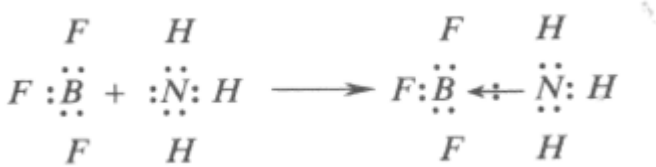
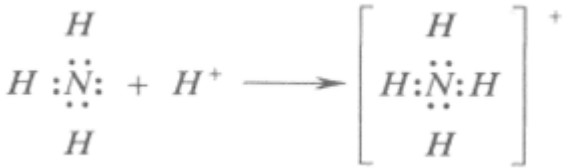
Si definisce ACIDO (di Lewis) una specie chimica in grado di accettare uno o più lone pairs; BASE (di Lewis) una specie in grado di fornire uno o più lone pairs





Complexes of the d-Block Elements

- Ions of d-block elements are excellent **Lewis acids** (electron pair acceptors).
- They form coordinate covalent bonds with molecules or ions that can act as **Lewis bases** (electron pair donors).
- Complexes formed in this way participate in many biological reactions (e.g., hemoglobin, vitamin B_{12}) and are important in other ways as well (e.g., catalysis, dyes, solar energy conversion).

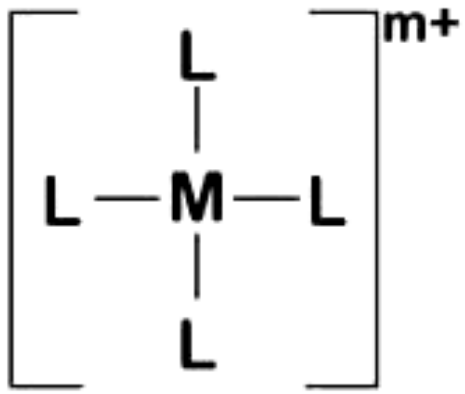
Terminology

- **ligand** - a molecule or ion attached to a central metal atom or ion. Typically, there are four or six ligands in a complex.
- **coordinate** (*verb*) - to attach. (Ligands coordinate to the metal when they form the complex.)
- **coordination compound** - a compound with a coordinate covalent bond.
- **coordination sphere** - the sphere around the central ion made up of the ligands directly attached to it.
- **coordination number** - the number of points where ligands are attached to the central metal atom.

COMPOSTI DI COORDINAZIONE

Complexes

General structure



X^{n+}

L - ligand

M - central species

X - counter ion

Specie centrale Deve essere in grado di accettare una o più coppie di elettroni negli orbitali d disponibili, tipicamente uno ione metallico

Leganti Anione, catione o specie neutre in grado di donare coppie di elettroni con formazione di legami di coordinazione (dativi)

Contro ione Necessario se il complesso presenta una carica elettrica

Tipicamente i leganti sono anioni o specie neutre polari quando agiscono in ambiente acquoso

I leganti possono essere classificati secondo il numero di "***denti***" o il numero di legami di coordinazione

Monodentati

1 legame di coordinazione - es. NH_3

Bidentati

2 legami di coordinazione – es. $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$

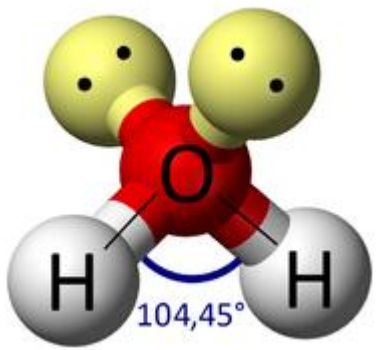
Polidentati

Numero variabile secondo le necessità – es. ***EDTA***

Monodentate ligands

Possess only one accessible donor group.

H_2O is a good example since all metal ions exist as aqua complexes in water.



Although two e^- pair are available, only one is accessible.

