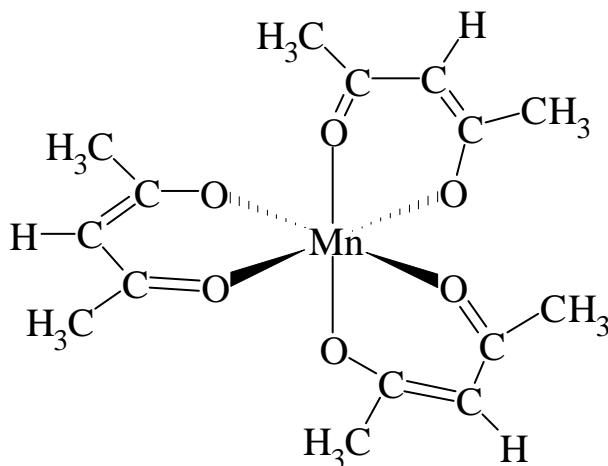


## Mn(acac)<sub>3</sub> Synthesis

- Manganese ( $Z = 25$ ) has a valence configuration  $3d^5 4s^2$ , and typically shows positive oxidation states of +2, +3, and +7, all of which are seen in this experiment.

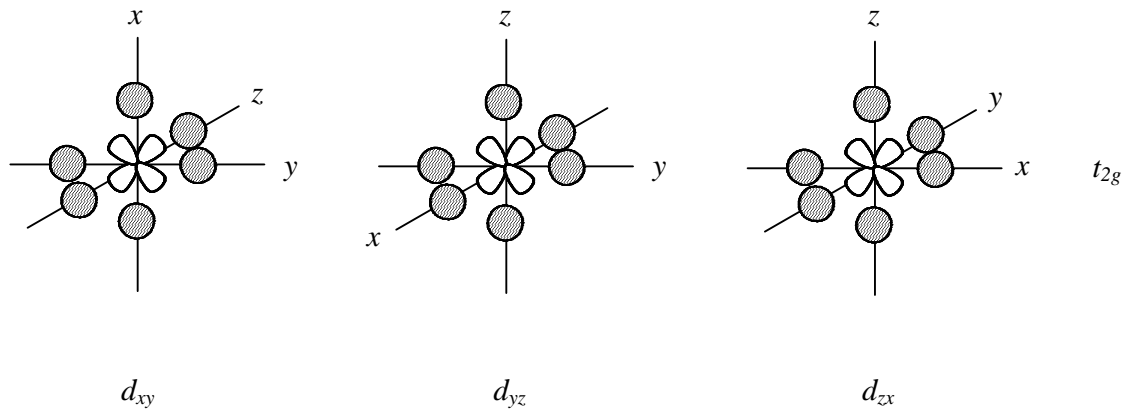
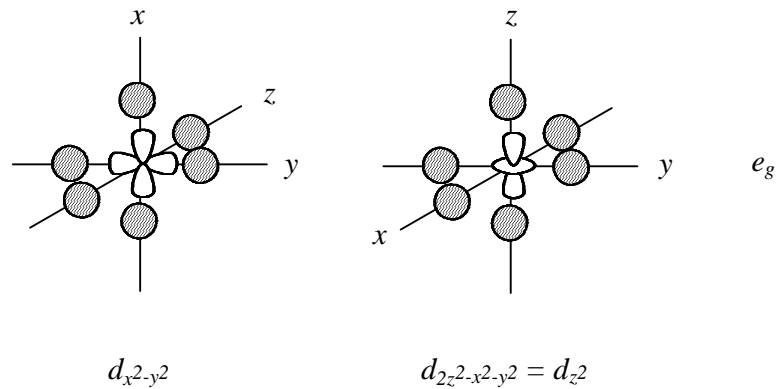
MnCl <sub>2</sub> ·4H <sub>2</sub> O	Mn(II)	pale pink
Mn(acac) <sub>3</sub>	Mn(III)	lustrous dark brown
KMnO <sub>4</sub>	Mn(VII)	deep purple

