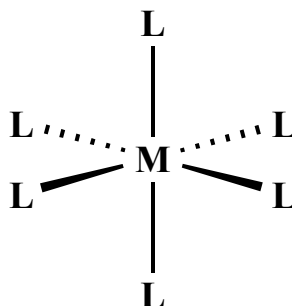
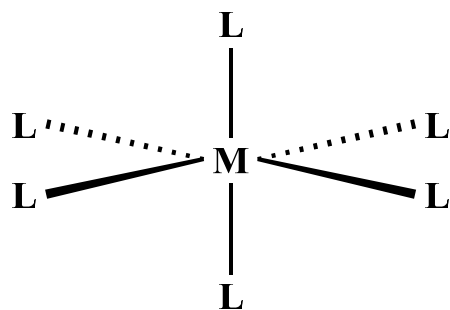


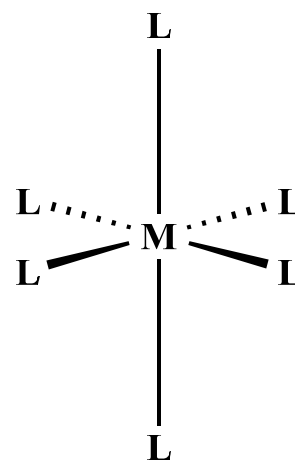
Distortions in Octahedral Geometry



Regular Octahedron: Complexes with regular octahedral geometry are expected to form, when all of the ligands are of the same kind



Compressed

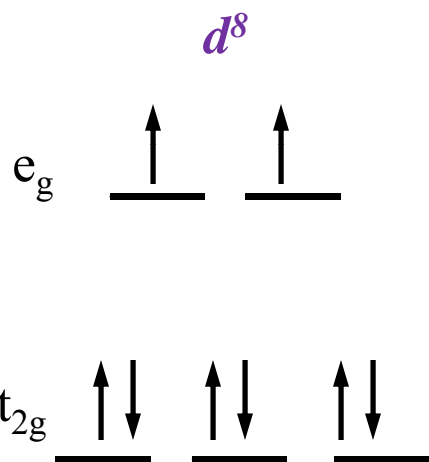


Elongated

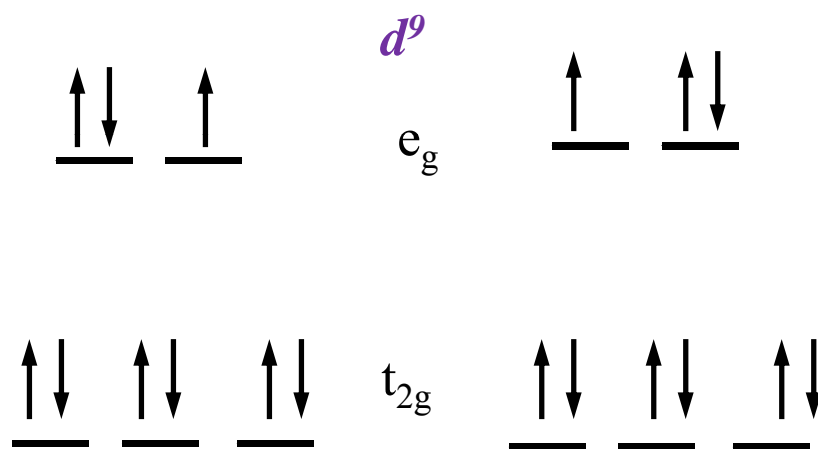
Distorted Octahedron: Complexes with distorted octahedral geometry are expected to form, when the ligands are of different kinds

Distortions in Octahedral Geometry

If the ground electronic configuration of a non-linear complex is orbitally degenerate, the complex will distort so as to remove the degeneracy and achieve a lower energy. This is called the **Jahn-Teller Effect**

