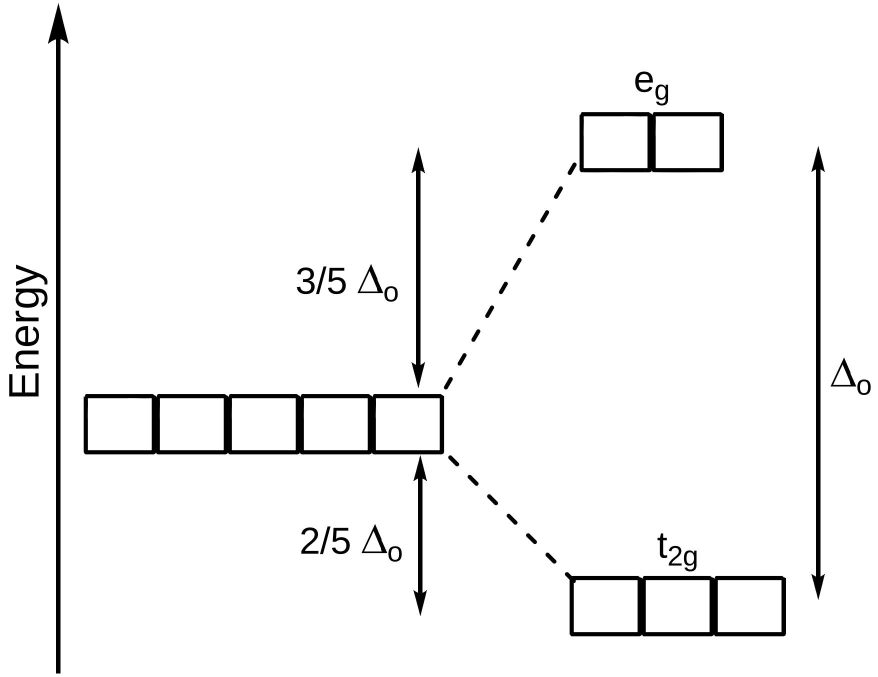
Crystal Field Splitting in an Octahedral Field

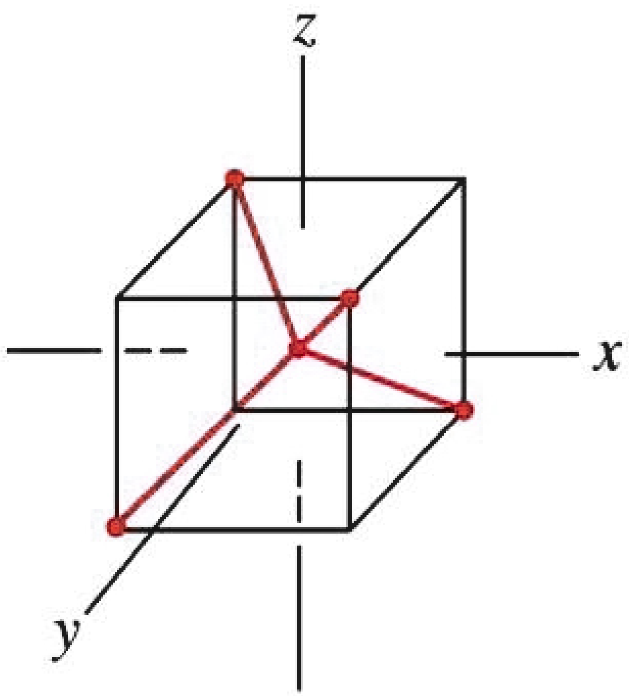


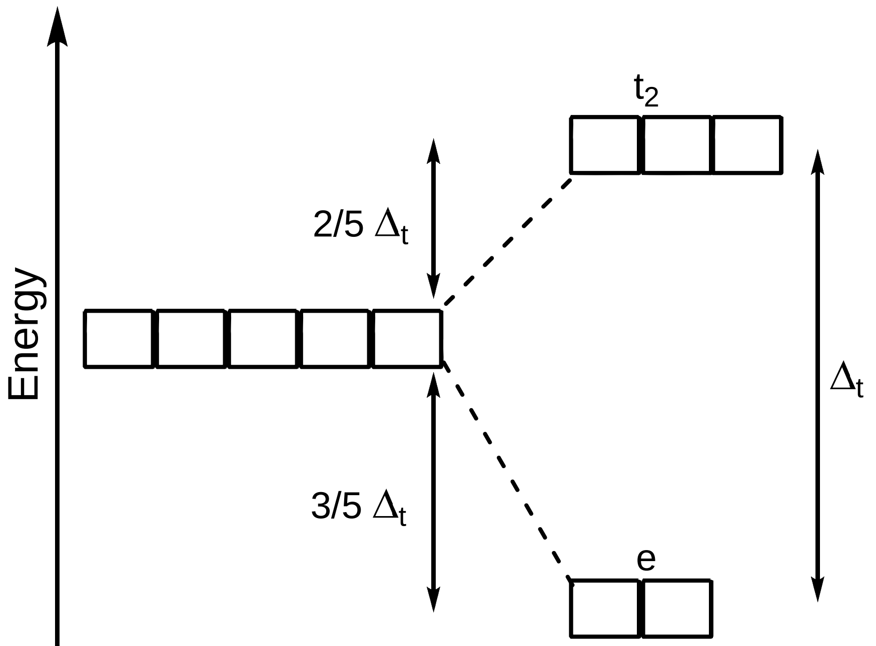
e_g - The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$)
t_{2g} - The lower energy set of orbitals (d_{xy}, d_{yz} *and* d_{xz})

