Aula 12 QE

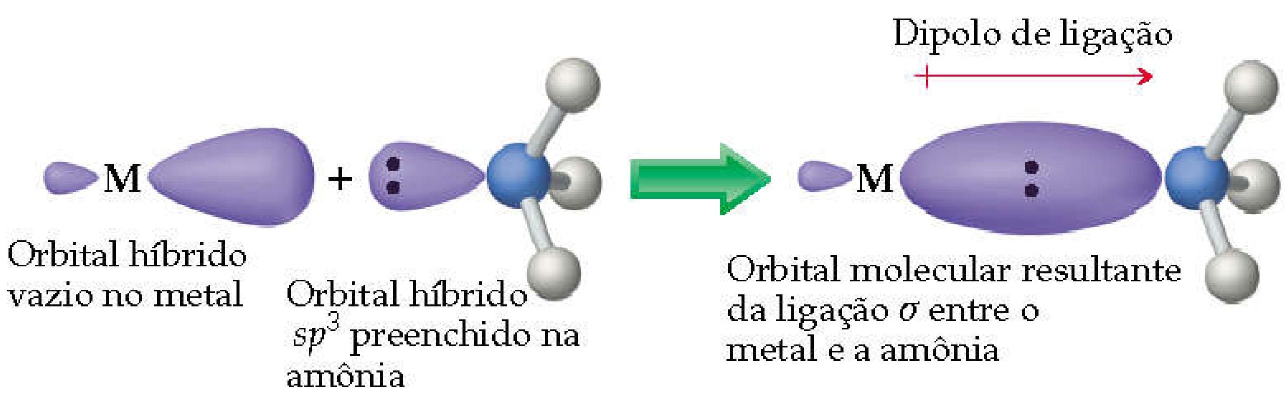
Teoria do campo cristalino

Teoria do campo cristalino

- A teoria do campo cristalino descreve a ligação em complexos de metais de transição.
- A formação de um complexo é uma reação ácido-base de Lewis.
- Ambos os elétrons na ligação vêm do ligante e são doados para um orbital vazio hibridizado no metal.
- A carga é doada do ligante para o metal.

