CHAPTER-III

MANGANESE(II), 3d$^5$

1.1 INTRODUCTION,

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CHAPTER-III

MANGANESE(II), 3d^5

1.1 INTRODUCTION:

Manganese is known to form compounds in all the oxidation state ranging from (+II) to (+VII). The most stable and most common oxidation state for manganese is +II. It has the electronic configuration (Ar)d^5. This spherically symmetrical configuration has several bearing on the biological activity of the metal ions. Mn^{2+} ion exists in the solid, in the solution and as well as in complexes^1-2.

Firstly, due to the absence of any ligand field stabilization energy, the formation constants of the Mn(II), complexes are smaller than those of other first transition series metals, so that one may predict the existence of few metal enzyme that contain manganese than those containing other transition metals^3-4.

Secondly, the large magnetic moments value resulting from five unpaired electrons has a large effect on the longitudinal proton relaxation rate of water protons, i.e. on the rate of attainment of equilibrium of nuclear spin states, induced by pulsed nuclear magnetic resonance. The increased rate is affected by promotion of proton electron dipolar magnetic interaction^5-6.

The (+II) oxidation state of manganese is also used to protect the living cells against the toxicity of hyoeroxia thus act as pharmaceutical compound. The importance of manganese in studies of biological system has two different aspects^7

(a) the direct implication of Mn(II) in enzyme action, mostly proteolytic enzymes and

(b) The ability of manganous ion to act as a paramagnetic probe.
The manganese has importance in both plants and animals enzymes. In mammals
the enzyme arginase is produced in the liver, which converts nitrogenous waste
products into urea in the ornithine-arginine-citrulline cycle. $\text{Mn}^{2+}$ can replace $\text{Mg}^{2+}$
in a large number of biological systems. $70\%$ of body magnesium occurs in the
bone in association with calcium and phosphorus. The rest is present in all the cells
of the other tissues, blood and body fluids. It is about equally distributed between
cells and plasma. Together with calcium and hydrogen ion it depresses neuro-
muscular activity and balance the action of $\text{Na}^+$ and $\text{K}^+$. Absorbed magnesium excreted through urine, bile and intestinal secretion. Increase
in plasma level of magnesium depresses the nervous system, can also induce
anesthesia and paralysis of skeletal muscle. Low level of serum magnesium
cause symptoms similar to tetany. Renal failure may produce a rise in plasma
magnesium level and this may explain some of the finding like depression and
muscular weakness.

1.2 EARLIER WORK ON MANGANESE(II) COMPLEXES:

Mn(II) complexes of thiosemicarbazone have been synthesized by Pradhan
et al. These were characterized by physico-chemical investigations. They were
found to have $[\text{Mn(TSC)}_3(\text{ClO}_4)_2]$ and $[\text{Mn (TSC)}_2X_2]$ composition, [where $X = \text{Cl}^-$ and $\text{Br}^-$]. Mn(II) complexes of 1-benzoyl-4-phenyl -3-thiosemicarbazone (HL)
have been reported by Aggarwal et al. These complexes have the general
compositions $[(\text{Mn(I,2)})]$ (violet) and $[\text{Mn(I,2)}].2\text{H}_2\text{O}$ (yellow). Both the complexes
show magnetic moments 5.73 and 6.33 B.M. respectively. On the basis of spectral studies an octahedral geometry has been suggested for the complexes.

Mn(II) complexes of 2, 4- diacetyl- pyridine bis-(semicarbazone) have been reported by Pelenik et.al\(^{13}\). These complexes were found to have composition \([\text{Mn(1.)(Cl)(H}_2\text{O)}]\). Mn(II) complexes of cyclohexanone semicarbazone and thiosemicarbazone have been synthesized by Chandra et.al\(^{14}\). These complexes were characterized by different physico-chemical techniques.

Mn(II) complexes of acetone, ethyl methyl ketone and 3-methyl cyclohexanone semicarbazones and thiosemicarbazones were synthesized by Chandra et.al\(^{15}\). They have the general composition \([\text{Mn(L)}_2\text{X}_2]\), where \(X = \text{Cl}^\text{-} \text{or SO}_4^{2-}\). These complexes were characterized by elemental analysis, molar conductance, IR and EPR spectral studies. Mn(II) complexes of phenyl-pyruvic acid semicarbazone, 4-methyl phenyl pyruvic acid semicarbazone, 4-methyl pyruvic acid thiosemicarbazone, phenyl pyruvic acid were synthesized by Chandra et.al\(^{16}\). These complexes were characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility, IR and EPR spectral studies.