Δ_o or 10 Dq - The energy separation between the two levels

The e_g orbitals are repelled by an amount of 0.6 Δ_o
The t_{2g} orbitals to be stabilized to the extent of 0.4 Δ_o.

Tetrahedral Field

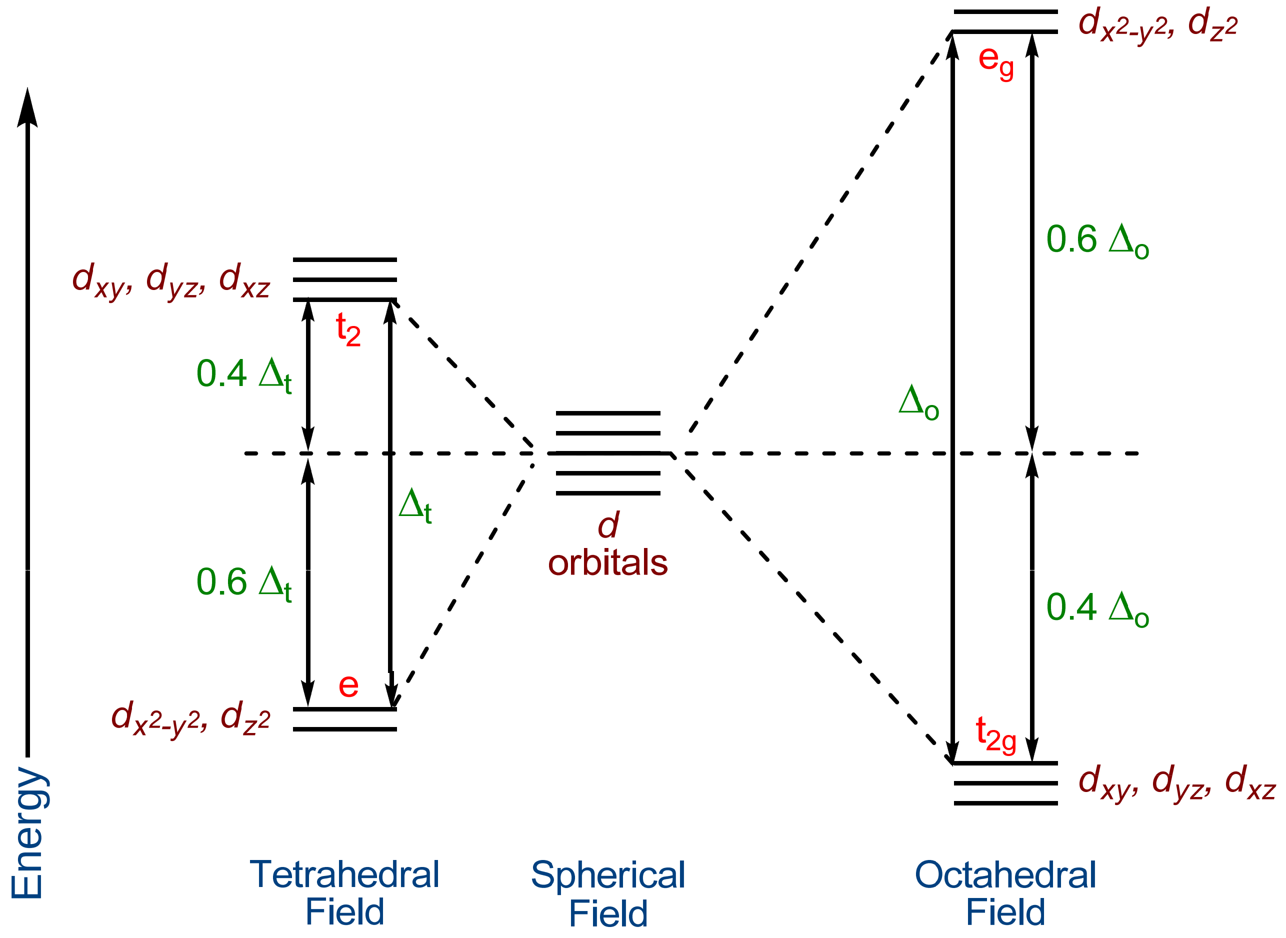




The higher energy set of orbitals (d_{xz}, d_{yz}, d_{xy}) is labeled as t_2 and the lower energy set (d_{z^2} and $d_{x^2-y^2}$) is labeled as e.

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 **$\Delta_t = 4/9\ \Delta_o$**

Octahedral Vs Tetrahedral



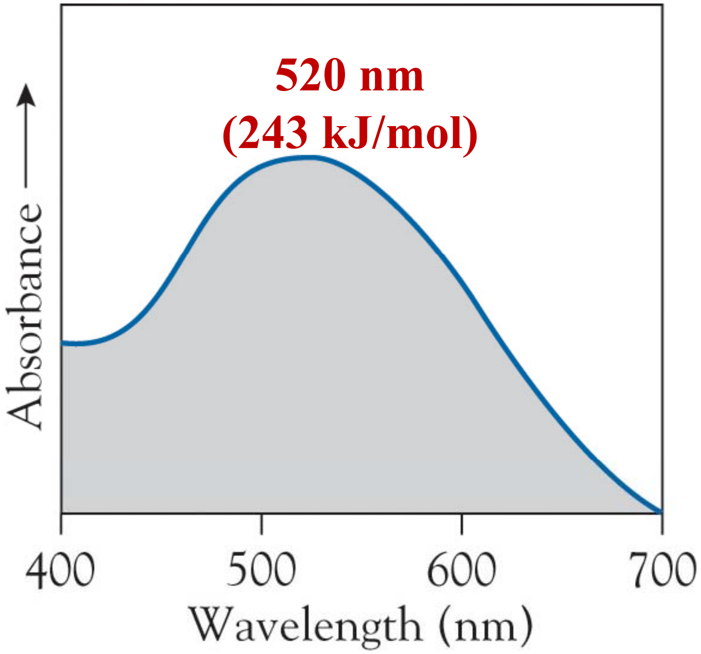
$[Ti(H_2O)_6]^{3+}$ – a d^1 system

Energy

Ground State

Excited State

