Stereoisomerism

❑ Octahedral Complexes

MA$_5$B Case:
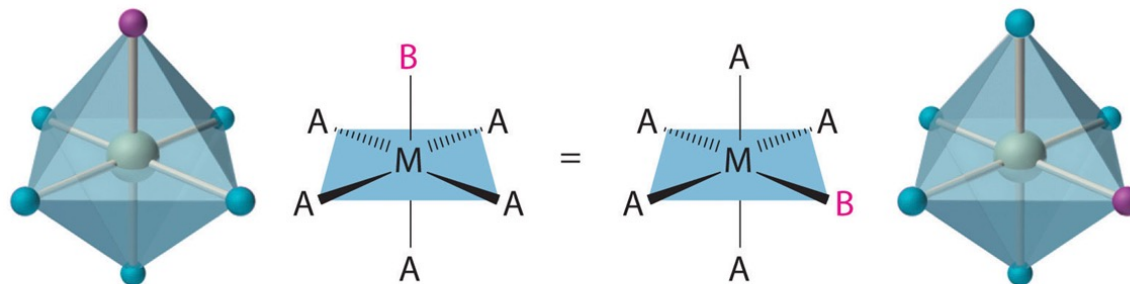
MA$_5$B octahedral complex

MA$_4$B$_2$ Case:
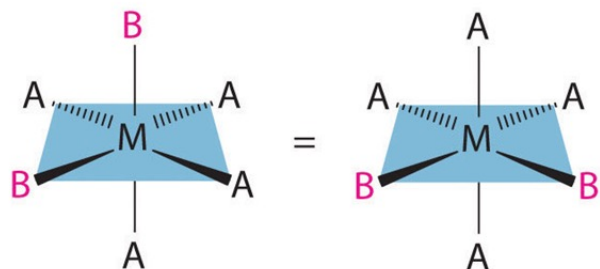
MA$_4$B$_2$ octahedral complex, *cis* isomer
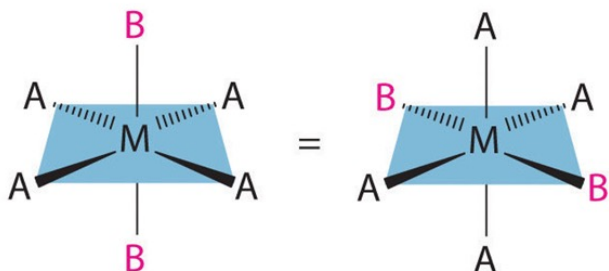
MA$_4$B$_2$ octahedral complex, *trans* isomer
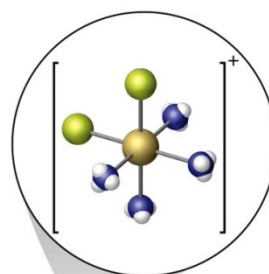
cis-tetraamminedichlorocobalt(III) chloride

cis-[Co(NH$_3$)$_4$Cl$_2$]Cl
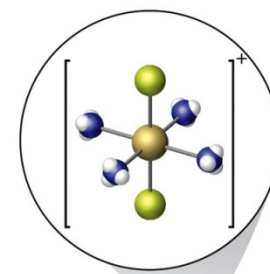
trans-tetraamminedichlorocobalt(III) chloride
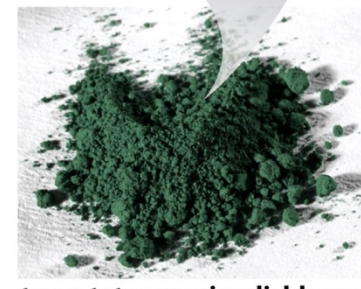
trans-[Co(NH$_3$)$_4$Cl$_2$]Cl
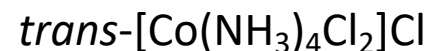
Stereoisomerism

