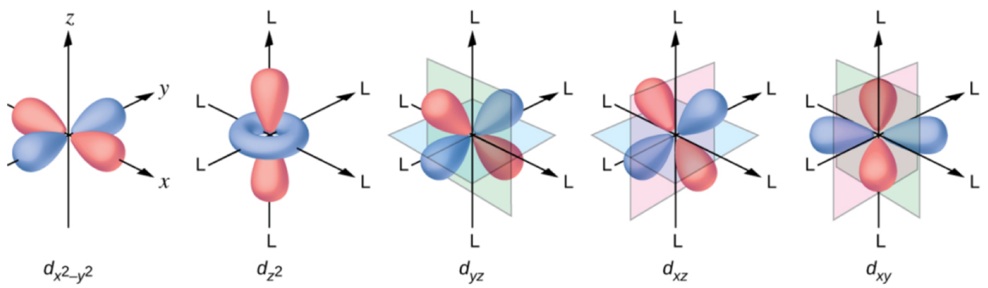
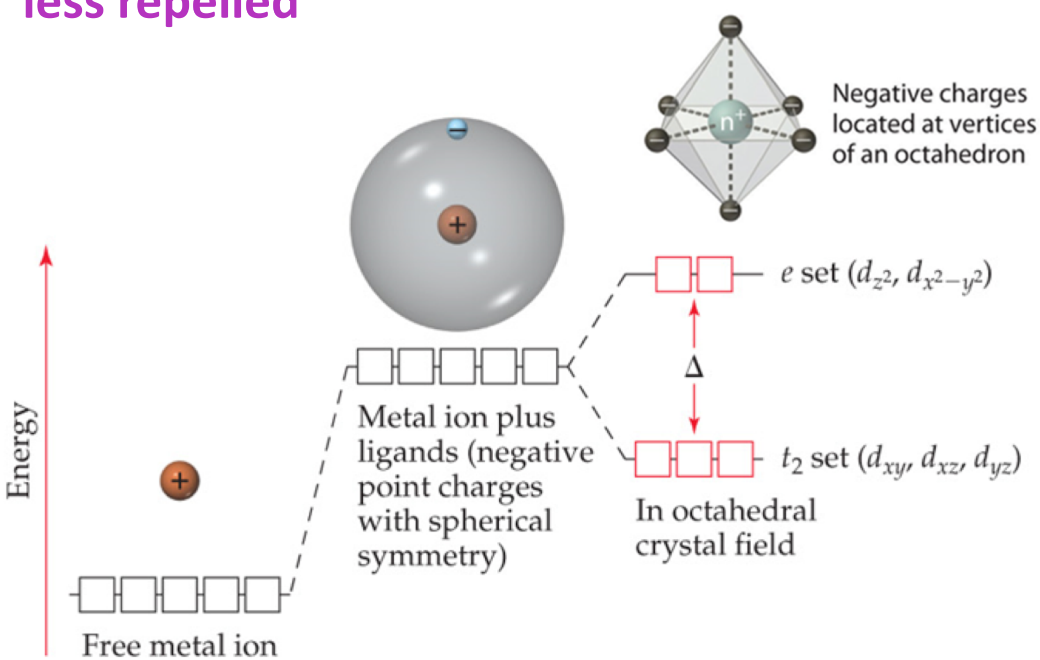
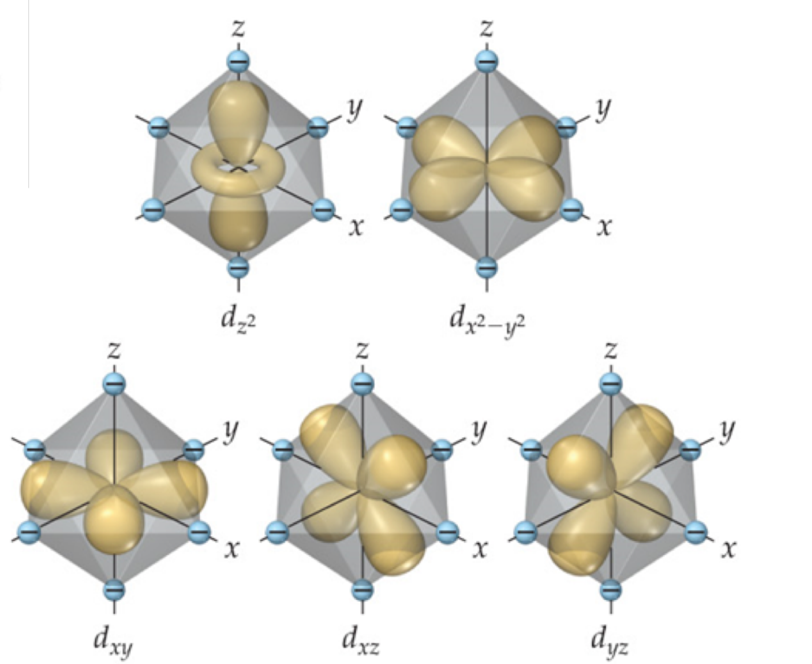
Metal Ion in an Octahedral Field