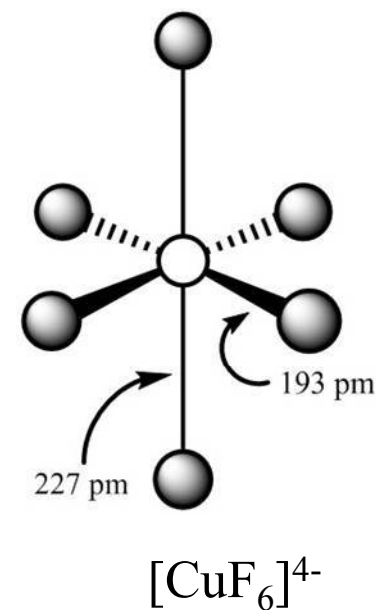
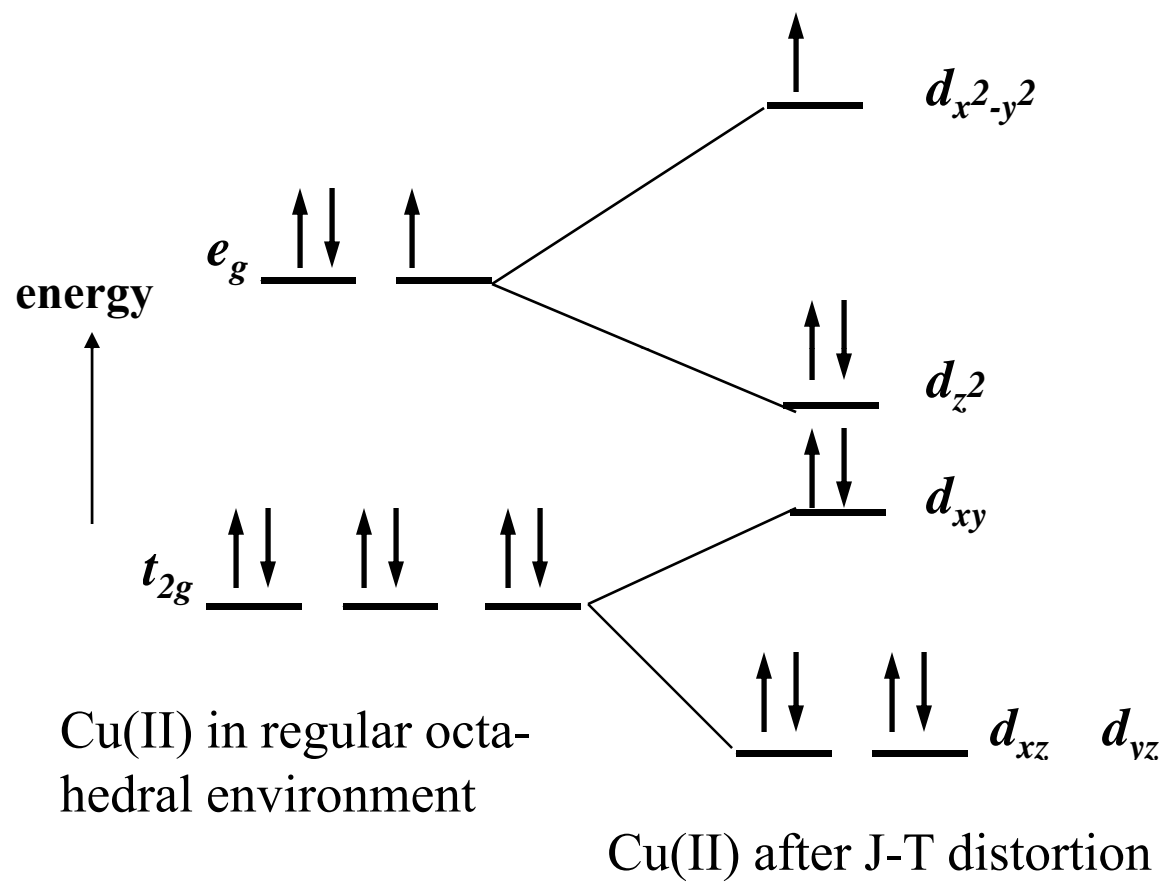


Ni^{2+} : Only one way of filling the orbitals; not degenerate and no Jahn-Teller Distortion

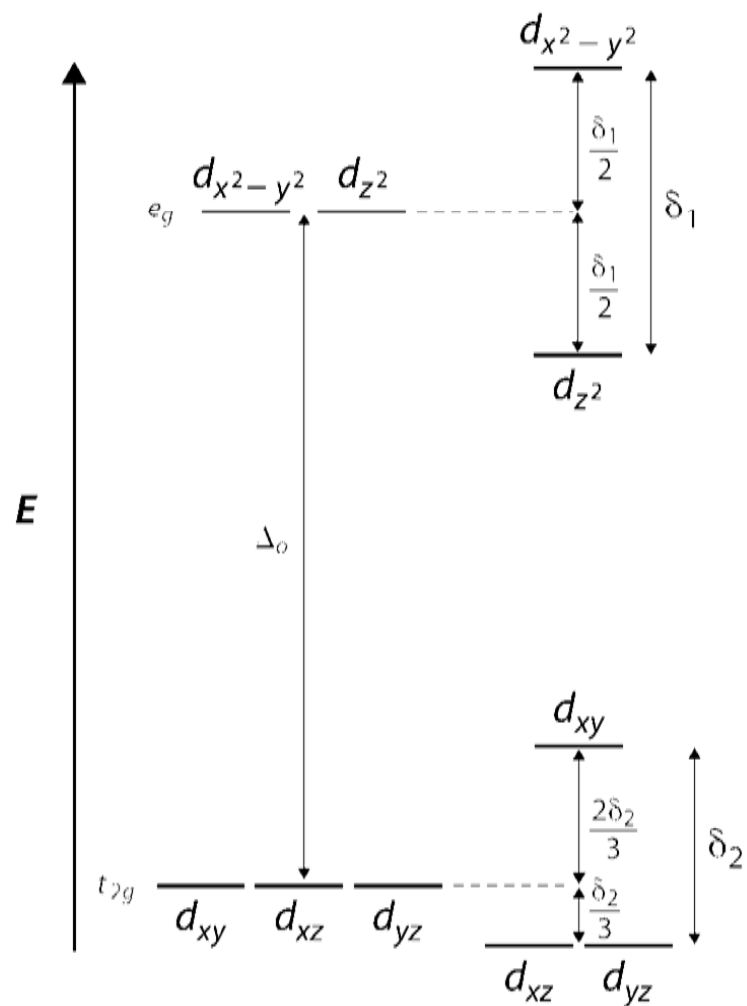


Cu^{2+} : Two ways of filling the e_g orbitals; there is degeneracy and Jahn-Teller Distortion is observed

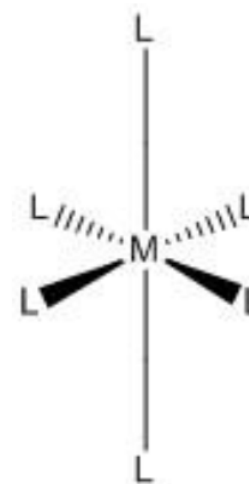
Jahn-Teller Distortion in Cu(II) Complexes