❑ Octahedral Complexes

MA$_3$B$_3$ Case: **facial and meridional isomers**
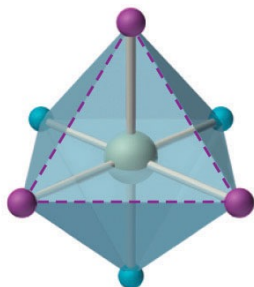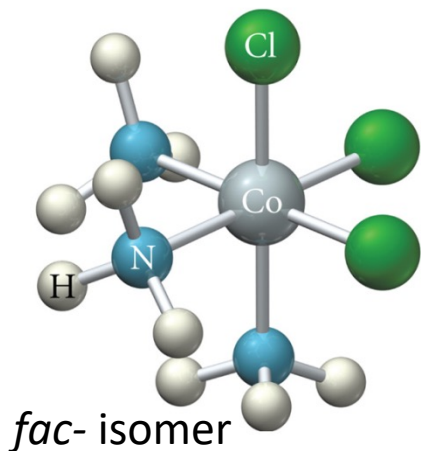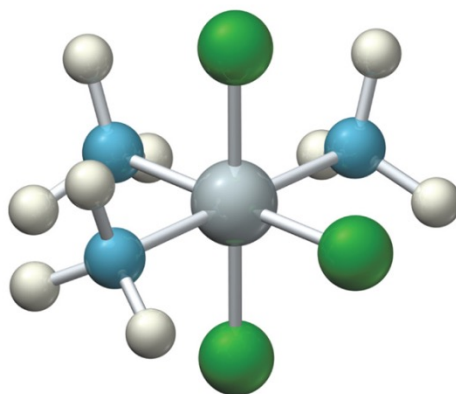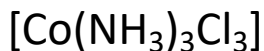
MA$_3$B$_3$ octahedral complex, *fac* isomer
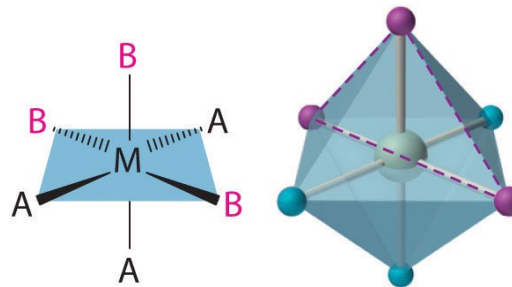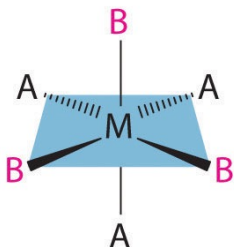
MA$_3$B$_3$ octahedral complex, *mer* isomer

❑ *fac*-isomers have 3 identical ligands on one triangular face
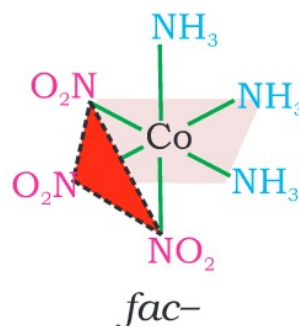❑ *mer*-isomers have 3 identical ligands in a plane bisecting the molecule

fac- isomer   *mer*- isomer

[Co(NH$_3$)$_3$Cl$_3$]

fac–   *mer*–

[Co(NH$_3$)$_3$(NO$_2$)$_3$]
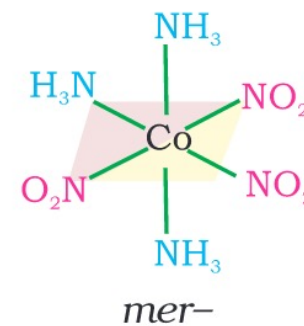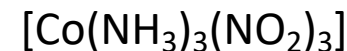
Bonding in Coordination Compounds

❑ Valence Bond Theory

- ❑ Proposed by Linus Pauling (Nobel Prize 1954) for nature of chemical bonds and elucidation of structure of complex systems.

- ❑ The model utilizes hybridization of metal valence orbitals to account for the observed structures and magnetic properties of complexes. *(n-1)d, ns and np undergo hybridization* to give hybridized orbitals. *An empty hybrid orbital on the metal center can accept a pair of electrons* from a ligand to form a σ-bond.

Vacant metal hybrid atomic orbital   Occupied ligand atomic orbital   Coordinate covalent bond

$[Cr(NH_3)_6]^{3+}$

$[Ni(CN)_4]^{2-}$
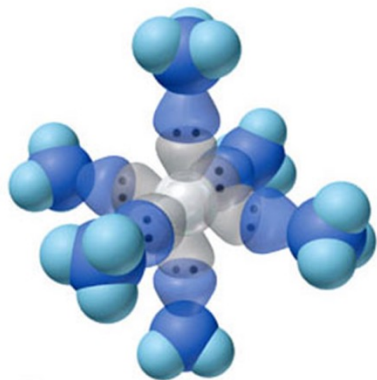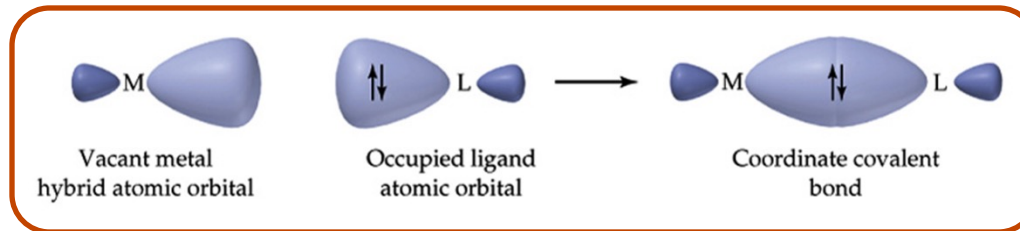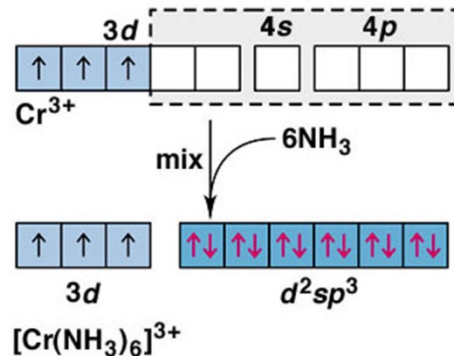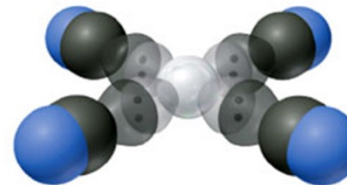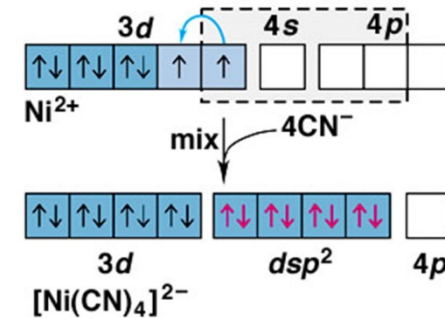
Valence Bond Theory: Limitations