The other will always point the wrong way

Monodentate ligands

Common monodentate ligands

anionic		neutral
X^-	OH^-	H_2O
SCN^-	$RCOO^-$	NH_3
CN^-	S^{2-}	RNH_2

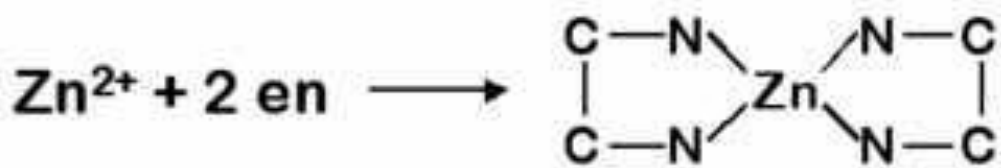
Bidentate ligands

Form two binds / central species.

A good example is ethylene diamine.

$NH_2CH_2CH_2NH_2$ - (en)

The amino groups are far enough apart to permit both to interact.

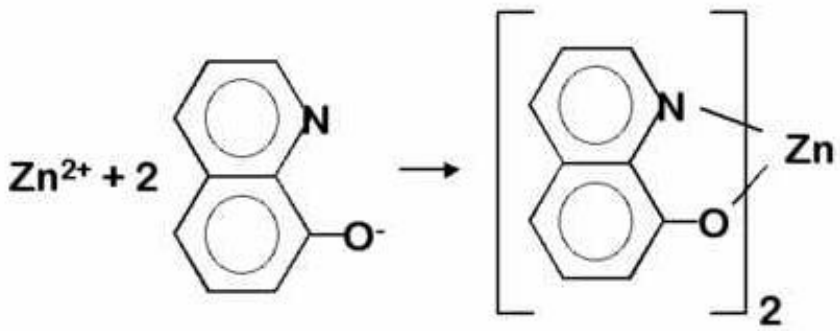


Other examples

Bidentate ligands

Other common bidentate ligands.

