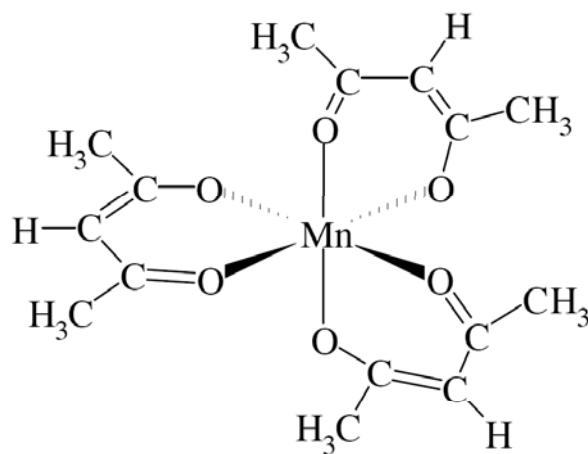
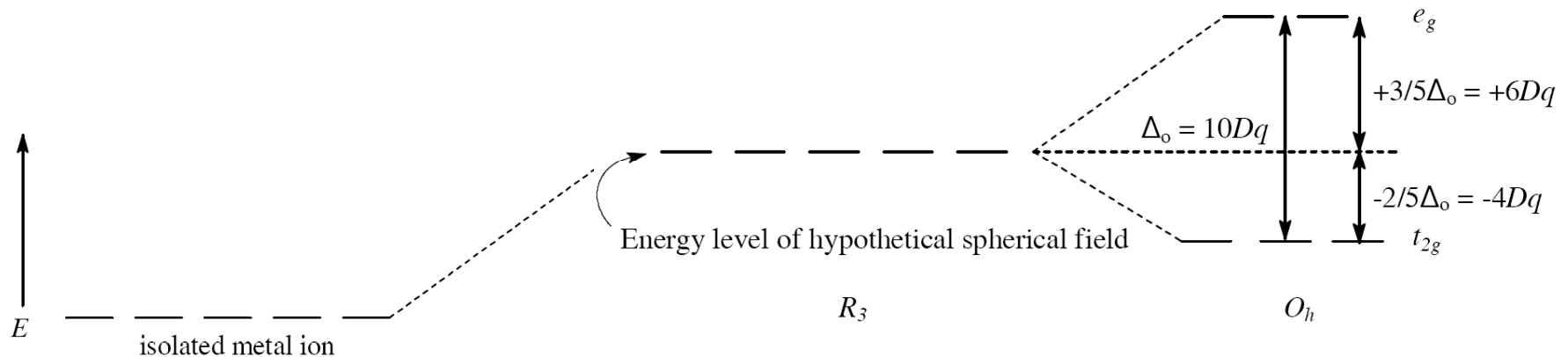