[PtCl$_4$]$^{2-}$ which is diamagnetic – d^8 square planar

[NiCl$_4$]$^{2-}$ which is paramagnetic – d^8 tetrahedral

❑ **Limitations of Valence Bond Theory**

❑ **Electronic and spectroscopic properties (color) of coordination complexes is not explained.**

❑ **Quantitative interpretation of magnetic data is impossible.**

❑ **Whether a complex of coordination number four is square planar or tetrahedral cannot be exactly predicted.**

❑ **Effect of ligands of different donor ability is neglected or high-spin and low-spin complexes cannot be distinguished.**

Crystal Field Theory (CFT)

❑ **Assumptions/Features of CFT**

❑ **The interaction between the metal ion and the ligand is assumed to be purely electrostatic (ionic) in nature.**

❑ **The ligands are treated as point charges.**

❑ **Examines the energetics (splitting) of d-orbitals in certain geometries.**

❑ **Nature of Interaction between Metal and Ligand**

❑ **The approaching ligand is considered to be a point charge repelled by the electrons in a metal's d-orbitals.**

❑ **Therefore, the d orbitals on a metal in a complex would not remain degenerate.**

❑ **Those that point toward ligands would be higher in energy than those that do not.**

d-Orbitals
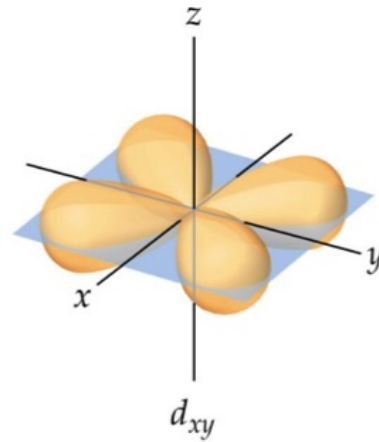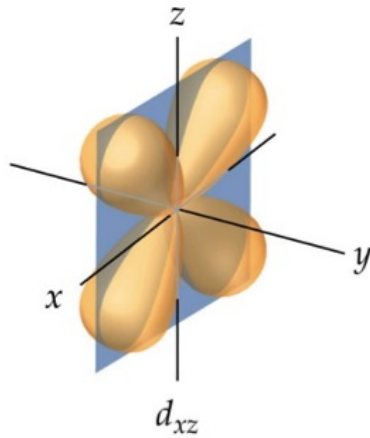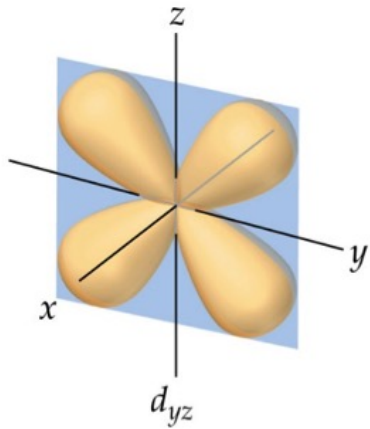
These three atomic orbitals point *in between the axes*
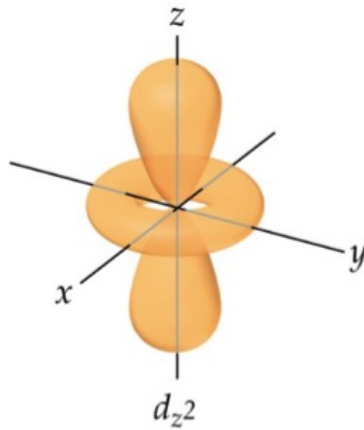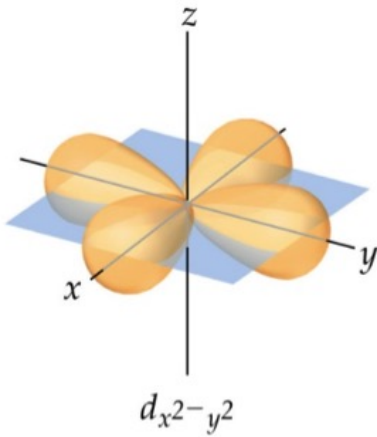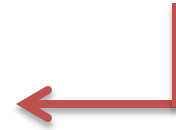
These two atomic orbitals point **along the axes**