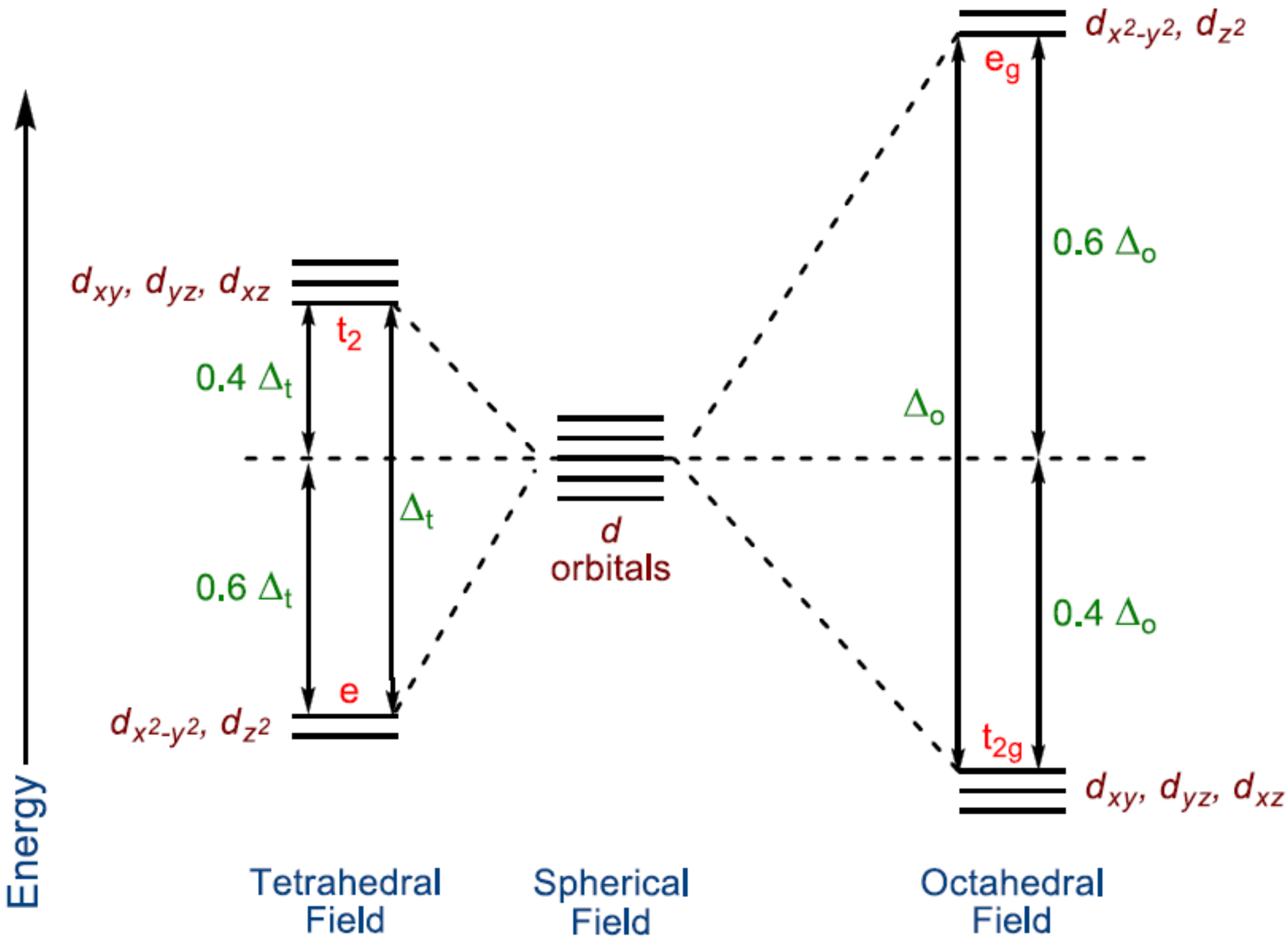
- ❑ The corners of octahedron are assumed to be placed on the axes.
- ❑ The ligands approach along the axes and occupy the corners
- ❑ Electrons in the *d* orbitals lying along the axes are repelled the most, while those lying in between the axes are less repelled



