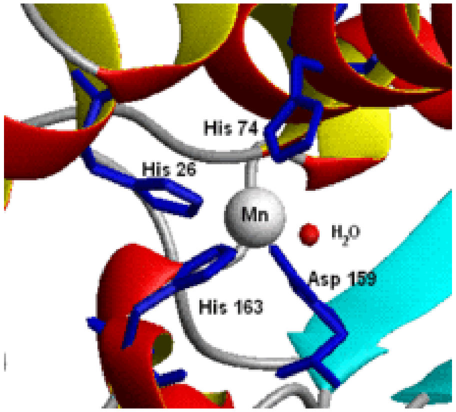
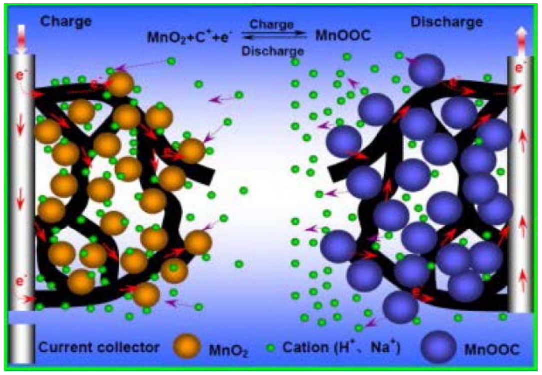
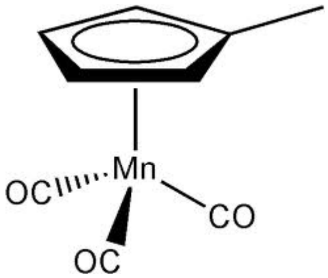
Group 7 :
Manganese Chemistry

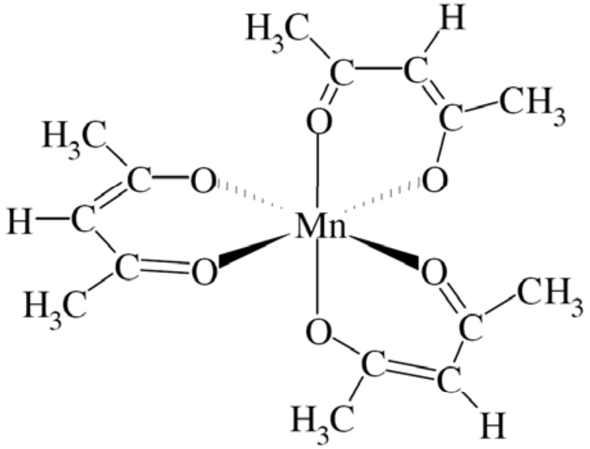
Mn : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$