Metal Ion in an Octahedral Field

- **The corners of octahedron are assumed to be placed on the axes.**
- **The ligands approach along the axes and occupy the corners**
- **Electrons in the *d* orbitals lying along the axes are repelled the most, while those lying in between the axes are less repelled**
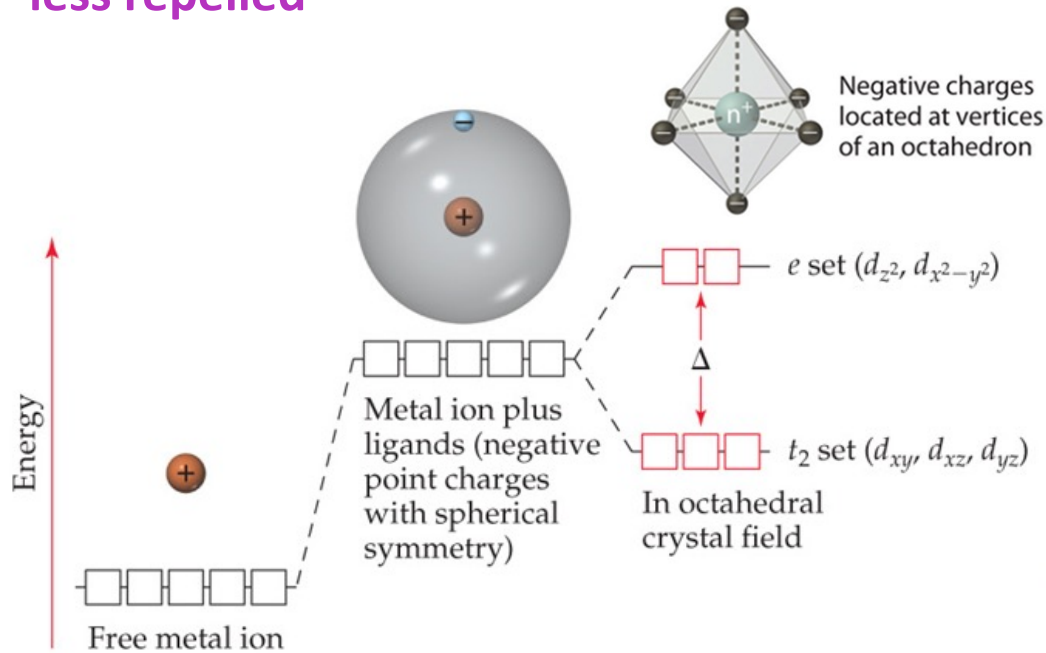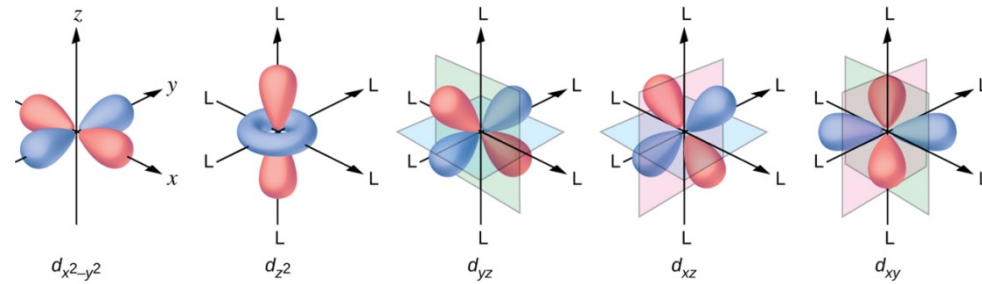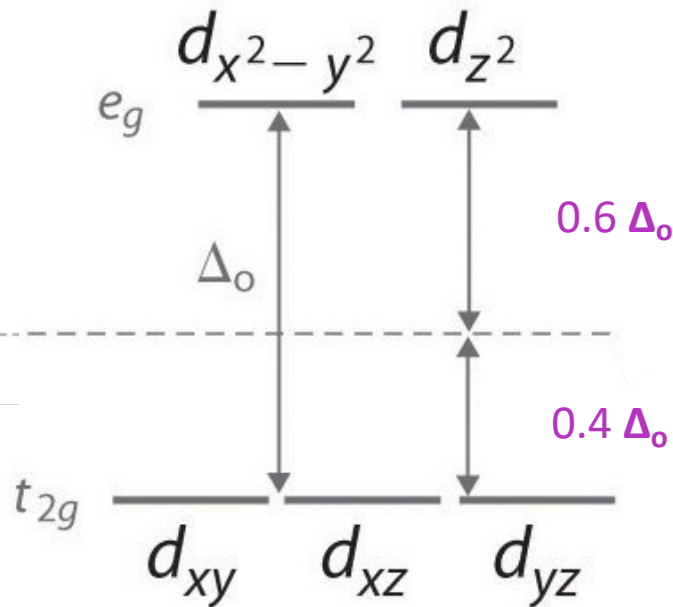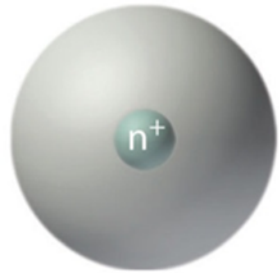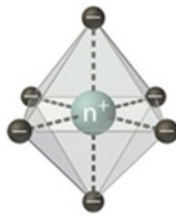
$d_{x^2-y^2}$ d_{z^2} d_{yz} d_{xz} d_{xy}