Jahn-Teller Distortion in d^9 Complexes

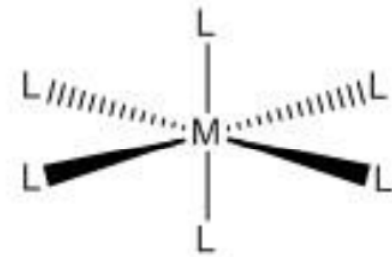
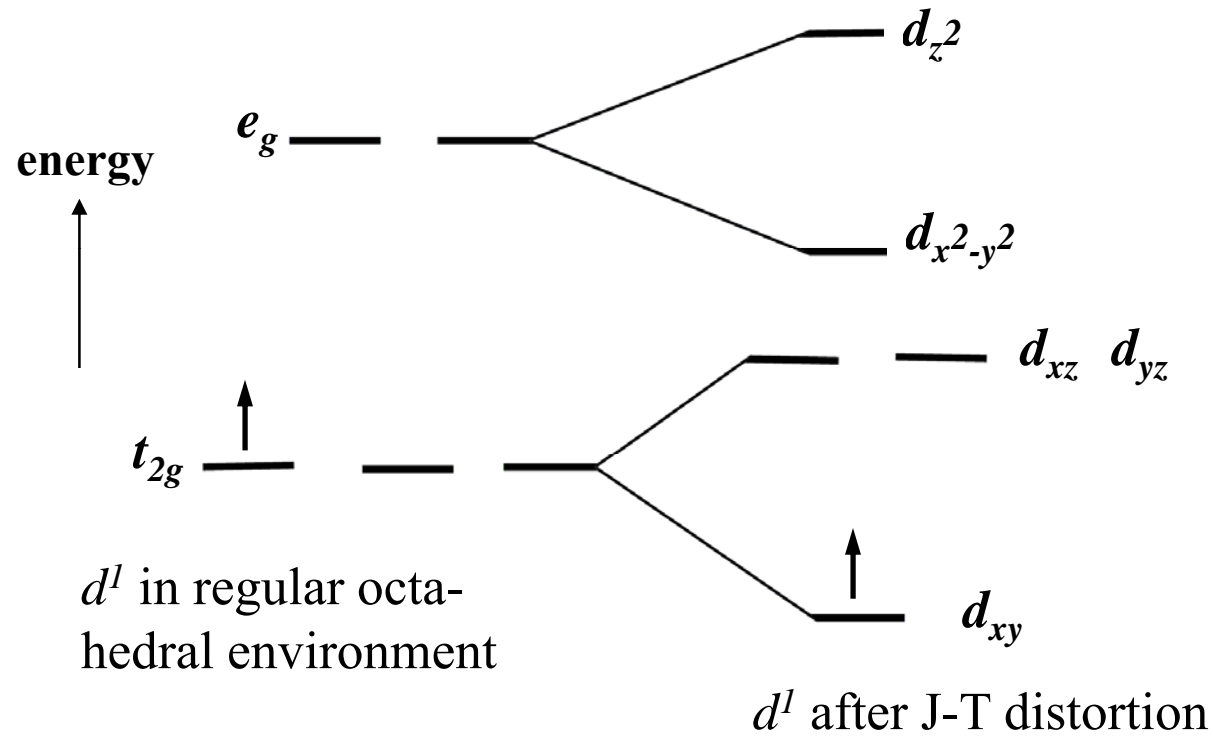