The single electron in the t_{2g} orbitals absorb energy in the form of light and gets excited to the e_g orbitals. In case of $[Ti(H_2O)_6]^{3+}$, this corresponds to 520 nm (20,300 cm^{-1}).



Factors Affecting the Magnitude of Δ

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

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

2. In groups, heavier analogues have larger Δ.

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

3. Geometry of the metal coordination unit affects Δ greatly.

Tetrahedral complexes $\mathrm{ML_4}$ have smaller Δ than octahedral ones $\mathrm{ML_6}$:
Δ = 10,200 cm^{-1} for $[\mathrm{Co^{II}(NH_3)_{\mathbf{6}}}]^{2+}$
5,900 cm^{-1} for $[\mathrm{Co^{II}(NH_3)_{\mathbf{4}}}]^{2+}$

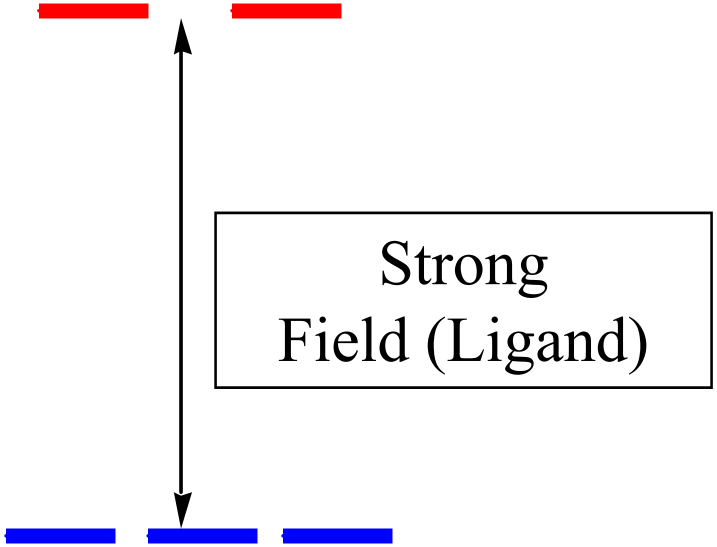
4. Nature of the ligands.

