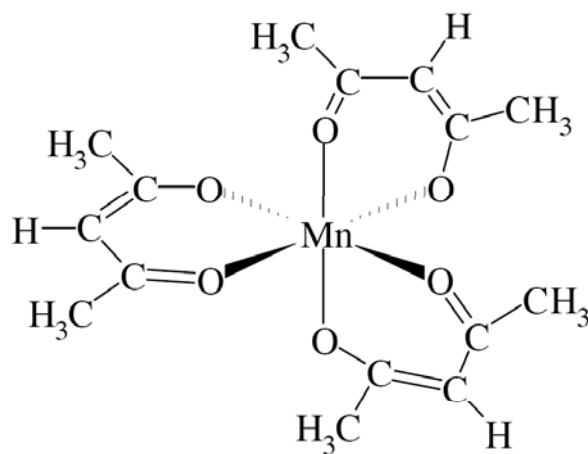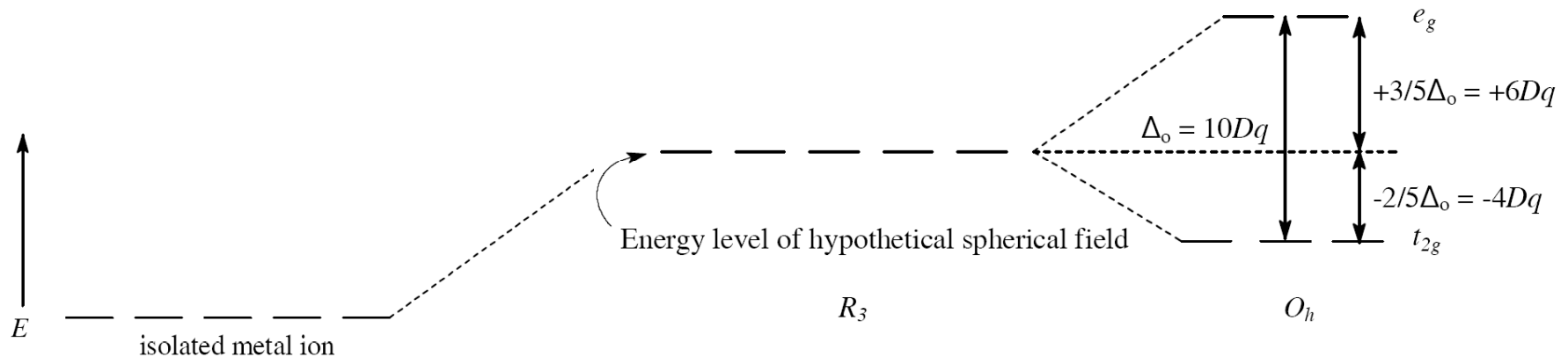# Crystal Field Splitting