Teoria do campo cristalino

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



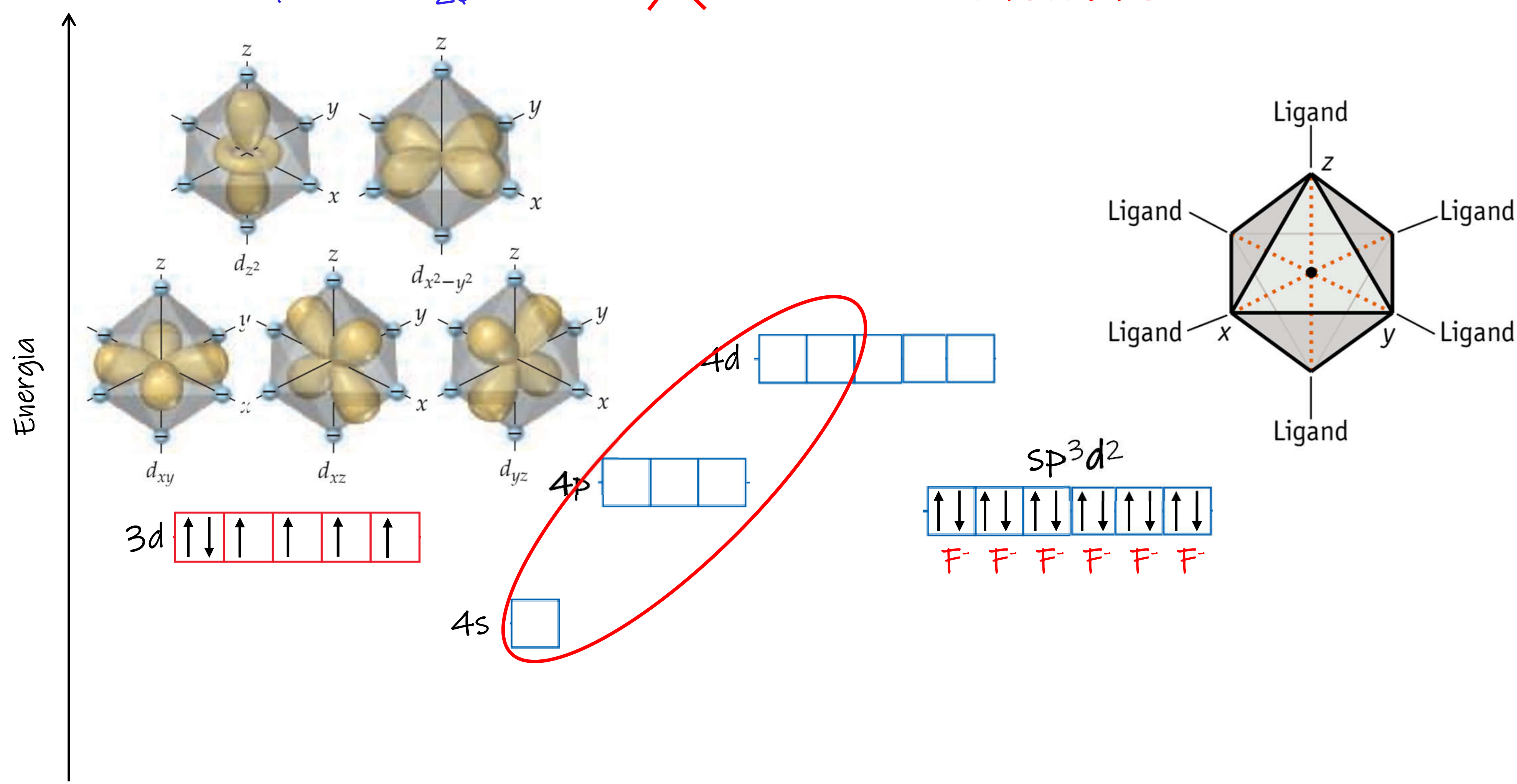
Teoria do campo cristalino

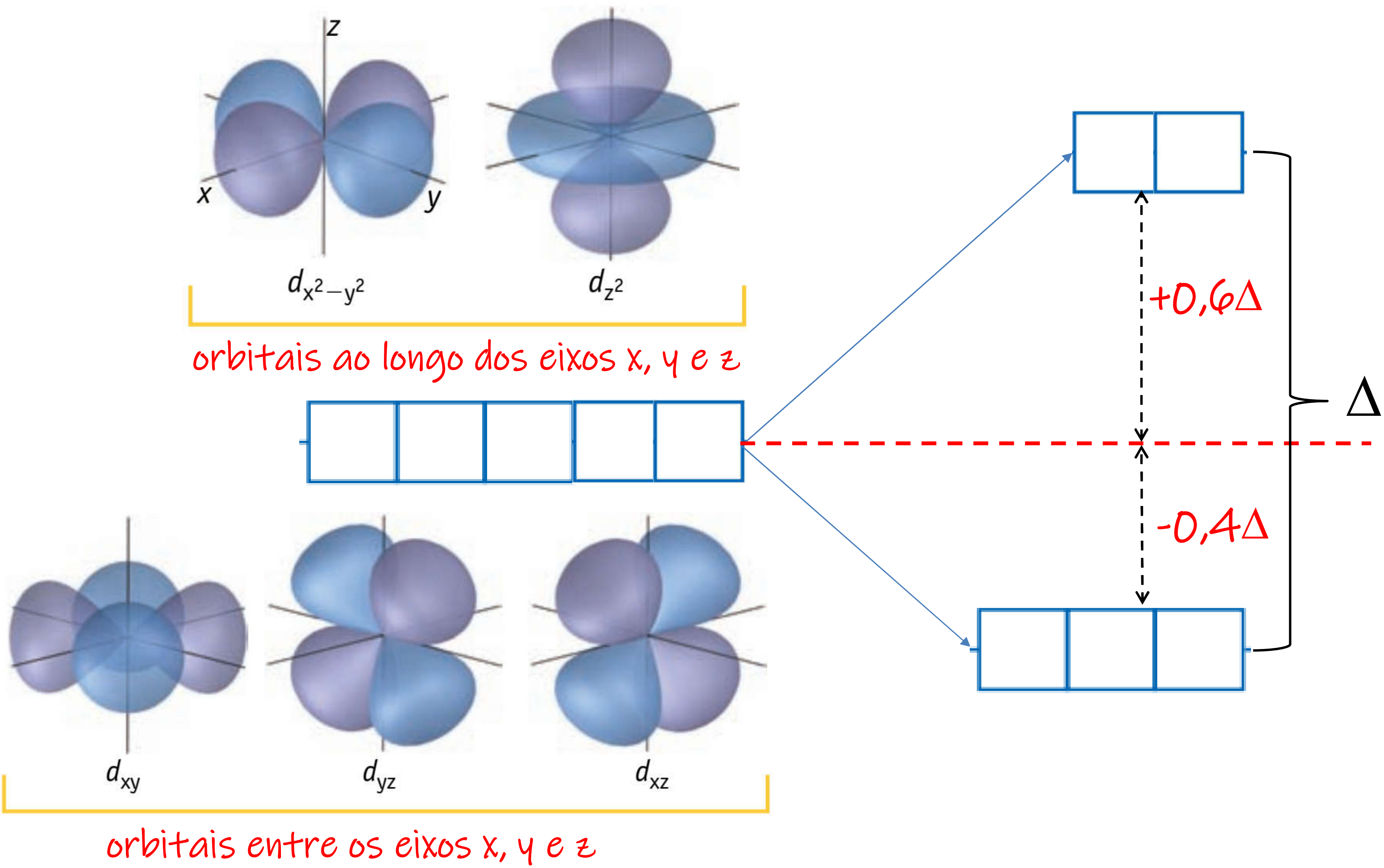
- O íon metálico complexo tem uma energia menor do que o metal e os ligantes separados.
- Entretanto, existem algumas repulsões ligante-elétron *d* que ocorrem, uma vez que o metal tem orbitais *d* parcialmente preenchidos.
- Em um campo octaédrico, a degenerecência dos cinco orbitais *d* é suspensa.
- Em um campo octaédrico, os cinco orbitais *d* não têm a mesma energia: três orbitais degenerados têm mais energia do que dois orbitais degenerados.

