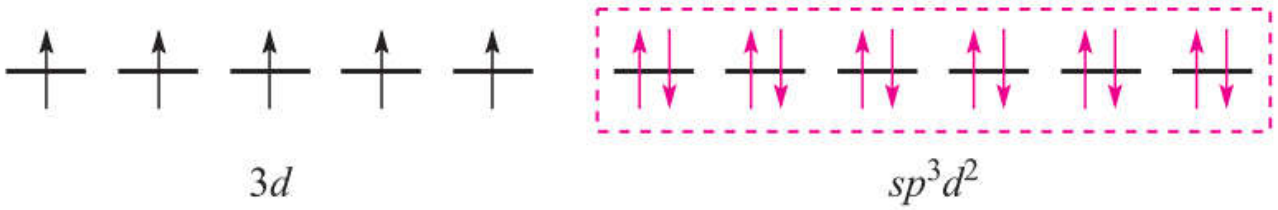
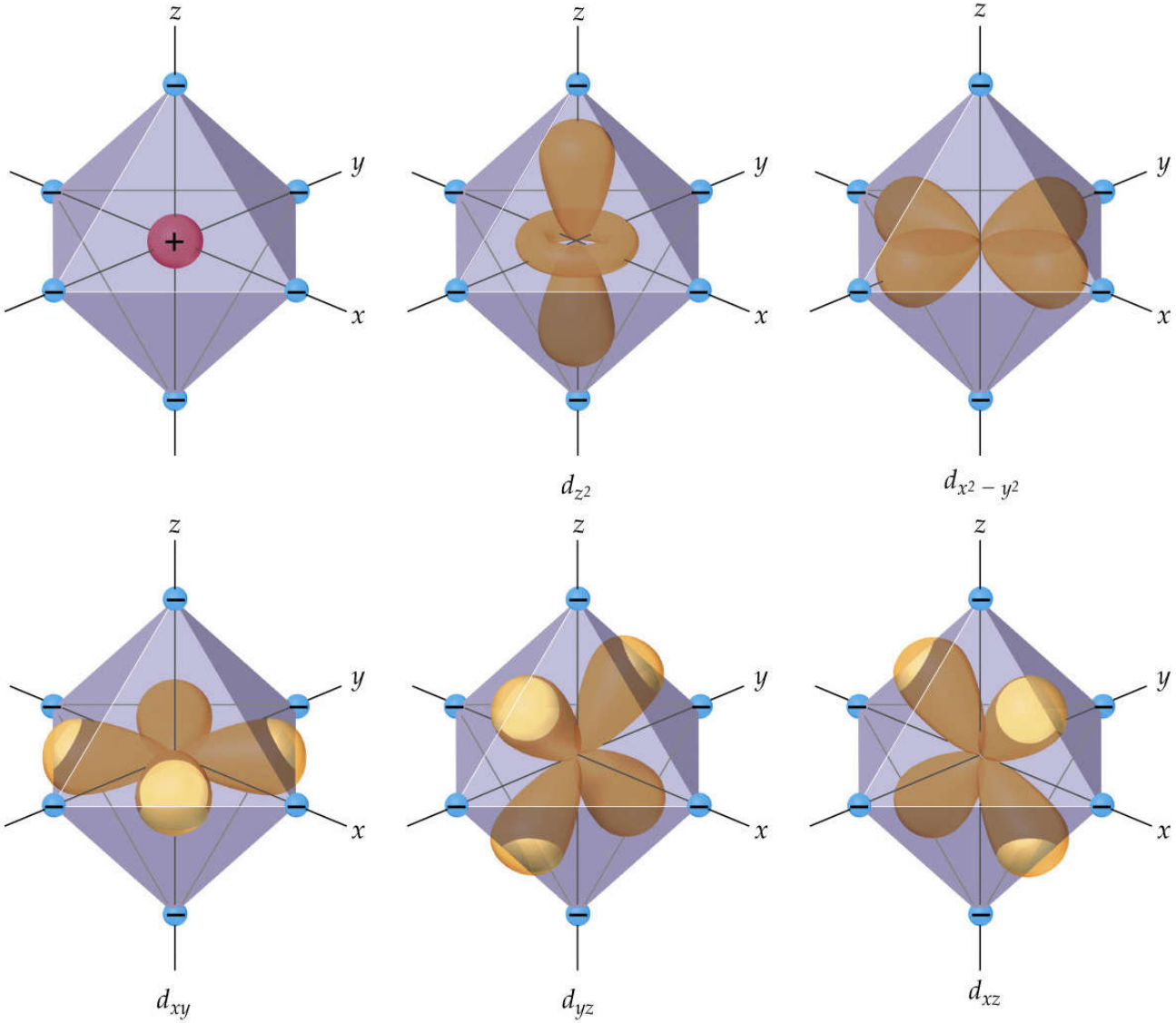
Aula 13 QE

Para um complexo octaédrico, como $[FeF_6]^{-3}$, os cinco elétrons 3d ocupam os cinco orbitais atômicos 3d (como no íon livre mostrado acima) e os dois orbitais d necessários para o esquema de hibridização sp_3d_2 deve vir do 4d. Com os elétrons do ligante incluídos, ligação de valência teoria descreve a ligação da seguinte forma, deixando três orbitais atômicos 4d vazios (não mostrados):

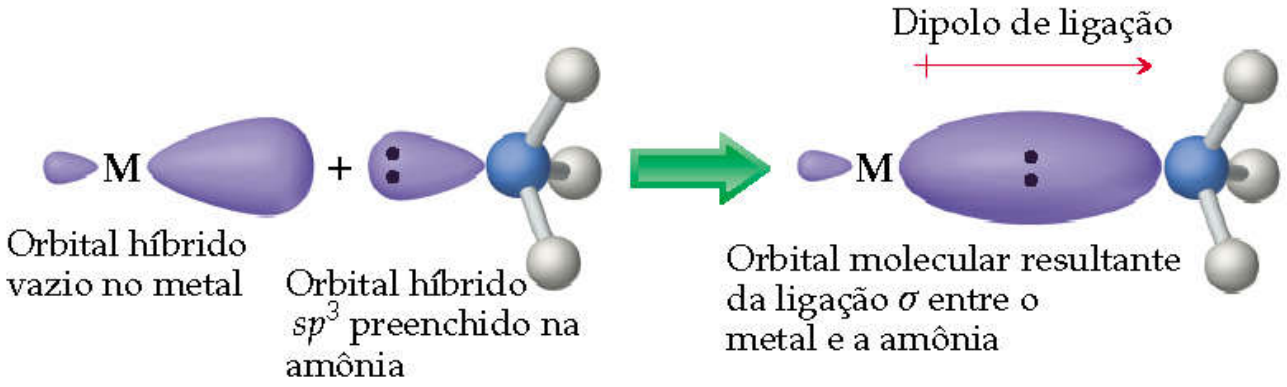
Fe^{3+} $[Ar]$ ~~$4s^2$~~ $3d^5$ $4s$ $4p$ $4d$