in
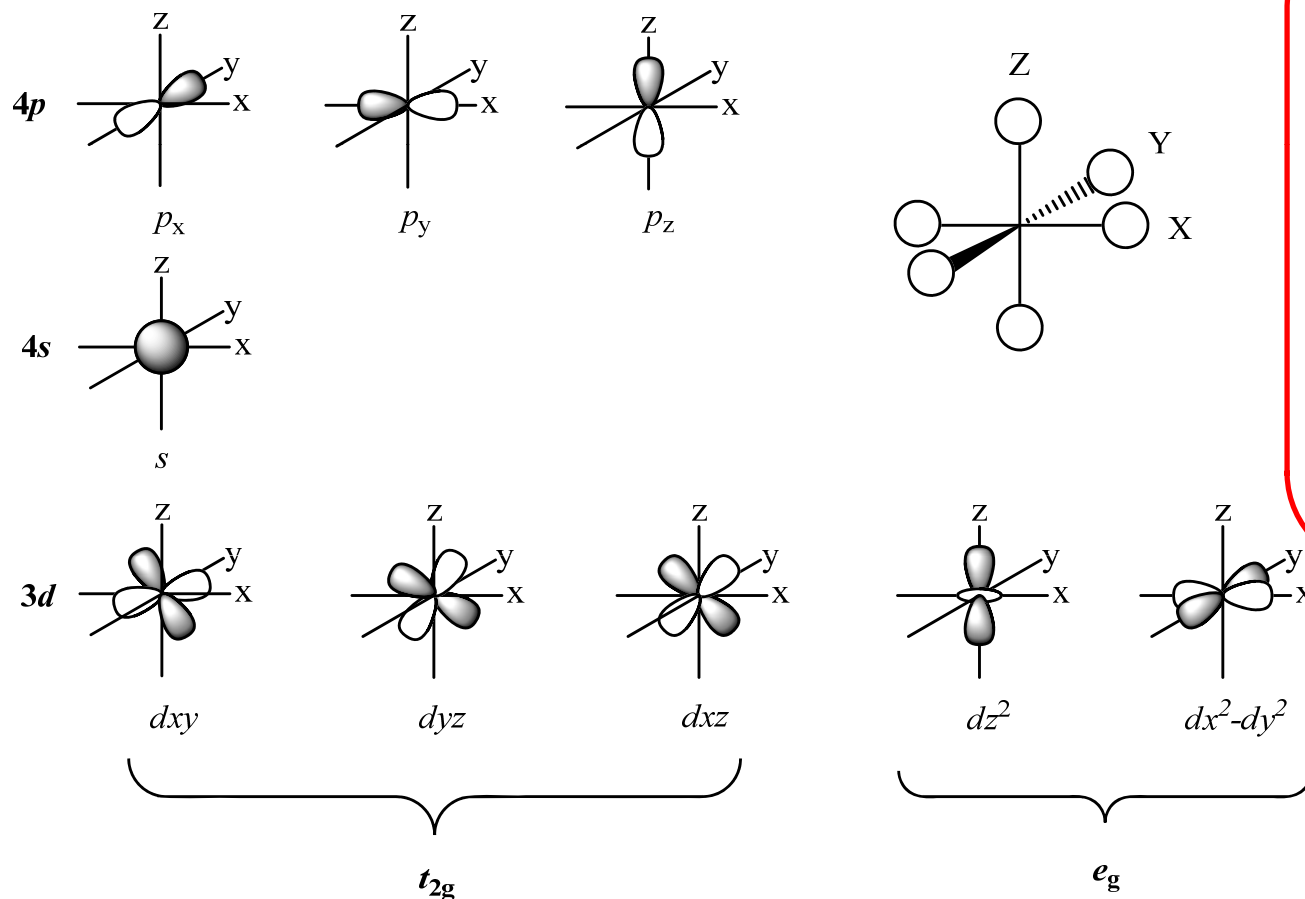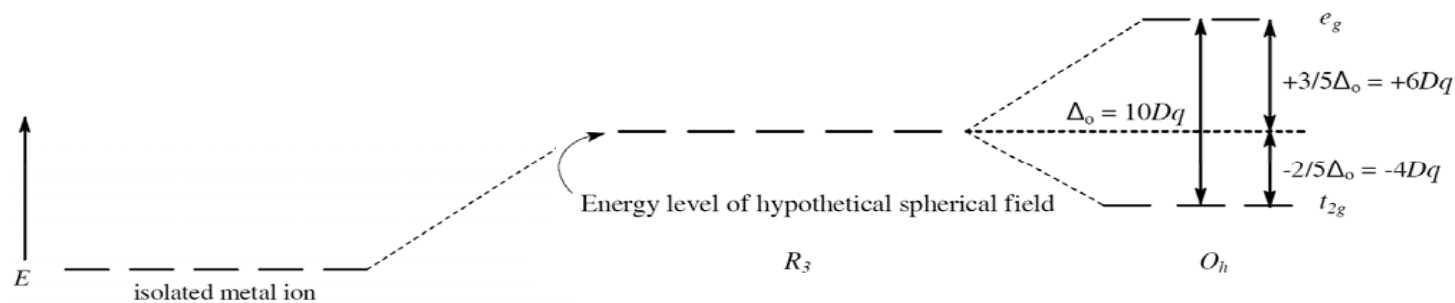# Octahedral