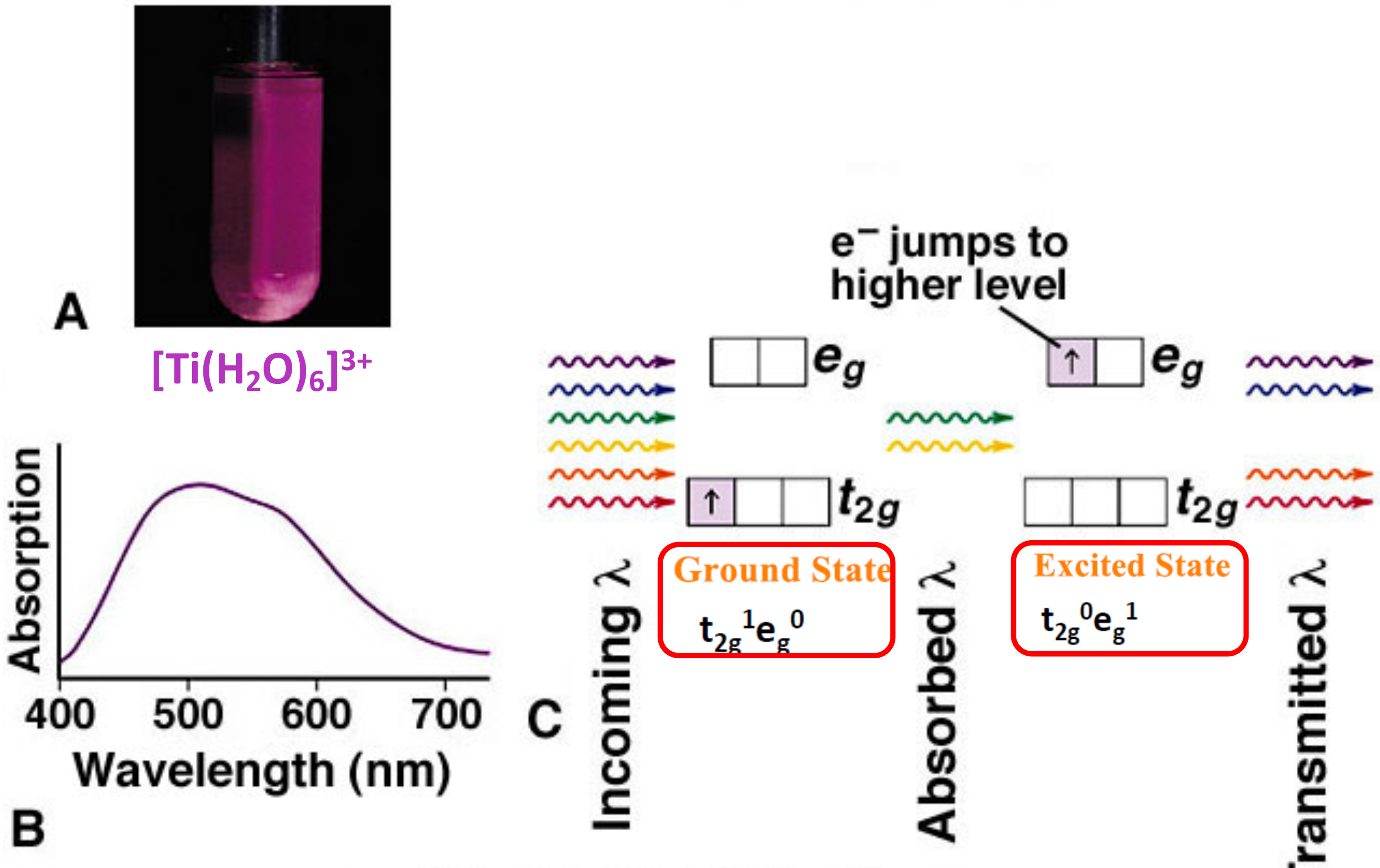


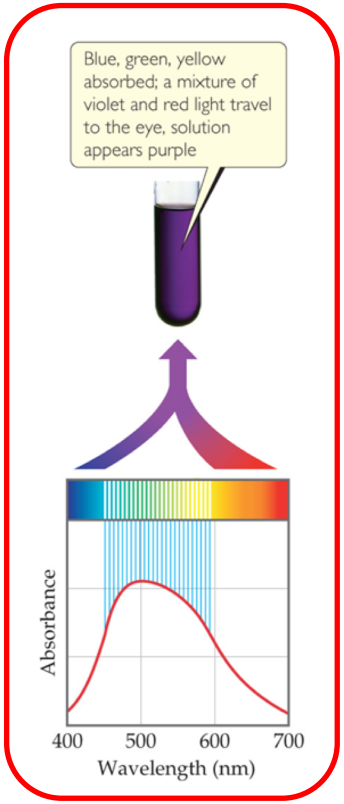


Comparison of Octahedral and Tetrahedral Fields



Determination of Δ



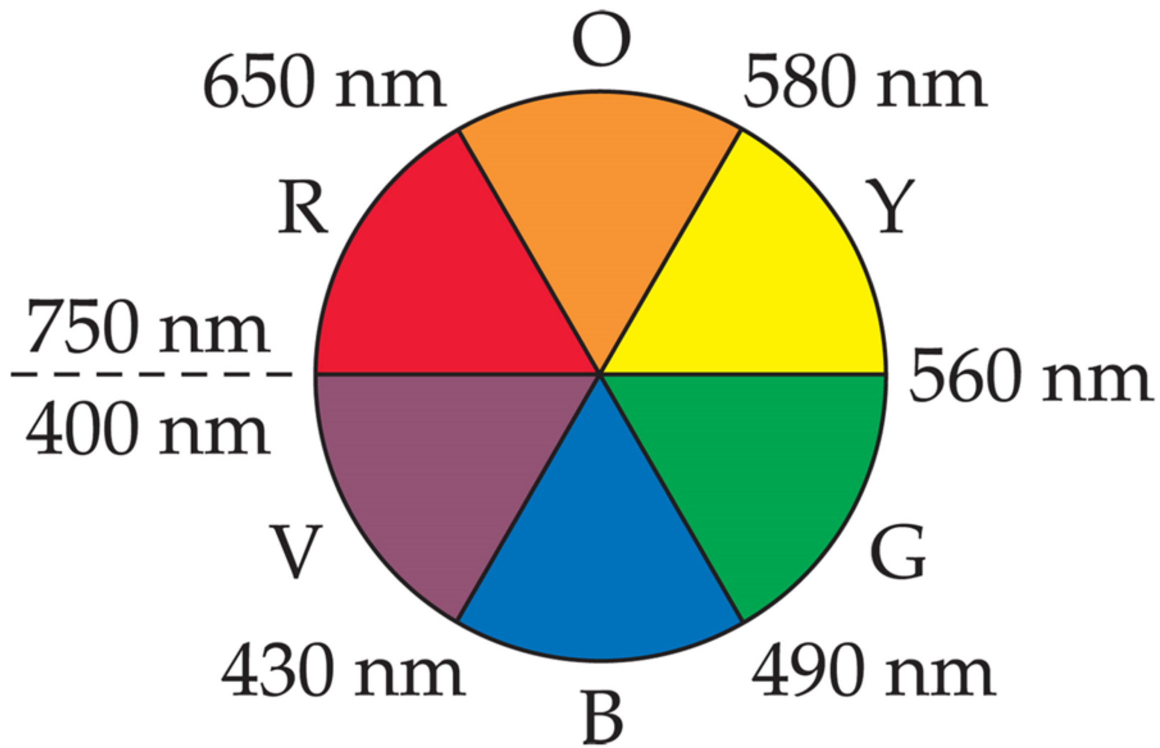


Δ is Relatable to Colour

- Complementary colour wheel.

  Absorb **Orange** See **Blue**

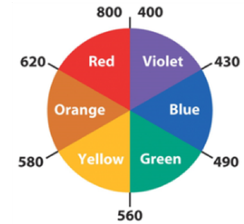
  Absorb **Red** See **Green**