Crystal Field Splitting in Octahedral Transition Metal Complexes

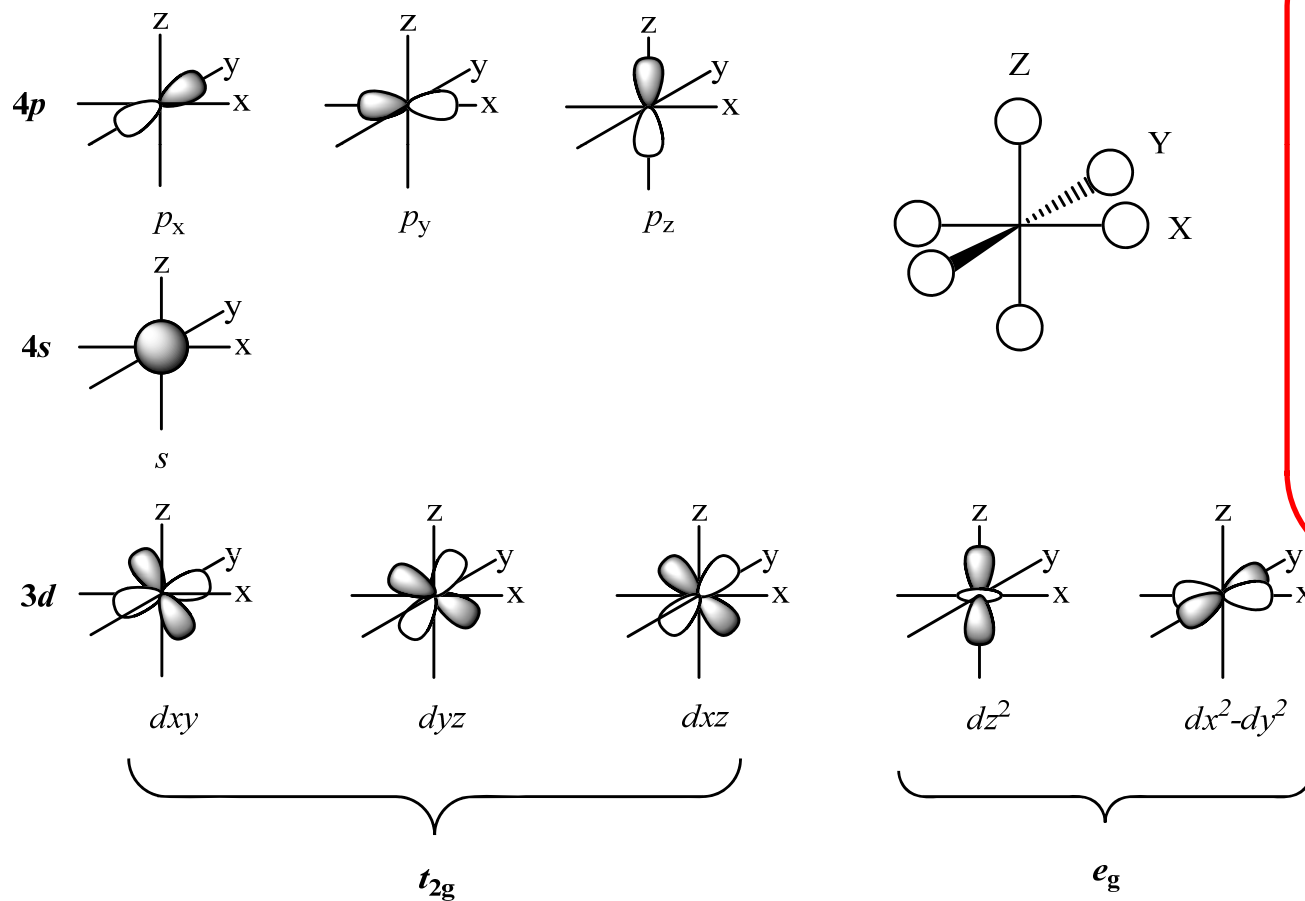
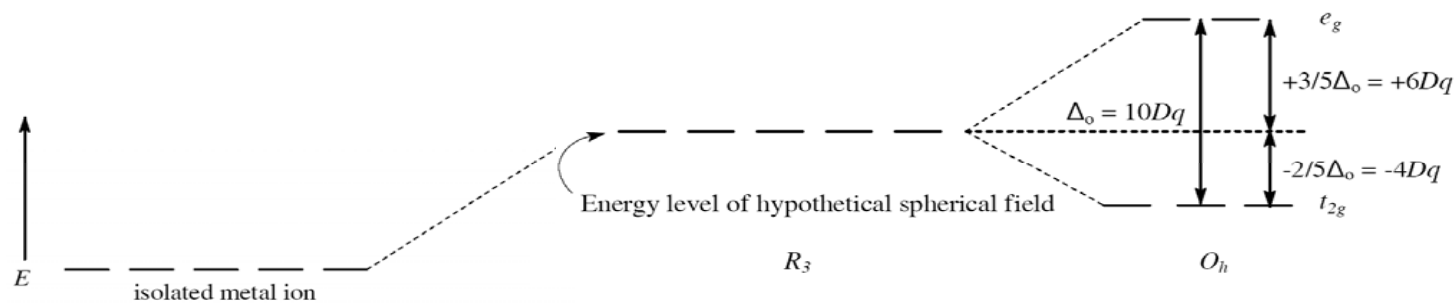