$[FeF_6]^{4-}$

$_{26}Fe^{2+}$: Ar ~~$4s^2$~~ $3d^6$

Octaédro

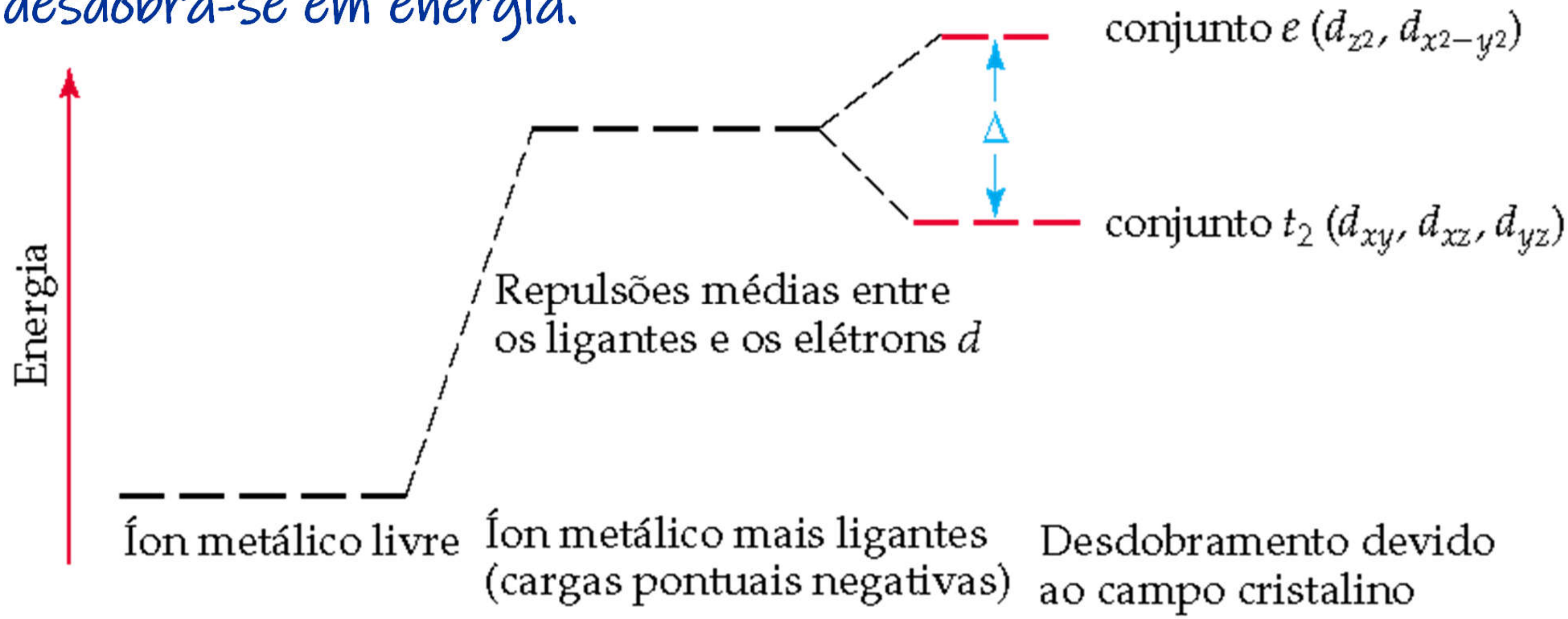


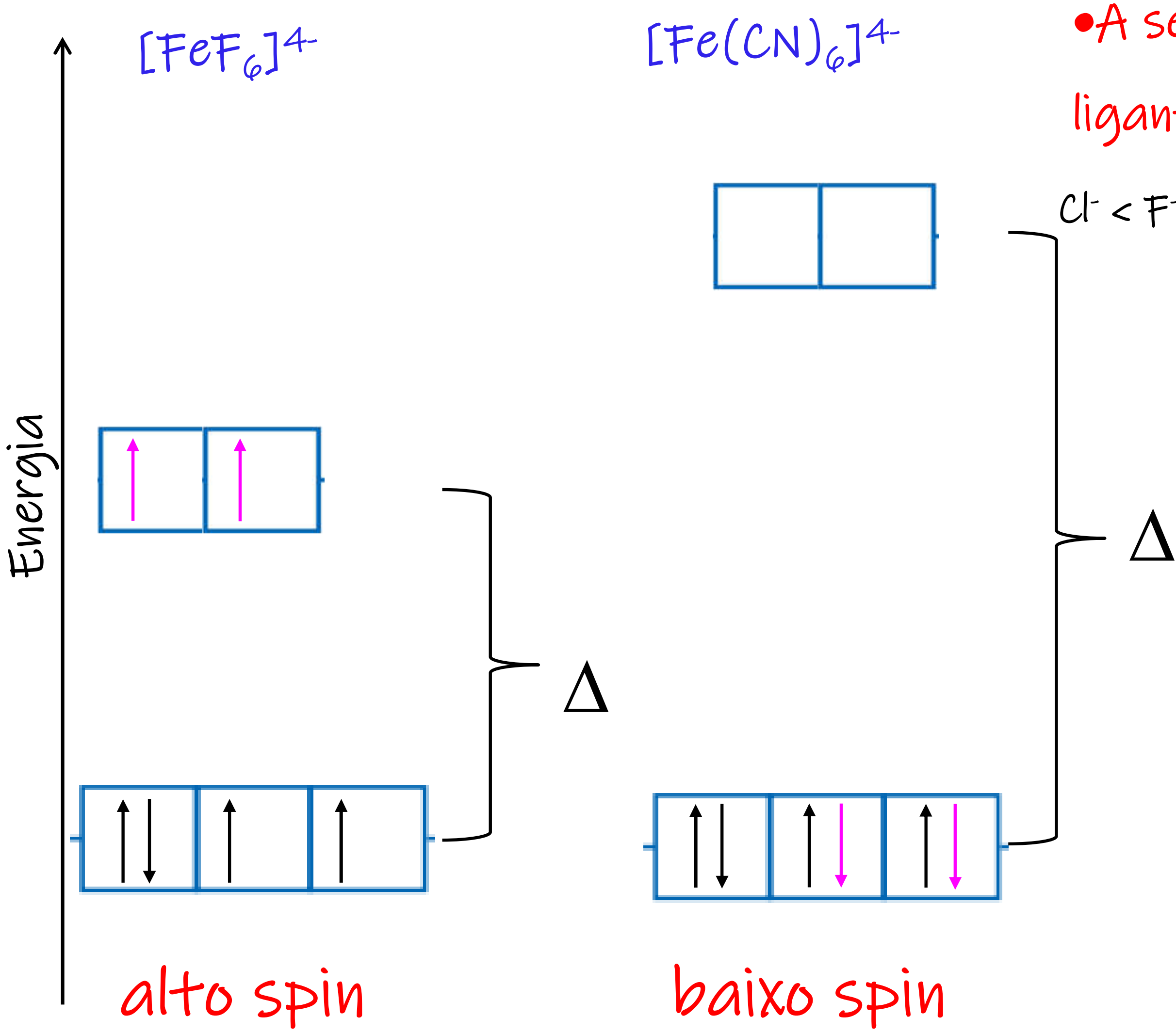


z
x
y
$d_{x^2-y^2}$
d_{z^2}
orbitais ao longo dos eixos x, y e z
+0,6Δ
Δ
-0,4Δ
d_{xy}