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

Teoria do campo cristalino

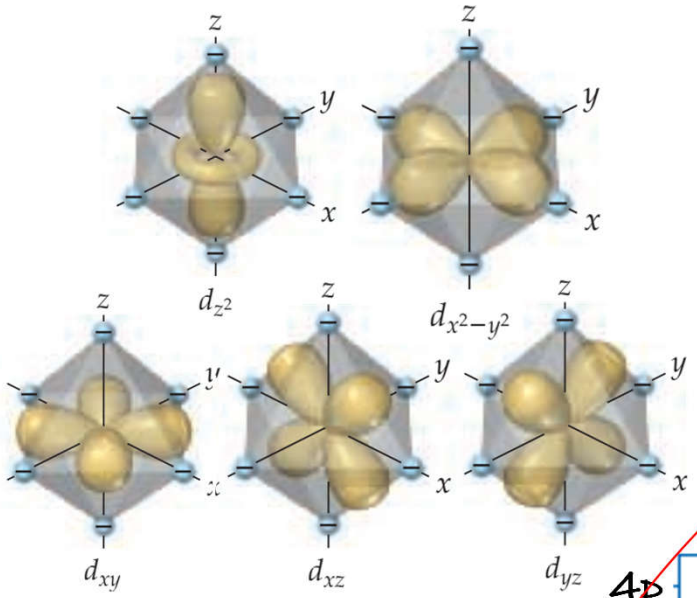
- Quanto mais diretamente o ligante ataca o orbital do metal, maior é a energia do orbital *d*.