d-Subshell Splitting in an O_h Field

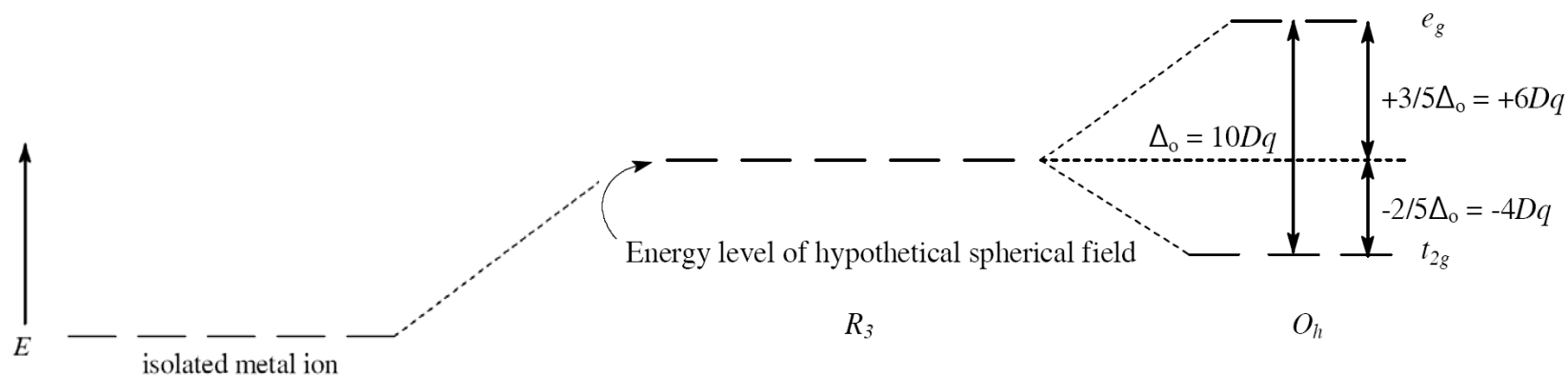
- In the octahedral (O_h) environment of three acac ligands, the fivefold degeneracy among the d orbitals in Mn^{3+} is lifted.
- To a first approximation, the ligand field is of O_h symmetry, and the $3d$ orbitals will separate into a set of three degenerate orbitals ($t_{2g} = dxy, dyz, dxz$) and a 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).



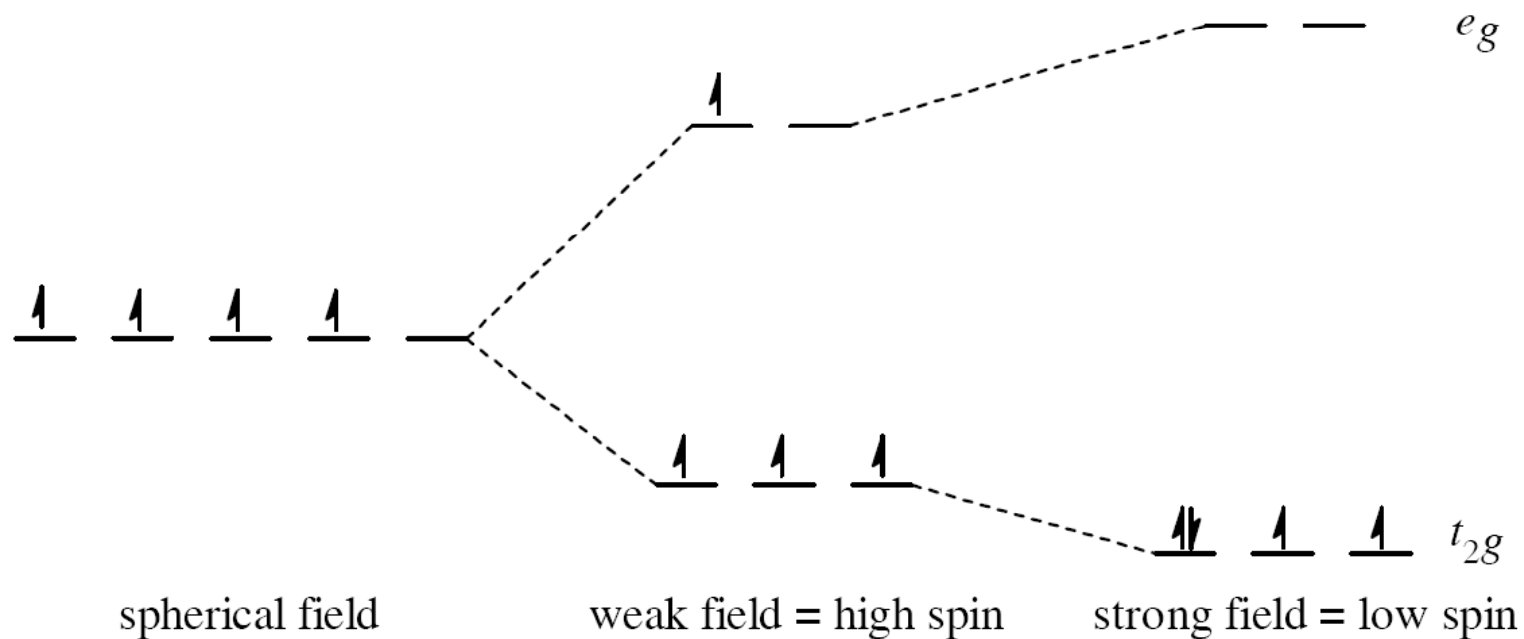
- The energy increase of the e_g orbitals and the energy decrease of the t_{2g} orbitals must be balanced relative to the energy of the hypothetical spherical field (*aka* the barycenter).
- The energy of each of the two orbitals of the e_g set rises by $+3/5 \Delta_o$ ($+6 Dq$) while the energy of each 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 $t_{2g}^4 e_g^0$.