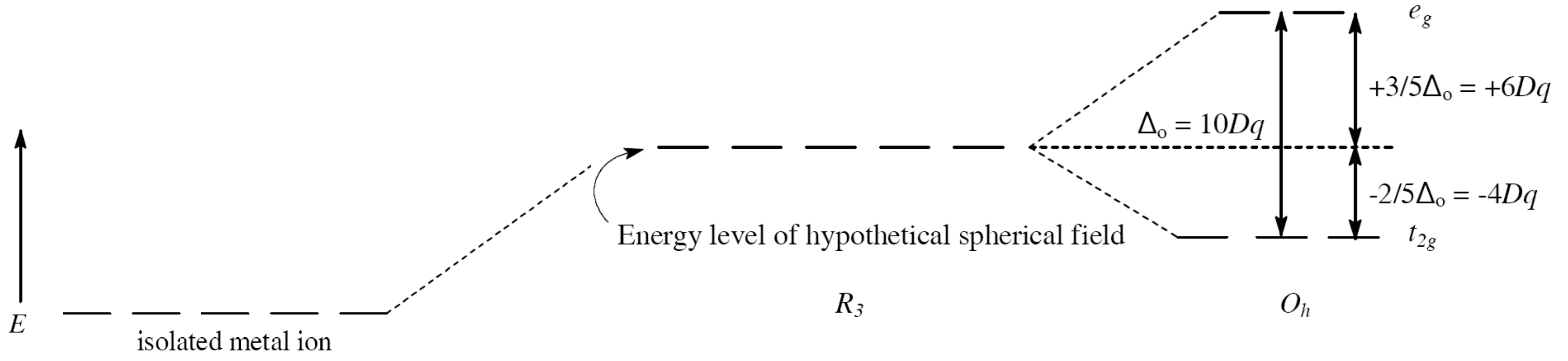


Crystal Field Splitting
in
Octahedral
Transition Metal Complexes

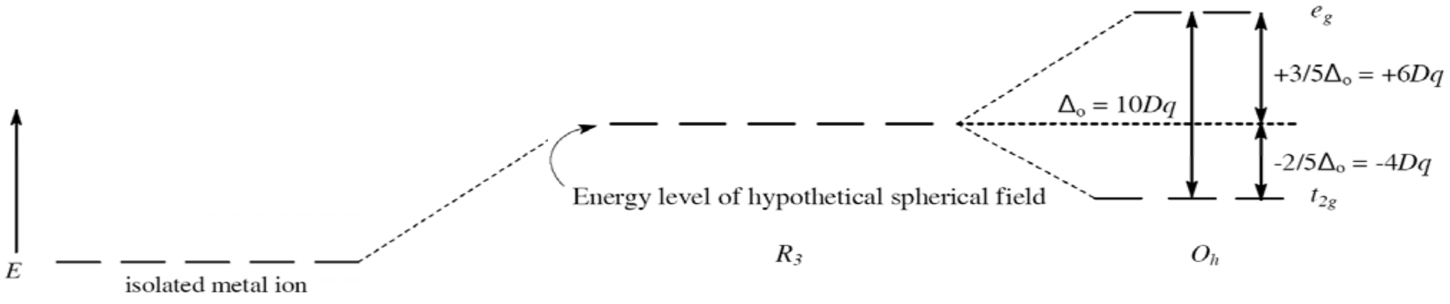


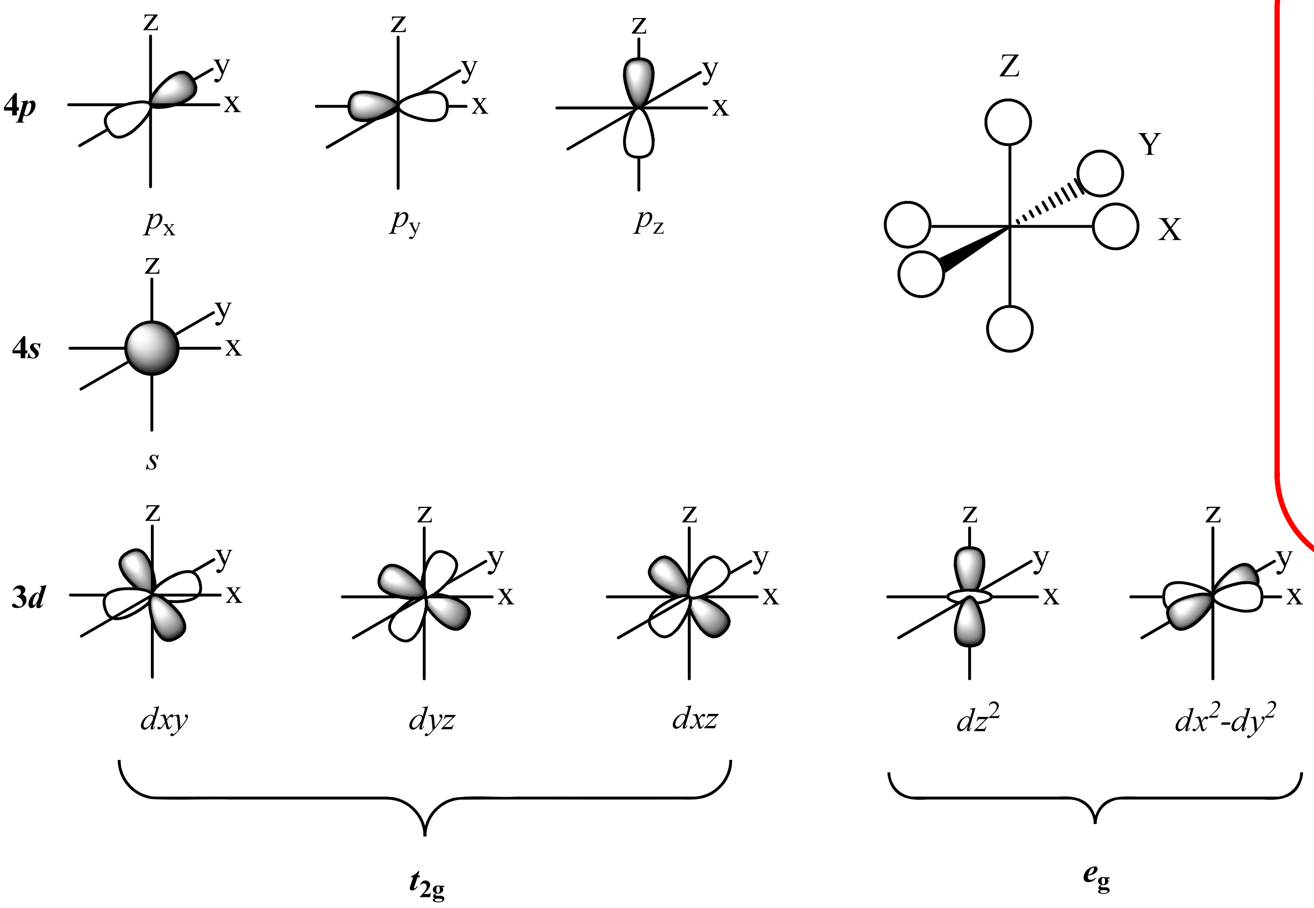
d-Subshell Splitting in an O$_h$ Field

- In the octahedral (O_h) environment of three acac ligands, the fivefold degeneracy among the *d* orbitals in Mn^{3+} is lifted.
- To a first approximation, the ligand field is of O_h symmetry, and the 3*d* orbitals will separate into a set of three degenerate orbitals (t_{2g} = *d*xy, *d*yz, *d*xz) and a set of two degenerate orbitals (e_g = $dx^2–y^2$, dz^2).