Mn(II) complexes of propiophenone and butyrophenone semicarbazones have been synthesized by Chandra et.al\(^{17}\). These complexes were characterized by elemental analysis; electrical conductance, magnetic moment, IR, electronic and electron spin resonance spectral studies. All the complexes show magnetic moments corresponding to five unpaired spins. On the basis of electronic and ESR spectral studies an octahedral geometry has been proposed for the complexes.
Chandra et al.\textsuperscript{18} have also prepared Mn L\textsubscript{2} X\textsubscript{2}, (L = C\textsubscript{6}H\textsubscript{5}C(R): NNHCONH\textsubscript{2}, R = et, Pr: X = Cl\textsuperscript{−}, Br\textsuperscript{−}, NO\textsubscript{3} and SO\textsubscript{4}\textsuperscript{2−}) complexes. These complexes were characterized by elemental analysis, molar conductance, magnetic moments, IR, electronic and ESR spectral studies. All complexes show magnetic moment corresponding to five unpaired electrons. An octahedral geometry has been proposed for all the complexes.

Mn(II) complexes of salicyldehyde or benzoin or 2-hydroxy-1-napthaldehyde thiosemicarbazones were synthesized by Behara et al.\textsuperscript{19}. These complexes were found to have [MnL\textsubscript{3}(SCN)\textsubscript{3}] type composition. Six coordinated geometry have been suggested for the complexes. Talwar et al.\textsuperscript{20} have been synthesized and characterized the complexes, [MnL\textsubscript{2}X\textsubscript{2}], (where L = MeRC: NNHC (E) NH\textsubscript{2}, (R = pentyl, hexyl: E = O, S); X = Cl\textsuperscript{−}, Br\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−}). These complexes were characterized by elemental analysis and molar conductance, magnetic susceptibility measurements, IR, electronic and ESR spectral studies. All the complexes exhibit magnetic moments corresponding to 5 unpaired electrons. Six coordinated octahedral geometry has been assigned for the complexes.

Mn(II) complexes of pyridine, 2-ethoxy carbonyl amino pyridine-N-oxide thiosemicarbazone have been synthesized by Aggrawal et al.\textsuperscript{21}. The complexes were found to have [MnL\textsubscript{2}(H\textsubscript{2}O)]\textsuperscript{2+} composition. These complexes were characterized by elemental analysis, magnetic moments, IR and EPR spectral studies. These complexes were also screened for antibacterial activities. Mn(II) complexes of 2-hydroxy napthaldehyde and 4-hydroxynaphthaldehyde semicarbazones and thiosemicarbazones were synthesized by Kumar et al.\textsuperscript{22}.
These complexes were found to have [Mn(L₂)] and [Mn(II₅)X₂] compositions. These complexes were characterized by physico-chemical techniques.

Mn(II) complexes of iso-nitrosoacetyl acetone di-thiosemicarbazone have been synthesized by Shreedhar et al. These complexes were characterized by E.S.R and electronic spectral studies. They have the general composition [MnL₅]. Mn(II) complexes of nitrogen-oxygen donor ligand were synthesized by Fahmi et al. These complexes were found to have [MnCl(TSCZ)H₂O] and [Mn(TSCZ)₂] composition. These complexes were characterized by elemental analysis, magnetic moment, IR and EPR spectral data. Molecular weight determination and conductivity measurements suggest that the complexes were non-electrolytic in nature. Tetrahedral geometry had been suggested for the complexes.

Mn(II) complexes of 2-acetylpyridine-2-methyl-3-thiosemicarbazone were synthesized by Grenifo et al. These complexes have the general composition [Mn(apmt)]. The tentative structure of the complexes was determined by using various spectral studies. Mn(II) complexes of p-chlorophenyl glyoxal and p-methoxy phenyl glyoxal semicarbazones have been synthesized by Singh et al. The complexes were characterized by various physico-chemical studies.