Factors Influencing the Magnitude of Δ

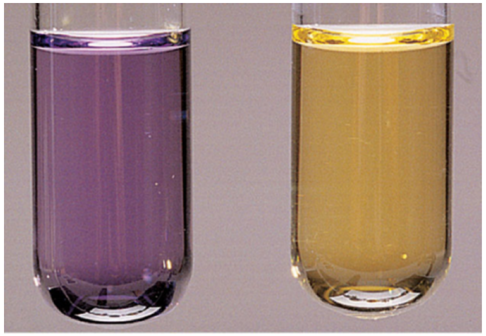
Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[TiF_6]^{3-}$	17 000	$[Fe(ox)_3]^{3-}$	14 100
$[Ti(OH_2)_6]^{3+}$	20 300	$[Fe(CN)_6]^{3-}$	35 000
$[V(OH_2)_6]^{3+}$	17 850	$[Fe(CN)_6]^{4-}$	33 800
$[V(OH_2)_6]^{2+}$	12 400	$[CoF_6]^{3-}$	13 100
$[CrF_6]^{3-}$	15 000	$[Co(NH_3)_6]^{3+}$	22 900
$[Cr(OH_2)_6]^{3+}$	17 400	$[Co(NH_3)_6]^{2+}$	10 200
$[Cr(OH_2)_6]^{2+}$	14 100	$[Co(en)_3]^{3+}$	24 000
$[Cr(NH_3)_6]^{3+}$	21 600	$[Co(OH_2)_6]^{3+}$	18 200
$[Cr(CN)_6]^{3-}$	26 600	$[Co(OH_2)_6]^{2+}$	9 300
$[MnF_6]^{2-}$	21 800	$[Ni(OH_2)_6]^{2+}$	8 500
$[Fe(OH_2)_6]^{3+}$	13 700	$[Ni(NH_3)_6]^{2+}$	10 800
$[Fe(OH_2)_6]^{2+}$	9 400	$[Ni(en)_3]^{2+}$	11 500