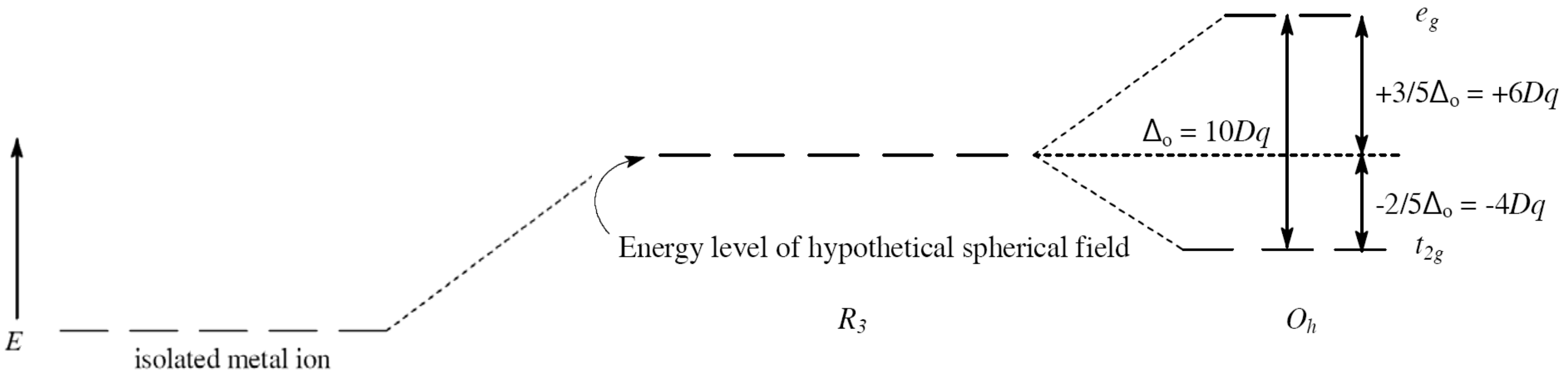


- Relative to the energy of the hypothetical spherical field, the e_g set will rise in energy and the t_{2g} set will fall in energy, creating an energy separation of Δ_o or 10 *Dq* between the two sets of *d* orbitals.





- The t_{2g} orbitals point between ligands.
- The e_g orbitals point directly at the ligands.
- Thus, the t_{2g} set is stabilized and the e_g set is destabilized *(relative to the energy of a hypothetical spherical octahedral field)*.



- The energy increase of the e_g orbitals and the energy decrease of the t_{2g} orbitals must be balanced relative to the energy of the hypothetical spherical field (*aka* the barycenter).
- The energy of each of the two orbitals of the e_g set rises by +3/5 Δ_o (+6 *Dq*) while the energy of each of the three t_{2g} orbitals falls by -2/5 Δ_o (-4 *Dq*).
- This results in no net energy change for the system:

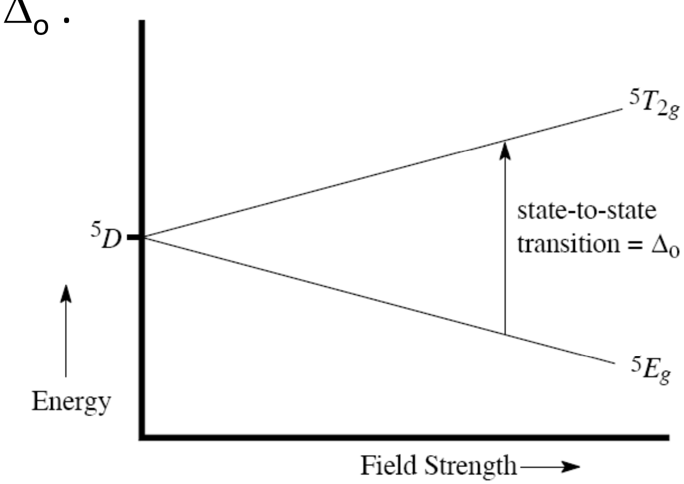
$$\begin{aligned} \Delta E &= E(e_g) + E(t_{2g}) \\ &= (2)(+3/5\ \Delta_o) + (3)(-2/5\ \Delta_o) \\ &= (2)(+6\mathrm{Dq}) + (3)(-4\mathrm{Dq}) = 0 \end{aligned}$$