Manganese(II) complexes of N-benzoyl, N-2-furanthiocarbohydrazone and have been synthesized by Singh et al. These complexes have been synthesized by elemental analysis, magnetic susceptibility measurements, I.R., ESR, NMR (¹H and ¹³C), mass/FAB mass and Mossbaeuer spectral studies. The biological activities have been screened against several bacteria and fungi.
Mn(II) complexes N-salicyldehyde-N-thiobenzhydrazone were synthesized by Singh et al. These complexes were found to have general composition [Mn(SBth)(H₂O)₂]. These complexes were characterized by elemental analysis, magnetic susceptibility measurements, I.R and NMR spectral studies. Ligands as well as its complexes have shown remarkable in vitro anti-tumour activity against P-8-15 (murine mastocytoma) tumour cells.

Mn(II) complexes of picolinaldehyde thiosemicarbazone have been prepared by Pawar et al. Manganese(II) forms a yellow colour complex with a reagent picolinaldehyde nicotinoyl hydrazone (PANH). These complexes were used for the spectrophotometric determination.

1-isonicotinoyl-4-benzoyl-3-thiosemicarbazone (IBtsc) and its Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been prepared by Singh et al. These complexes were characterized by elemental analysis, magnetic susceptibility measurements, I.R, N.M.R and F.A.B mass spectral data. On the basis of above spectral data an octahedral geometry was assigned for the complexes. Chandra et al. prepared a new ligand, α-methyl, acetophenone semicarbazone (HL₁) and thiosemicarbazone (HL₂). The complexes having the general composition: [Mn(L)₂X₂], (where L =α-methyl, acetophenone semicarbazone (HL₁) and thiosemicarbazone (HL₂) and X = Cl, Br, 1/2SO₄). All the complexes were characterized by elemental analysis, magnetic moments, electronic and ESR spectral studies. These complexes were found to have magnetic moments corresponding to five unpaired electrons. Possible geometries of the complexes were deduced on the basis of above spectral studies.
Mn(II) complexes of vitamin K$_3$ thiosemicarbazone have been synthesized by Tang et al.$^{32}$ These were characterized on the basis of elemental analysis, IR, molar conductance and thermal analysis. All the complexes possess strong inhibitory action against G (+) staphylococcus aureus, G (-) Hay basicllus, and G (-) Eschericha coli. The antibacterial activities of the complexes are stronger than those of the thiosemicarbazone itself. Mn(II) complexes of 2–amino-4–benzamido thiosemicarbazone were synthesized by Ansari et al.$^{33}$ The complexes were found paramagnetic high spin with octahedral geometry.

Mn(II) complexes of 2-methylcyclohexanone thiosemicarbazone and 2-methyl cyclohexanone 4-methyl-3-thiosemicarbazones were synthesized by Chandra et al.$^{34}$ The complexes were found to have the general composition [Mn L $X_2$], (where $X = C{l}^-, S C N^-, N O_3^-$ and 1/2$S O_4^{2-}$). These were characterized by the elemental analysis, molar conductance, magnetic moment measurement, electronic, IR and EPR spectral studies. All the complexes were found to have an octahedral geometry. Mn(II) and Co(II) complexes of salicylidine–4, 4–dimethyl 3-thiosemicarbazone (H$_2$salmtsc), salicylidenemorpholine–N–thiohydrazine (H$_2$Salmth) and salicylideneepiperidine–N–thiohydrazide (H$_2$Salpth) have been synthesized by Choudhary et al.$^{35}$ The complexes were found to have [(Mn L $L (1 H)$) and [CoL$_3$]$nH_2O$, where (H$_2$L = H$_2$Salmtsc, H$_2$Salmth or H$_2$Salpth and $n = 1$ or 3). All the complexes were of high spin type. On the basis of spectral data an octahedral geometry have been suggested.
Mn(II) complexes of the salicylaldehyde, 5-bromo salicylaldehyde, and 5-nitrosalicylaldehyde and naphthaldehyde thiosemicarbazones have been synthesized by Yildiz et. al\(^6\). These were characterized by the elemental analysis, magnetic susceptibility measurements, \(^1\)H NMR, IR and UV. On the basis of spectral data an octahedral geometry had been suggested. The antibacterial activities of the ligands and its metal complexes have been screened in the vitro against the organism Escherichia coli ATCC-11230, Staphylococcus aureus ATCC-6538P, Bacillus cereus ATCC-7064, Prteus vulgaris ATCC-8427. It is observed that the coordination of the metal ions has pronounced effect on the microbial activities of the ligands.