$[FeF_6]^{3-}$

Octaédro

Energia

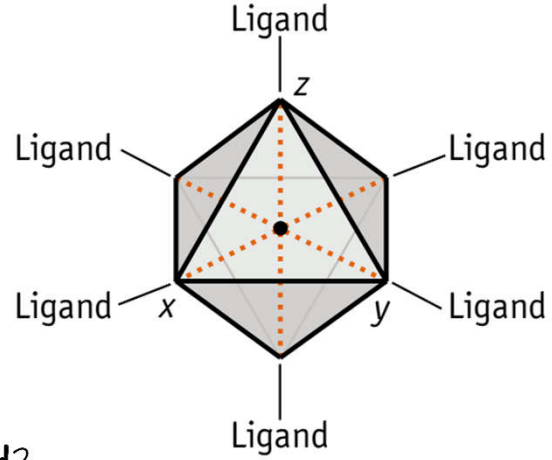


3d

4s

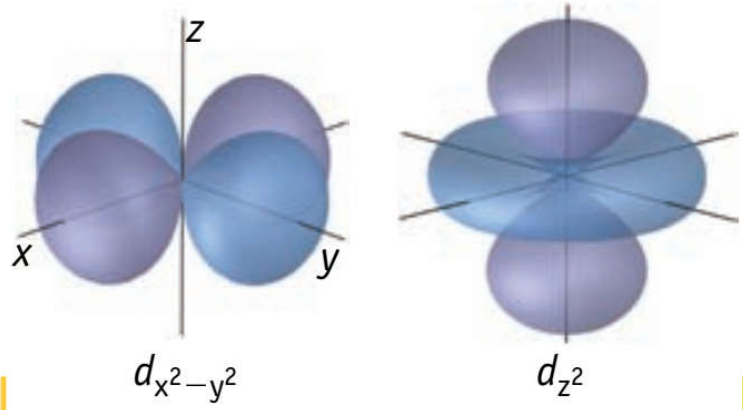
4p

4d

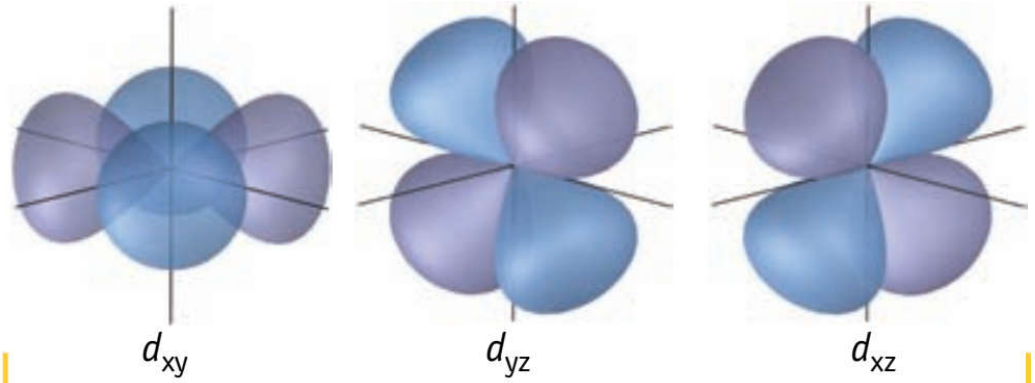


sp^3d^2

F^- F^- F^- F^- F^- F^-



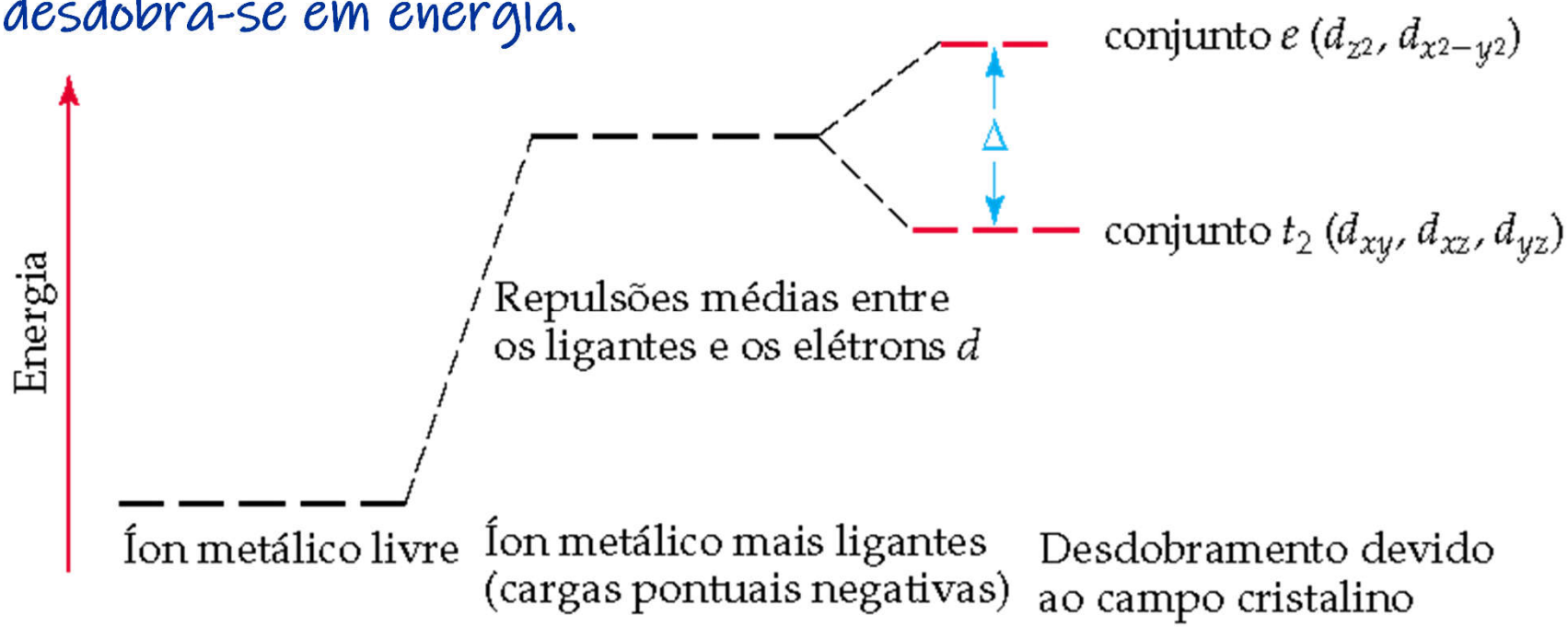
orbitais ao longo dos eixos x, y e z

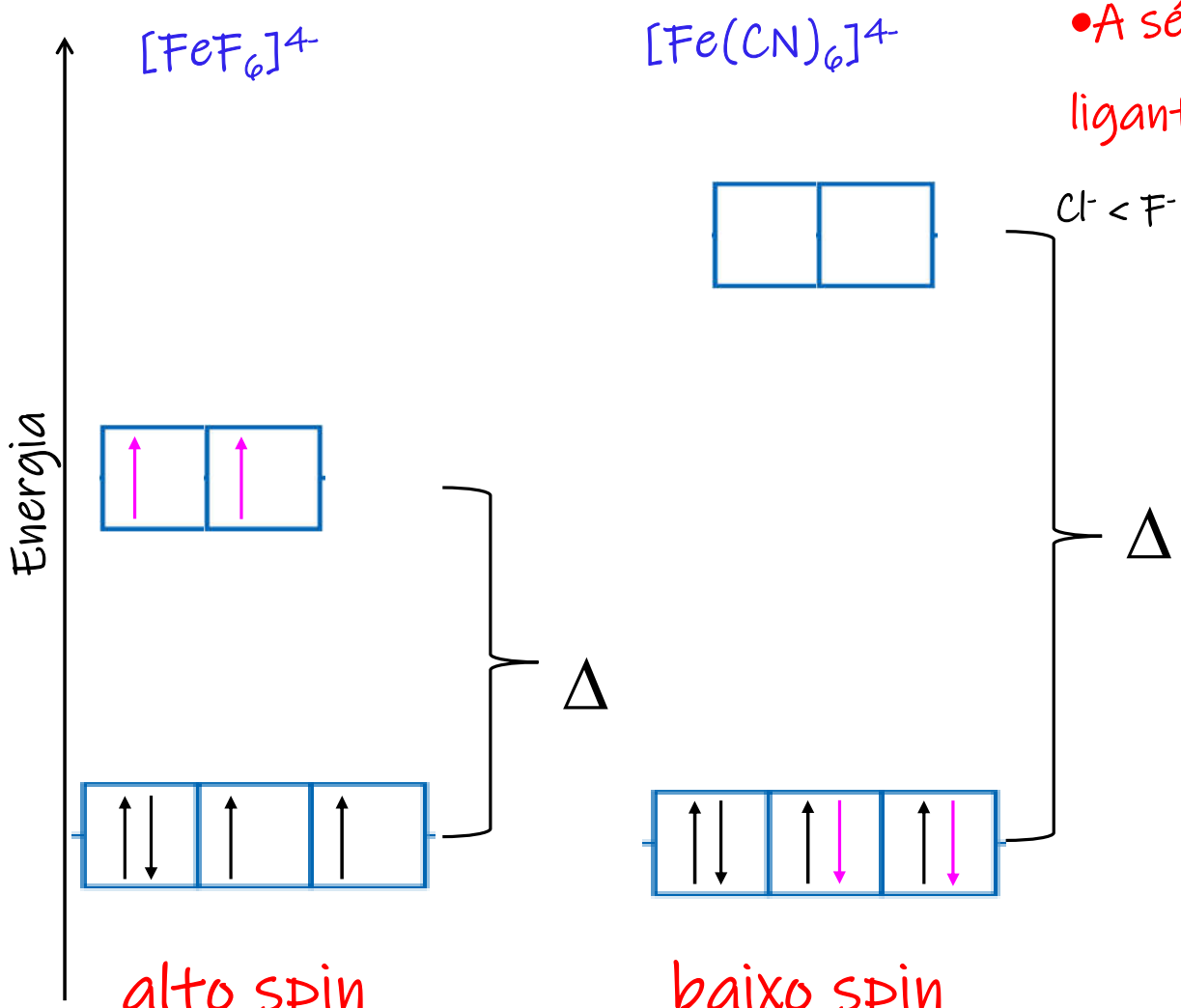


orbitais entre os eixos x, y e z

Teoria do campo cristalino

- A distância em energia entre eles é chamada Δ, o campo cristalino desdobra-se em energia.





