which displayed similar properties, i.e., i.r. absorptions at 645 and 631 cm$^{-1}$ and $\mu = 1.96$ BM. The reaction of excess oxygen with Mn(salen) and Mn(saltm) in benzene or dimethylsulfoxide yields a second insoluble product which was formulated as a polymeric $\mu$-oxo - manganese (IV) complex, $[\text{Mn(salen)}\text{O}]_n$.

Five coordinate cationic complexes of Mn(III), $[\text{Mn(SB)}\text{H}_2\text{O}]\text{ClO}_4$, where SB is the dianion of the tetradeinate Schiff-base busalen and busaltm have been synthesized and characterised by Boucher et al. in 1975. Hydrolysis by 0.005 M NaOH of chloroform solutions of these complexes in air led to the formation of six-coordinate species $[(\text{Mn}_2(\text{busalen})_2\text{O}_2)]\text{H}_2\text{O}$. and $[\text{Mn}_2(\text{busaltm})\text{O}_2]_2\text{H}_2\text{O}$. These Mn(IV) complexes are dimeric in chloroform solutions and show reduced room temperature magnetic moments, $\mu = 2.5$ BM. I.r and visible bands were inconsistent with Mn$_2$(IV)O$_2$ ring in these complexes.

The same authors have synthesised and characterised several optically active complexes of Mn(III), $[\text{Mn(SB)}\text{H}_2\text{O}]\text{ClO}_4$ and $[\text{Mn(SB)}\text{Cl}]$ and the Mn(III, IV) dimers, $[\text{Mn}_2(\text{SB})_2(\text{OH})^+(\text{O})]_n\text{H}_2\text{O}$, where SB was a dianion of the optically active tetradeinate Schiff-base derived from $(-)-1,2$-diaminopropane and 4-sec - butylsalicylaldehyde or 4-sec-butyl-2- acetylphenol. The electronic absorption bands around 14-21 kK, 21 - 30 kK and 30-45 kK were observed.
The band around 22 kK was assigned to mixed-valence intervalence transition.

**Complexes with other ligands:**

Oxo-bridged dimeric manganese(IV) porphyrin complexes have been reported including crystal and molecular structures. The complexes were found to be e.s.r. silent. These were found to oxidise cyclohexane at room temperature to give cyclohexyl azide. Thermal decomposition of these μ-oxo-bridged [X Mn (IV) TPP]₂ O (X = N₃⁻, OCN⁻) complexes yielded deeply trapped mixed-valence dimeric complexes which show 16 line e.s.r. spectrum.

Very recently Wijegahardt et al have reported dinuclear

$$[\text{L} \text{Mn}^{III} (\mu_{-} \text{Q} (\mu_{-} \text{CH₃CO₂})_{2} \text{Mn}^{IV} \text{L})_{2} \text{ClO}_4]_{3}^{-}, \text{ where}$$

L = tmtc. Crystal and molecular structure have been reported. On oxidation of Mn₂ (II) complex synthesised it formed Mn₂(III) complex, the Mn (III, IV) mixed-valence complex and a Mn₂(IV) complex. The Mn₂(II) complex was found to show weak antiferromagnetic coupling where \( J = -9 \text{ cm}^{-1} \). However, the Mn (II, III) complex remained unisolable. The same authors have isolated Mn₂ (III) complex which on electrochemical oxidation yields Mn (III, IV) mixed-valence dimer. This dimer was also obtained by chemical oxidation and was isolated in crystalline form. The Mn₂(III) was found to be ferromagnetically coupled where \( J = +18 \text{ cm}^{-1} \). The electronic spectra of the mixed-valent dimer in acetonitrile had IVTA band at 12.7 kK. Interestingly, there was another IVTA band around 7.14 kK. Similar electronic
spectra were recorded for manganese containing metalloprotein of a pseudocatalase isolated from Lactobacillus planarum suggesting this complex to be a model for water oxidation in photosystem II of photosynthesis in plants. Magnetic data for the Mn (III, IV) complex was calculated which found that the atoms are intramolecularly coupled antiferromagnetically. Further electrochemical oxidation of this complex led to the formation of Mn\(_2\) (IV) complex which was unstable. C.v in liquid SO\(_2\) (0.1M TBA - PF\(_6\)) at - 40\(^\circ\)C showed two reversible one-electron transitions at 1.25 V and 1.92 V (with NHE). The first corresponds to Mn\(_2\) (III) + Mn (III, IV) and the second to Mn (III, IV) + Mn\(_2\)(IV). Mn\(_2\)(IV) complex was found unstable even in liquid SO\(_2\).