For $[\mathrm{Co^{III}L_6}]$, Δ in cm^{-1}: 13,100 ($\mathrm{F^-}$); 20,760 ($\mathrm{H_2O}$); 22,870 ($\mathrm{NH_3}$)
For $[\mathrm{Cr^{III}L_6}]$, Δ in cm^{-1}: 15,060 ($\mathrm{F^-}$); 17,400 ($\mathrm{H_2O}$); 26,600 ($\mathrm{CN^-}$)

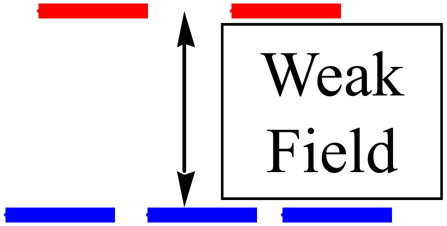
Spectrochemical Series

An arrangement of ligands according to their ability to increase Δ for a given metal center

Weak – I^-, Br^-, SCN^-, Cl^-, N_3^-, F^-, $H_2NC(O)NH_2$, OH^-, ox^{2-}, O^{2-}, H_2O, NCS^-, py, NH_3, en , bpy, phen, NO_2^-, CH_3^-, $C_6H_5^-$, CN^-, CO – Strong

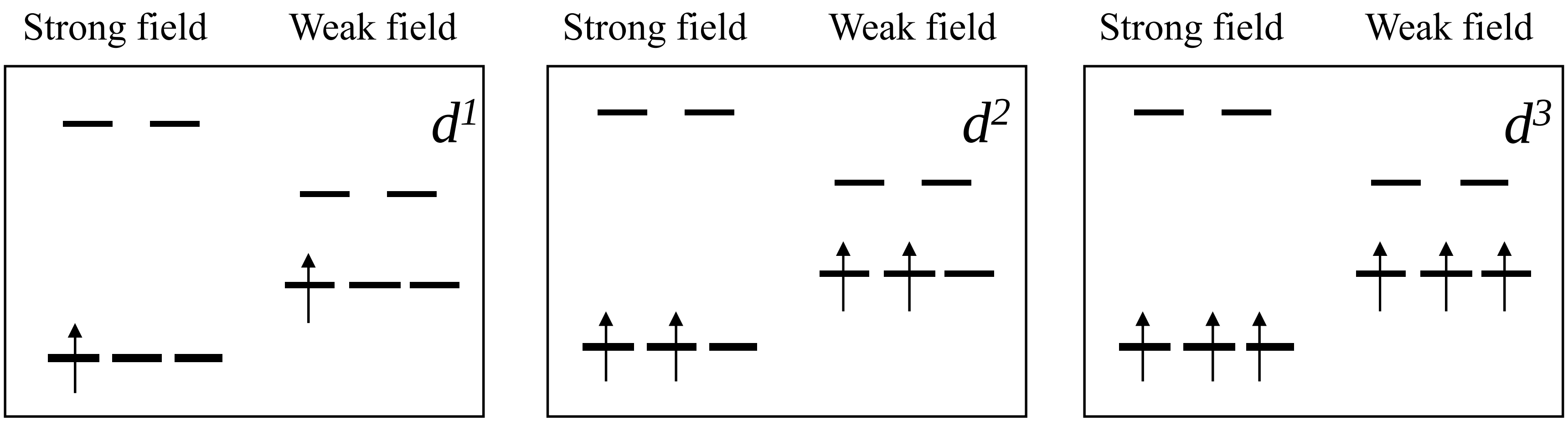


Strong
Field (Ligand)



Weak
Field

Distribution of Electrons in an Octahedral Complex



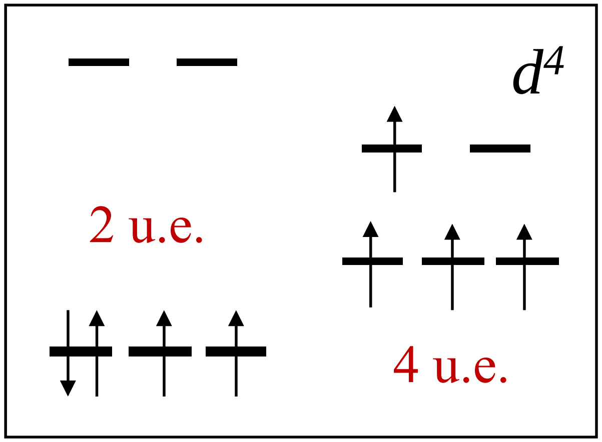
Net energy decrease is called crystal field stabilization energy (CFSE)