Transition Metal Complexes
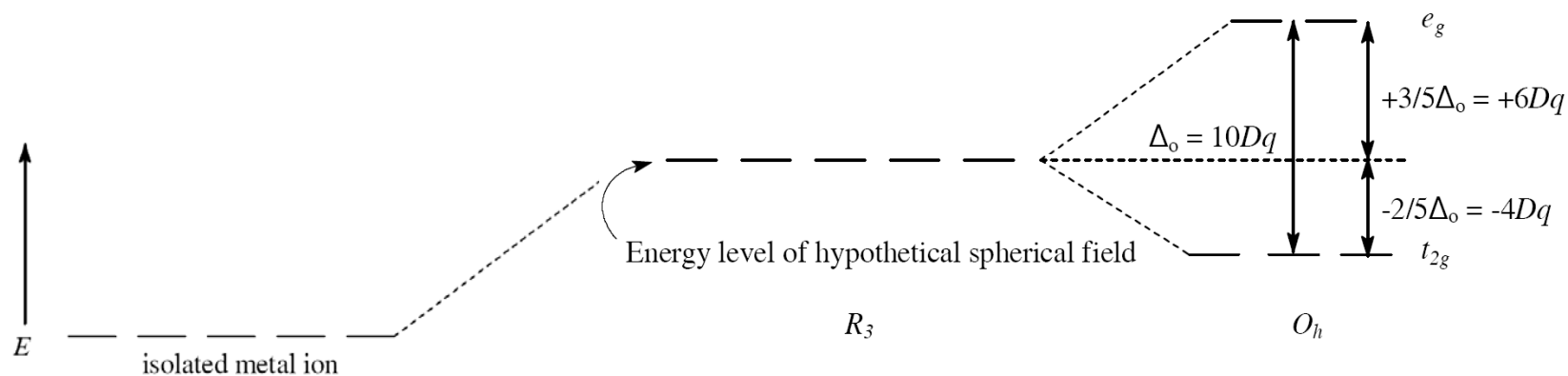
d-Subshell Splitting in an O*h* Field