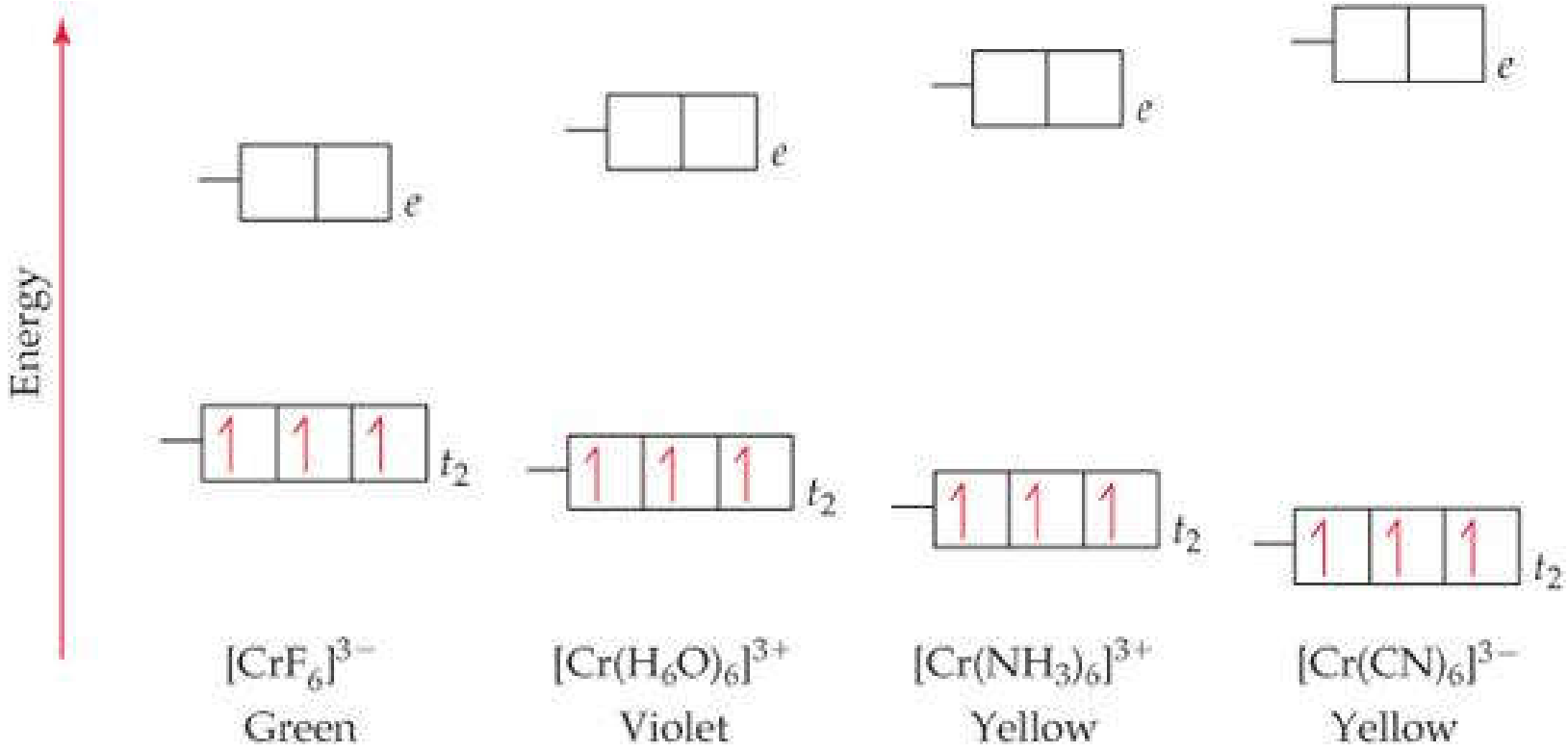
- A série espectroquímica é uma lista de ligantes em ordem crescente de Δ:

$Cl^- < F^- < H_2O < NH_3 < en < NO_2^-$ (ligado aN) $< CN^-$

Δ

vs

Energia de pareamento



$Cl^- < F^- < H_2O < NH_3 < en < NO_2^-$ (ligado aN) $< CN^-$

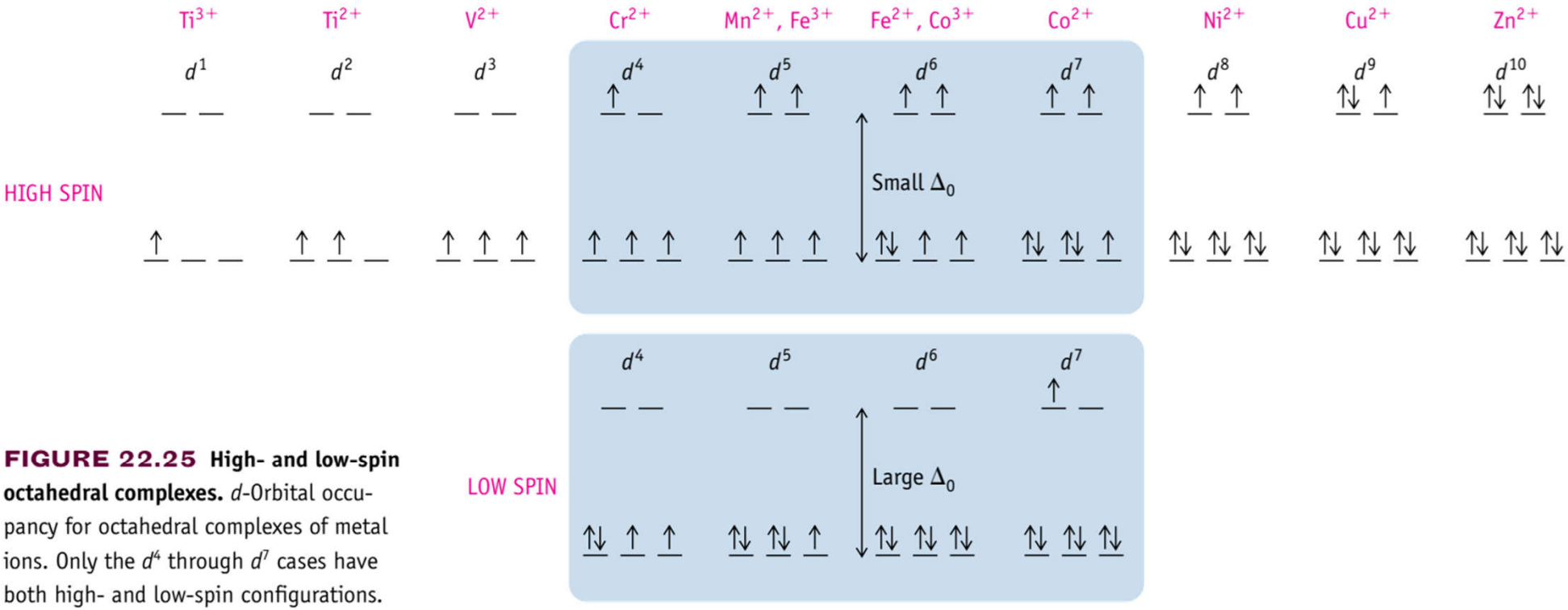
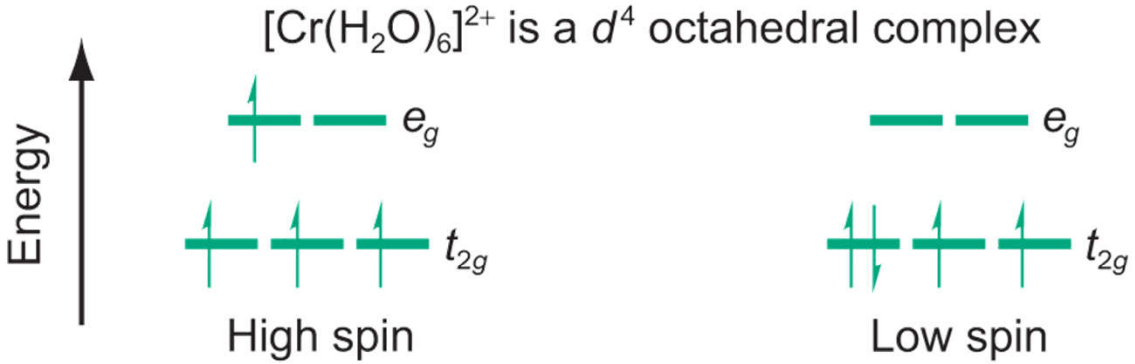


FIGURE 22.25 High- and low-spin octahedral complexes. *d*-Orbital occupancy for octahedral complexes of metal ions. Only the d^4 through d^7 cases have both high- and low-spin configurations.



$\Delta = 170\ KJ.mol^{-1}$ $P = 245\ KJ.mol^{-1}$

$EECC = 3x(-0,4\Delta)+1x(+0,6\Delta)$

$EECC = -0,6\Delta = -0,6x170$

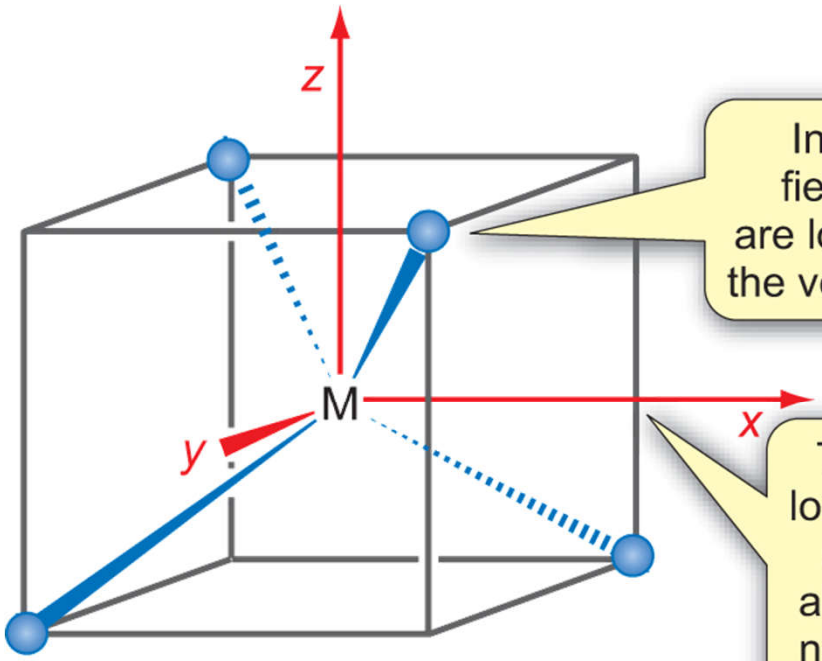
$EECC = -102\ KJ.mol^{-1}$

$EECC = 4x(-0,4\Delta)+P$

$EECC = -1,6\Delta+P$

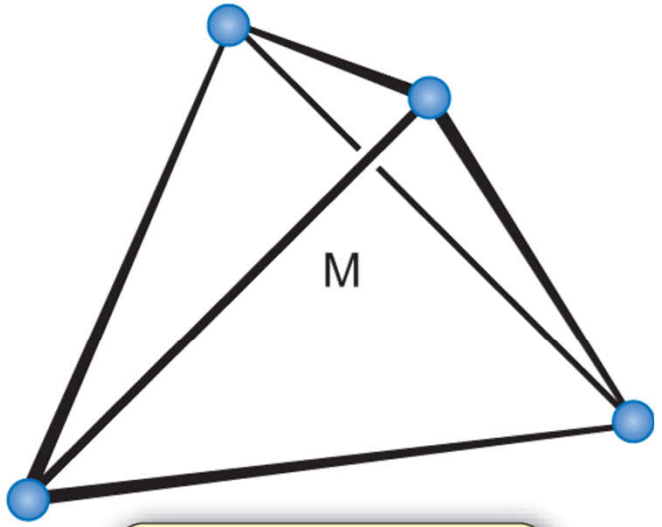
$EECC = -1,6x170 + 245 = -27\ KJ.mol^{-1}$

Tetraedro

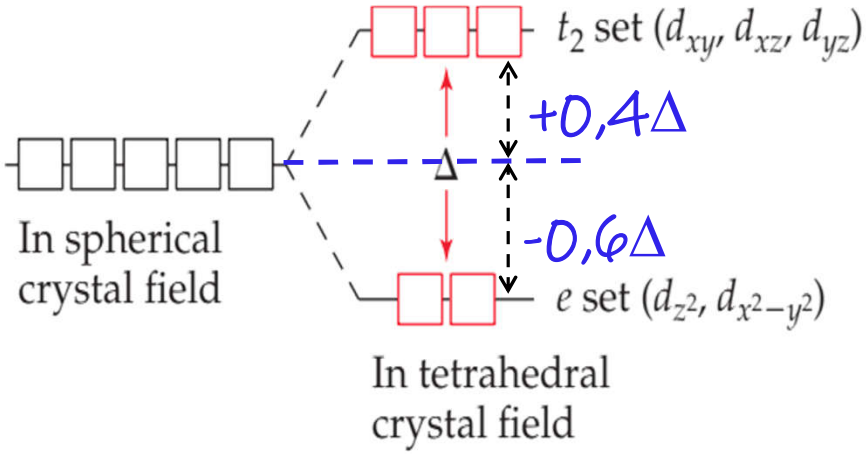


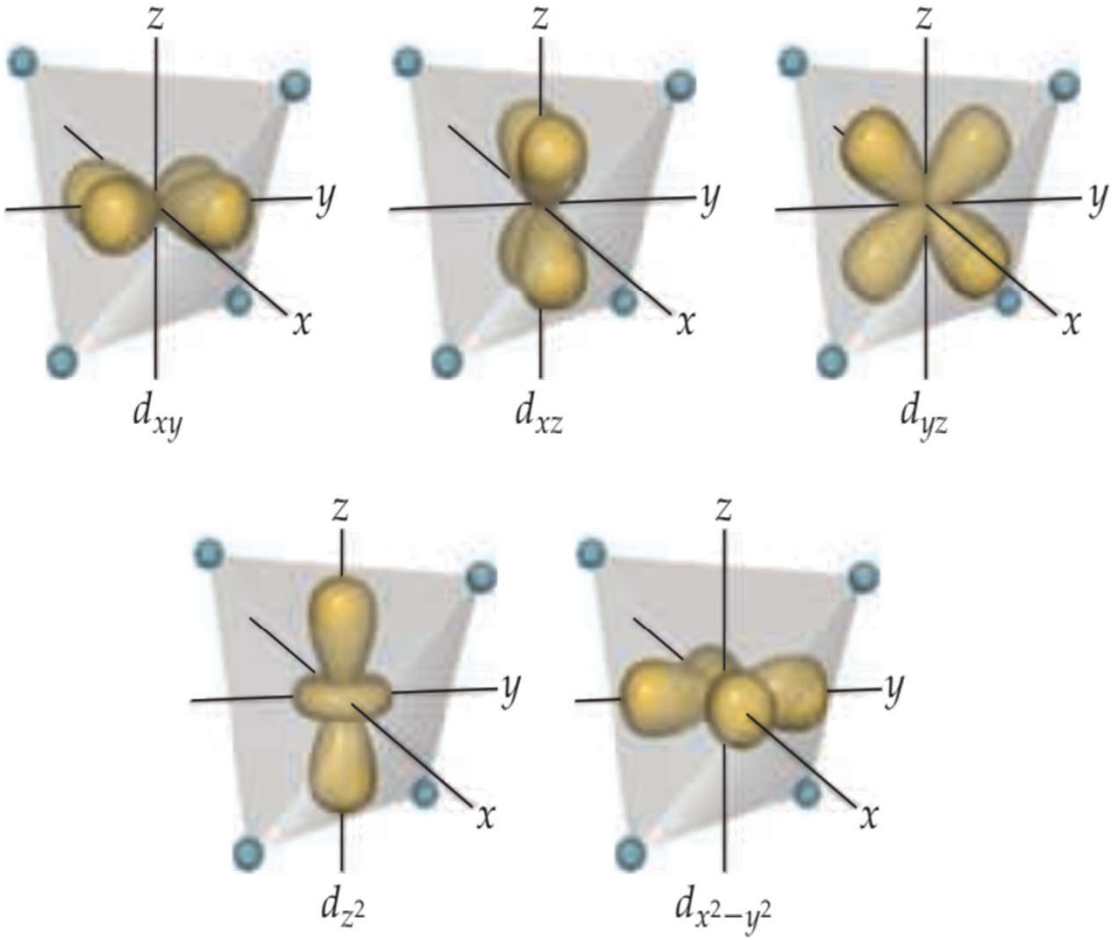
In a tetrahedral field, the ligands are located on four of the vertices of a cube.

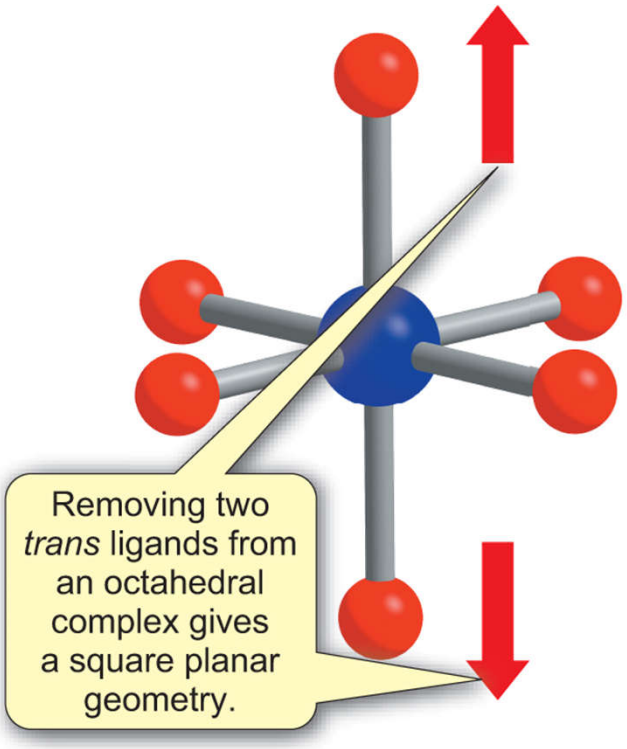
The *d* orbitals are located in the *xy*, *xz*, and *yz* planes or along the *z*-axis, so none points directly at the charges.

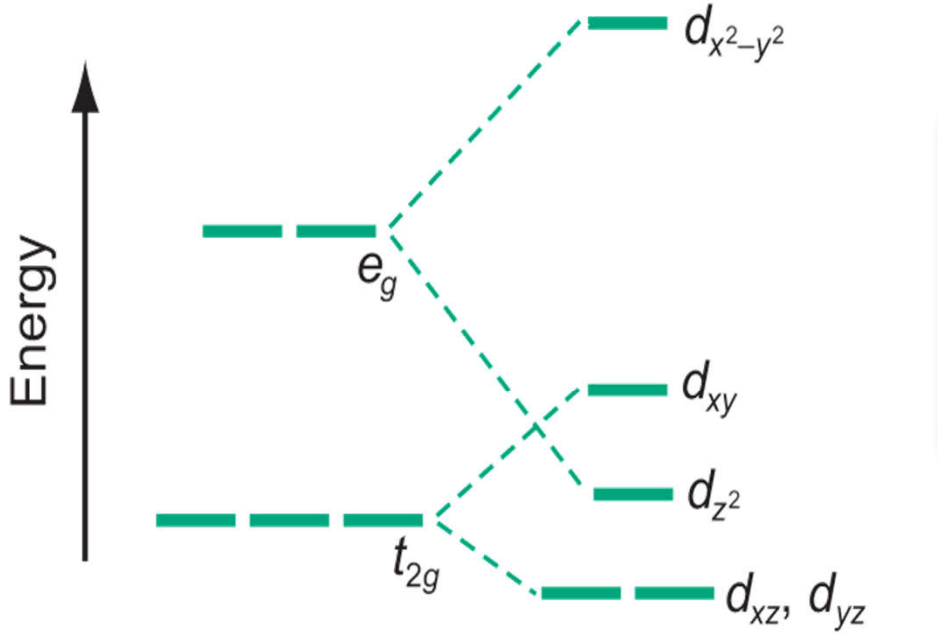


The four positions define the vertices of a tetrahedron.


t_2 set (d_{xy}, d_{xz}, d_{yz})
+0,4Δ
Δ
-0,6Δ
e set (d_{z^2}, $d_{x^2-y^2}$)
In spherical crystal field
In tetrahedral crystal field

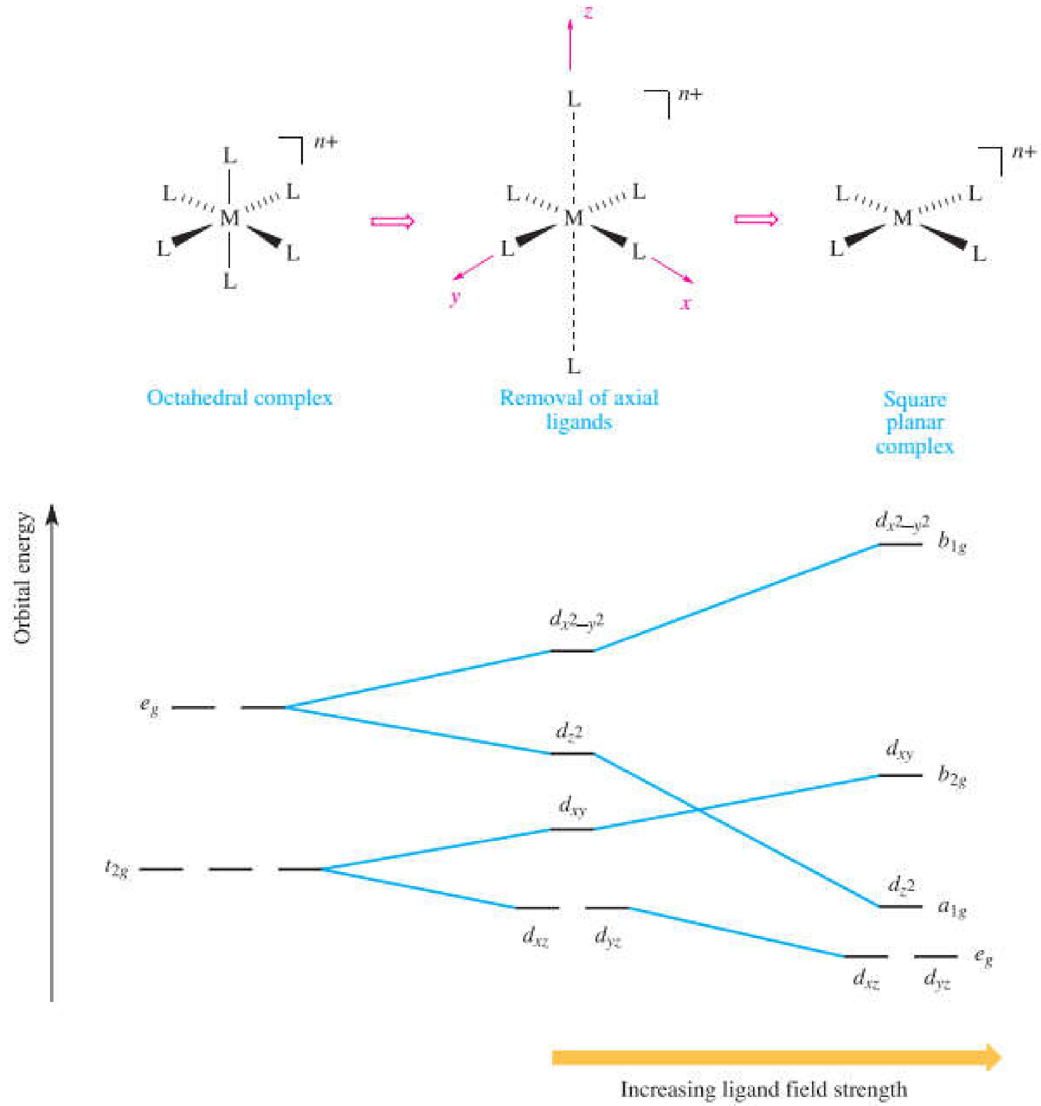

z
y
x
d_{xy}
d_{xz}
d_{yz}
d_{z^2}
$d_{x^2-y^2}$





campo Octaedrico

campo quadrado planar



Octahedral complex
Removal of axial ligands
Square planar complex
Orbital energy
Increasing ligand field strength

$_{28}Ni^{2+}$: $Ar\cancel{4s^2}3d^8$

paramagnético


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


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

tetraedro

diamagnético


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


d_{xy}


d_{z^2}


d_{xz}, d_{yz}

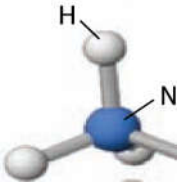
quadrado planar

Efeito Quelato

$$[Ni(H_2O)_6]^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6\,H_2O(l)$$

$$K_f = 1.2 \times 10^9$$

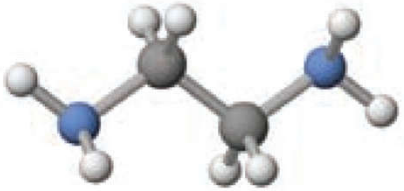
ΔH=-109 KJ/mol



$$[Ni(H_2O)_6]^{2+}(aq) + 3\,en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6\,H_2O(l)$$