$$\Delta_o \gg \delta_1 > \delta_2.$$

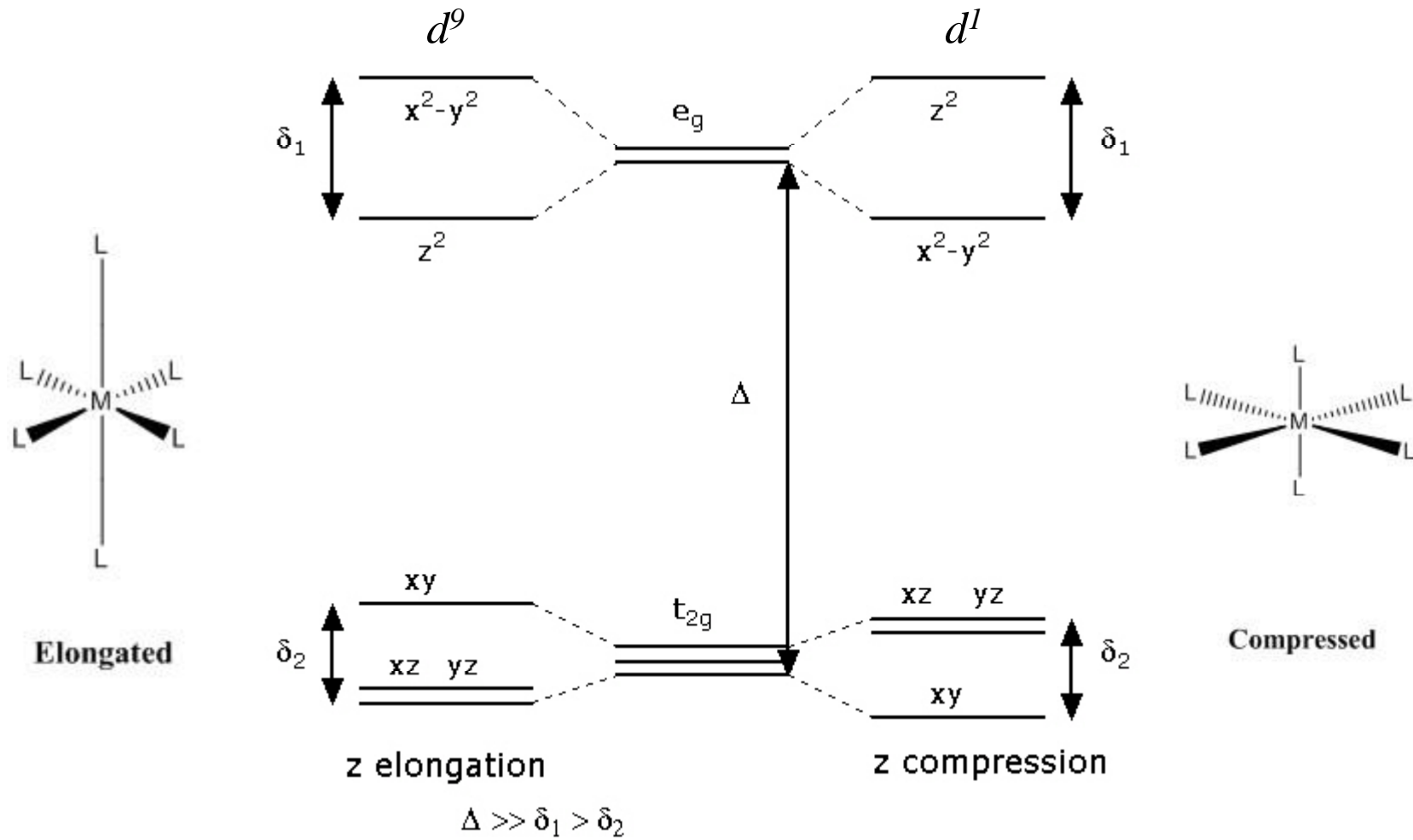


Elongated

Jahn-Teller Distortion in d^1 Complexes

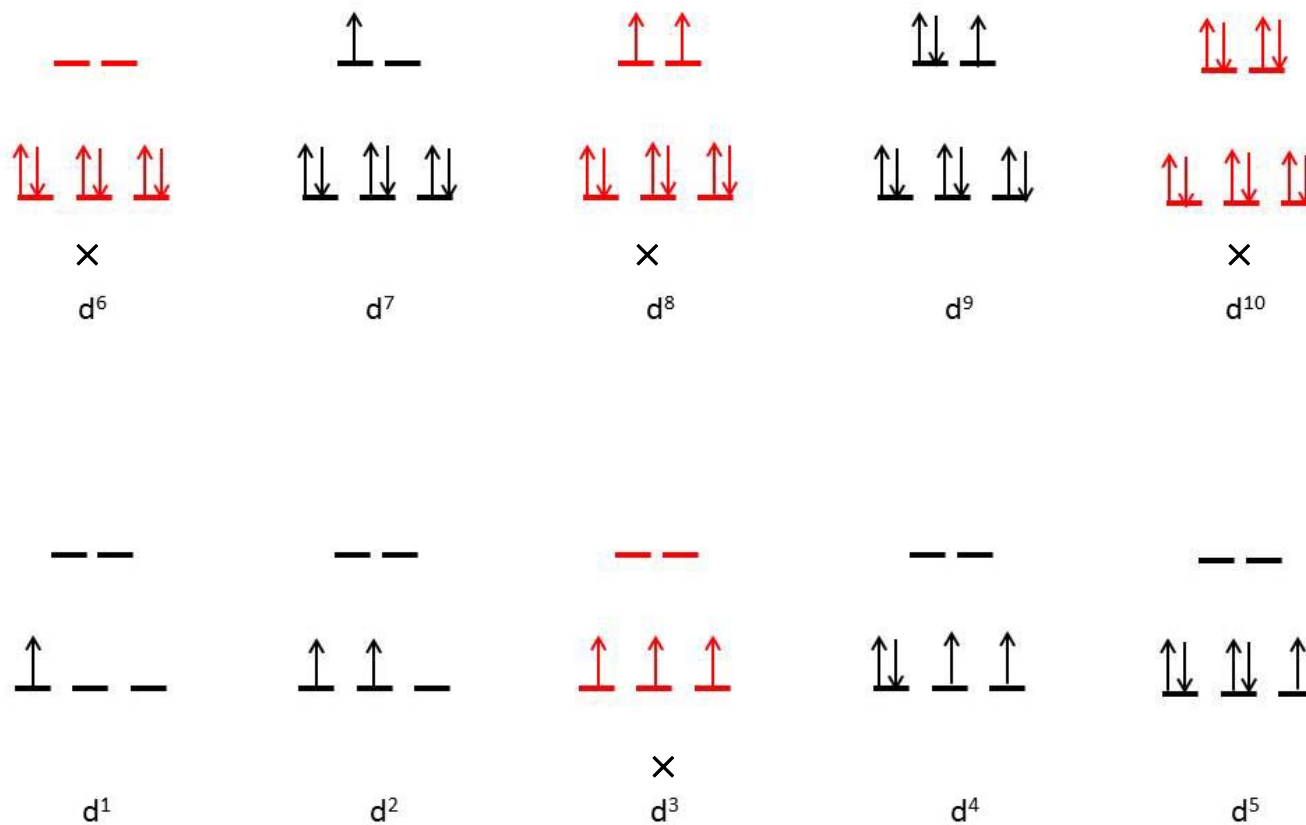


d^1 Vs d^9

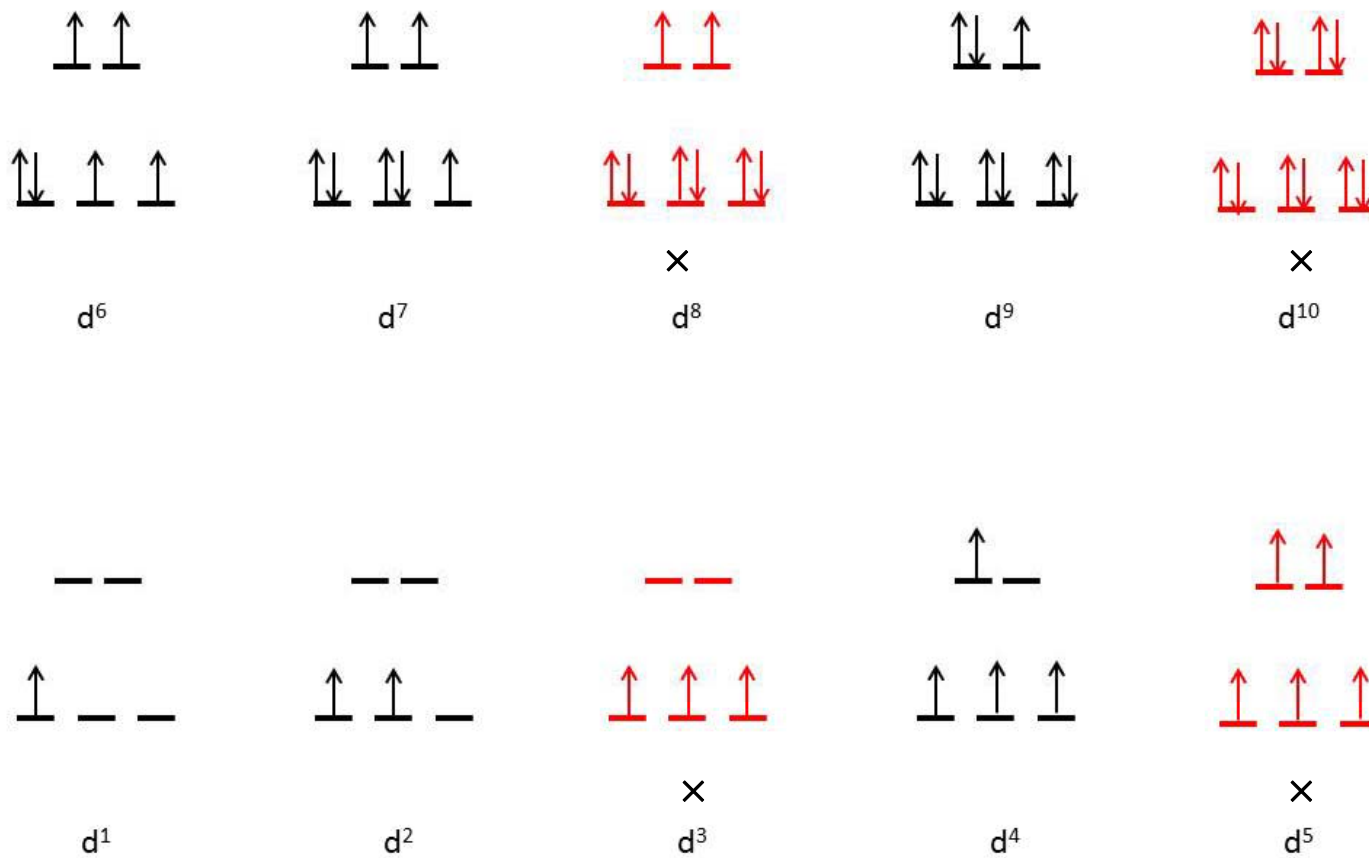


Distortions are more pronounced if the degeneracy occurs in an e_g orbital

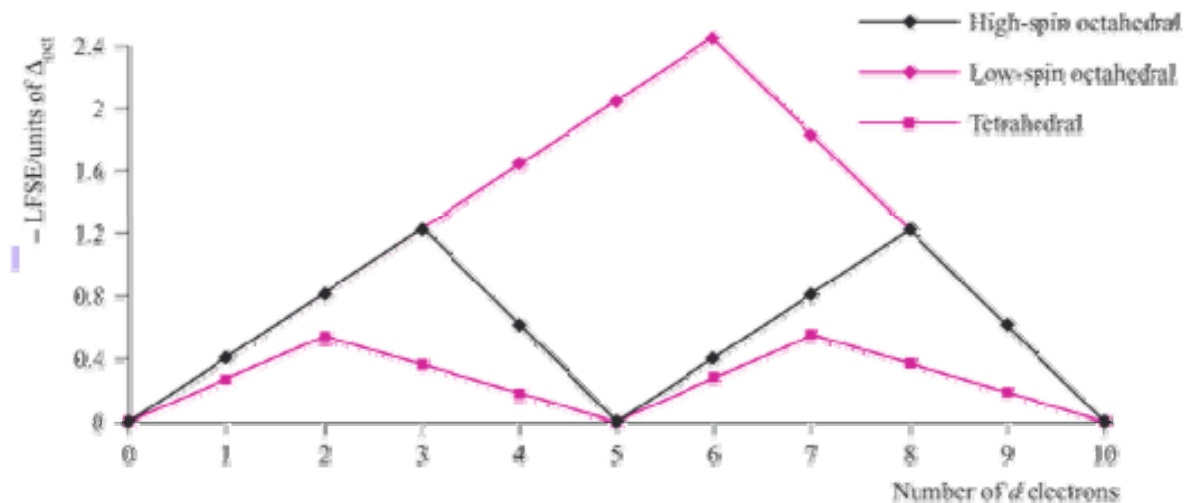
Distortions in Low-Spin Complexes



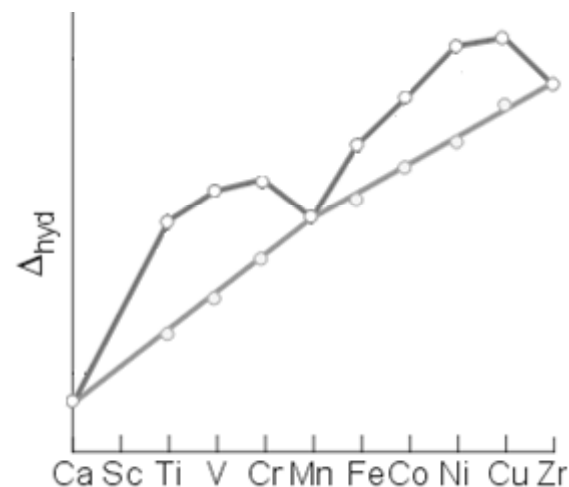
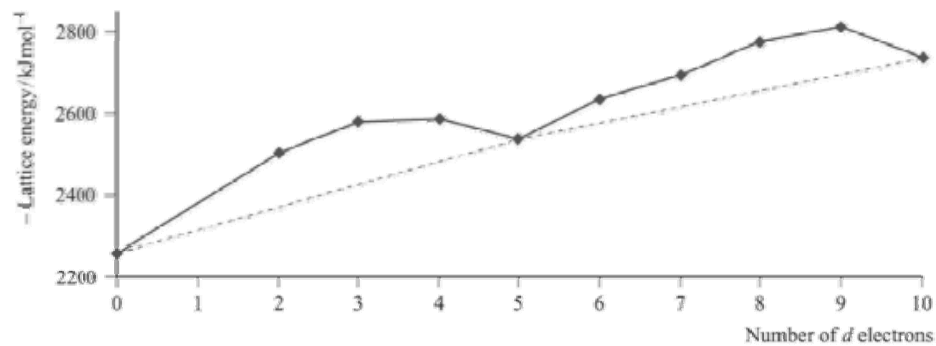
Distortions in High-Spin Complexes



Thermodynamic Aspects of CFSE



Lattice Energy: Estimated using Borne-Lande equation



Heats of hydration for M^{2+} ions

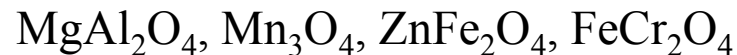
Site Preference in Spinel



The oxide ions form a close packed arrangement with octahedral and tetrahedral voids and the metal ions occupy the voids.