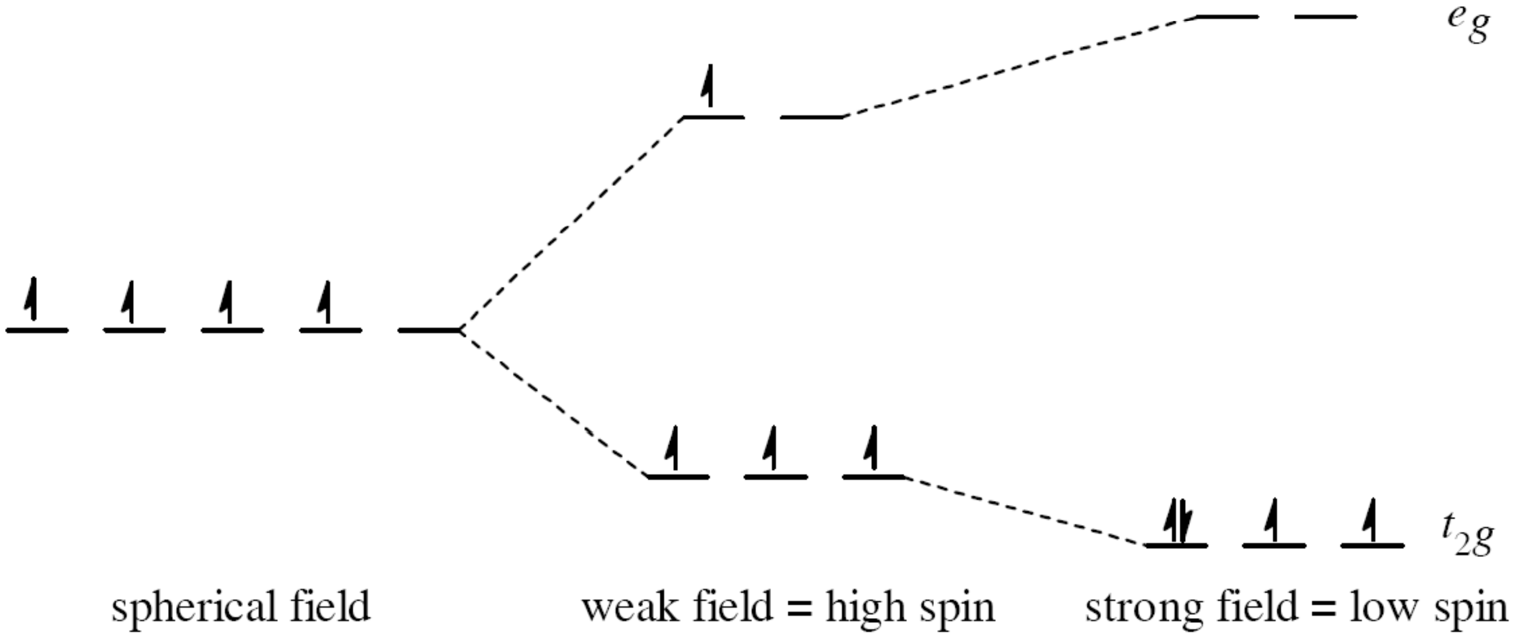
(The magnitude of Δ_o depends upon both the metal ion and the attaching ligands)

High-Spin and Low-Spin Configurations

- In an octahedral complex, electrons fill the t_{2g} and e_g orbitals in an aufbau manner, but for configurations $d^4 - d^7$ there are two possible filling schemes depending on the magnitude of Δ_o relative to the *mean pairing energy*, P.
- A *high-spin configuration* avoids pairing by spreading the electrons across both the t_{2g} and e_g levels.
- A *low-spin configuration* avoids occupying the higher energy e_g level by pairing electrons in the t_{2g} level.
- For a given metal ion, the pairing energy is relatively constant, so the spin state depends upon the magnitude of the field strength, Δ_o .
- Low field strength results in a high-spin state.
- High field strength results in a low-spin state.
- For a d^4 configuration, the high-spin state is $t_{2g}^{3}e_g^{1}$,

  and the low-spin state is $t_{2g}^{4}e_g^{0}$.





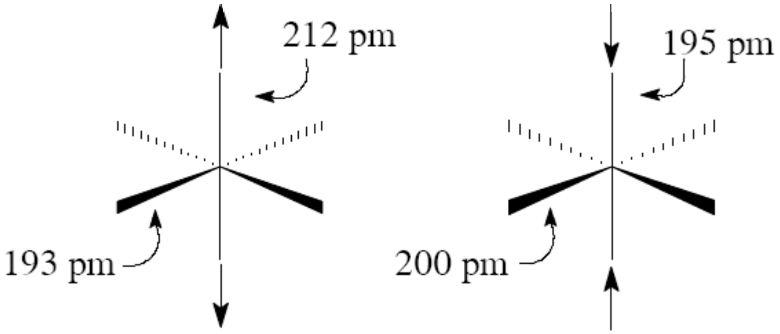
- Low field strength results in a high-spin state.
- High field strength results in a low-spin state.
- For a d^4 configuration, the high-spin state is $t_{2g}^3 e_g^1$, and the low-spin state is $t_{2g}^4 e_g^0$.
- $Mn(acac)_3$ is a weak-field/high-spin case with the configuration $t_{2g}^3 e_g^1$.