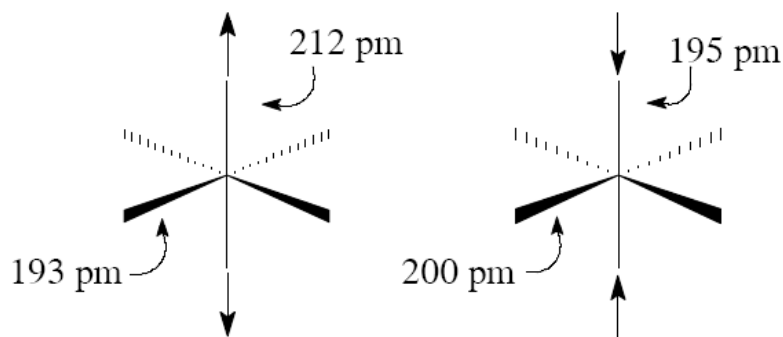
- Low field strength results in a high-spin state.
- High field strength results in a low-spin state.
- For a d^4 configuration, the high-spin state is $t_{2g}^3 e_g^1$, and the low-spin state is $t_{2g}^4 e_g^0$.
- $\text{Mn}(\text{acac})_3$ is a weak-field/high-spin case with the configuration $t_{2g}^3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

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.

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

- 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 $\text{Mn}(\text{acac})_3$ 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. $\text{Mn}(\text{acac})_3$ 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:

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

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

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

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

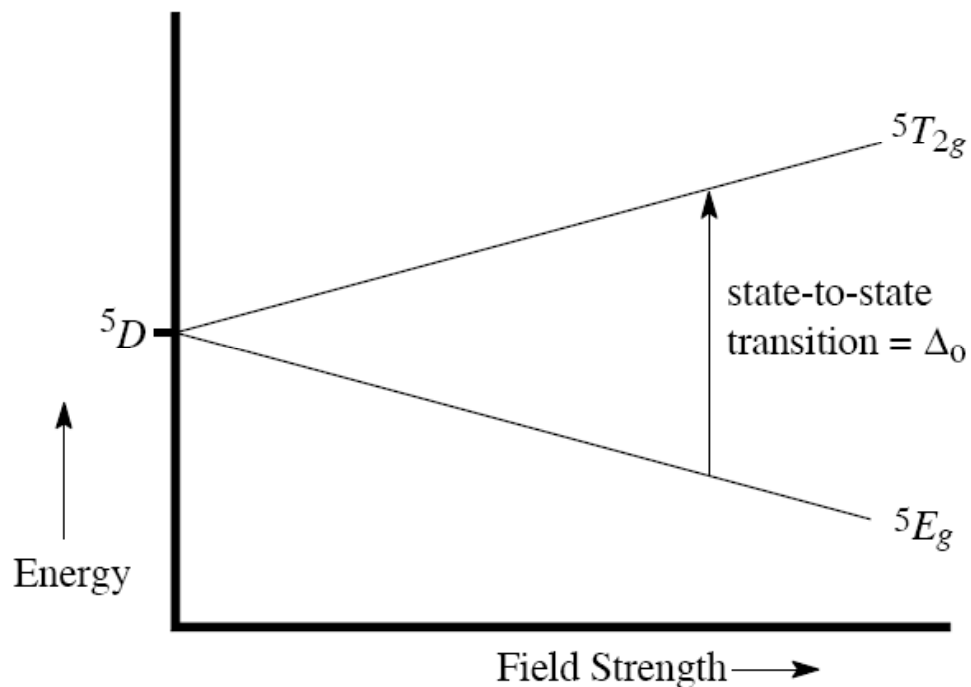
$$(dxy)^1 (dyz)^0 (dxz)^1 (e_g)^2$$

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

- 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 ($h\nu$) 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.



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

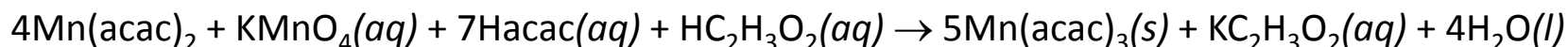
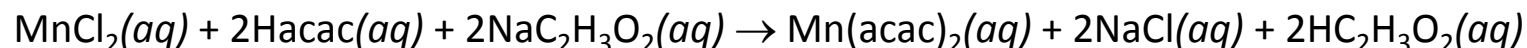


deep purple

- 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.

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).



- 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).