Factors Influencing the Magnitude of Δ



1. Higher oxidation states of the metal atom correspond to larger Δ.

Δ = 10,200 cm^{-1} for $[Co^{II}(NH_3)_6]^{2+}$ and 22,870 cm^{-1} for $[Co^{III}(NH_3)_6]^{3+}$
Δ = 32,200 cm^{-1} for $[Fe^{II}(CN)_6]^{4-}$ and 35,000 cm^{-1} for $[Fe^{III}(CN)_6]^{3-}$

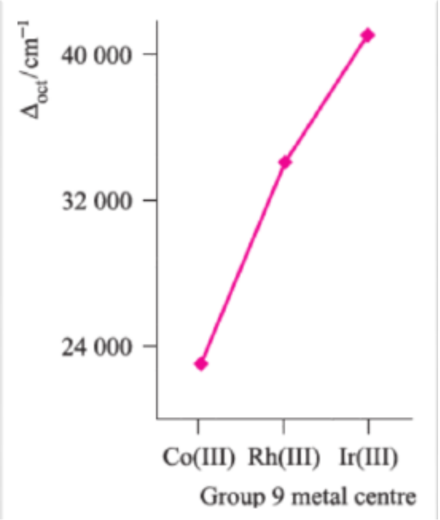


$[V(H_2O)_6]^{2+}$ $[V(H_2O)_6]^{3+}$

- ❑ **Higher ionic charge on the metal ion, pulls the ligands closer towards it and higher electrostatic repulsion results in larger splitting of *d*-orbitals**

2. In groups, heavier analogues have larger Δ.

For hexaammine complexes
$[M^{III}(NH_3)_6]^{3+}$: **Δ** = 22,870 cm^{-1} (Co)
34,100 cm-1(Rh)
41,200 cm-1(Ir)



- ❑ **Larger size of 4d and 5d orbitals results in stronger interactions with ligands.**
- ❑ **For larger metal ion, the ligands experience less steric crowding and thus approach closer. Thus results in stronger interaction and larger crystal field splitting.**