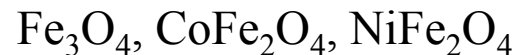
Normal Spinel: $(\text{A}^{\text{II}})^{\text{tet}}(\text{B}^{\text{III}}_2)^{\text{oct}}\text{O}_4$

The divalent A^{II} ions occupy the tetrahedral voids, whereas the trivalent B^{III} ions occupy the octahedral voids in a close packed arrangement of oxide ions.



Inverse Spinel: $(\text{B}^{\text{III}})^{\text{tet}}(\text{A}^{\text{II}}\text{B}^{\text{III}})^{\text{oct}}\text{O}_4$

The A^{II} ions occupy the octahedral voids, whereas half of B^{III} ions occupy the tetrahedral voids.



Site Preference in Spinel



Ni is in +2 oxidation state and has 8 electrons in the d orbitals

In a tetrahedral void,

Configuration – $e^4t_2^4$; CFSE – $0.8 \Delta_t$ (**$0.4 \Delta_o$**)

In an octahedral void,

Configuration – $t_{2g}^6e_g^2$; CFSE – **$1.2 \Delta_o$**

Fe is in +3 oxidation state and has 5 electrons in the d orbitals

In a tetrahedral void,

Configuration – $e^2t_2^3$; CFSE – 0

In an octahedral void,

Configuration – $t_{2g}^3e_g^2$; CFSE – 0

Hence, it is advantageous to have Ni^{2+} ion in the octahedral voids. This results in an inverse spinel structure for the compound.



Site Preference in Spinel



When Mn is in +2 oxidation state, it has 5 electrons in the d orbitals

In a tetrahedral void,

Configuration – $e^2t_2^3$; CFSE – 0

In an octahedral void,

Configuration – $t_{2g}^3e_g^2$; CFSE – 0

When Mn is in +3 oxidation state, it has 4 electrons in the d orbitals

In a tetrahedral void,

Configuration – $e^2t_2^2$; CFSE – $0.4 \Delta_t$ (**$0.2 \Delta_o$**)