d_{yz}
d_{xz}
orbitais entre os eixos x, y e z

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 a N) $< CN^-$

Δ

vs

Energia de pareamento

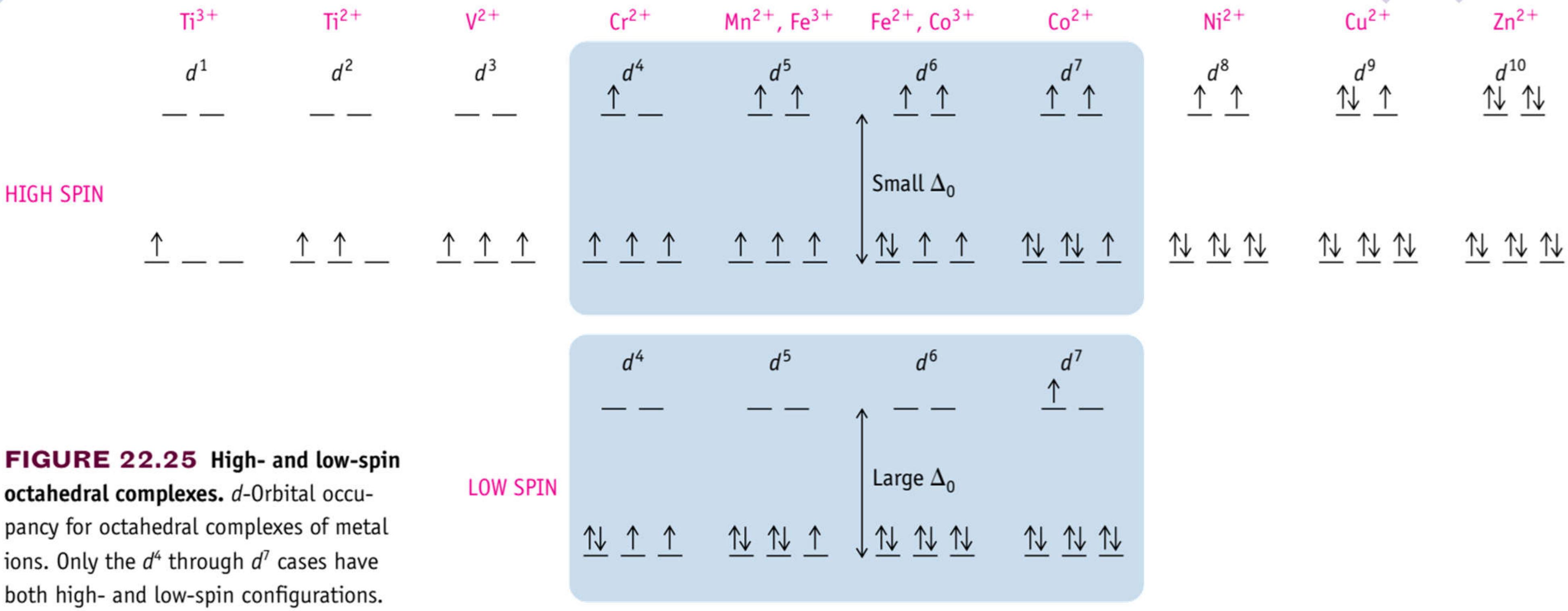
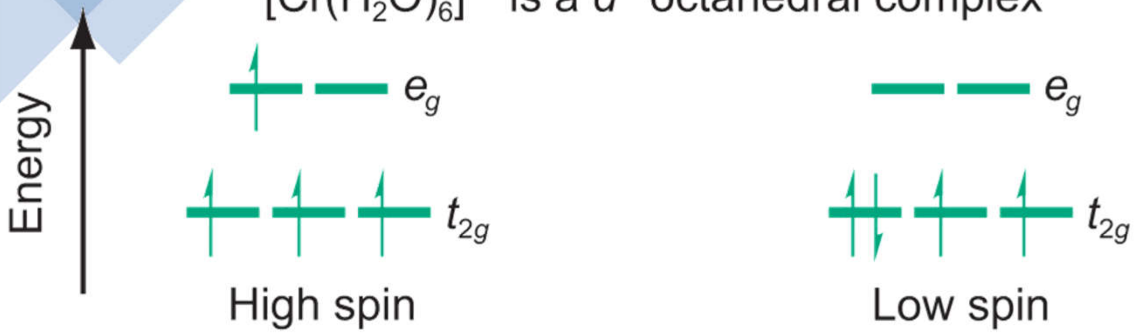