- 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 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 = dx²–y², dz²).

e_g

$+3/5\Delta_o = +6Dq$

$\Delta_o = 10Dq$

Energy level of hypothetical spherical field

$-2/5\Delta_o = -4Dq$

t_{2g}

R_3

O_h

E

isolated metal ion

- 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.

Energy level of hypothetical spherical field

R_3

e_g

$+3/5\Delta_o = +6Dq$

$\Delta_o = 10Dq$

$-2/5\Delta_o = -4Dq$

t_{2g}

O_h

E

isolated metal ion

4p

p_x p_y p_z

4s

s

3d

dxy dyz dxz dz^2 dx^2-dy^2

t_{2g} e_g

- 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)*.

Energy level of hypothetical spherical field

$\Delta_o = 10Dq$

$+3/5\Delta_o = +6Dq$

$-2/5\Delta_o = -4Dq$

e_g

t_{2g}

R_3

O_h

E

isolated metal ion

- 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:

$$\Delta E = E(e_g) + E(t_{2g})$$

$$= (2)(+3/5 \Delta_o) + (3)(-2/5 \Delta_o)$$

$$= (2)(+6Dq) + (3)(-4Dq) = 0$$

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

spherical field   weak field = high spin   strong field = low spin
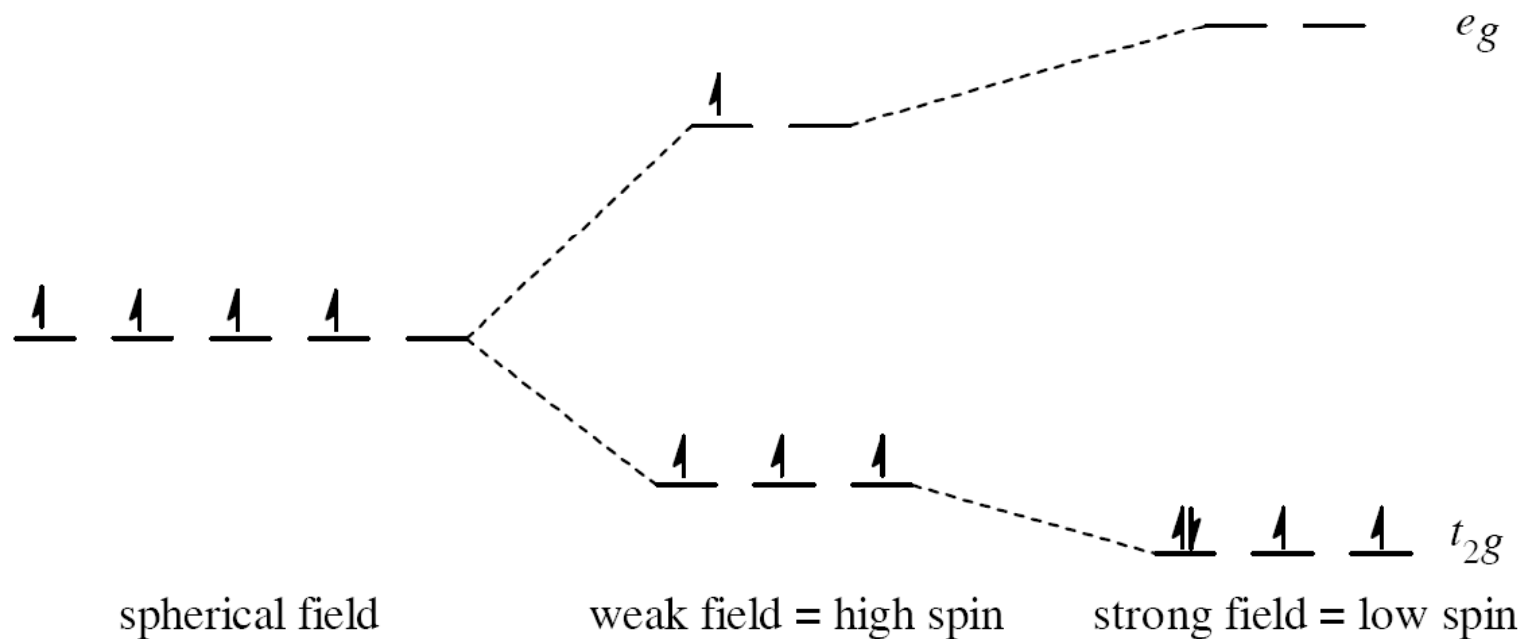
- Low field strength results in a high-spin state.

- 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.

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

- 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, $O_h \rightarrow D_{4h}$.

- 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.

212 pm   195 pm

193 pm   200 pm
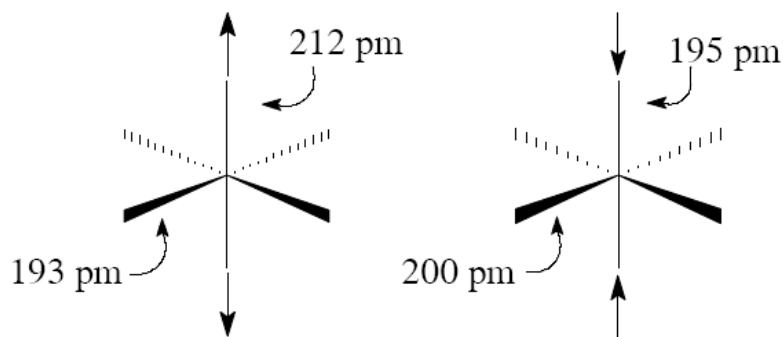
State Splitting in an Octahedral Field

- 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:

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

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

- 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 from four unpaired electrons.