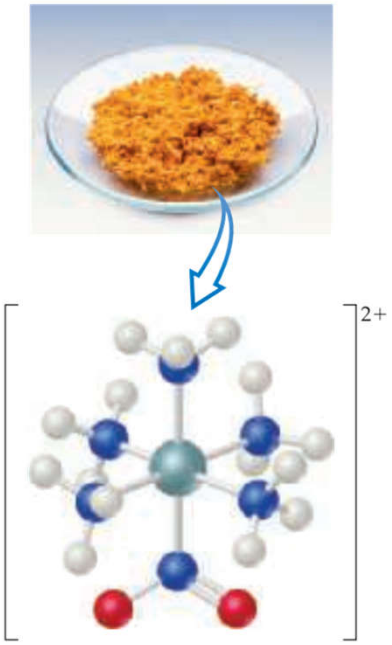
$$K_f = 6.8 \times 10^{17}$$

ΔH=-117 KJ/mol

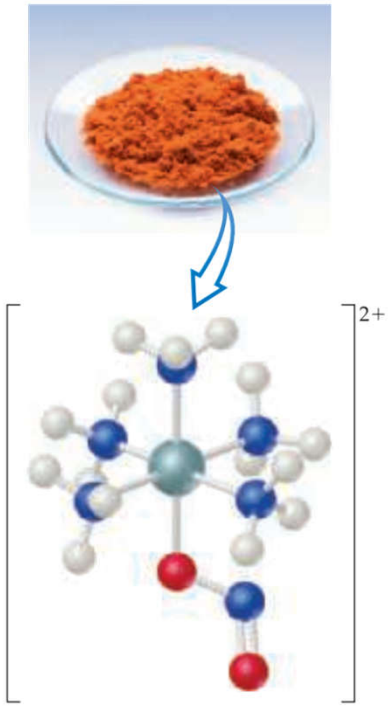


$\Delta G = -RT\ln K$ $\Delta G = \Delta H - T\Delta S$

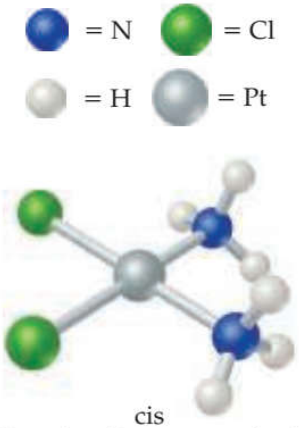
ISOMERIA



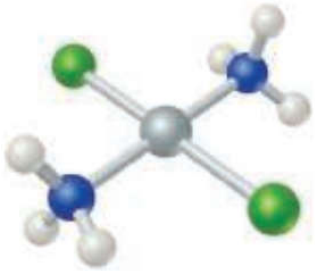
Nitro isomer
Bonding via ligand N atom



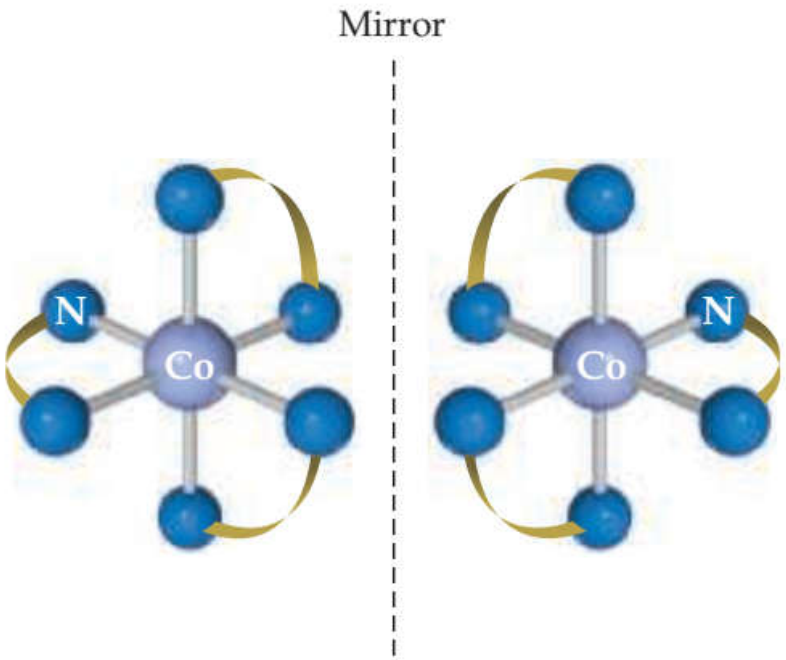
Nitrito isomer
Bonding via ligand O atom



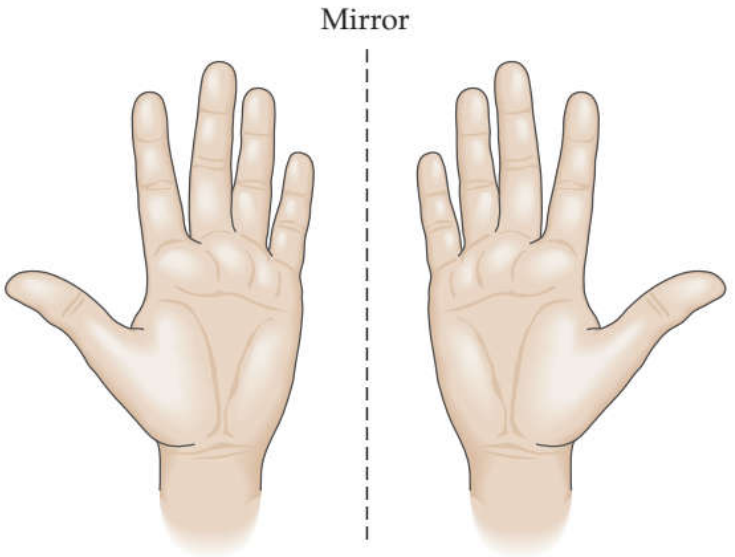
cis
Cl ligands adjacent to each other
NH_3 ligands adjacent to each other



trans
Cl ligands on opposite sides of central atom
NH_3 ligands on opposite sides of central atom



Enantiomers of $[Co(en)_3]^{3+}$



Left hand

Mirror image of left hand is identical to right hand

Obrigado !!