Nair et al\(^5\) have attempted the preparation of a mixed-valent manganese species with \(\beta\)-cyclodextrin ligand. They have synthesised a Mn\(_2\)(III) complex which was soluble in water, dimethylformamide and dimethylsulfoxide. However in water it was found unstable decomposing to hydrated oxides of managanese. The electronic spectra were recorded in dimethylformamide and magnetic moments were determined by the n.m.r. method which was found to be 3.51BM/Mn at 302\(^\circ\)K decreasing to 3.38BM/Mn at 224\(^\circ\)K, well below spin-only value (4.9BM) for a mononuclear species suggesting a weak antiferromagnetic coupling of the manganese spins. The c.v. studies in dimethylformamide showed a quasi-reversible two electron oxidation wave. No mixed-valent Mn (III, IV) product expected for a one-electron oxidation of Mn\(_2\)(III) was formed. Mn\(_2\)(IV) obtained was unstable and at room temperature decomposed within a few hours.
Matsushita et al.\textsuperscript{58} have prepared binuclear manganese complexes by using bridging quadridentate bis (Schiff-bases) and dipicolinates and with bis(μ-oxo) groups and one or two picolinate ligands per manganese. Their redox chemistry has been characterised by c.v and controlled-potential coulometry. They indicate that the electron-transfer mechanisms are ligand-centered rather than metal-centered. They show that the bpy ligands in the bis(μ-oxo) bridged complexes can be substituted by 2 or more picolinate anions like (Mn\textsubscript{2}O\textsubscript{2}bpy\textsubscript{3}PA\textsubscript{2})\textsuperscript{+} and (Mn\textsubscript{2}O\textsubscript{2}PA\textsubscript{4})\textsuperscript{−}. Several of these complexes were thought to be good models for water oxidation in photosystem II.

Suzuki et al.\textsuperscript{59} reported preparation of dinuclear manganese (III, IV) and manganese (IV, IV) complexes with N\textsubscript{4}-pyridine. The analytically pure samples were determined by redox titrations and their conductivity was measured. C.v in CH\textsubscript{3}CN was recorded and magnetic moments at 300 K - 80 K were measured. They were found to exhibit strong antiferromagnetic interaction with J = -159 and -137 cm\textsuperscript{-1}, respectively. E.s.r spectrum of the (III, IV) complex showed a 16-line \textsuperscript{55}Mn hyperfine pattern at g=2 indicating a trapped valence state. Absorption bands in CH\textsubscript{3}CN in the visible region were shown. A preliminary simulation of the spectrum was also given. The resonance fields were almost reproduced. Introduction of small anisotropies in g and A tensors caused no significant change in spectrum. Little anisotropy in g and A tensors implies that the structures of two manganese units are close to the regular octahedron. This complex was reported not to oxidise water under similar conditions as that reported by Ramaraj et al.\textsuperscript{45}.
Manganese complexes as models for photosystem II:—

Current literature on photo-synthesis in green plants has accepted the involvement of manganese in the evolution of oxygen. Kok et al. have proposed the 'S states' mechanism to account for the periodic release of \( \text{O}_2 \) from chloroplasts. Short pulses of light oxidise each reaction centre by one electron producing one electron oxidation of the \( \text{O}_2 \) evolving centres on each flash that yields states \( S_2, S_3, S_4, S_5, S_6 \ldots \) etc. in a cycle. By using light of sufficient intensity to turn over all reaction centres on each flash this synchronization is preserved. Water is then oxidised to \( \text{O}_2 \) with a yield that reaches a maximum every fourth flash of light eventually damping to a steady state level. \( S_4 \) is the state associated with \( \text{O}_2 \) release. This behaviour established that the \( \text{O}_2 \) evolving centres function independently, yielding intermediate states which can persist for tens of seconds and longer before deactivation.

