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 $\text{Mn}^{3+}$ 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 ($e_g = dx^2-y^2, dz^2$).

- 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 $\Delta_o$ 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 $+3/5 \Delta_o (+6Dq)$ while the energy of each of the three $t_{2g}$ orbitals falls by $-2/5 \Delta_o (-4Dq)$.

• 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 $\Delta_o$ 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 $\Delta_o$ 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, $\Delta_o$.

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

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

- 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.
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 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]$4s^23d^5$, and typically shows positive oxidations states of +2, +3, and +7, all of which are seen in this experiment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation State</th>
<th>Configuration</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl$_2$.4$\text{H}_2$O</td>
<td>Mn(II)</td>
<td>[Ar]$3d^5$</td>
<td>pale pink</td>
</tr>
<tr>
<td>Mn(acac)$_3$</td>
<td>Mn(III)</td>
<td>[Ar]$3d^4$</td>
<td>lustrous dark brown</td>
</tr>
<tr>
<td>KMnO$_4$</td>
<td>Mn(VII)</td>
<td>[Ar]</td>
<td>deep purple</td>
</tr>
</tbody>
</table>

- Pale color of MnCl$_2$.4H$_2$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 KMnO₄ 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).

\[
\text{MnCl}_2(aq) + 2\text{Hacac}(aq) + 2\text{NaC}_2\text{H}_3\text{O}_2(aq) \rightarrow \text{Mn(acac)}_2(aq) + 2\text{NaCl}(aq) + 2\text{HC}_2\text{H}_3\text{O}_2(aq)
\]

\[
4\text{Mn(acac)}_2 + \text{KMnO}_4(aq) + 7\text{Hacac}(aq) + \text{HC}_2\text{H}_3\text{O}_2(aq) \rightarrow 5\text{Mn(acac)}_3(s) + \text{KC}_2\text{H}_3\text{O}_2(aq) + 4\text{H}_2\text{O}(l)
\]
• The ligand acetylacetonate (acac) is the anion of acetylacetone (aka 2,4-pentanediione; 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).