FIGURE 22.25 High- and low-spin octahedral complexes. *d*-Orbital occupancy for octahedral complexes of metal ions. Only the d^4 through d^7 cases have both high- and low-spin configurations.

$[Cr(H_2O)_6]^{2+}$ is a d^4 octahedral complex



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

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

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

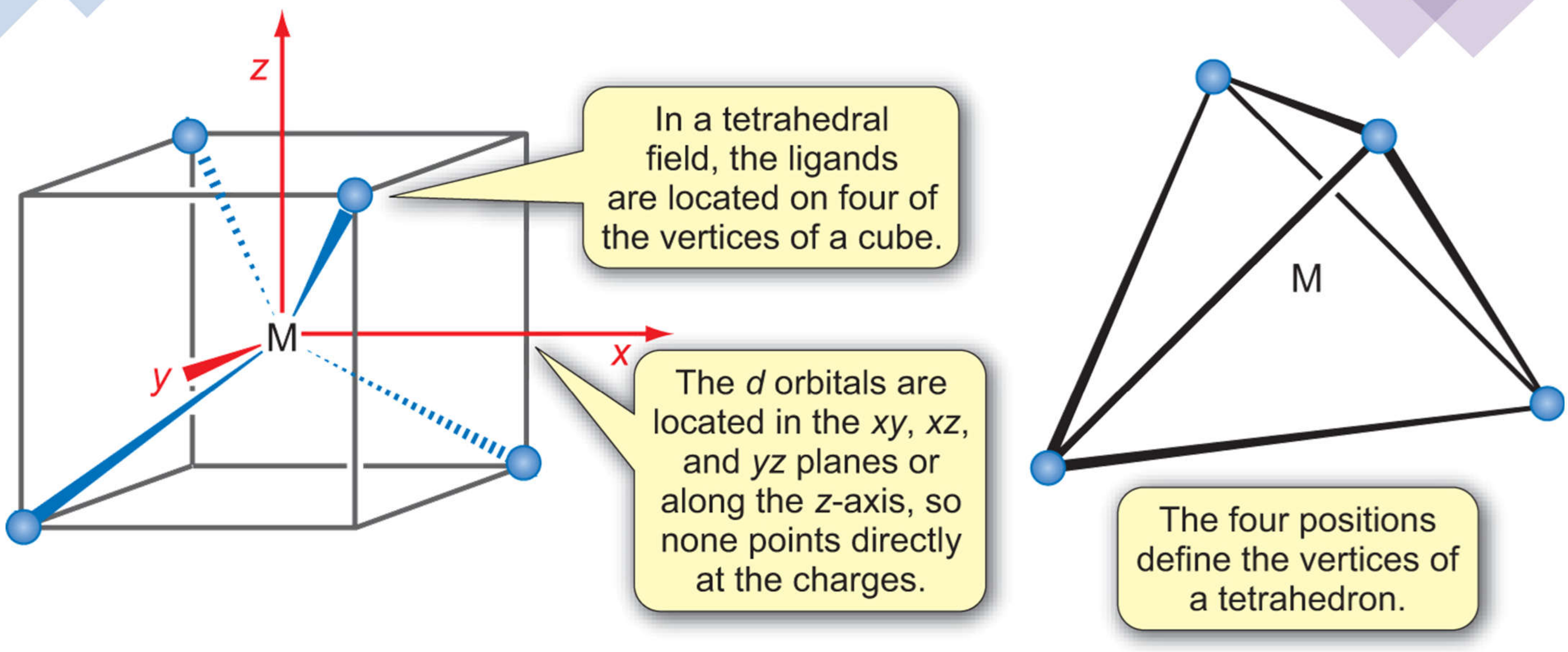
$EECC = -102$ KJ.mol^{-1}

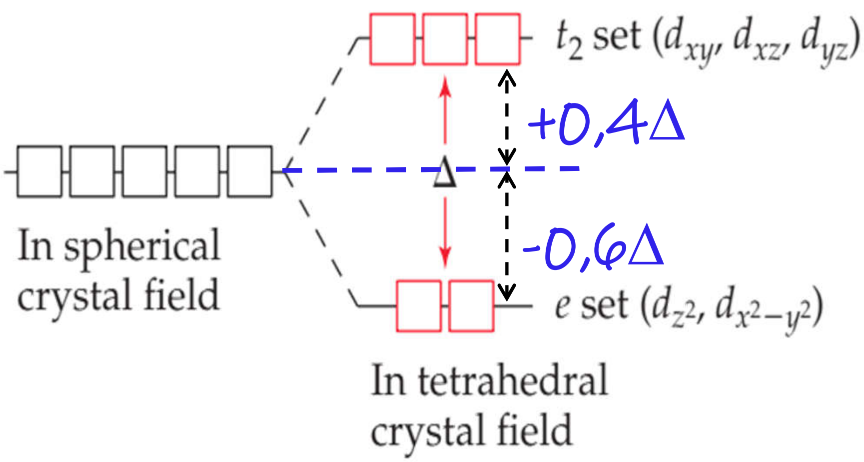