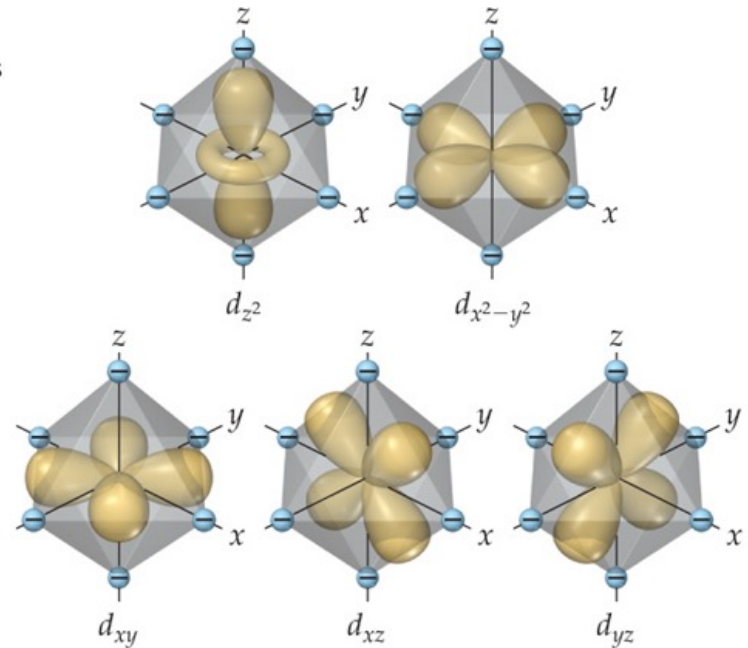Negative charges located at vertices of an octahedron

Metal ion plus ligands (negative point charges with spherical symmetry)

In octahedral crystal field

e set $(d_{z^2}, d_{x^2-y^2})$

Δ

t_2 set (d_{xy}, d_{xz}, d_{yz})

Energy

Free metal ion

d_{z^2} $d_{x^2-y^2}$

d_{xy} d_{xz} d_{yz}

Barycenter

❑ Δ_o = crystal field splitting parameter; The energy separation between the two levels is denoted by Δ_o or 10 D*q*.

❑ The higher energy set of orbitals (d_{z2} and d_{x2-y2}) are labeled as e_g and the lower energy set is labeled as t_{2g}. These notations are based on the symmetry of the orbitals.

❑ To maintain the average energy, the e_g orbitals need to be destabilized by 0.6 Δ_o (6 Dq) and the t_{2g} orbitals to be stabilized to the extent of 0.4 Δ_o (4 Dq)

The Complete Picture

Negative charges distributed uniformly over surface of a sphere

Negative charges located at vertices of an octahedron

Metal cation, M^{n+}

E

$d_{x^2-y^2}$ d_{z^2}

e_g

Δ_o

t_{2g} d_{xy} d_{xz} d_{yz}

e_g

Δ_o

t_{2g}

Electrostatic attractions $(+/-)$ considered

(a)

$d_{x^2-y^2}$ d_{z^2} d_{xy} d_{xz} d_{yz}

e_g orbitals go up in energy by $\frac{3}{5}\Delta_o$

t_{2g} orbitals go down in energy by $\frac{2}{5}\Delta_o$

(b)