Jahn-Teller Distortion

- Jahn-Teller Theorem: ***For any nonlinear system in a degenerate state, a distortion will occur that will lift the degeneracy.***
- $Mn(acac)_3$ has a ^5E_g ground state, which has an imbalance in the filling of electrons in orbitals that point directly at ligands.

$$(t_{2g})^3\,(dx^2\text{–}y^2)^1(dz^2)^0 \quad \textit{or} \quad (t_{2g})^3\,(dx^2\text{–}y^2)^0(dz^2)^1$$

- This results in significant distortion from ideal octahedral symmetry (O_h).
- Jahn-Teller corollary**:** ***If the system is centrosymmetric, the distorted configuration will also be centrosymmetric.***
- For $Mn(acac)_3$ this suggests tetragonal distortion, *pseudo* $O_h \rightarrow D_{4h}$.
- Most probable distortions are equally elongating or shortening two trans-related positions, relative to the four remaining equal positions in a plane. $Mn(acac)_3$ exists in two tetragonally distorted forms.



State Splitting in an Octahedral Field

- In the absence of the octahedral field (point group R_3), the ground state of a $3d^4$ configuration is ^5D.
- A weak O_h field causes this to split into two states:

  Ground state: $^5E_g = t_{2g}{}^3\, e_g{}^1$

  Excited state: $^5T_{2g} = t_{2g}{}^2 e_g{}^2$

- The ^5E_g ground state is doubly-degenerate, because there are two ways of placing the $e_g{}^1$ electron:

  $(t_{2g})^3\ (dx^2\text{–}y^2)^1(dz^2)^0$

  $(t_{2g})^3\ (dx^2\text{–}y^2)^0(dz^2)^1$

- The $^5T_{2g}$ excited state is triply degenerate, because there are three ways of placing the vacant orbital:

  $(dxy)^1(dyz)^1(dxz)^0\ (e_g)^2$

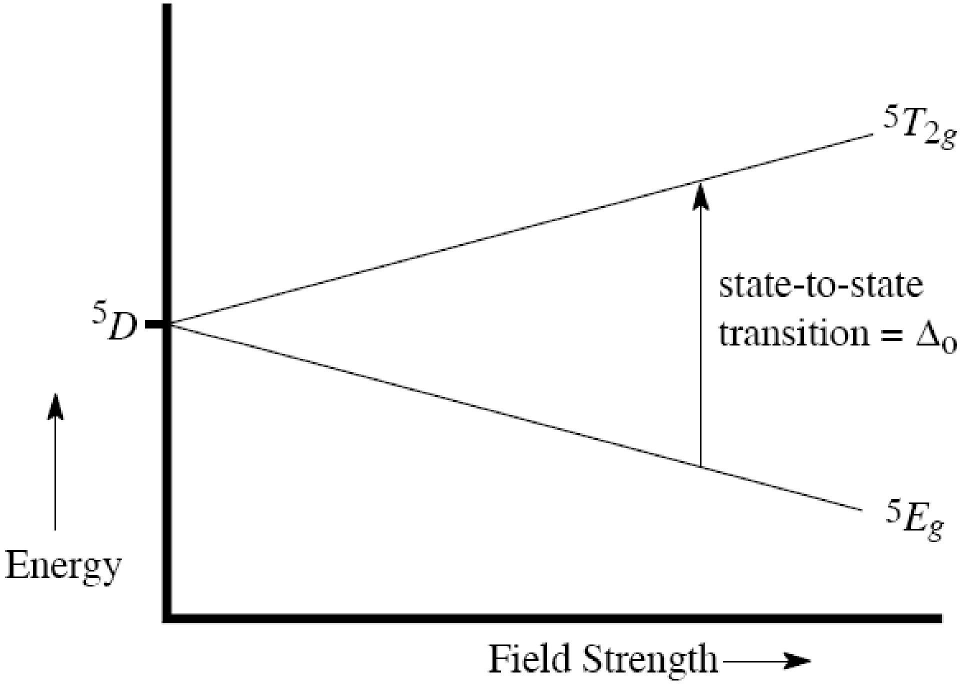
  $(dxy)^1(dyz)^0(dxz)^1\ (e_g)^2$

  $(dxy)^0(dyz)^1(dxz)^1\ (e_g)^2$

- ^5E_g state is paramagnetic from four unpaired electrons.

Absorption Spectra and State-to-State Transitions

- When a transition metal complex absorbs visible light, the energy absorbed causes a transition from the ground state to an excited state, corresponding to a change in electronic configuration.
- For a high-spin d^4 complex like $\mathrm{Mn(acac)_3}$, only one same-spin state-to-state transition is possible: $^5E_g \rightarrow {}^5T_{2g}$
- The $^5E_g \rightarrow {}^5T_{2g}$ gives rise to a single absorption band in the visible spectrum at ~ 500 nm, absorbing red-orange light and transmitting green light.



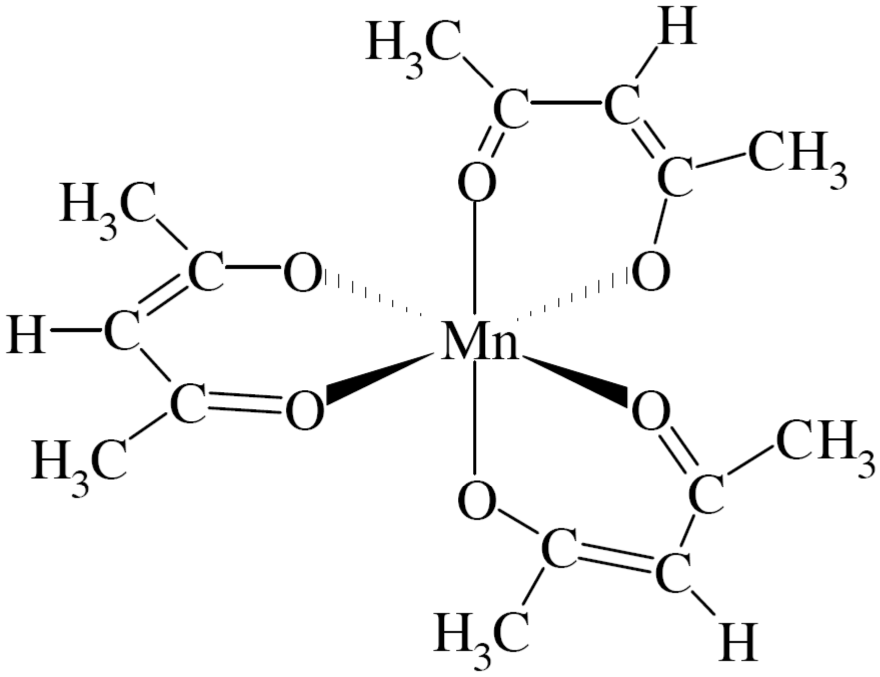
$Mn(acac)_3$ Synthesis

- Manganese (Z = 25) has a valence configuration $[Ar]4s^2 3d^5$, and typically shows positive oxidations states of +2, +3, and +7, all of which are seen in this experiment.

$MnCl_2.4H_2O$	**Mn(II)**	**$[Ar]3d^5$**	**pale pink**
$Mn(acac)_3$	**Mn(III)**	**$[Ar]3d^4$**	**lustrous dark brown**
$KMnO_4$	**Mn(VII)**	**[Ar]**	**deep purple**