$EECC = 4x(-0,4\Delta)+P$

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

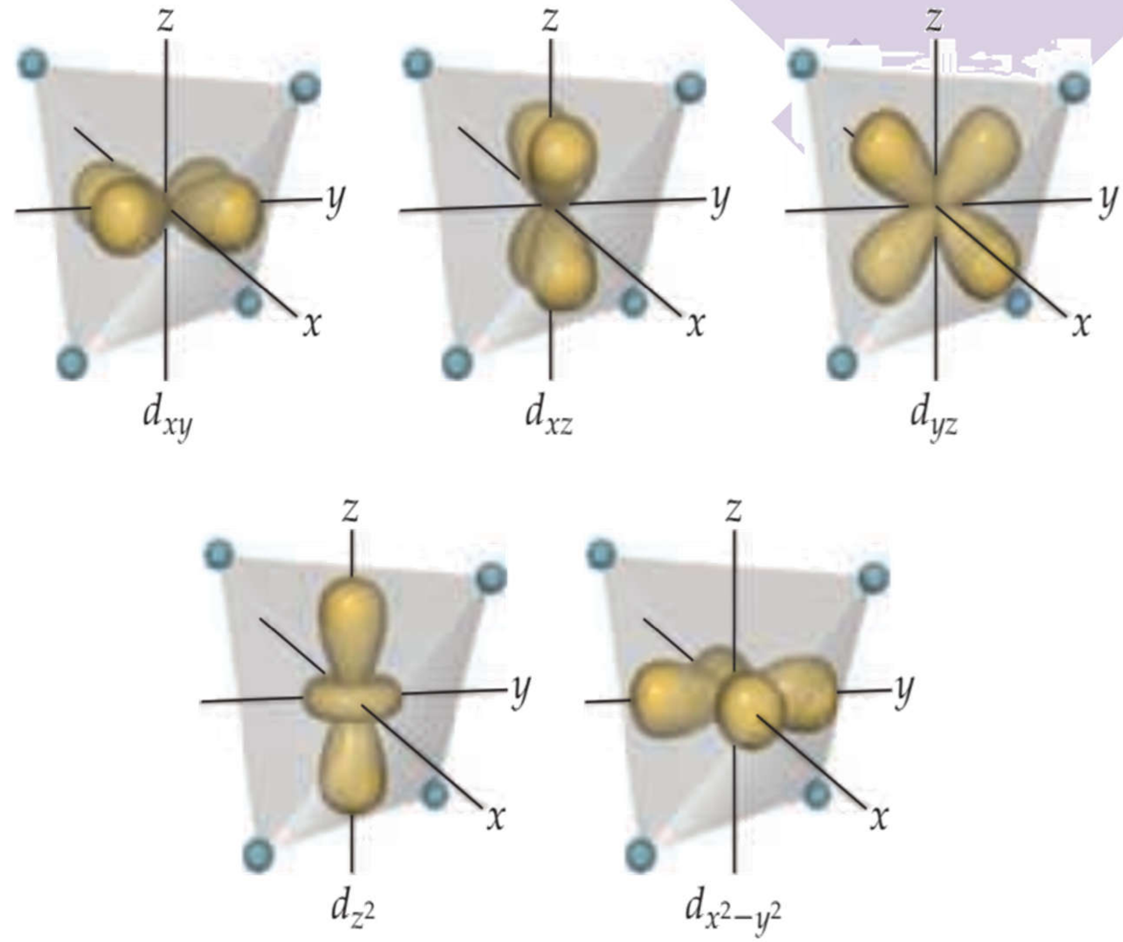
$EECC = -1,6x170 + 245 = -27$ KJ.mol^{-1}

Tetraedro

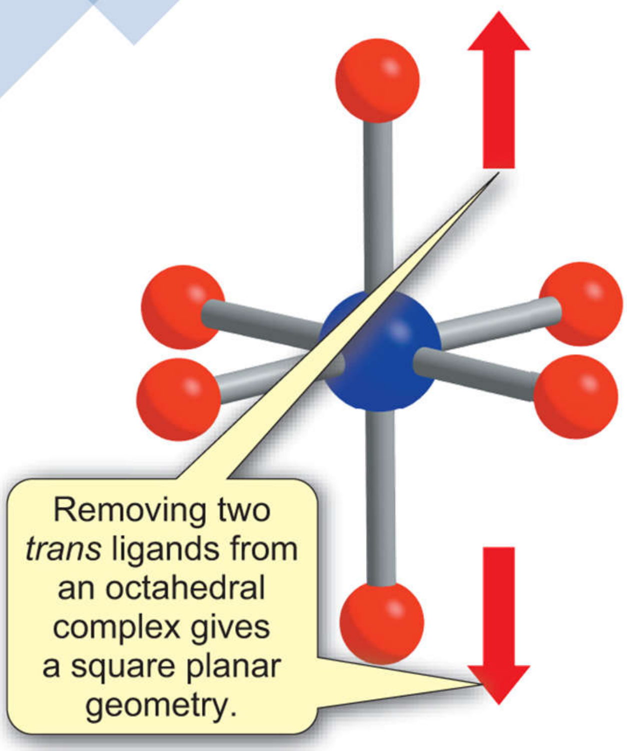

z
M
x
y
In a tetrahedral field, the ligands are located on four of the vertices of a cube.
The d orbitals are located in the xy, xz, and yz planes or along the z-axis, so none points directly at the charges.
M
The four positions define the vertices of a tetrahedron.