Tetrahedral Field

d_{xy}
Tetrahedral
©NCSSM 2003

d_{yz}
Tetrahedral
©NCSSM 2003

d_{xz}
Tetrahedral
©NCSSM 2003

"t_2" set

$d_{x^2-y^2}$
Tetrahedral
©NCSSM 2003

d_{z^2}
Tetrahedral
©NCSSM 2003

"e" set

❑ **No orbitals directly pointing toward the ligands.**
❑ **The *e* orbitals point between the two ligands present at opposite corners of a cube (thereby being less effected than the t_2 orbitals).**
❑ **The t_2 orbitals lie half an edge of the cube from ligand and point more directly toward ligands (destabilized).**
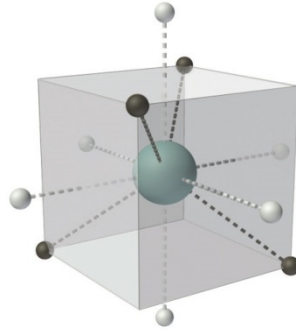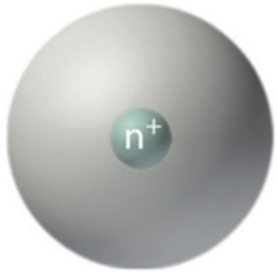
Tetrahedral Field
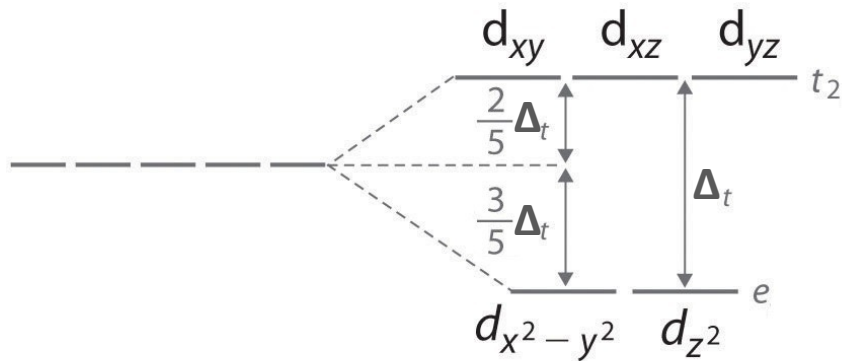
Spherical field   tetrahedral field
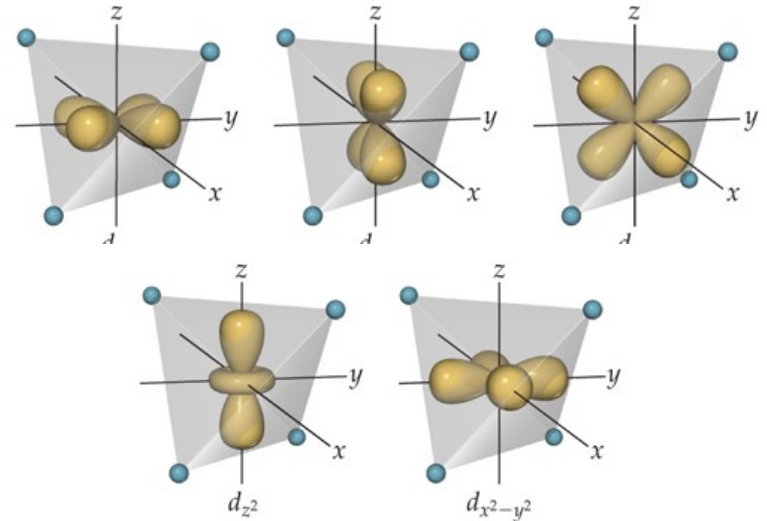
❑ **The crystal field splitting in the tetrahedral field is intrinsically smaller than in the octahedral field. For most purposes the relationship may be represented as $\Delta_t = 4/9 \ \Delta_o$**