Mn(II), Ti(II) and Cu(II) complexes of bis-(cinnamaldehyde) semicarbazone, bis-(4-chlorobenzaldehyde) semicarbazone, bis-3,4,5-trimethoxy benzaldehyde semicarbazone, bis-(pyridine-2-aldehyde) semicarbazone, bis- (thiophene-2-aldehyde) semicarbazone were synthesized by Ahmad et. al\(^7\). All the complexes were screened for their antimicrobial activity by agar disc diffusion method against the bacteria X. citri and the fungi A. soleni. All the complexes show an octahedral geometry.

Mn(II) complexes of isopropyl methyl ketone semicarbazone (Ismsc), isopropyl methyl ketone thiosemicarbazone (Ismtsc), 4-aminoacetophenone thiosemicarbazones (Aatsc) have been synthesized by Chandra et. al\(^8\). The complexes were found to have general composition [Mn (L)\(_2\) X\(_2\)], [where L = (Ismsc), (Ismtsc), (Aatsc) and \(X = \text{Cl}^-\) and \(1/2\text{SO}_4^{2-}\)]. These complexes were
characterized by elemental analysis, molar conductance, magnetic moment, EI-mass, $^1$H NMR, IR, EPR and electronic spectral studies.

Mn(II) complexes of cis- 3, 7-dimethyl-2, 6-octadiensemicarbazone have been synthesized by Nagar et al.$^{39}$ The complexes were found to have the general compositions \([\text{ML}_2\text{Cl}_2]\) and \([\text{ML}_2\text{Cl}_2]\) Cl type. Structure of the complexes was determined by using elemental analysis, molar conductivity, magnetic measurements, IR and electronic spectral data. The metal complexes as well as ligand were screened for their antibacterial activity. All the complexes exhibit strong inhibitory action against Gram (+) bacteria Staphylococcus aureus and Gram (-) bacteria coli.

Mn(II) complexes of 2-benzoyl pyridine -3- (tetra methyleneiminy1 thiosemicarbazone (HBpypTsc), 2-benzoyl pyridine N-(4)- cyclohexyl thiosemicarbazone (HBpychTsc) and 2-benzoyl pyridine N-(4) phenyl thiosemicarbazone (HBpyph Tsc) were synthesized by Kurup et al.$^{40}$ They have the general composition 1. \([\text{Mn(BpyphTsc)}_2]\), 2.\([\text{Mn(BpychTsc)}_2]\) H$_2$O, and 3.\([\text{Mn(BpyphTsc)}_2]\). These complexes were characterized by elemental analyses, molar conductance, magnetic measurements, electronic, infrared and EPR spectral studies. The structure of the complexes was found distorted octahedral.

Mn(II) complexes of di-2- pyridyl ketones thiosemicarbazone have been synthesized by Kurup et al.$^{41}$ They have the general composition [Mnl$_2$]. These complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility, IR and EPR spectral data. On the basis of reported spectral data distorted octahedral geometry had been suggested for all the complexes.
1.3 PRESENT WORK:

The present work is relates to the synthesis and characterization of Mn(II) complexes with four ligands pvsc \( (L^1) \), pvts\( (L^2) \), ptasc \( (L^3) \) and ptatsec \( (L^4) \). These complexes were characterized on the basis of elemental analysis, molar conductance, magnetic moment, I.R., electronic and EPR spectral studies.

(p-vanillin semicarbazone)  \( (pvsc-L^1) \)

(p-vanillin thiosemicarbazone)  \( (pvts-L^2) \)

(p-tolualdehyde semicarbazone)  \( (ptasc-L^3) \)

(p-tolualdehyde thiosemicarbazone)  \( (ptatsec-L^4) \)
PREPARATION OF THE COMPLEXES:

A hot ethanolic / aqueous ethanolic solution (20mL.) of the manganese salt (MnCl₂ or MnSO₄.6H₂O (0.001mole) was mixed with a hot ethanolic solution of semicarbazones and thiosemicarbazones of p-vanillin or p-tolualdehyde (0.44g, 0.002mol). The mixture was refluxed on a water bath for about 6-10 hrs at 68-80°C. On cooling cream to yellowish crystals of the complexes precipitated out. The separated crystals were filtered, washed with 50% ethanol, and finally dried over P₄O₁₀.

1.4 RESULT AND DISCUSSION:

On the basis of elemental analysis all the complexes were found to have the general composition MnL₂X₂, [where L = pvsc (L¹), pvtsc (L²), ptasc (L³), ptatsc (L⁴) and X= Cl⁻, 1/2SO₄²⁻]. Molar conductance has been measured in DMSO solution. It indicates that all the complexes are non electrolyte in nature. Thus the complexes may be formulated as [Mn (L)₂ X₂] (where X= Cl⁻, 1/2SO₄²⁻) Table - 1.