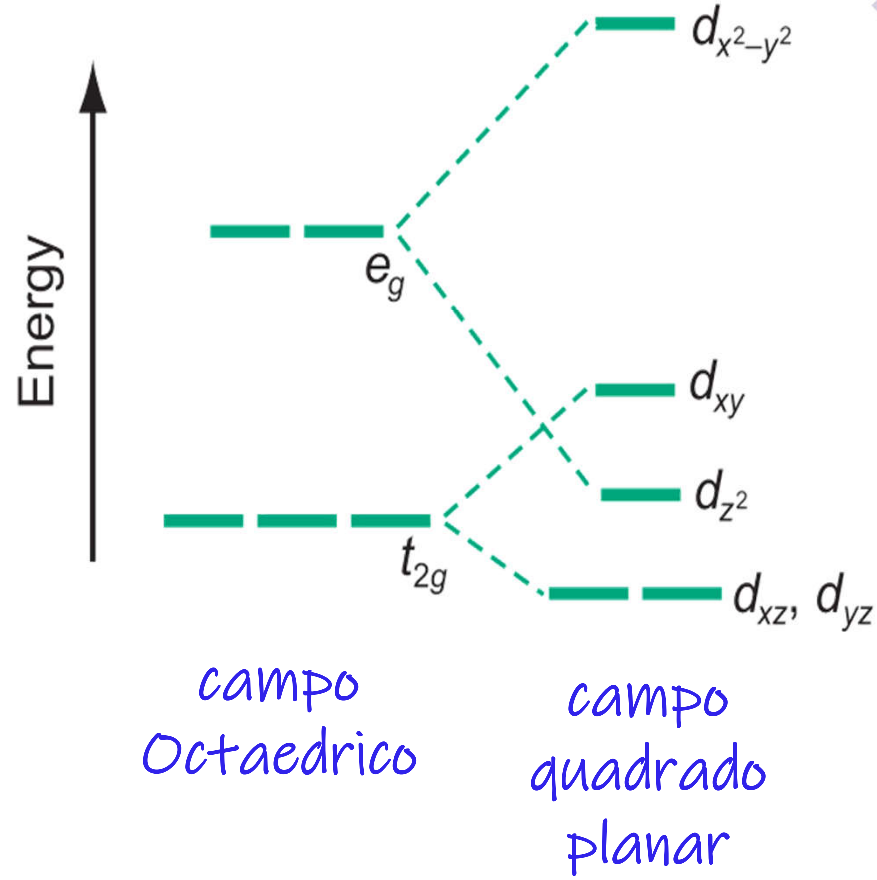


t_2 set (d_{xy}, d_{xz}, d_{yz})
+0,4Δ
Δ
-0,6Δ
In spherical crystal field
e set (d_{z^2}, $d_{x^2-y^2}$)
In tetrahedral crystal field



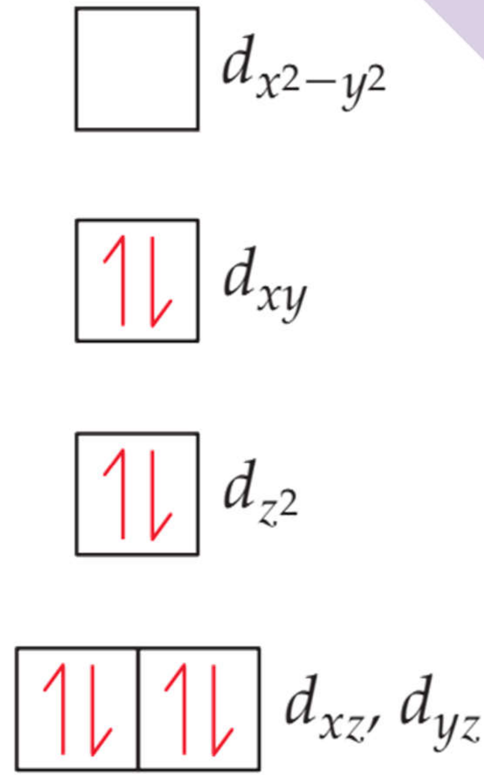
d_{xy}
d_{xz}
d_{yz}
d_{z^2}
$d_{x^2-y^2}$


Removing two *trans* ligands from an octahedral complex gives a square planar geometry.