Comparison of Octahedral and Tetrahedral Fields

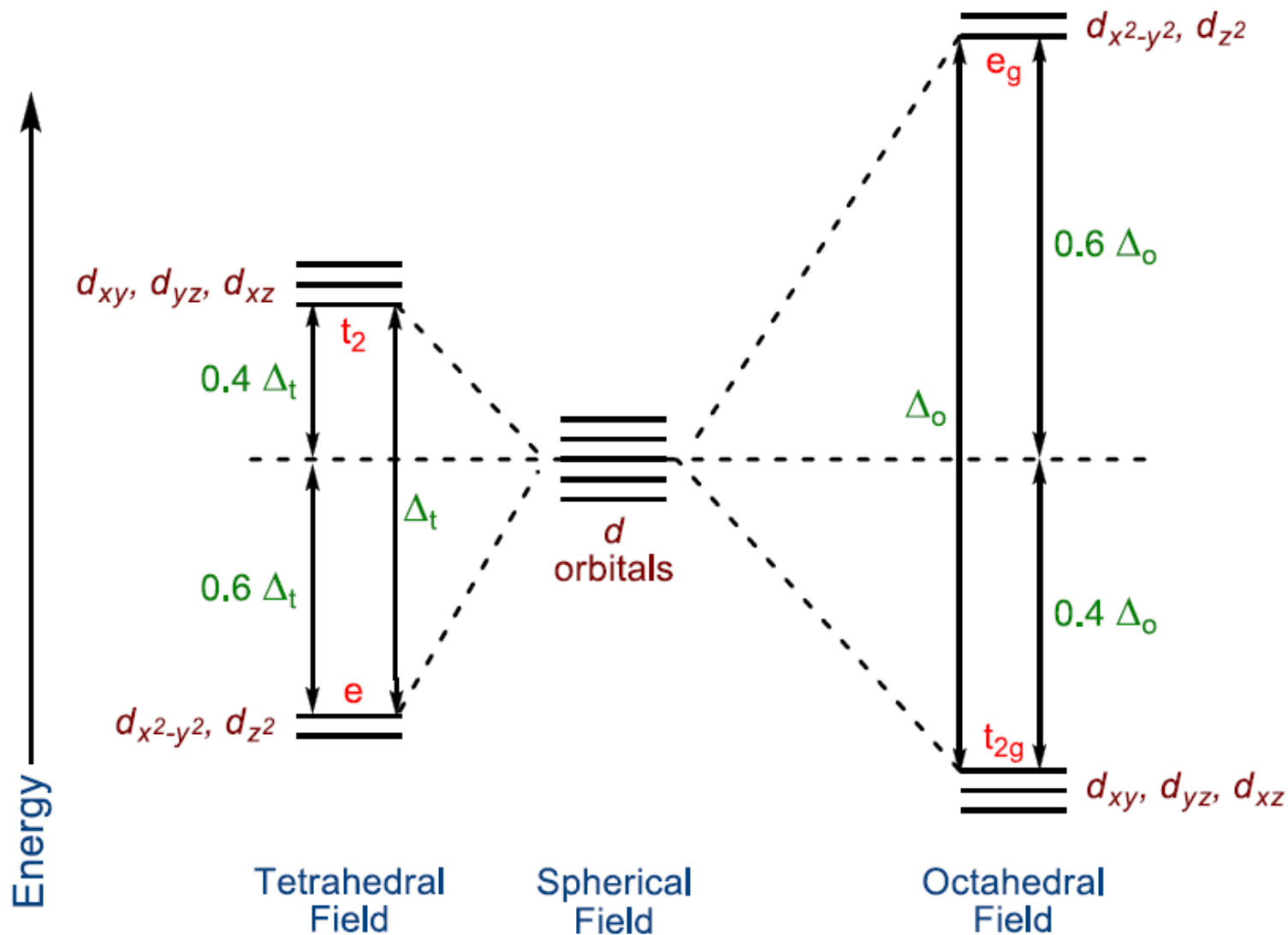# Determination of Δ

[Ti(H₂O)₆]³⁺

Blue, green, yellow absorbed; a mixture of violet and red light travel to the eye, solution appears purple

e⁻ jumps to higher level

Ground State
$t_{2g}^{1}e_{g}^{0}$

Excited State
$t_{2g}^{0}e_{g}^{1}$

Incoming λ   Absorbed λ   Transmitted λ
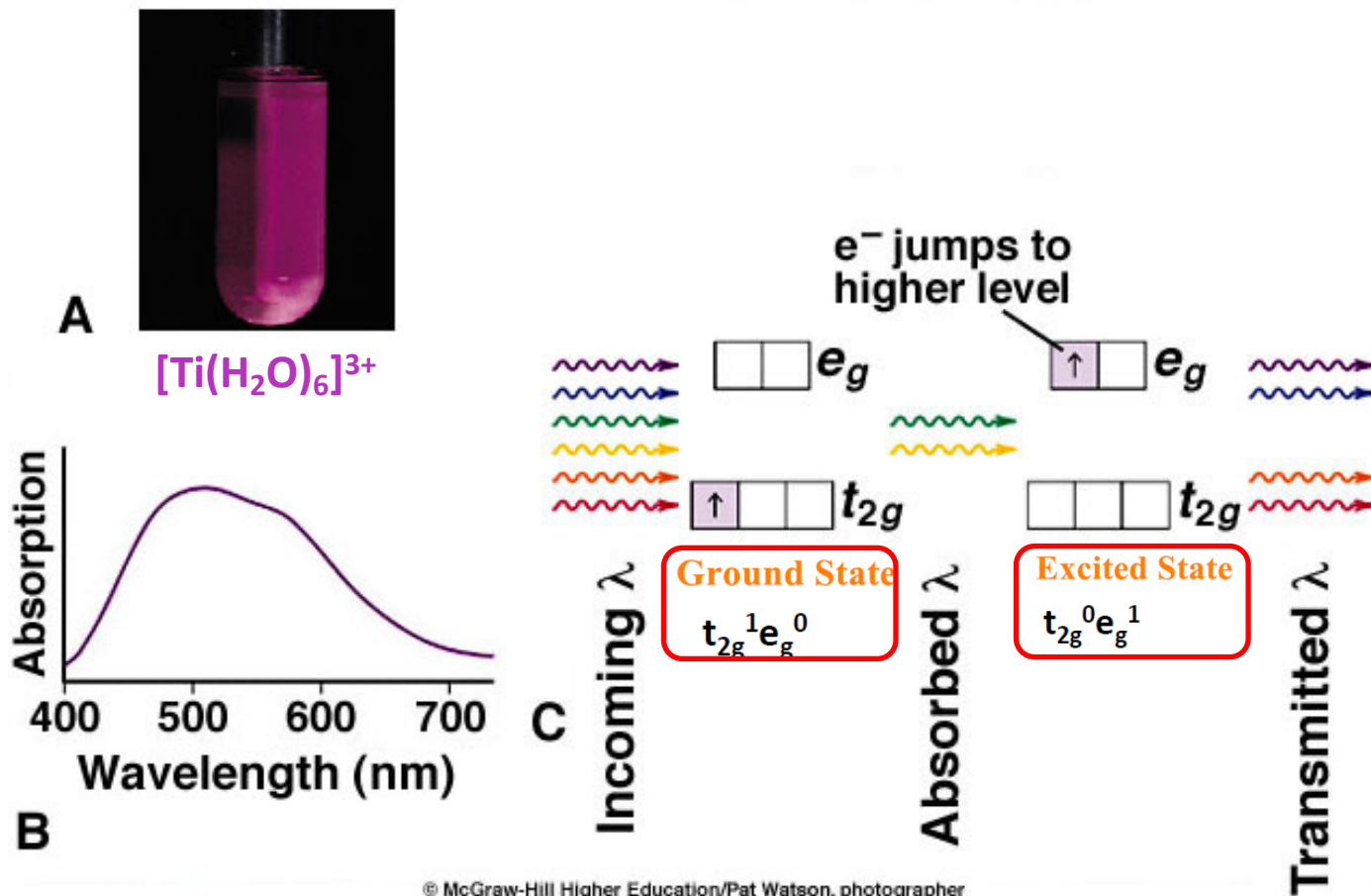
© McGraw-Hill Higher Education/Pat Watson, photographer