MAGNETIC MOMENT:

The ground state term in this case is ⁶A₁g. This corresponds to half-filled d shell and is spherically symmetrical. There is no temperature independent paramagnetic effect and no reduction of the magnetic moment below the spin - only value by spin orbit coupling with higher ligands field terms. The magnetic
moment is indeed found very close to spin only value of 5.92 B.M. The magnetic moment of complexes under study at room temperature lies in range of 5.91-5.99 B.M. corresponding to five unpaired electrons.

IR SPECTRA OF THE COMPLEXES:
As discussed in the chapter-II, that all the ligands acts as bi-dentate. They coordinated through either O or S and the nitrogen of the N(C=N) group.

BANDS DUE TO ANIONS:

IR SPECTRA OF SULPHATO COMPLEXES:
The sulphato complexes show three bands in the region 1149 (3s) (v₃), 1088 (v₃), 1064 (v₃), and 931cm⁻¹ (v₁) indicating the bidentate nature of sulphate group.²²

ELECTRONIC SPECTRA:
In the high spin six coordinated Mn(II) complexes, has a d⁵ electronic configuration i.e. t₂g³,e₆² gives rise to ground state ⁶A₁g. It is derived from the free ion ⁶S state, which is orbitally non degenerate. It cannot be split by crystal field (of any symmetry). The absence of any other spin sextet terms implies that all crystal field transitions will be spin forbidden as well as Laporte forbidden. The crystal field spectra of high spin d⁵ complexes are therefore expected to very weak. There is number of lower spin terms with three (quartets) or one (doublets) unpaired electron.
Figure 2. IR Spectrum Of [Mn (pv'sc)_2SO_4]
Figure 2: IR Spectrum of MnSO₄.
Orgel energy level diagram for Mn^{2+} (d^5) octahedral.
Transitions to spin doublet levels are highly forbidden, there being a change in
the spin quantum number 2 in such case, and thus they are not expected to be
observed. The spin quartets $^4F$, $^4G$ and $^4D$ arise from the configuration $t_{2g}^3e_g^1$,
t$_{2g}^3e_g^2$ and $t_{2g}^2e_g^3$ with strong field crystal energies
-10Dq, 0 and +10Dq respectively. Thus the quartet term $^4G$ splits into $^4T_{1g}$, $^4T_{2g}$,
$^4A_{1g}$, $^4E_g$ and $^4D$ splits into $^4T_{2g}$, $^4E_g$, while $^4F$ splits into $^4A_{2g}$ which is
independent of the crystal field.

Thus the possible transitions for octahedral Mn(II) complexes are as follows.

$^6A_{1g} \rightarrow ^4T_{1g}(G)$ near 18900 cm$^{-1}$

$^6A_{1g} \rightarrow ^4E_g$ $^4A_{1g}(G)$ near 25300 cm$^{-1}$

$^6A_{1g} \rightarrow ^4T_{2g}(D)$ near 28000 cm$^{-1}$

$^6A_{1g} \rightarrow ^4E_g(D)$ near 29700 cm$^{-1}$

Electronic spectra of complexes show bands in the region of 17241-18700 ($v_1$),
20300-24800 ($v_2$), 27397-28800 ($v_3$) and 29000-31500 ($v_4$) cm$^{-1}$ which is
characteristics of octahedral geometry. The assignments are obtained by fitting the
observed spectra to the Tanabe-sugano diagram. Thus these bands may be assigned
to following transitions.

$^6A_{1g} \rightarrow ^4T_{1g}(G)$ (10B+5C) ($v_1$) $^6A_{1g} \rightarrow ^4E_g$ $^4A_{1g}$($^4G$) (10B+5C) $v_2$,

$^6A_{1g} \rightarrow ^4E_g$ (17B+5C) ($v_3$) and $^6A_{1g} \rightarrow ^4T_{1g}$($^4P$) ($v_4$) respectively (Table-2).
Figure 2.40 Electronic Spectrum of [Mn (ptâsc)_2Cl_2]
Figure 2.6 Electronic Spectrum of [Mn (pvsc)$_2$SO$_4$]
Figure 2.142: Electronic Spectrum of [$\text{Mn (ptatse)}_2\text{SO}_4$]
The experimentally observed transition energies are used to calculate the value of parameters B, C, Dq and $\beta$ Table-3. The best set of values for parameters B and C could be obtained using transitions