For d^1, CFSE = $1 \times 0.4 = \mathbf{0.4\ \Delta_o}$

For d^2, CFSE = $2 \times 0.4 = \mathbf{0.8\ \Delta_o}$

For d^3, CFSE = $3 \times 0.4 = \mathbf{1.2\ \Delta_o}$

Distribution of Electrons in an Octahedral Complex

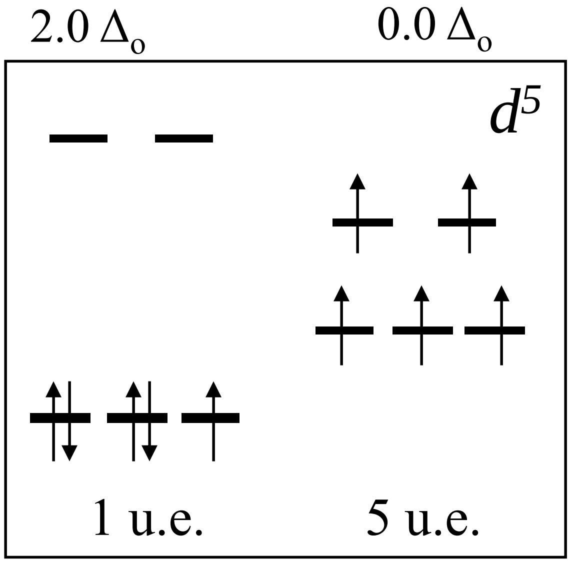


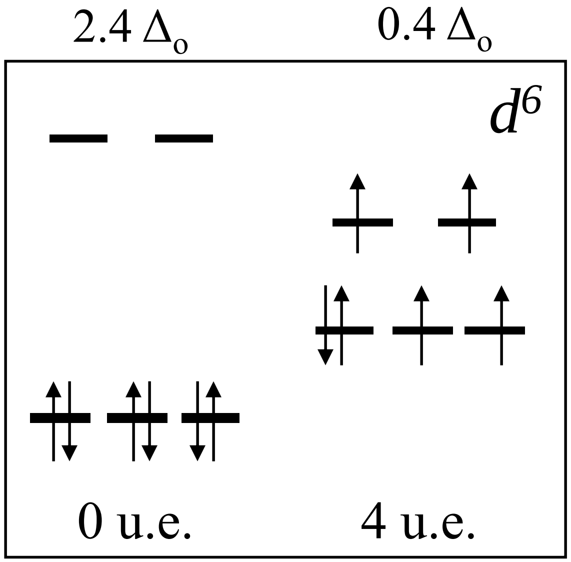
There are two possibilities for metal ions having d^4-d^7 electronic configuration. Depending on the nature of the ligands and the metal they could be **high-spin** or **low-spin** complexes.