Determination of Δ

ground state   excited state

e_g

Δ_o $h\nu$

t_{2g}

Ground State   **Excited State**

$t_{2g}{}^1 e_g{}^0$ $t_{2g}{}^0 e_g{}^1$
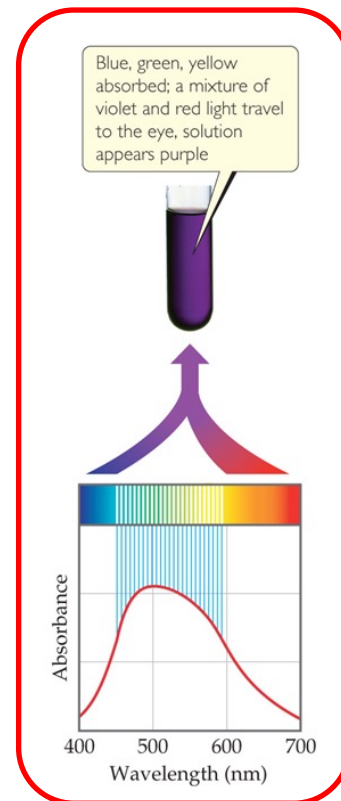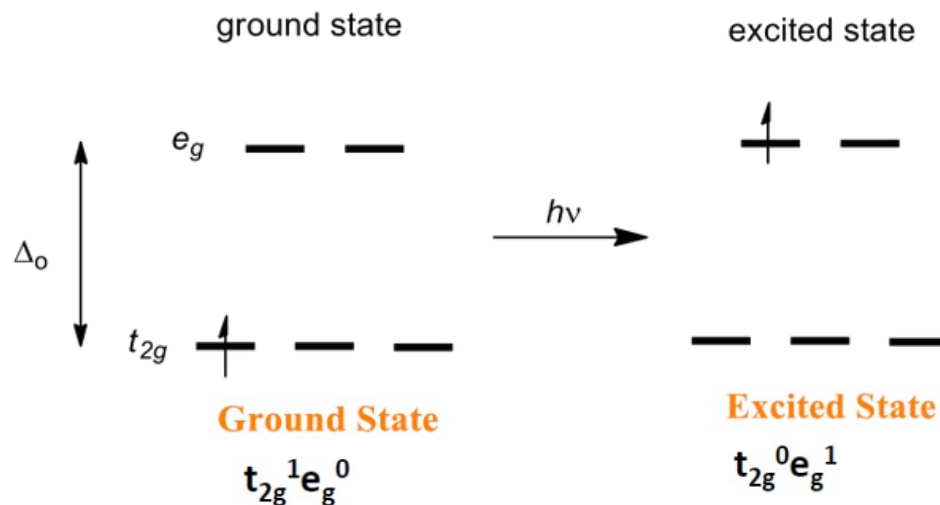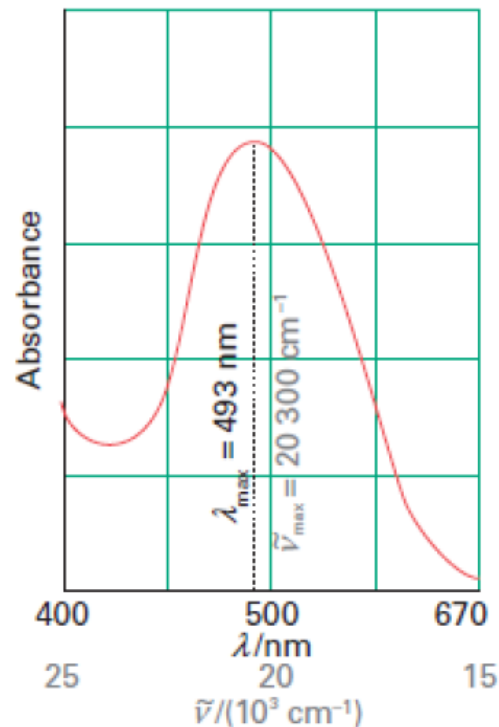
❑ **[Ti(H$_2$O)$_6$]$^{3+}$ is a d^1 complex. The single electron in the t$_{2g}$ orbitals absorb energy in the form of light and gets promoted to the e$_g$ orbitals to show it's purple color.**

❑ **For [Ti(H$_2$O)$_6$]$^{3+}$, this corresponds to 493 nm (Δ$_o$ = 20,300 cm^{-1} = 243 kJ/mol).**

❑ **For t$_{2g}{}^1$e$_g{}^0$ configuration:**
stabilization energy = 243 x 0.4 = 97 kJ/mol,
this extra stabilization due to the splitting of *d*-orbitals called
crystal field stabilization energy (CFSE).

octahedral
[M(H$_2$O)$_6$]$^{3+}$

e_g

$3/5\Delta_o$

$2/5\Delta_o$ Δ_o

t_{2g}

Ti^{3+}, d^1