$^6A_{1g} \rightarrow ^4E_g^0 A_{1g}^{(4G)} (10B+5C) (\nu_2)$

$^6A_{1g} \rightarrow ^4E_g^{(4D)} = (17B+5C) (\nu_3)$

This is due to the fact that the energies of these two transitions are independent of the crystal field splitting energy and depends only on the parameters B and C. The values for Dq could be evaluated with the help of the curve transition energy versus Dq, given by orgel, using the energy level due to transition $^6A_{1g} \rightarrow ^4T_{1g}$. The value of the Dq parameter could not be obtained using transition $^6A_{1g} \rightarrow ^4E_g^0 A_{1g}^{(4G)}$ and $^6A_{1g} \rightarrow ^4E_g^{(4D)}$ because, having almost zero or negative slope. These transitions are independent of the Dq value.

**Racah and Slater Condon shortly parameters:**

Parameters B and C are linear combination of certain coulomb and exchange integrals and are generally treated as empirical parameters obtained from the spectra of the free ions. Slater, Condon-Shortley parameters $F_2$ and $F_4$ are related to the Racah inter-electronic repulsion parameters B and C as follows:

$$B = F_2 - 5F_4$$

$$C = 35F_4$$

The values of parameters $F_2$ and $F_4$ are also listed in the Table 3. The electron-electron repulsion in the complexes is less than in the free ion, resulting in an increased distance between electrons and thus an effective increase in the size of
the orbitals. On increasing delocalization the value of β decreases and is less than 1 in the complexes. An estimate of β has been obtained from the nephelauxetic parameter for the ligand (hx) and nephelauxetic parameters of the metal ions $K_m$ as $(1 - \beta = \text{hx} \times K_m)$. The values of the parameter $^4\beta$ of the metal (hx) for the complexes have been calculated using the covalency contribution of Mn(II) ions i.e. $K_m = 0.07$ while the numerical value $786 \text{ cm}^{-1}$ for $B$ of the free Mn(II) ion has been used to calculate the value for β. The calculated values of β and hx indicate that the complexes under study have appreciable ionic character. The values of various parameters are listed in the Table-3.

**EPR SPECTRA:**

The high spin Mn(II) has an orbital $^6S_{5/2}$ ground state term, which should not interact with the electric field in the first order case. However, the combined action of the electric field gradient and the spin –spin interaction produces splitting of the energy levels due to second order spin –orbit coupling between the $^6A_1$ ground state and the lowest level of the manifold $^4A_2$ state. The axial field splitting parameter D in the case of an axially distorted octahedral field expects the magnitude of the zero –field splitting. The spin Hamiltonian for Mn(II) can be defined as

$$\mathcal{H} = g\beta \ H \cdot S + D \ [(S_x^2 - 1/3S(S+1)) + A.S.I]$$

Where $H$ is the magnetic field vector, $g$ is the spectroscopic splitting factor, $\beta$ the Bohr magneton, $A$ is the manganese hyperfine splitting constants, $S$ is the
Figure 2.10: EPR Spectra of [Mn(pvtsc)$_2$Cl$_2$]
electron spin vector, and \( I \) is the nuclear vector. \( S = 5/2 \) and \( S_z \) is the diagonal spin operator.

For \( S = 5/2 \) and noting selection rule \( \Delta m_s = \pm 1 \), five allowed transitions should arise when field separation are dependent on \( \theta \), the angle between the applied magnetic field and the symmetry axis. These transitions are:\footnote{48}

\[
\Delta m_s = \pm 5/2 \leftrightarrow 3/2; \ H = H_0 \pm 2D (3\cos^2\theta - 1)
\]

\[
\Delta m_s = \pm 3/2 \leftrightarrow 1/2; \ H = H_0 \pm D (3\cos^2\theta - 1)
\]

\[
\Delta m_s = +1/2 \leftrightarrow -1/2; \ H = H_0
\]

Where \( H = \hbar \omega / g \beta \) and \( \theta \) is the angle between the applied magnetic field and the direction of the axial distortion\footnote{49}. When the complex is octahedral only the central \( \Delta m_s = -1/2 \leftrightarrow +1/2 \) transition will be observed since it has a second order dependence split into a sextet due to electron spin nuclear spin hyperfine coupling (\(^{55}\text{Mn}, \ I = 5/2\)). However, the zero fields splitting are an appreciable than the other electronic transition will appear in the powder spectrum and the values of zero fields splitting can thus be evaluated. In addition to these allowed transition the frozen solution spectra give low intensity pair of forbidden between each pair of allowed lines. These lines are due to simultaneous change of the electron and nuclear spin by \( \pm 1 \).