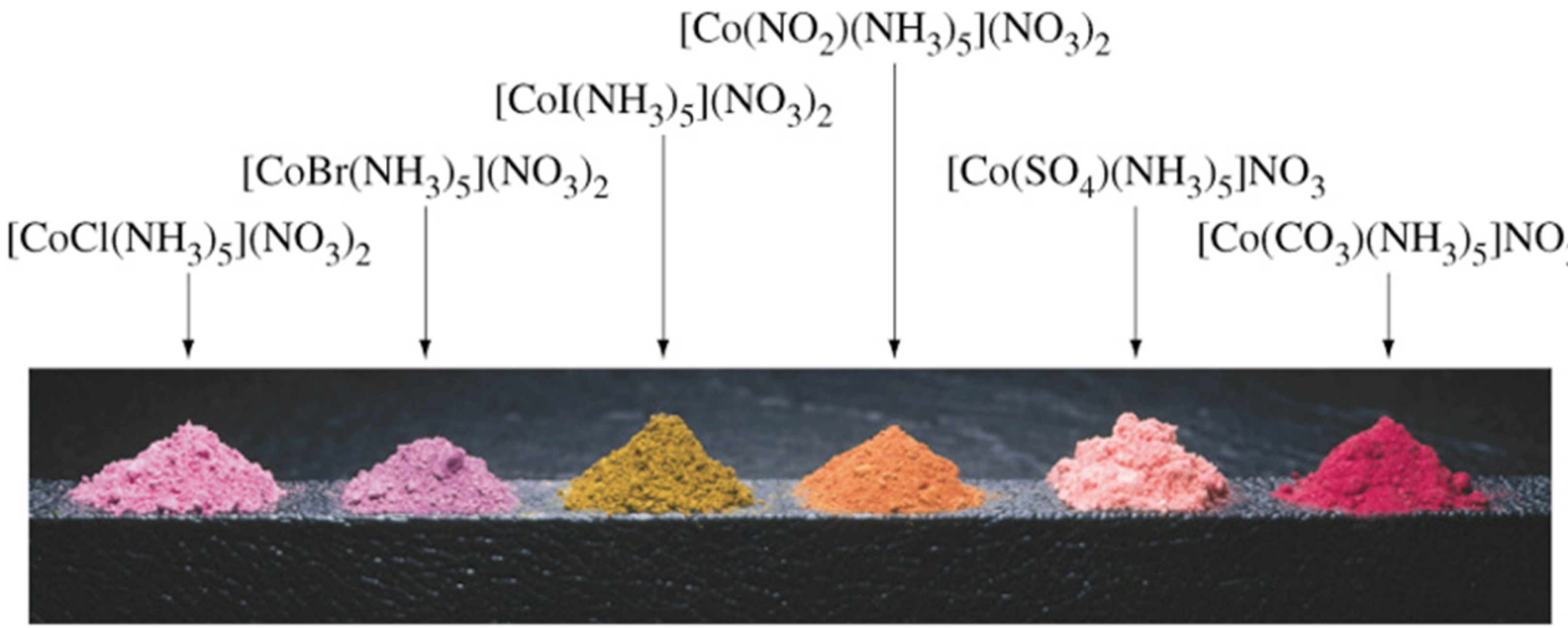
Factors Influencing the Magnitude of Δ

3. Coordination number/ Geometry has significant effect on Δ.

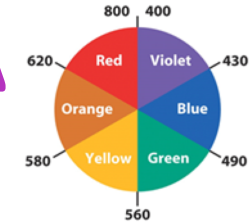
Tetrahedral complexes ML_4 have smaller **Δ** than octahedral ones (ML_6):

Δ = 10,200 cm^{-1} for $[Co^{II}(NH_3)_6]^{2+}$
5,900 cm^{-1} for $[Co^{II}(NH_3)_4]^{2+}$

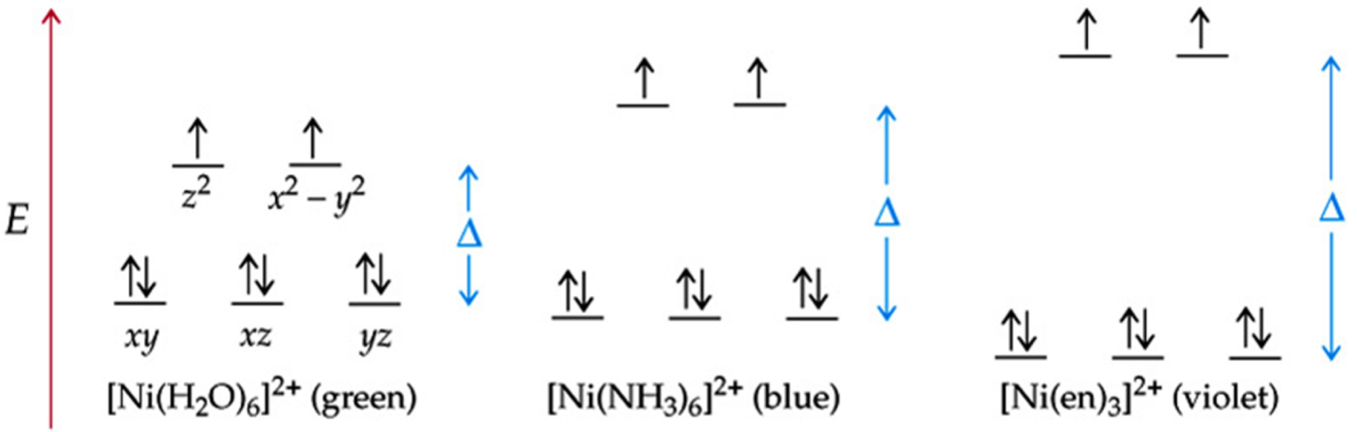
4. Nature of the ligands.



Effect of Ligands on the Magnitude of Δ



- Example nickel complexes



- Example chromium complexes