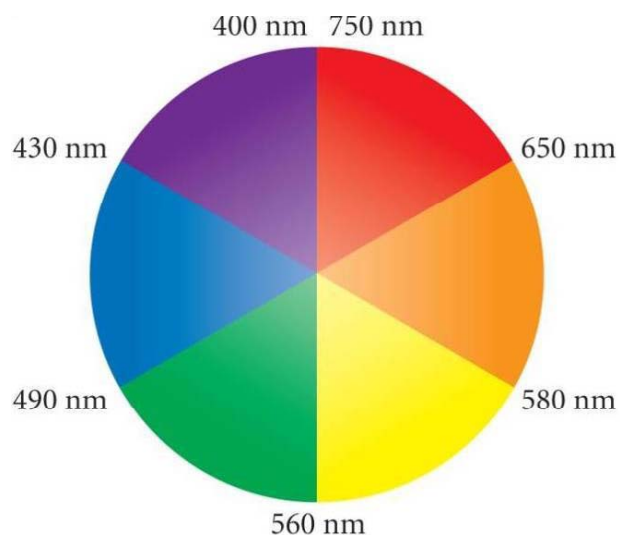
In an octahedral void,

Configuration – $t_{2g}^3e_g^1$; CFSE – **$0.6 \Delta_o$**

Hence, it is advantageous to have Mn^{3+} ions in the octahedral voids. This results in a normal spinel structure for the compound.



Origin of Color



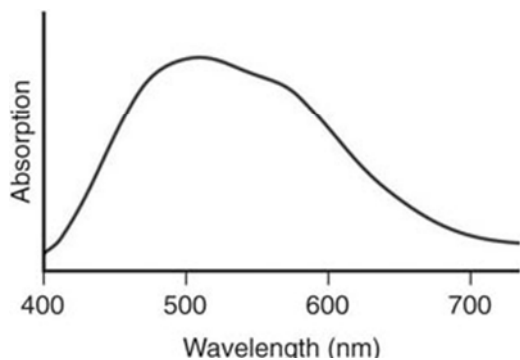
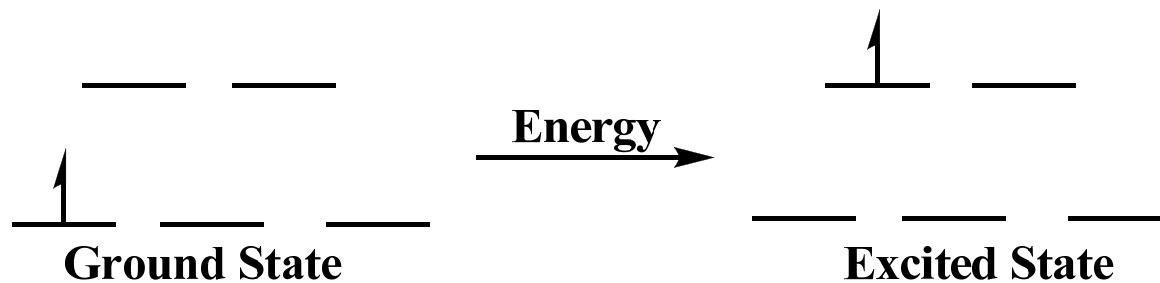
Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520

The Beer-Lambert Law

$$A = \log_{10}(I_0/I) = \epsilon cl$$

where ϵ is the molar extinction coefficient (in $L\text{ cm}^{-1}\text{ mole}^{-1}$), c is concentration in mole L^{-1} and l is the path length in cm. A is known as ‘Absorbance’ and it is dimensionless.

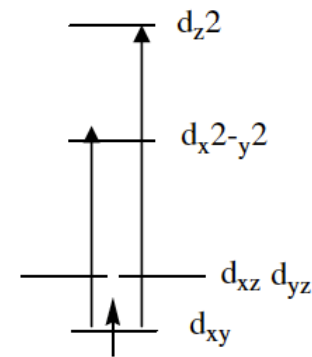
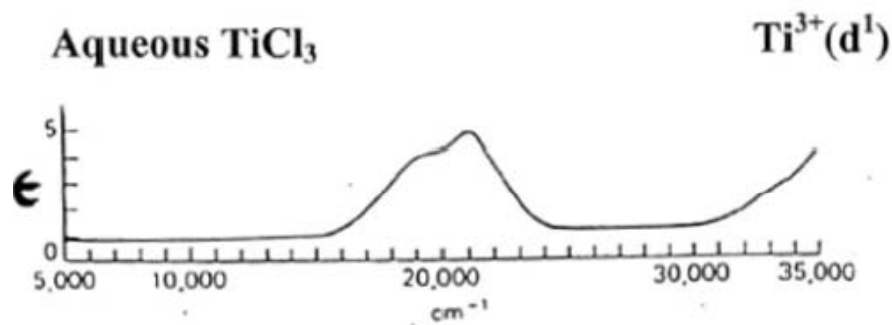
Color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



Absorption at 520 nm gives the complex its purple color

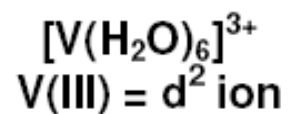


A more resolved absorption spectrum of the complex has a shoulder

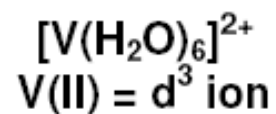
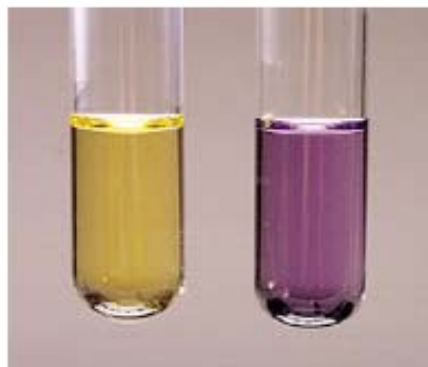
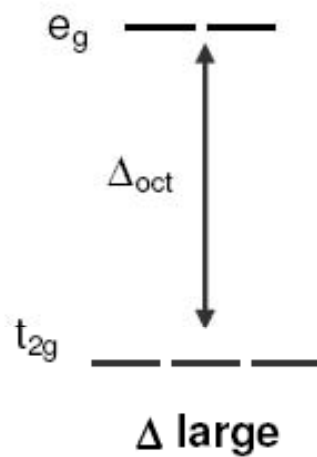