Absorption Spectra and State-to-State Transitions

- When a transition metal complex absorbs visible light, the energy absorbed (h<) 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 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.
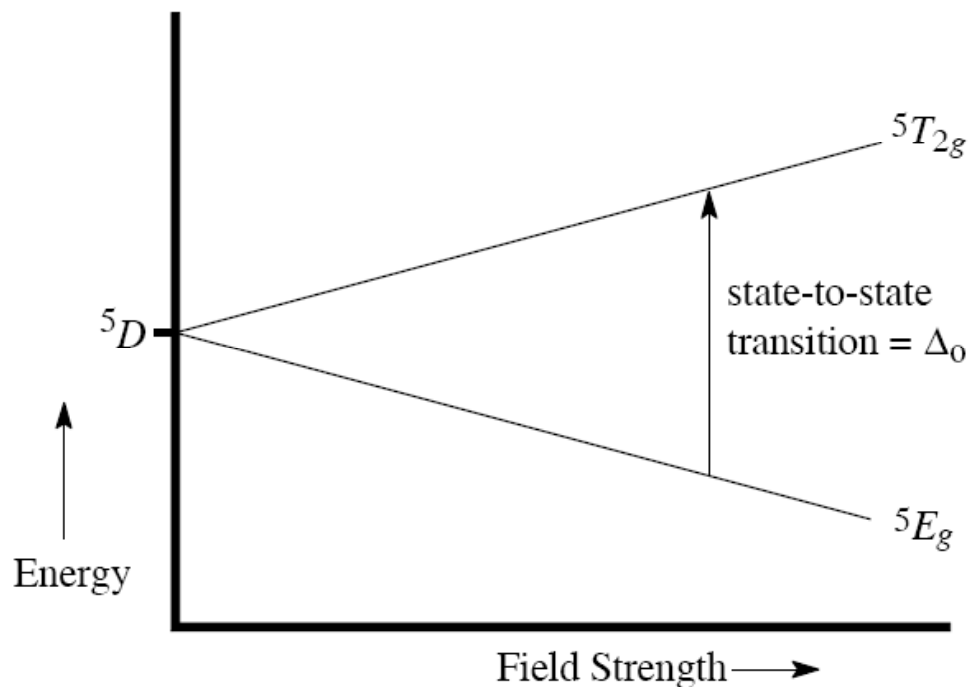
Mn(acac)$_3$ Synthesis

- 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.
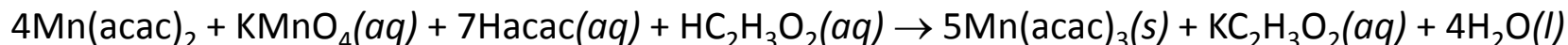
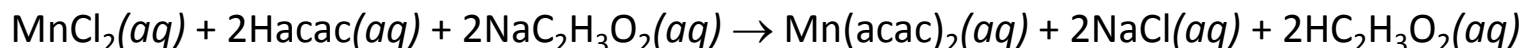|			
MnCl$_2$.4H$_2$O	Mn(II)	[Ar]$3d^5$	pale pink
Mn(acac)$_3$	Mn(III)	[Ar]$3d^4$	lustrous dark brown
KMnO$_4$	Mn(VII)	[Ar]	deep purple

- Pale color of MnCl$_2$.$_4$H$_2$O 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.

Procedure Notes

- Two-step preparation.

- Make certain that all $KMnO_4$ is dissolved before adding to the solution in the second step.

- Use filter paper /Büchner funnel or Hirsh funnel for first crude product collection (not sintered glass).