- Pale color of MnCl<sub>2</sub>·4H<sub>2</sub>O is due to the absence of any same-spin (spin-allowed)  $d-d$  transitions for a  $d^5$  high-spin complex.
  - Mn(acac)<sub>3</sub> is green by transmitted light, owing to a single broad  $d-d$  transition at about 500 nm.
  - KMnO<sub>4</sub> 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<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>, Hacac.
  - Mn(acac)<sub>3</sub> has octahedrally coordinated Mn<sup>3+</sup> ( $D_3 \approx O_h$ ).



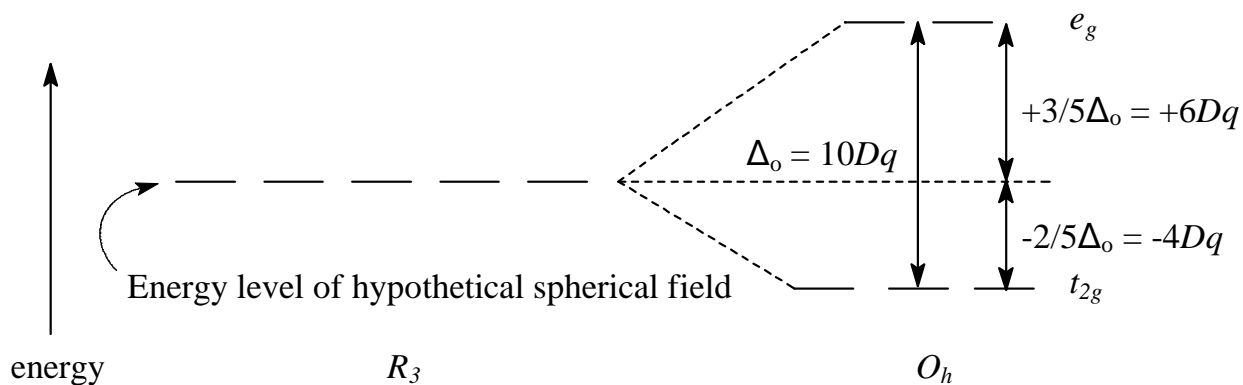
## ***d*-Subshell Splitting in an Octahedral Field**

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



- 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).

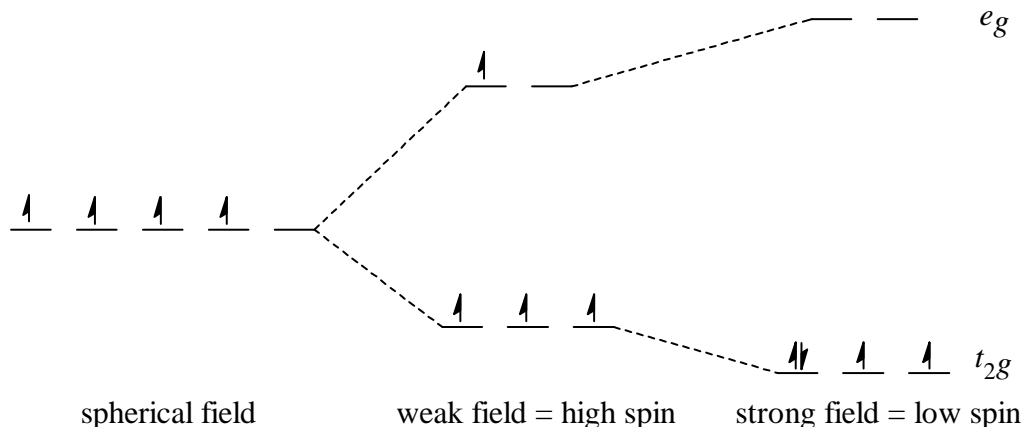
- The energy of each of the two orbitals of the  $e_g$  set rises by  $+3/5\Delta_o = +6Dq$  while the energy of each of the three  $t_{2g}$  orbitals falls by  $-2/5\Delta_o = -4Dq$ . This results in no net energy change for the system; i.e.,

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

- The magnitude of  $\Delta_o$  depends upon both the metal ion and the attaching ligands.