The EPR spectra of the present complexes have been recorded as polycrystalline samples as well as in DMSO solution. The spectra of polycrystalline sample at \( RT \) are isotropic in nature, it does not show splitting and \( g_{iso} \) value lie in the range of 1.84 -1.99.
Thus on the basis of magnetic susceptibility, molar conductance measurements, IR, electronic and EPR spectral studies and the subsequent discussion for the complexes given above, the following structure may be proposed for these complexes.
$L = \text{pvtsc and ptatsc}$

$L = \text{pvsc, pvtsc, ptasc and ptatsc}$

$X = \text{SO}_4^-$
### Elemental Analysis and Molar Conductance Data of Mn(II) Complexes:

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Colour</th>
<th>MP °C</th>
<th>Molar Conductance Ω Mol⁻¹ cm⁻¹</th>
<th>Yield %</th>
<th>Elemental analyses found and (calculated) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mn</td>
</tr>
<tr>
<td>[Mn(pvsc)₂Cl₂]</td>
<td>Cream</td>
<td>175</td>
<td>12</td>
<td>60</td>
<td>10.02 (10.09)</td>
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<tr>
<td>[Mn(pvtsc)₂Cl₂]</td>
<td>Cream</td>
<td>180</td>
<td>15</td>
<td>75</td>
<td>9.45 (9.53)</td>
</tr>
<tr>
<td>[Mn(ptasc)₂Cl₂]</td>
<td>Cream</td>
<td>190</td>
<td>16</td>
<td>65</td>
<td>11.34 (11.30)</td>
</tr>
<tr>
<td>[Mn(ptatsc)₂Cl₂]</td>
<td>Cream</td>
<td>180</td>
<td>9</td>
<td>68</td>
<td>10.58 (10.68)</td>
</tr>
<tr>
<td>[Mn(pvsc)₂SO₄]</td>
<td>Off/White</td>
<td>200</td>
<td>14</td>
<td>70</td>
<td>9.59 (9.65)</td>
</tr>
<tr>
<td>[Mn(pvtsc)₂SO₄]</td>
<td>Off/White</td>
<td>210</td>
<td>18</td>
<td>75</td>
<td>9.10 (9.15)</td>
</tr>
<tr>
<td>[Mn(ptasc)₂SO₄]</td>
<td>Cream</td>
<td>218</td>
<td>16</td>
<td>68</td>
<td>10.66 (10.78)</td>
</tr>
<tr>
<td>[Mn(ptatsc)₂SO₄]</td>
<td>Cream</td>
<td>240</td>
<td>20</td>
<td>66</td>
<td>10.12 (10.18)</td>
</tr>
</tbody>
</table>
### ELECTRONIC BANDS OF Mn (II) COMPLEXES:

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$v_1$ (cm$^{-1}$)</th>
<th>$v_2$ (cm$^{-1}$)</th>
<th>$v_3$ (cm$^{-1}$)</th>
<th>$v_4$ (cm$^{-1}$)</th>
</tr>
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<td>24100</td>
<td>28490</td>
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<tr>
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<td>652</td>
<td>1192</td>
<td>254</td>
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<td>[Mn(ptasc)$_2$Cl$_2$]</td>
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<td>24200</td>
<td>28800</td>
<td>29500</td>
</tr>
<tr>
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<td>1760</td>
<td>657</td>
<td>1192</td>
<td>254</td>
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<td>28750</td>
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</tr>
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### TABLE – 3

**LIGAND FIELD PARAMETERS AND EPR DATA OF THE Mn(II) COMPLEXES:**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Dq(cm⁻¹)</th>
<th>B(cm⁻¹)</th>
<th>β</th>
<th>F₄</th>
<th>F₂'</th>
<th>Hₓ</th>
<th>g</th>
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<tr>
<td>[Mn(pvsc)₂Cl₂]</td>
<td>1724</td>
<td>699</td>
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<td>657</td>
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<td>107</td>
<td>1192</td>
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<td>0.72</td>
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<td>1069</td>
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1.5 REFERENCES:


