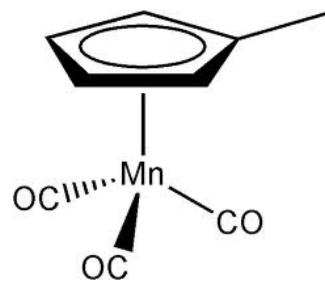
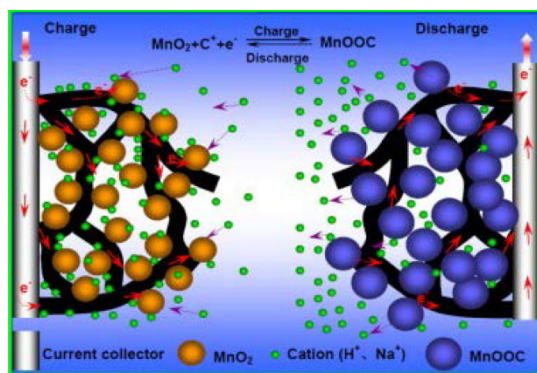
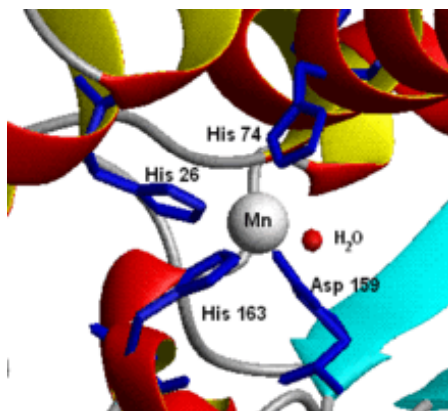
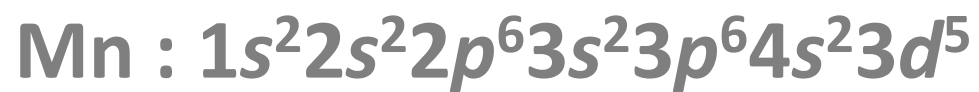


Group 7 : Manganese Chemistry



Mn(acac)₃ Synthesis

- Manganese (Z = 25) has a valence configuration [Ar]4s²3d⁵, and typically shows positive oxidation states of +2, +3, and +7, all of which are seen in this experiment.



pale pink



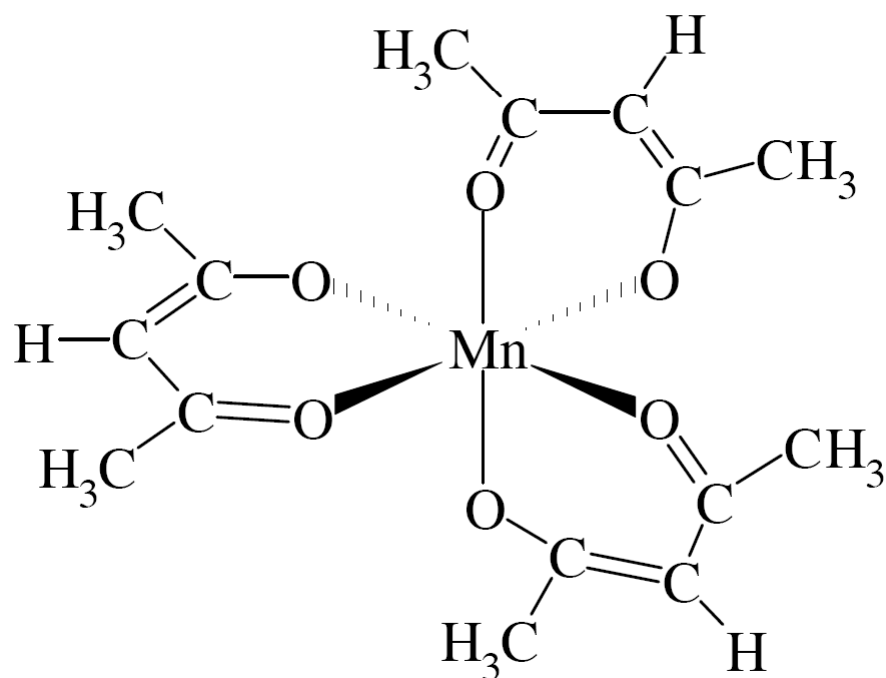
lustrous dark brown



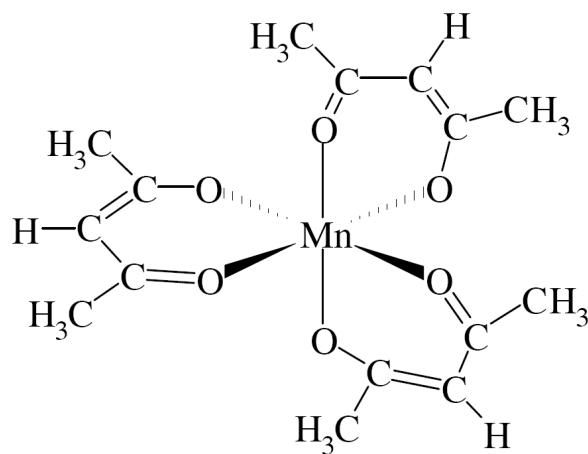
deep purple

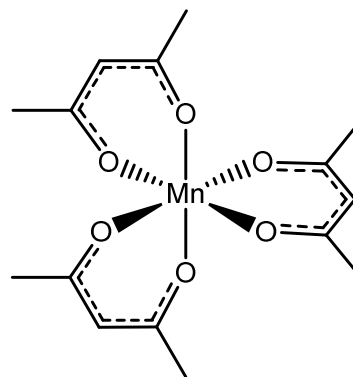
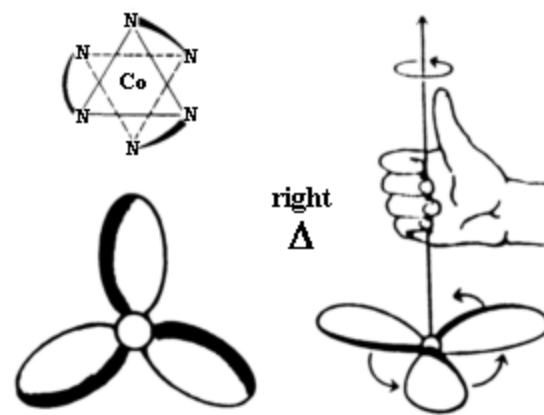
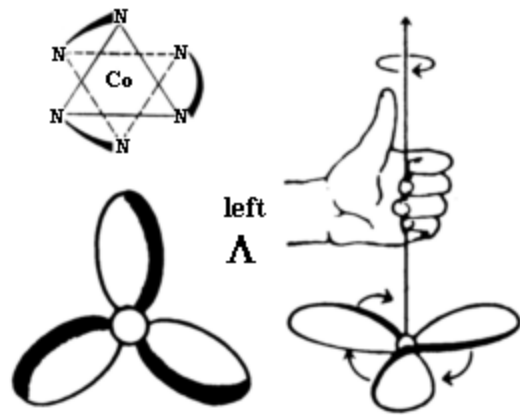
- Pale color of MnCl₂·4H₂O is due to the absence of any *spin-allowed d-d* transitions for a d⁵ high-spin complex.
- Mn(acac)₃ is green by transmitted light, owing to a single broad *d-d* transition at about 500 nm.
- KMnO₄ is deep purple, owing to a ***ligand-to-metal charge-transfer (LMCT)*** transition 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 $\text{Mn}(\text{acac})_3$ the Mn^{3+} centre is ligated by three surrounding *acac* ligands in an octahedral geometry (point group: $D_3 \rightarrow \text{pseudo } O_h$ symmetry).
- We can still describe the arrangement of coordinating point charges at the metal center as an octahedral “geometry” even though its “symmetry” is not pure octahedral.

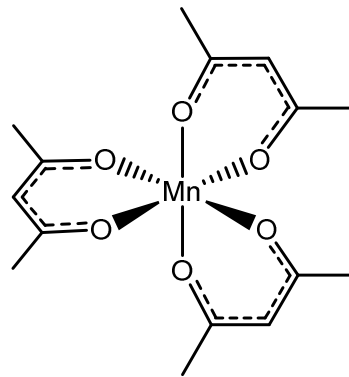


Crystal Field Splitting in Octahedral Transition Metal Complexes





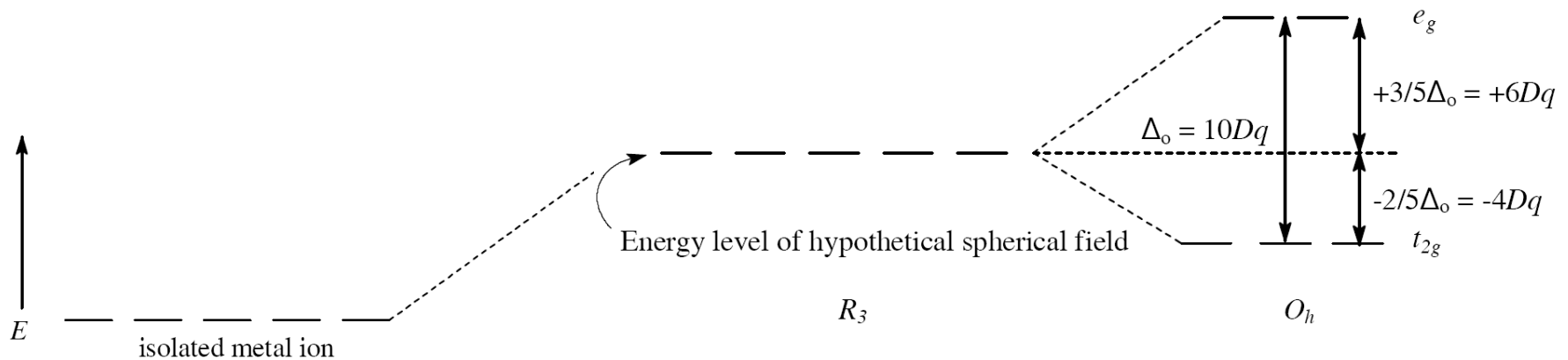
Λ -isomer



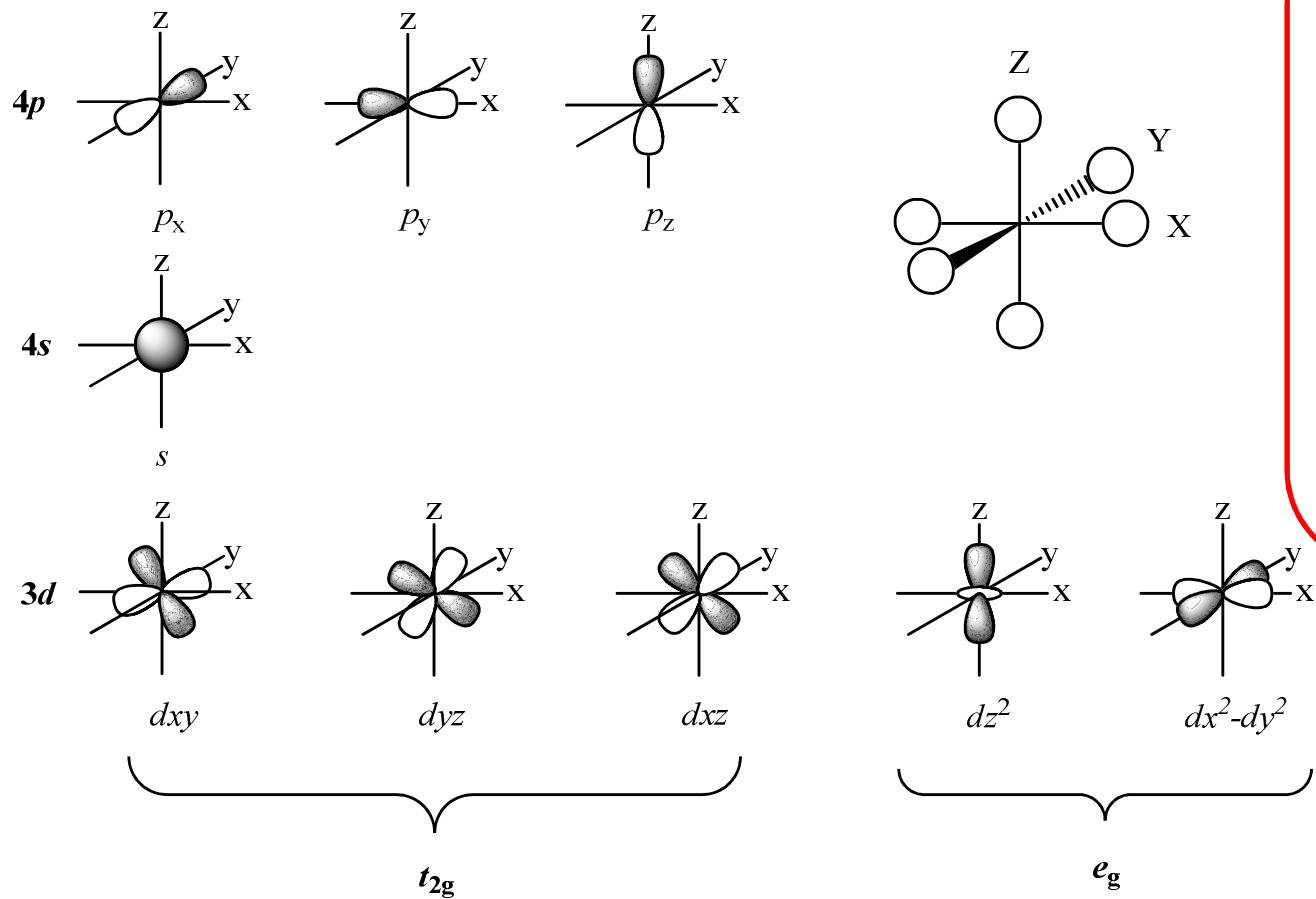
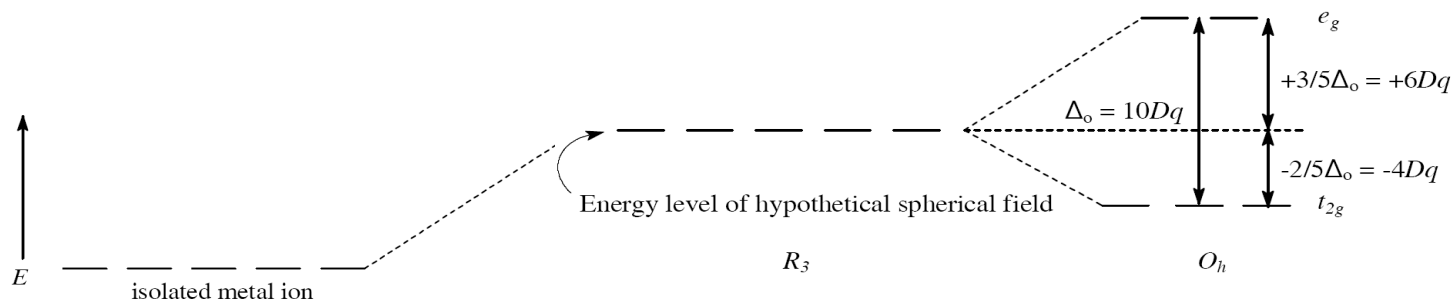
Δ -isomer

d-Subshell Splitting in an O_h Field

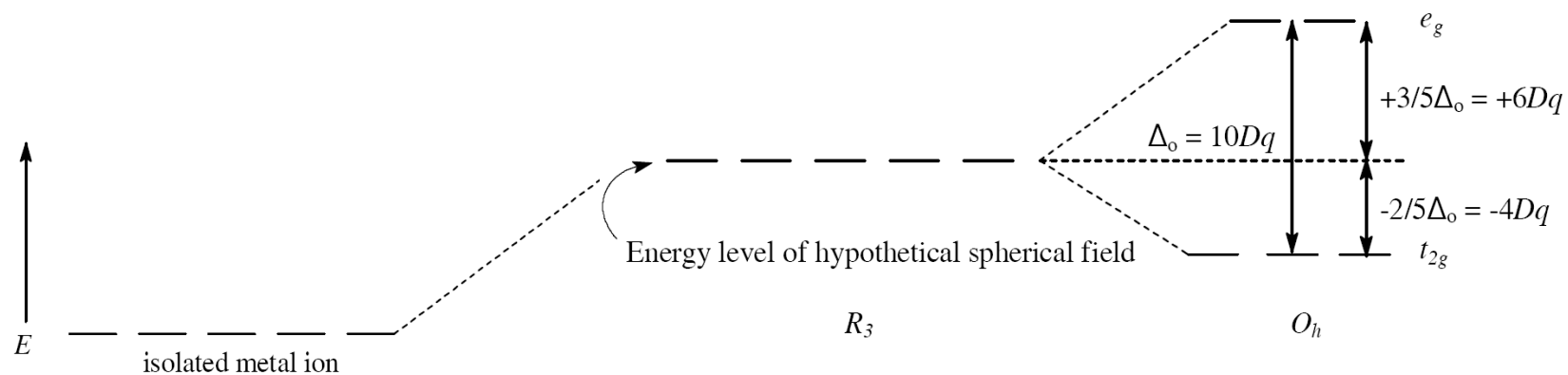
- In the octahedral (O_h) environment of three acac ligands, the fivefold degeneracy among the d orbitals in Mn^{3+} is lifted.
- To a first approximation, the ligand field is of O_h symmetry, and the $3d$ orbitals will separate into a set of three degenerate orbitals ($t_{2g} = d_{xy}, d_{yz}, d_{xz}$)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



- 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 electric field).



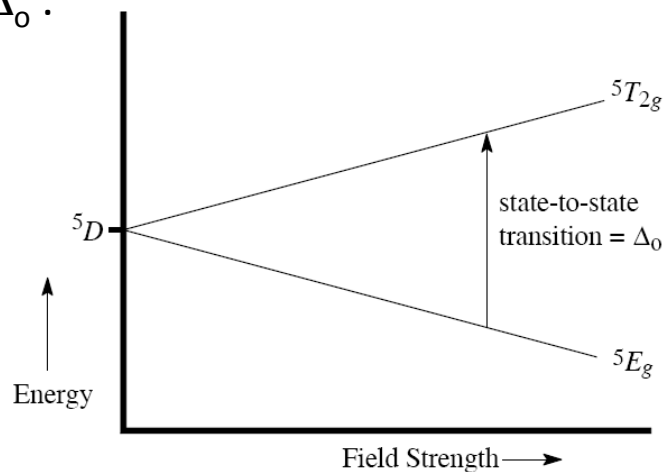
- The energy increase of the e_g orbitals and the energy decrease of the t_{2g} orbitals must be balanced relative to the energy of the hypothetical spherical field (*aka* the barycenter).
- The energy of each of the two orbitals of the e_g set rises by $+3/5 \Delta_o$ ($+6 Dq$) while the energy of each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

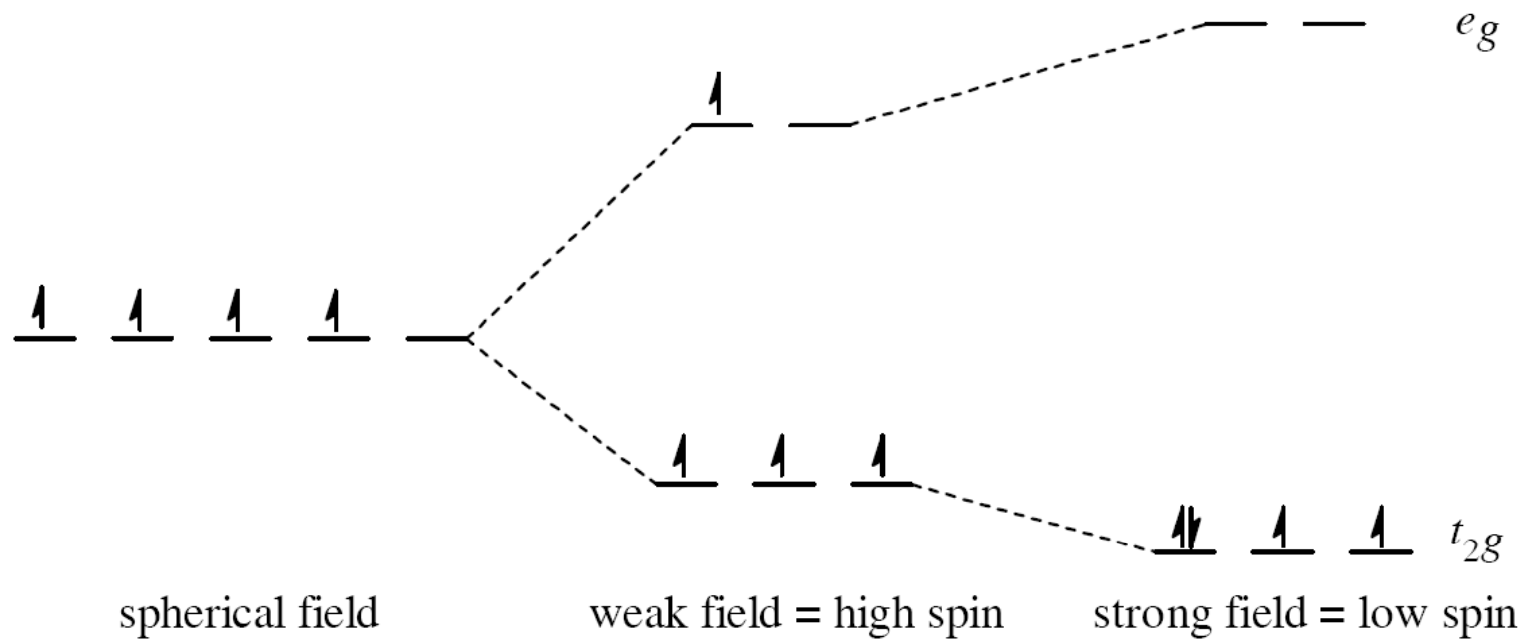
$$\begin{aligned}
 \Delta E &= E(e_g) + E(t_{2g}) \\
 &= (2)(+3/5 \Delta_o) + (3)(-2/5 \Delta_o) \\
 &= (2)(+6Dq) + (3)(-4Dq) = 0
 \end{aligned}$$

(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 $t_{2g}^4 e_g^0$.

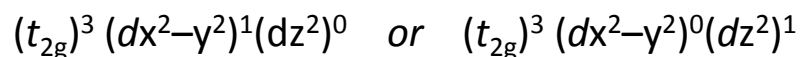




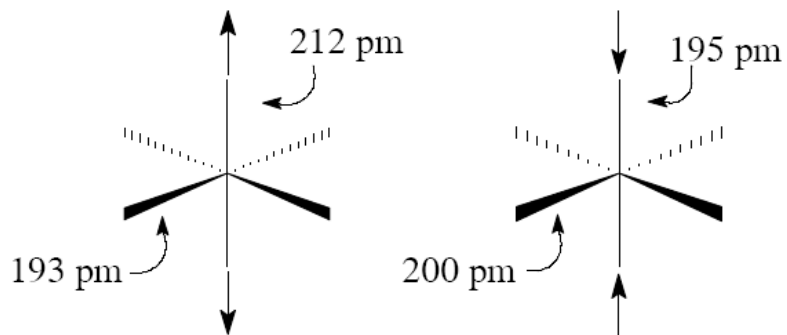
- Low field strength results in a high-spin state.
- High field strength results in a low-spin state.
- For a d^4 configuration, the high-spin state is $t_{2g}^3 e_g^1$, and the low-spin state is $t_{2g}^4 e_g^0$.
- $\text{Mn}(\text{acac})_3$ is a weak-field/high-spin case with the configuration $t_{2g}^3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

Jahn-Teller Distortion

- Jahn-Teller Theorem: ***For any nonlinear system in a degenerate state, a distortion will occur that will lift the degeneracy.***
- $\text{Mn}(\text{acac})_3$ has a 5E_g ground state, which has an imbalance in the filling of electrons in orbitals that point directly at ligands. (5E_g = multiplicity of 5, doubly degenerate (E) + centrosymmetric (g) electronic configuration.



- 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 $\text{Mn}(\text{acac})_3$ this suggests tetragonal distortion, $\text{pseudo } O_h \rightarrow D_{4h}$.
- Most probable distortions are equally elongating or shortening two trans-related positions, relative to the four remaining equal positions in a plane. $\text{Mn}(\text{acac})_3$ exists in two tetragonally distorted forms.



State Splitting in an Octahedral Field

- In the absence of the octahedral field (totally symmetric point group R_3), the ground state of a $3d^4$ configuration is described by the 5D term symbol (fivefold degeneracy).

- A weak O_h field causes this to split into two states (twofold + threefold degeneracy)

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:

$$(t_{2g})^3 (dx^2-y^2)^1 (dz^2)^0$$

$$(t_{2g})^3 (dx^2-y^2)^0 (dz^2)^1$$

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

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

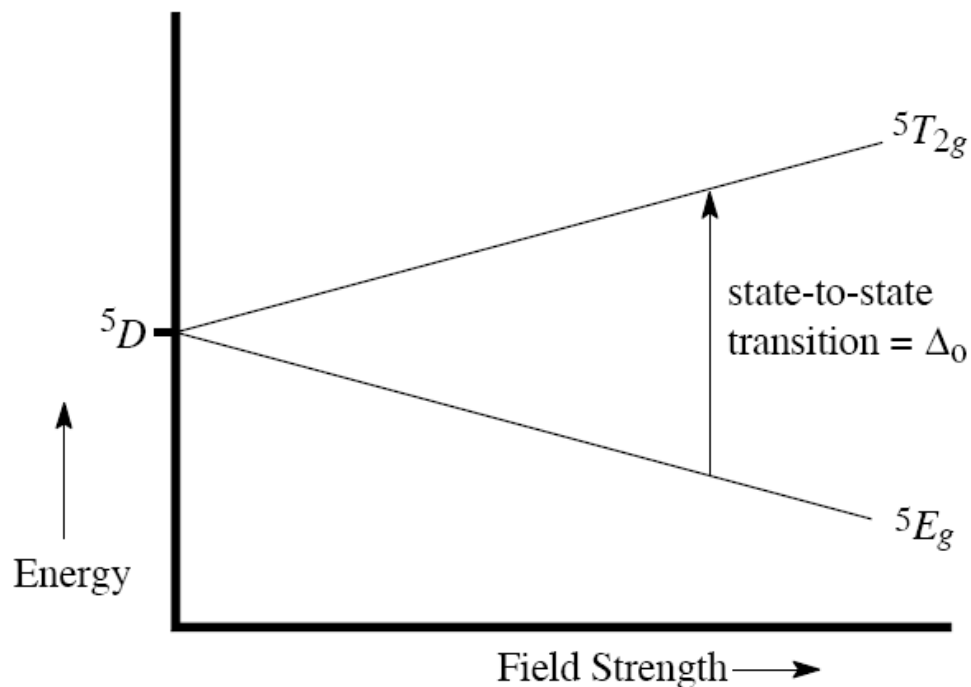
$$(dxy)^1 (dyz)^0 (dxz)^1 (e_g)^2$$

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

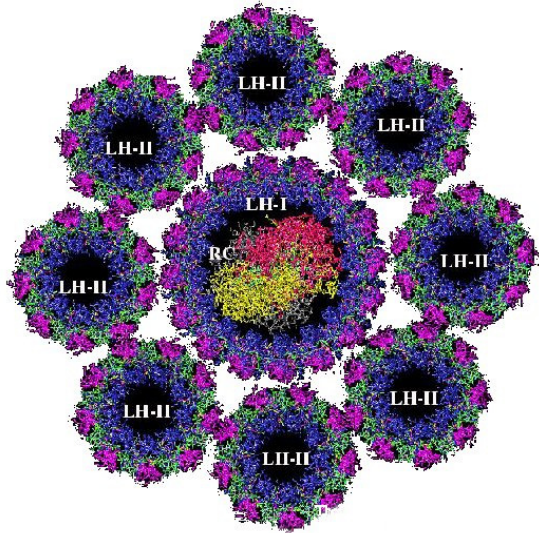
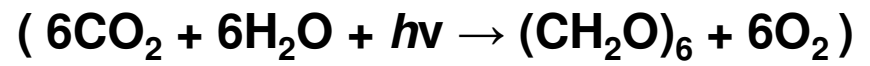
- 5E_g state is paramagnetic as a result of having four unpaired electrons.

Absorption Spectra and State-to-State Transitions

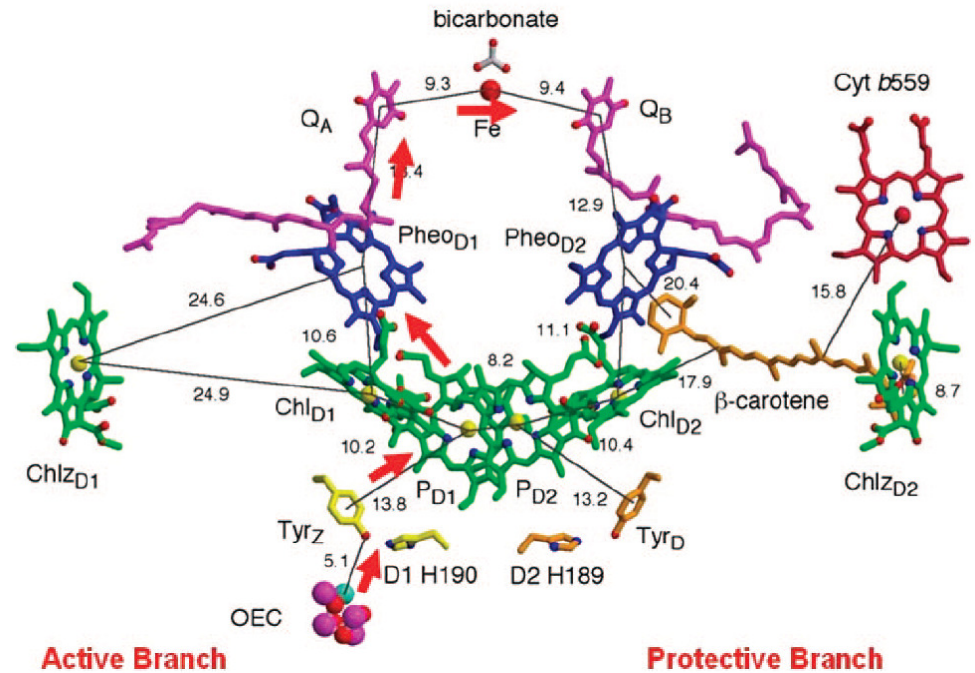
- When a transition metal complex absorbs visible light, the energy absorbed causes a transition from the ground state to an excited state, corresponding to a change in electronic configuration.
- For a high-spin d^4 complex like $\text{Mn}(\text{acac})_3$, only one same-spin state-to-state transition 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.



Photosynthesis



Light-Harvesting
(energy transfer)



Reaction Center

(charge separation via e^- transfer)

**H₂O oxidation by OEC via
proton-coupled e^- transfer
(dark reaction)**

H₂O oxidation by OEC via proton-coupled e⁻ transfer (dark reaction)