## High-Spin and Low-Spin Configurations

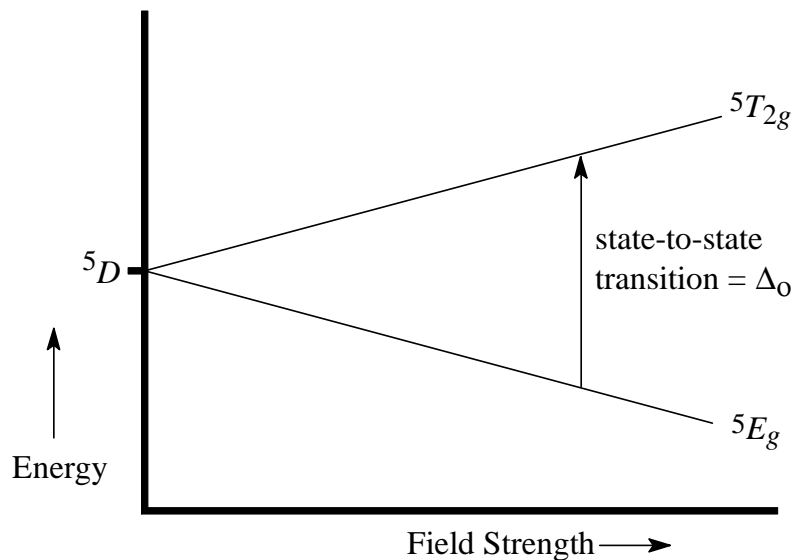
- In an octahedral complex, electrons fill the  $t_{2g}$  and  $e_g$  orbitals in an aufbau manner, but for configurations  $d^4 - d^7$  there are two possible filling schemes depending on the magnitude of  $\Delta_o$  relative to the mean pairing energy,  $P$ .
  - A high spin configuration avoids pairing 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  $t_{2g}^3 e_g^1$ , and the low-spin state is  $t_{2g}^4 e_g^0$ .



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

## 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  $^5T_{2g} = t_{2g}^2 e_g^2$



- The  $^5E_g$  ground state is doubly-degenerate, because there are two ways of placing the  $e_g^1$  electron:

$$\begin{aligned} &(t_{2g})^3 (d_{x^2-y^2})^1 (d_{z^2})^0 \\ &(t_{2g})^3 (d_{x^2-y^2})^0 (d_{z^2})^1 \end{aligned}$$

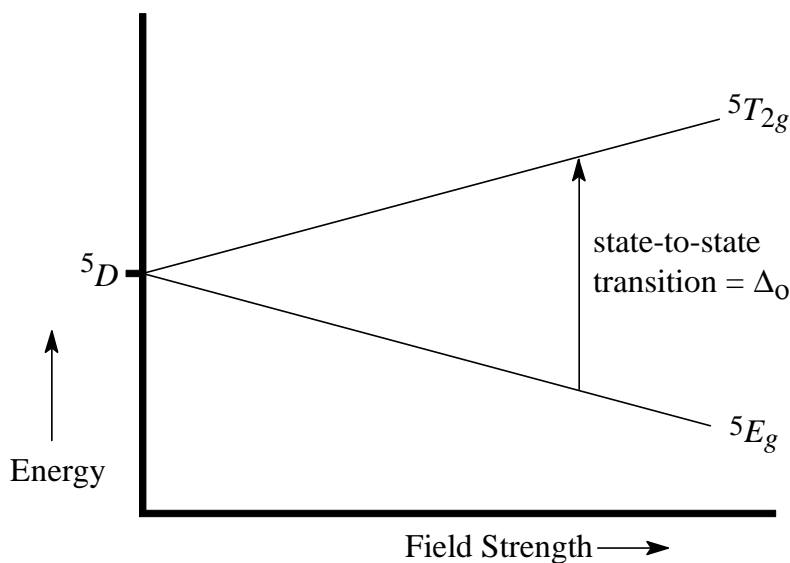
- The  $^5T_{2g}$  excited state is triply degenerate, because there are three ways of placing the vacant orbital:

$$\begin{aligned} &(d_{xy})^1 (d_{yz})^1 (d_{xz})^0 (e_g)^2 \\ &(d_{xy})^1 (d_{yz})^0 (d_{xz})^1 (e_g)^2 \\ &(d_{xy})^0 (d_{yz})^1 (d_{xz})^1 (e_g)^2 \end{aligned}$$

- $^5E_g$  state is paramagnet from four unpaired electrons.

## Absorption Spectra and State-to-State Transitions

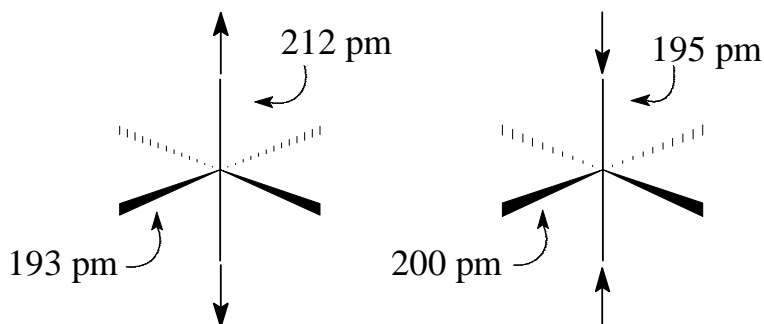
- When a transition metal complex absorbs visible light, the energy absorbed ( $h\nu$ ) causes a transition from the ground state to an excited state, corresponding to a change in electronic configuration.
- For a high-spin  $d^4$  complex like  $\text{Mn}(\text{acac})_3$ , only one same-spin state-to-state transition is possible:  ${}^5E_g \rightarrow {}^5T_{2g}$ .



- The energy of this transition occurs at  $\sim 500$  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  $\sim 500$  nm.

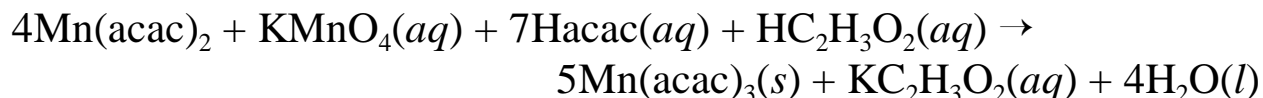
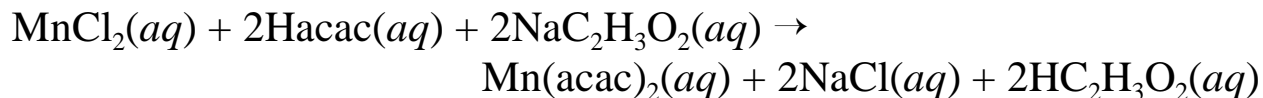
## Jahn-Teller Distortion

- ☛ Jahn-Teller Theorem: For any nonlinear system in a degenerate state, a distortion will occur that will lift the degeneracy.
- $\text{Mn}(\text{acac})_3$  has a  ${}^5E_g$  ground state, which has an imbalance in the filling of electrons in orbitals that point directly at ligands.  
 $(t_{2g})^3 (d_{x^2-y^2})^1 (d_{z^2})^0$  or  $(t_{2g})^3 (d_{x^2-y^2})^0 (d_{z^2})^1$ 
  - 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.



## Synthetic Procedure

- Two-step preparation:



- 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  $\text{KMnO}_4$  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).