Mn(acac)$_3$ Synthesis

- Manganese ($Z = 25$) has a valence configuration $3d^54s^2$, 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>Charge</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl$_2$·4H$_2$O</td>
<td>Mn(II)</td>
<td>pale pink</td>
</tr>
<tr>
<td>Mn(acac)$_3$</td>
<td>Mn(III)</td>
<td>lustrous dark brown</td>
</tr>
<tr>
<td>KMnO$_4$</td>
<td>Mn(VII)</td>
<td>deep purple</td>
</tr>
</tbody>
</table>

- Pale color of MnCl$_2$·4H$_2$O is due to the absence of any same-spin (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 charge transfer transition with high molar absorptivity.

- The ligand (acac) in the product is the anion of acetylacetone, 2,4-pentanedione, CH$_3$COCH$_2$COCH$_3$, Hacac.

- Mn(acac)$_3$ has octahedrally coordinated Mn$^{3+}$ ($D_3 \cong O_h$).
In the octahedral environment of three acac ligands, the five-fold degeneracy among $d$ orbitals in $\text{Mn}^{3+}$ is lifted.

- To a first approximation, the ligand field is octahedral ($O_h$), 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 ($e_g = d_{x^2-y^2}, d_{z^2}$).
- The $t_{2g}$ orbitals point between ligands, but the $e_g$ orbitals point at ligands, so the $t_{2g}$ set is stabilized and the $e_g$ is destabilized relative to the energy of a hypothetical spherical octahedral field.


$d$-Subshell Splitting in an Octahedral Field - cont.

- 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 $\Delta_0$ or $10Dq$ between the two sets of $d$ orbitals.

  \[
  \Delta_0 = 10Dq
  \]

  \[
  e_g
  \]

  \[
  +3/5\Delta_0 = +6Dq
  \]

  \[
  t_{2g}
  \]

  \[
  -2/5\Delta_0 = -4Dq
  \]

- 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 (sometimes called the barycenter).
  - The energy of each of the two orbitals of the $e_g$ set rises by $+3/5\Delta_0 = +6Dq$ while the energy of each of the three $t_{2g}$ orbitals falls by $-2/5\Delta_0 = -4Dq$. This results in no net energy change for the system; i.e.,
    \[
    \Delta E = E(e_g) + E(t_{2g}) = (2)(+3/5\Delta_0) + (3)(-2/5\Delta_0)
    \]
    \[
    = (2)(+6Dq) + (3)(-4Dq)
    \]
    \[
    = 0
    \]

- The magnitude of $\Delta_0$ 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 $\Delta_0$ 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, $\Delta_0$.
  - 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 $t_{2g}^3e_g^1$, and the low-spin state is $t_{2g}^4e_g^0$.

- Mn(acac)$_3$ is a weak-field/high-spin case ($t_{2g}^3e_g^1$).
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 $^5T_{2g} = t_{2g}^2 e_g^2$

![Diagram of state splitting](image)

• The $^5E_g$ ground state is doubly-degenerate, because there are two ways of placing the $e_g^1$ electron:
  \[
  (t_{2g})^3 (d_{x^2-y^2})^1 (d_{z^2})^0 \\
  (t_{2g})^3 (d_{x^2-y^2})^0 (d_{z^2})^1
  \]

• The $^5T_{2g}$ excited state is triply degenerate, because there are three ways of placing the vacant orbital:
  \[
  (d_{xy})^1 (d_{yz})^1 (d_{xz})^0 (e_g)^2 \\
  (d_{xy})^1 (d_{yz})^0 (d_{xz})^1 (e_g)^2 \\
  (d_{xy})^0 (d_{yz})^1 (d_{xz})^1 (e_g)^2
  \]

• $^5E_g$ state is paramagnet 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 energy of this transition occurs at ~500 nm, removing red-orange light and transmitting green light.

- The $^5E_g \rightarrow ^5T_{2g}$ gives rise to a single absorption band in the visible spectrum at ~500 nm.
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. $\left(t_{2g}\right)^3 \left(d_{x^2-y^2}\right)^1 \left(d_{z^2}\right)^0$ or $\left(t_{2g}\right)^3 \left(d_{x^2-y^2}\right)^0 \left(d_{z^2}\right)^1$
  - 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.
Synthetic Procedure

- Two-step preparation:

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

\[
4\text{Mn(acac)}_2 + \text{KMnO}_4(aq) + 7\text{Hacac}(aq) + \text{HC}_2\text{H}_3\text{O}_2(aq) \rightarrow 5\text{Mn(acac)}_3(s) + \text{KC}_2\text{H}_3\text{O}_2(aq) + 4\text{H}_2\text{O}(l)
\]

- Crude product is obtained by chilling the final mixture.

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

- Procedure notes:
  1. Make certain that all KMnO\textsubscript{4} is dissolved before adding to the solution in the second step.
  2. Use filter paper /Büchner funnel or Hirsh funnel for first crude product collection (not sintered glass).
  3. Filter benzene solution through a sintered glass filter that is already discolored brown.
  4. Discard all solutions (esp., benzene/petroleum ether mixture) in waste containers (nothing down the drain).