Just after Cooper et al. have studied e.s.r. of the Mn (III, IV) dimers in detail, Dismukes et al. in 1981, have proposed them as models for photosynthetic oxidation of water. They have performed e.s.r. of spinach chloroplasts giving a series of laser flashes, \( n = 0, 1, \ldots, 6 \) at room temperature and rapidly cooling to \(-140^\circ\text{C}\) revealing 16 lines and possibly 21 or more hyperfine lines when observed below 35 K. The spectrum was consistent with a pair of antiferromagnetically coupled manganese ions, or possibly a tetramer of manganese ions, in which Mn (III) and Mn (IV) ions are present. The intensity of the signals from these flashes indicated that the paramagnetic signal was monitoring oxidation state changes in the enzyme involved in oxidation of water.
Goed in et al.\textsuperscript{62} in 1984 reported e.s.r. and x-ray absorption K-edge measurements of a spinach photosystem II preparation in $S_1$, $S_2$ or $S_3$ states. The changes observed in the edge properties between samples prepared in $S_1$ to $S_3$ states were in direct agreement with changes of signal intensity in e.s.r. A Mn (II, III) complex was suggested for $S_1$ state and Mn (III, IV) complex for a $S_2$ or $S_3$ state. A mechanism was proposed to show the changes of oxidation states of manganese in the S-states model (Sub-section 1.6.2).

Continuous power saturation and temperature dependence of e.s.r. signals which are generated by low-temperature illumination of dark-adapted photosystem II membranes associated with $S_2$ state of the $O_2$ evolving complex of photosynthesis were reported by Paula et al.\textsuperscript{63} in 1985. The data showed that the $S_2$ state e.s.r. signals arise from more than one paramagnetic site. A model was proposed for the species giving rise to the $S_2$ state e.s.r. signal in which an antiferromagnetically exchange coupled Mn(III, IV) dimer which is ferromagnetically exchange coupled to another site with $s = 1$ was likely to be present. The second site could be low-spin Mn (III), low-spin Fe (IV), or even a second manganese dimer.

Spectroscopic evidence for manganese:
E.s.r. spectroscopy has revealed the presence of multiline signal attributed to an oxidised form of the terminal electron donor in the $S_2$ state in thalakoid membranes. By comparison with synthetic manganese complexes\textsuperscript{64} and from simulations of the e.s.r. spectrum it has been identified with a cluster of two, or possibly four, interacting manganese ions present in a mixed-valence oxidation state.
Mn$_2$ (III, IV) or Mn$_4$ (III, IV) respectively. The Mn$_2$ (II, III) oxidation state was also proposed based on e.s.r. simulations.

**Mechanism for the role of manganese:**

Goodin et al. have proposed a scheme for the change in manganese oxidation associated with S states cycle. In state S$_0$, the metal centres are in the Mn(II, III) state. Transition from S$_0$ to S$_1$ occurs by the oxidation of one of the donor species which releases a proton. This transition occurs first by oxidation of the unstable intermediate S$_1^*$. This state relaxes to S$_2$ after two charge equivalents are transferred from the donor species to manganese, giving the Mn (III, IV) complex with no net proton release. Transition from S$_2$ to S$_3$ is analogous to the S$_0$ to S$_1$ step. The final light-induced step proceeds as before with the formation of an unstable intermediate S$_3^*$, which relaxes to a peroxo-bridged species with the Mn(III, IV) species containing the reduced donors. A water to ligand exchange reaction may then accompany the release of O$_2$, regenerating S$_0$. The last step proposes the release of two protons, one before and one after release of O$_2$. The mechanism is shown in figure 3.
Figure 3: Higher oxidation states of manganese suggested for Oxygen evolution by water oxidation associated with 5 states cycle (Ref. 62).