Color and CFT

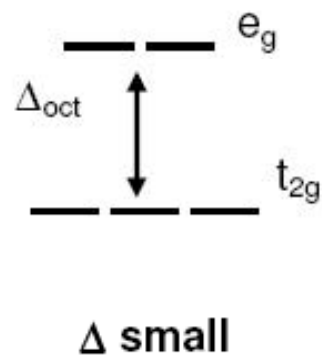
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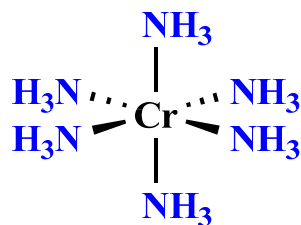
violet light absorbed
complex appears yellow



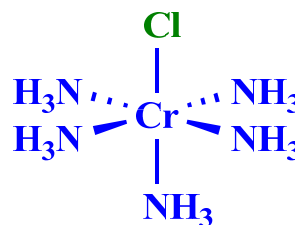
yellow light absorbed
complex appears violet



Color and CFT



Strong ligands, leading to high Δ_o . Absorbs violet and appears yellow.



Relatively weak set of ligands, leading to reduced Δ_o . Absorbs yellow and appears magenta.

Laporte Rule

In a molecule or ion possessing center of symmetry, transitions are not allowed between orbitals of same parity. Transitions are only possible between orbitals that differ by $\Delta l = \pm 1$; 'l' is the orbital quantum number.

Examples of forbidden transitions are: *s* to *s*, *d* to *d*, *p* to *f* etc.

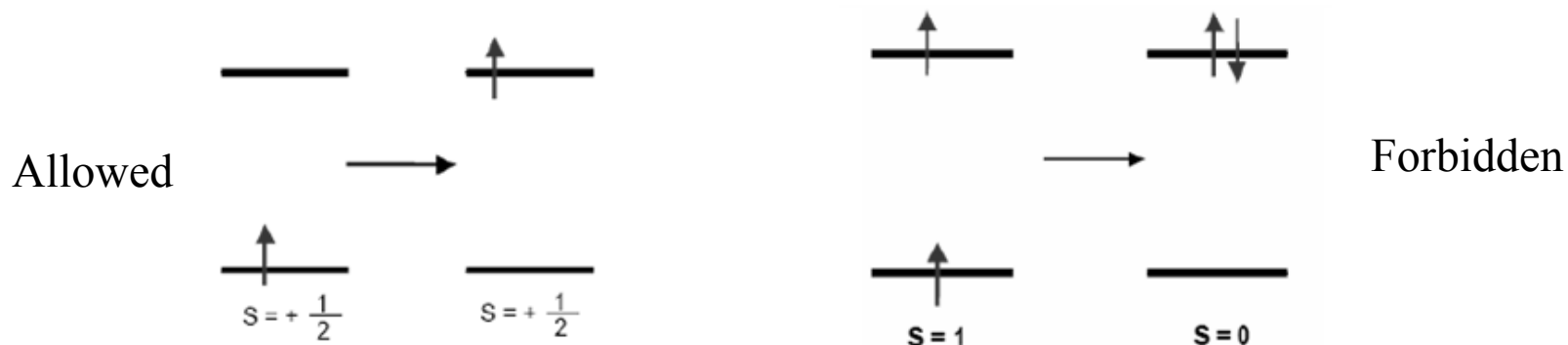
Tetrahedral geometry is not affected by this rule as it does not have a center of symmetry.

As a consequence, ϵ for tetrahedral complexes are 100 times more than the ϵ for octahedral complexes.

Even octahedral complexes lose their center of symmetry transiently due to unsymmetrical vibrations. This leads to color in octahedral and square planar complexes

Spin-forbidden and Spin-allowed Transitions

Any transition for which $\Delta S \neq 0$ is *strongly forbidden*; that is, in order to be allowed, a transition must involve no change in spin state.



$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ has a d^5 metal ion and is a high-spin complex. Electronic transitions are not only Laporte-forbidden, but also spin-forbidden. The dilute solutions of Mn^{2+} complexes are therefore colorless.

However, certain complexes such as MnO_4^- , CrO_4^{2-} etc are intensely colored even though they have metal ions without electrons in the d orbitals. The color of these complexes are not from d-d transitions, but from charge-transfer from ligand to metal orbitals.

d^0 and d^{10} ions have no $d-d$ transitions

Zn^{2+}	d^{10} ion	white
TiF_4	d^0 ion	white
TiCl_4	d^0 ion	white
TiBr_4	d^0 ion	orange
TiI_4	d^0 ion	dark brown
$[\text{MnO}_4]^-$ Mn(VII)	d^0 ion	extremely purple
$[\text{Cr}_2\text{O}_7]^-$ Cr(VI)	d^0 ion	bright orange
$[\text{Cu}(\text{MeCN})_4]^+$ Cu(I)	d^{10} ion	colourless
$[\text{Cu}(\text{phen})_2]^+$ Cu(I)	d^{10} ion	dark orange