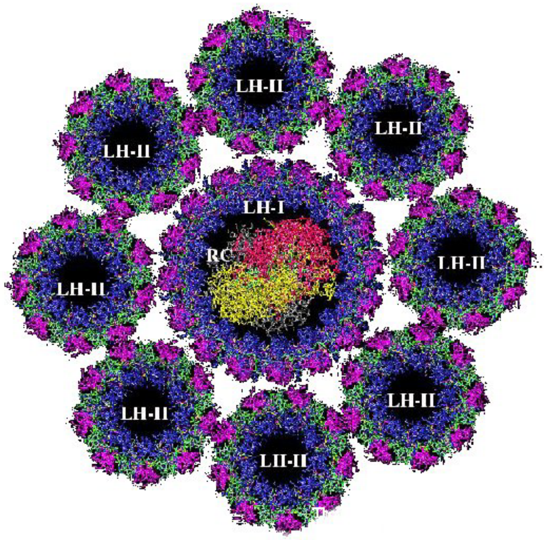
- Pale color of $MnCl_2.{}_4H_2O$ is due to the absence of any *spin-allowed d-d* transitions for a d^5 high-spin complex.
- $Mn(acac)_3$ is green by transmitted light, owing to a single broad *d-d* transition at about 500 nm.
- $KMnO_4$ is deep purple, owing to a ***ligand-to-metal charge-transfer (LMCT)*** transition with high molar absorptivity.

- The ligand *acetylacetonate (acac)* is the anion of acetylacetone (aka 2,4-pentanedione; Hacac) produced in-situ by deprotonation with an acetate base.
- In Mn(acac)$_3$ the Mn^{3+} centre is ligated by three surrounding acac ligands in an octahedral geometry (point group: *D*$_3$ $\rightarrow$ *pseudo O*$_\mathrm{h}$ symmetry).

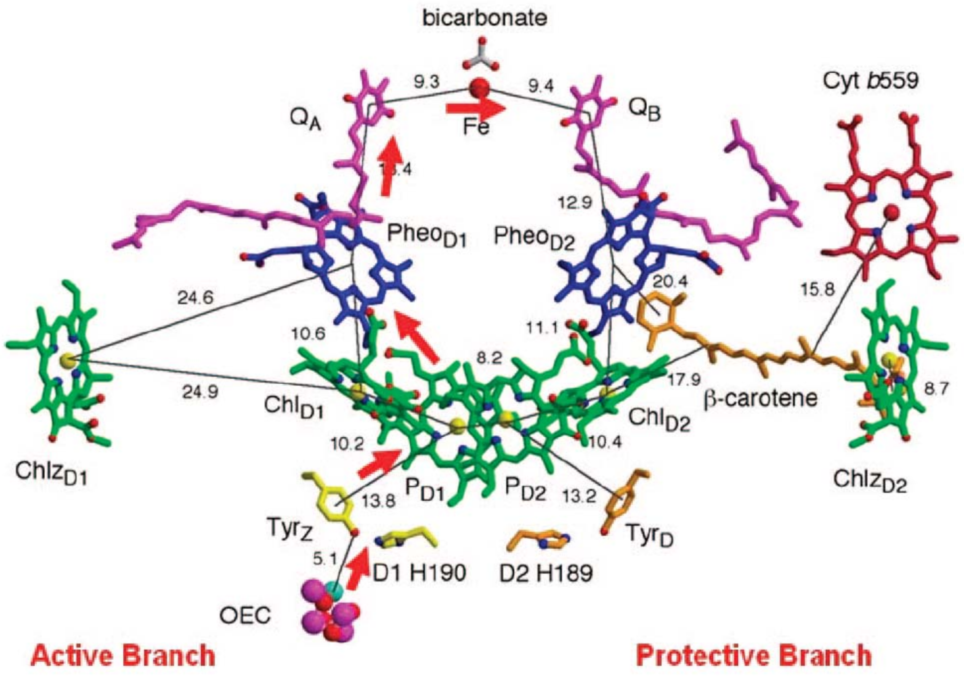


Photosynthesis

$(6CO_2 + 6H_2O + h\nu \rightarrow (CH_2O)_6 + 6O_2)$



Light-Harvesting
(energy transfer)



Reaction Center

(charge separation via e^- transfer)

H_2O oxidation by OEC via

proton-coupled e^- transfer

(dark reaction)

H_2O oxidation by OEC via proton-coupled e^- transfer

(dark reaction)