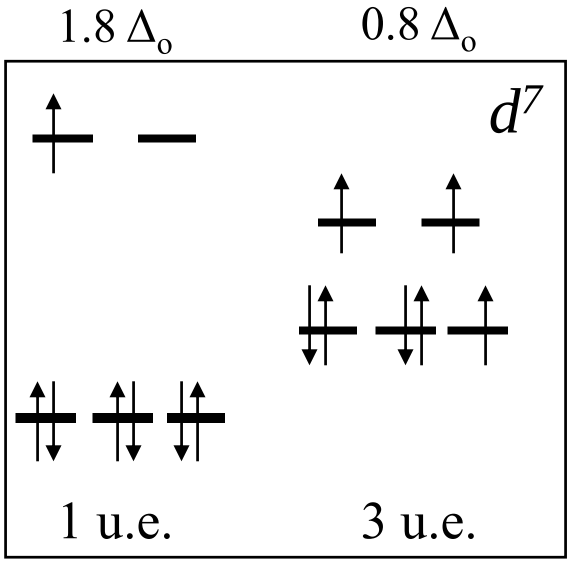
For the d^4 system, CFSE =

For high-spin, $(3 \times 0.4) - (1 \times 0.6)$ = **0.6 Δ_o** and

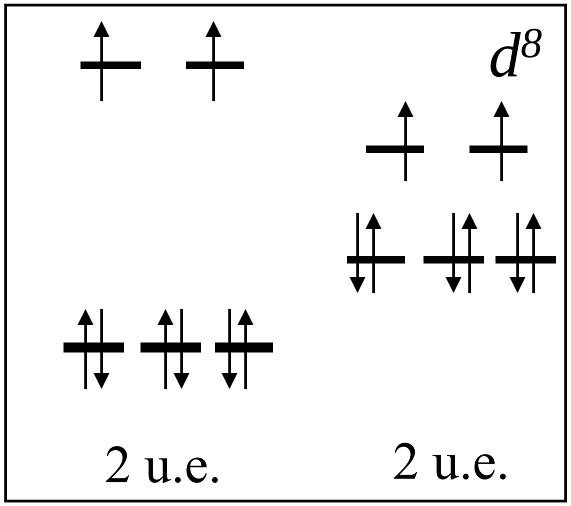
for low-spin, 4×0.4 = **1.6 Δ_o**

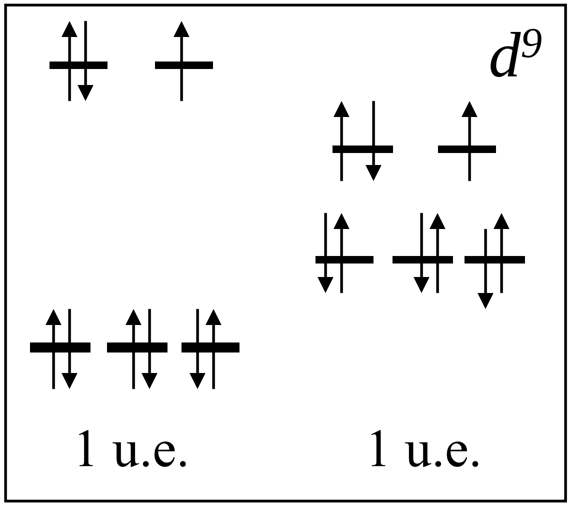


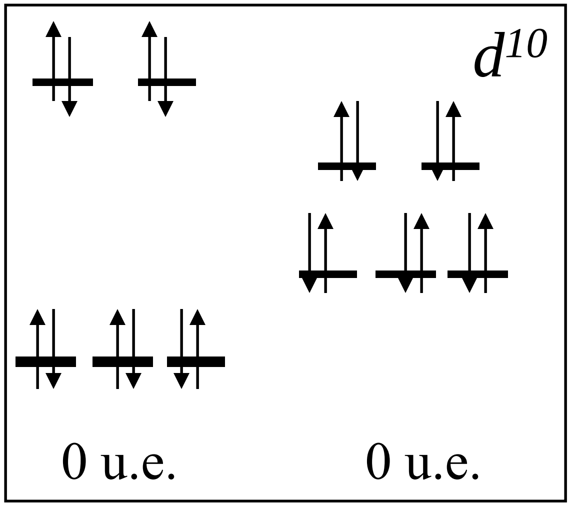




Distribution of Electrons in an Octahedral Complex







For d^8, CFSE = $(6 \times 0.4) - (2 \times 0.6) = 1.2\ \Delta_o$

For d^9, CFSE = $(6 \times 0.4) - (3 \times 0.6) = 0.6\ \Delta_o$

For d^{10}, CFSE = $(6 \times 0.4) - (4 \times 0.6) = 0.0\ \Delta_o$

In all electronic configurations involving two electrons in the same orbital, the actual CFSE is reduced by the energy spent on pairing the electrons.

Metal ions with 4 – 7 electrons in the *d* orbital can exist as high-spin or low-spin complexes. Weaker ligands tend to give high-spin complexes, whereas stronger ligands tend to give low-spin complexes.

Distribution of Electrons in an Octahedral Complex

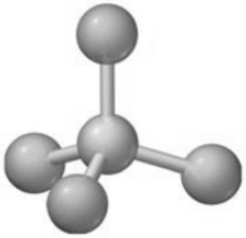
	High-spin		Low-spin	
d^1	$t_{2g}^1e_g^0$	$0.4\ \Delta_o$	$t_{2g}^1e_g^0$	$0.4\ \Delta_o$
d^2	$t_{2g}^2e_g^0$	$0.8\ \Delta_o$	$t_{2g}^2e_g^0$	$0.8\ \Delta_o$
d^3	$t_{2g}^3e_g^0$	$1.2\ \Delta_o$	$t_{2g}^3e_g^0$	$1.2\ \Delta_o$
d^4	$t_{2g}^3e_g^1$	$0.6\ \Delta_o$	$t_{2g}^4e_g^0$	$1.6\ \Delta_o$
d^5	$t_{2g}^3e_g^2$	$0.0\ \Delta_o$	$t_{2g}^5e_g^0$	$2.0\ \Delta_o$
d^6	$t_{2g}^4e_g^2$	$0.4\ \Delta_o$	$t_{2g}^6e_g^0$	$2.4\ \Delta_o$
d^7	$t_{2g}^5e_g^2$	$0.8\ \Delta_o$	$t_{2g}^6e_g^1$	$1.8\ \Delta_o$
d^8	$t_{2g}^6e_g^2$	$1.2\ \Delta_o$	$t_{2g}^6e_g^2$	$1.2\ \Delta_o$
d^9	$t_{2g}^6e_g^3$	$0.6\ \Delta_o$	$t_{2g}^6e_g^3$	$0.6\ \Delta_o$
d^{10}	$t_{2g}^6e_g^4$	$0.0\ \Delta_o$	$t_{2g}^6e_g^4$	$0.0\ \Delta_o$