- Crude product is obtained by chilling the final mixture.

- Pure product is obtained by recrystallization from benzene solution on adding petroleum ether.

- Filter benzene solution through a sintered glass filter that is already discolored brown.

- Discard all solutions (esp., benzene/petroleum ether mixture) in waste containers (nothing down the drain).

$$MnCl_2(aq) + 2Hacac(aq) + 2NaC_2H_3O_2(aq) \rightarrow Mn(acac)_2(aq) + 2NaCl(aq) + 2HC_2H_3O_2(aq)$$

$$4Mn(acac)_2 + KMnO_4(aq) + 7Hacac(aq) + HC_2H_3O_2(aq) \rightarrow 5Mn(acac)_3(s) + KC_2H_3O_2(aq) + 4H_2O(l)$$

- 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: $D_3 \rightarrow pseudo\ O_h$ symmetry).

Photosynthesis

$$6CO_2 + 6H_2O + h\nu \rightarrow (CH_2O)_6 + 6O_2$$
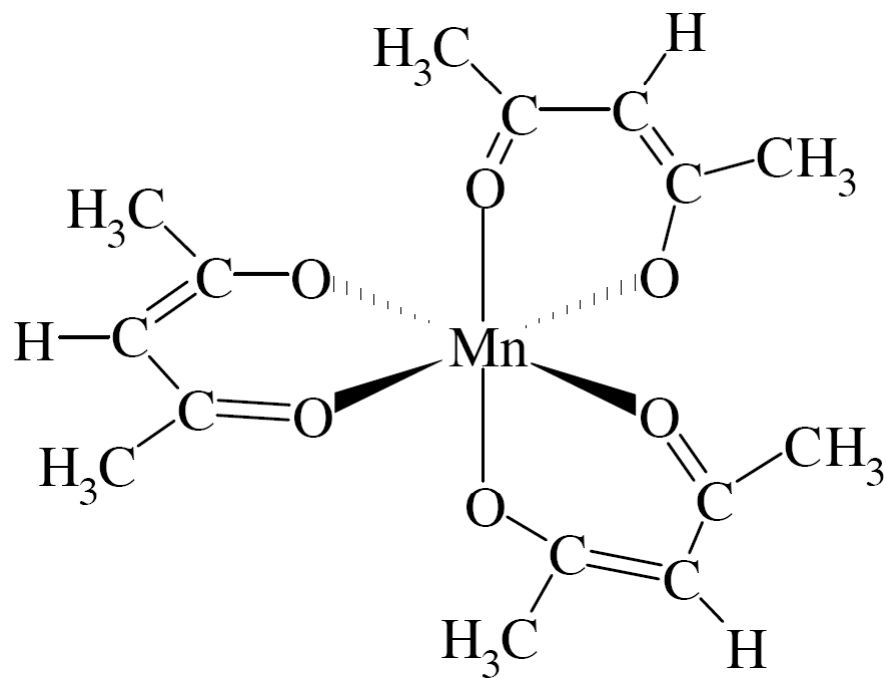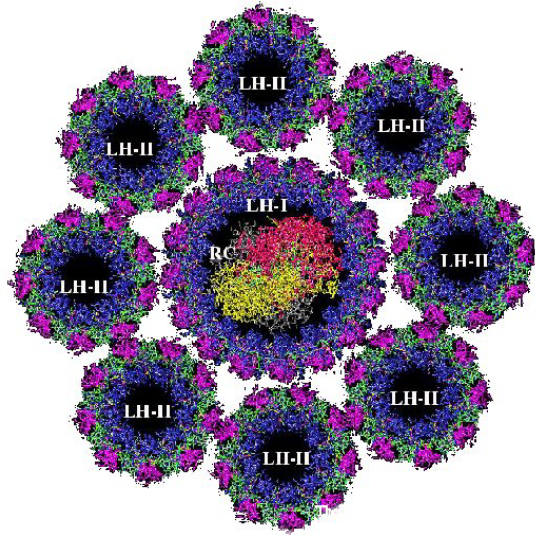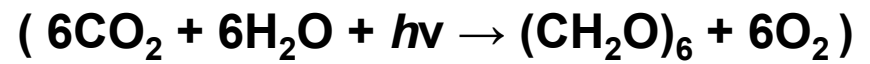
Light-Harvesting
(energy transfer)
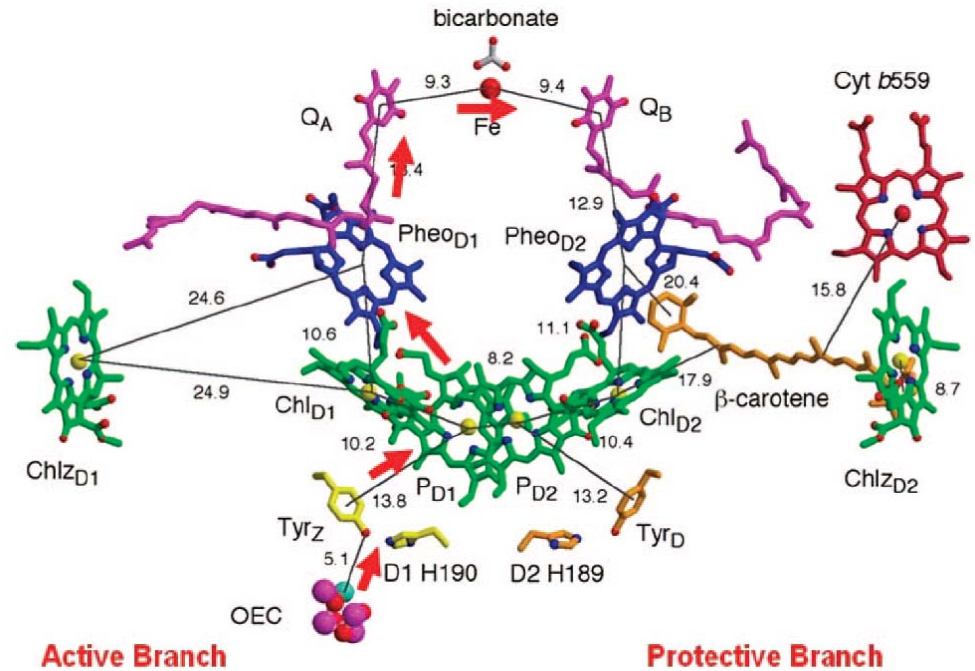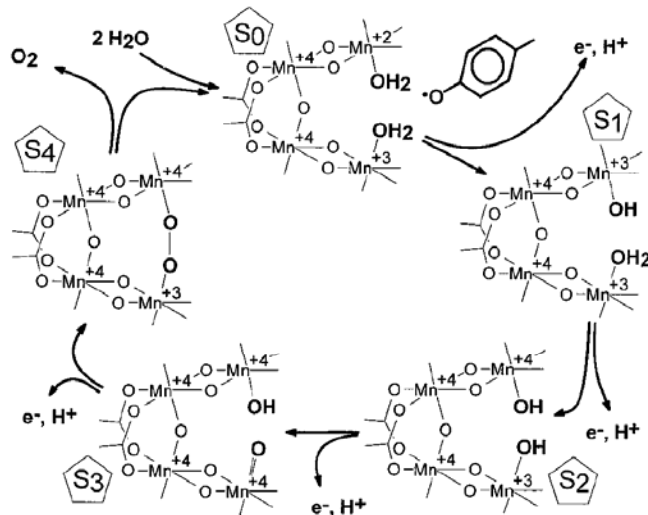
Reaction Center

(charge separation via e^- transfer)

H_2O oxidation by OEC via

proton-coupled e^- transfer

(dark reaction)