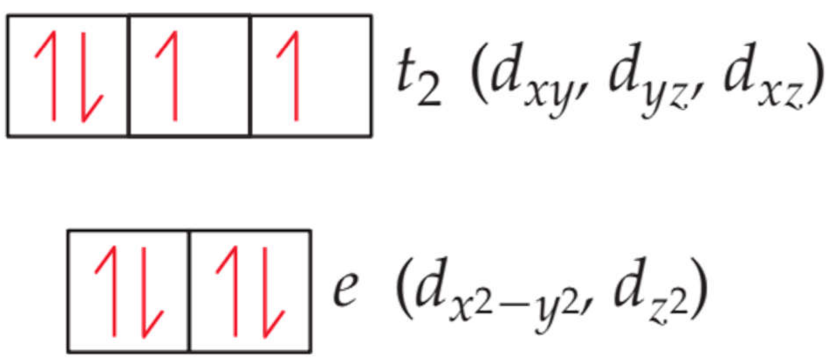

Energy
$d_{x^2-y^2}$
e_g
d_{xy}
d_{z^2}
t_{2g}
d_{xz}, d_{yz}
campo Octaedrico
campo quadrado planar

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

diamagnético



paramagnético



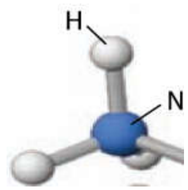
tetraedro

quadrado planar

Efeito Quelato

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

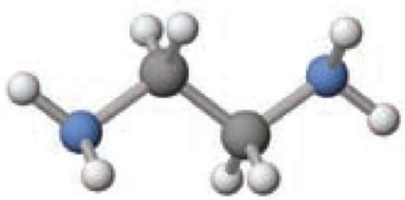
ΔH=-109 KJ/mol



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

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

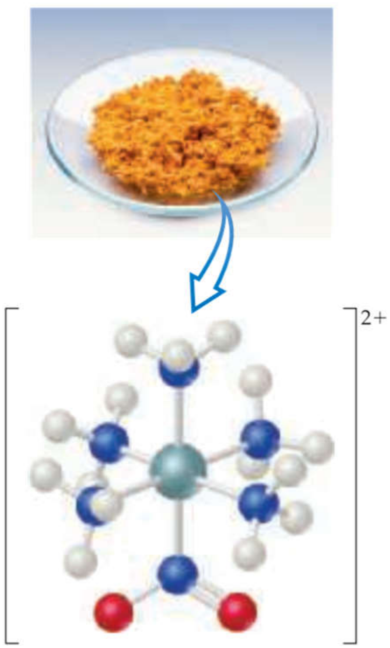
ΔH=-117 KJ/mol



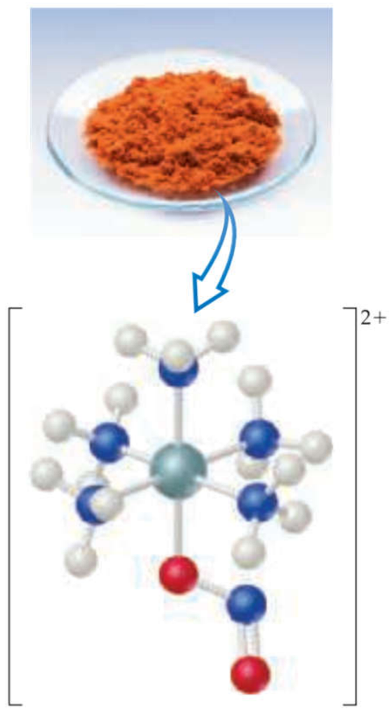
$$K_f = 6.8 \times 10^{17}$$

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

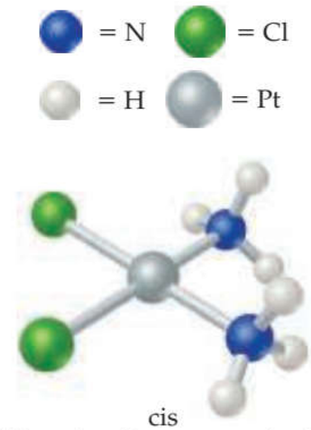
ISOMERIA



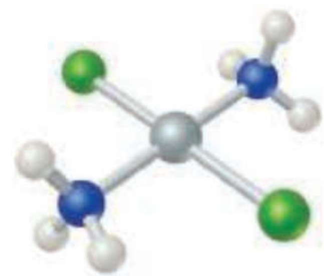
Nitro isomer
Bonding via ligand N atom



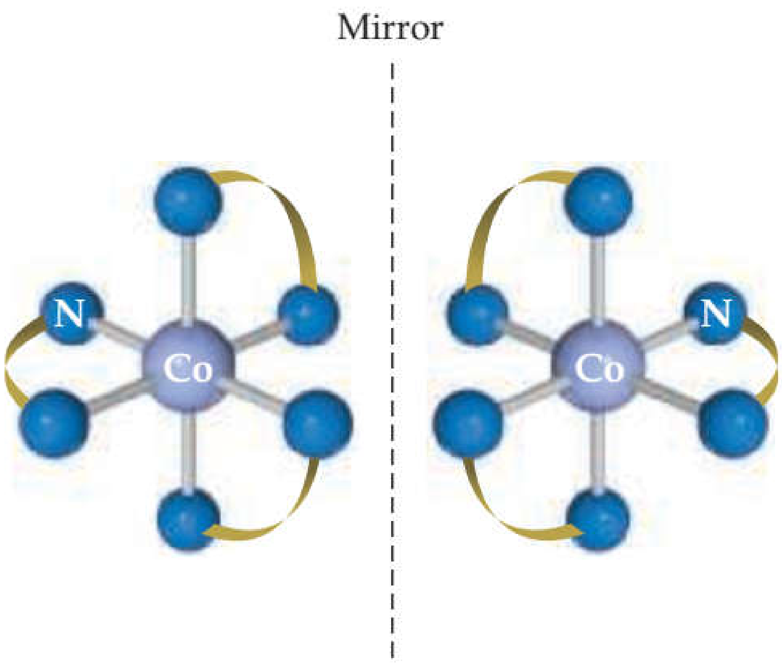
Nitrito isomer
Bonding via ligand O atom



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