Distribution of Electrons in a Tetrahedral Complex

Tetrahedral splitting is seldom large enough to result in pairing of the electrons.
As a result, low-spin tetrahedral complexes are not common.
A rare example is **$Cr[N(SiMe_3)_2]_3[NO]$**

d^1	$e^1\ t_2^0$	$0.6\ \Delta_t$
d^2	$e^2\ t_2^0$	$1.2\ \Delta_t$
d^3	$e^2\ t_2^1$	$0.8\ \Delta_t$
d^4	$e^2\ t_2^2$	$0.4\ \Delta_t$
d^5	$e^2\ t_2^3$	$0.0\ \Delta_t$
d^6	$e^3\ t_2^3$	$0.6\ \Delta_t$
d^7	$e^4\ t_2^3$	$1.2\ \Delta_t$
d^8	$e^4\ t_2^4$	$0.8\ \Delta_t$
d^9	$e^4\ t_2^5$	$0.4\ \Delta_t$
d^{10}	$e^4\ t_2^6$	$0.0\ \Delta_t$

When to Expect Tetrahedral Geometry

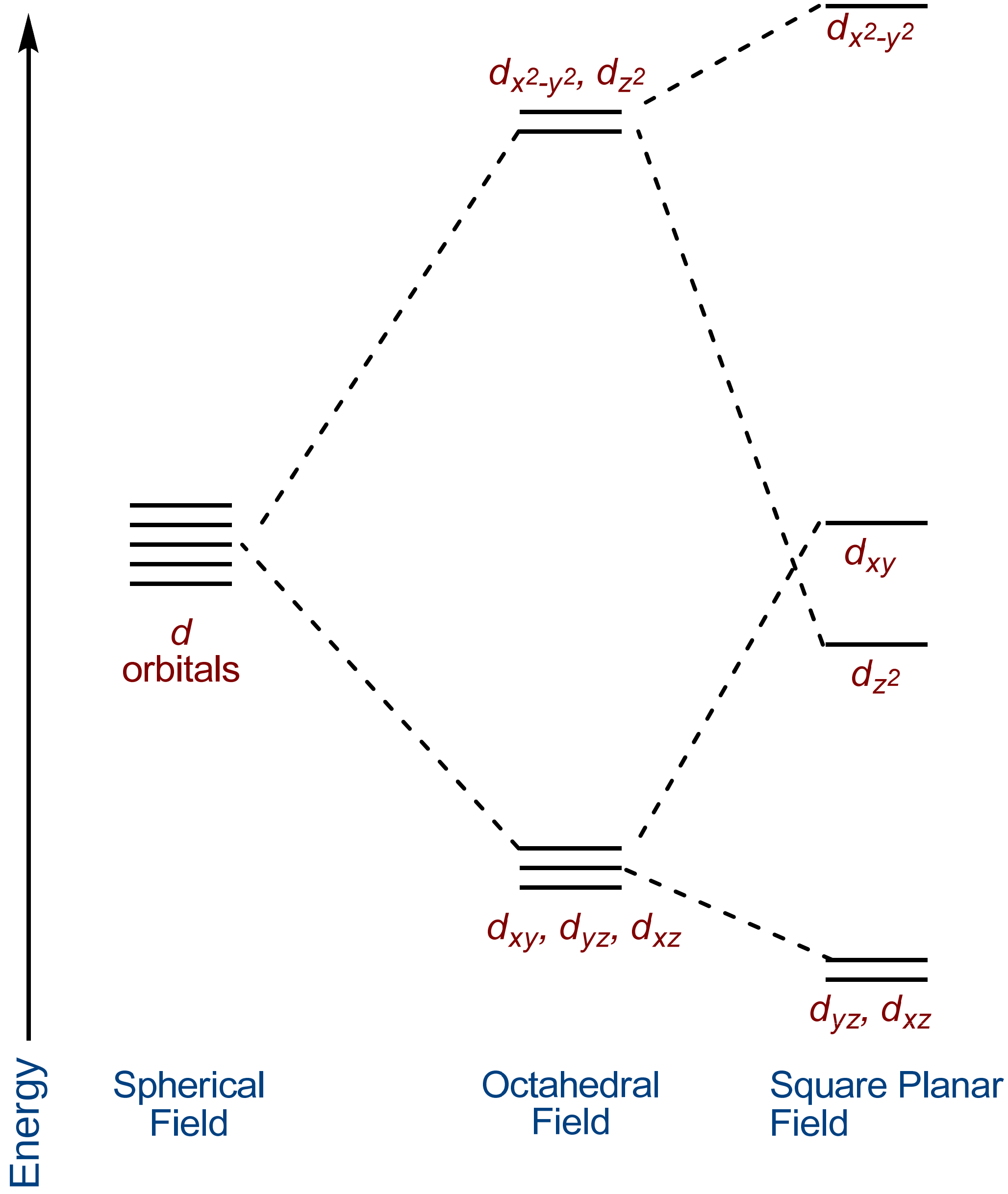


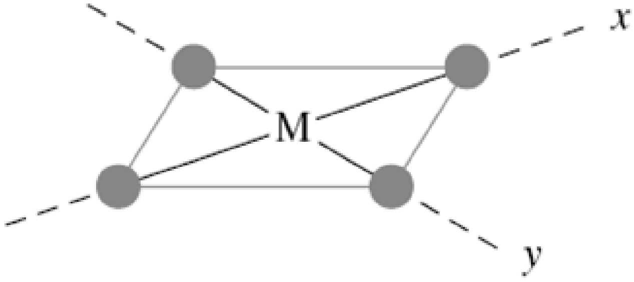
If ligands are large; so as to avoid ligand-ligand repulsion

In case of metal ions with zero CFSE (d^0, d^5 and d^{10}) or
MnO_4^- (d^0), $FeCl_4^-$ (d^5, h.s.), $ZnCl_4^{2-}$ (d^{10})

In case of metal ions with small CFSE (d^2 and d^7)
$CoCl_4^{2-}$ (d^7, h.s.) – $0.8\ \Delta_o$ vs $1.2\ \Delta_t$

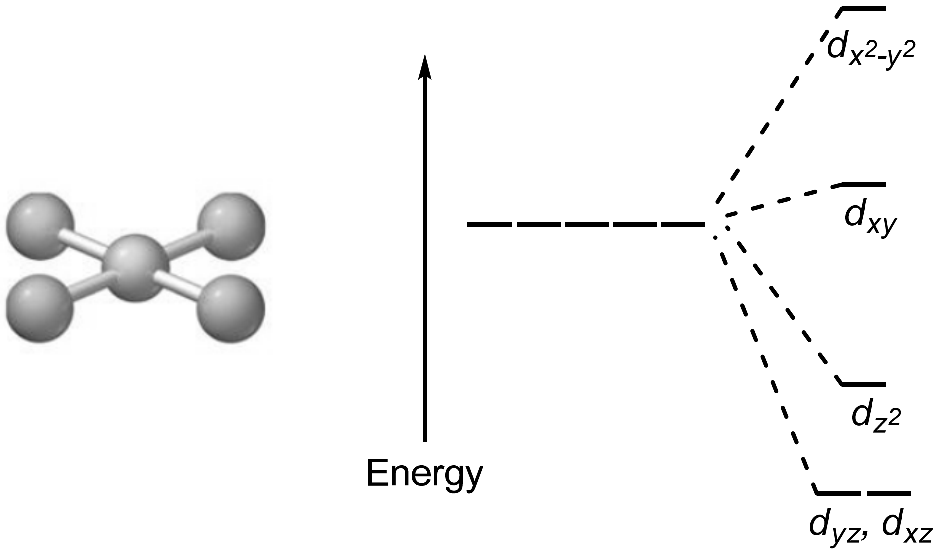
Square Planar Field





Ligands along the Z axis are removed from an octahedral complex to get a square planar complex

When to Expect Square Planar Geometry



In the case of d^8 metals and strong ligands:
Ni^{2+}, in the presence of strong field ligands such as CN^- forms a square planar complex.

2nd and 3rd row d^8 metals form square planar geometry irrespective of the nature of the ligand:
With Pd^{2+} (which already generates a strong field) even a weak field ligand such as Cl^- leads to the formation of a square planar complex, for example, $[PdCl_4]^{2-}$.