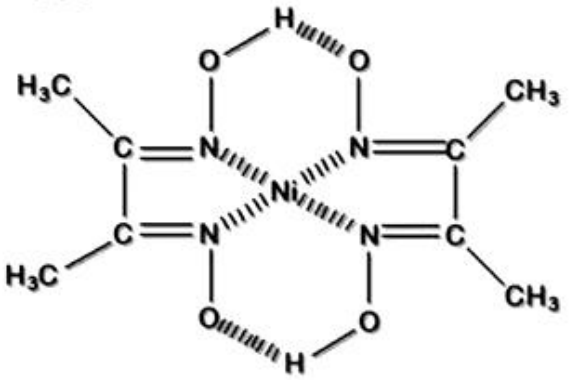
8 - hydroxyquinoline



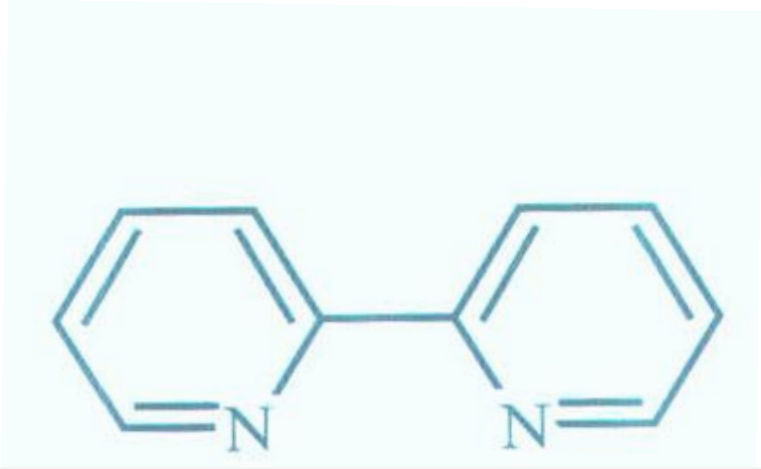
Bidentate ligands

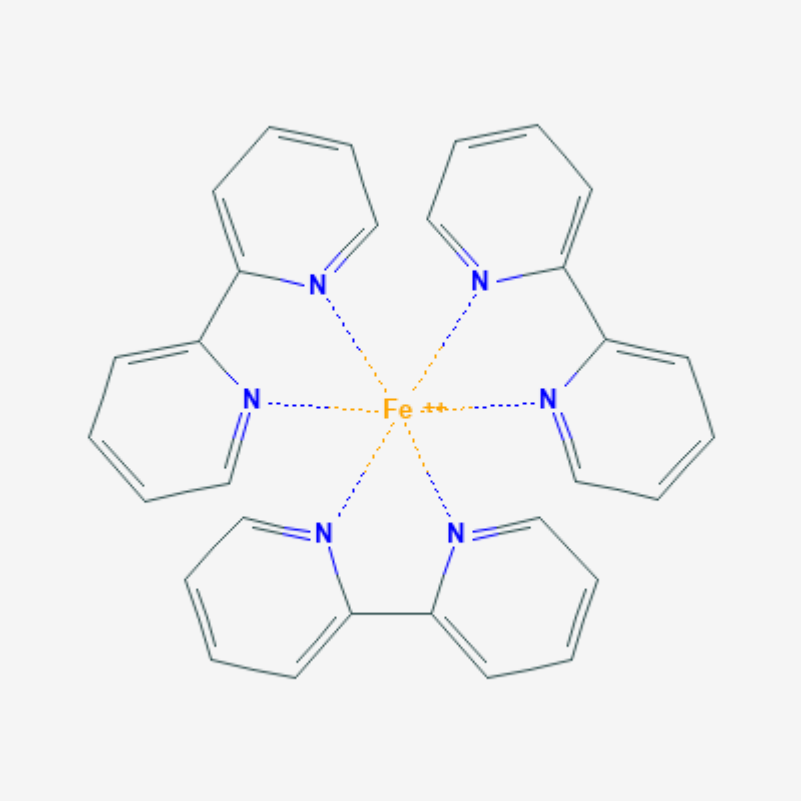
Other common bidentate ligands.

Dimethylglyoxime - DMG



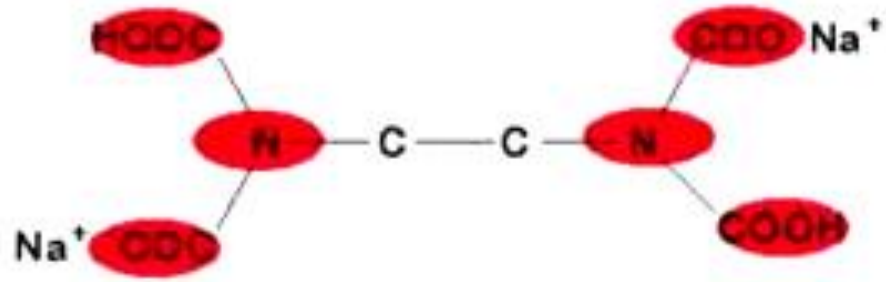
2,2’-Dipiridina





EDTA

The molecule contains 6 donor groups.

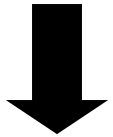


Regardless of the coordination number of the central species, the molecule will adapt to the number needed.

$$Mg^{2+} + H_2Y^{2-} \longrightarrow MgY^{2-} + 2H^+$$

$$Fe^{3+} + H_2Y^{2-} \longrightarrow FeY^- + 2H^+$$

Numero di coordinazione



Non è collegato allo stato di ossidazione dello ione metallico!

Numeri di coordinazione più comuni

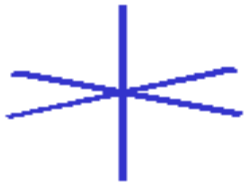
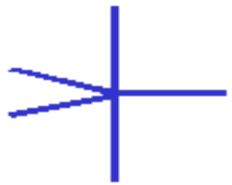
2 - Geometria lineare

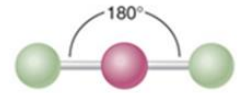
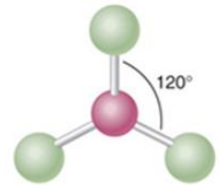
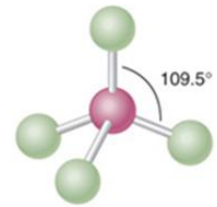
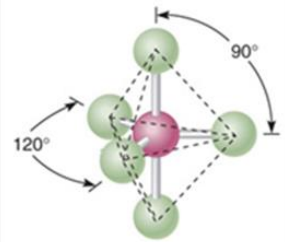
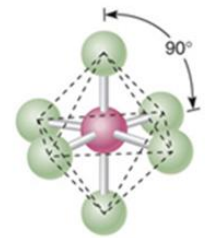
4 - Geometria tetraedrica /planare quadrata

6 - Geometria ottaedrica

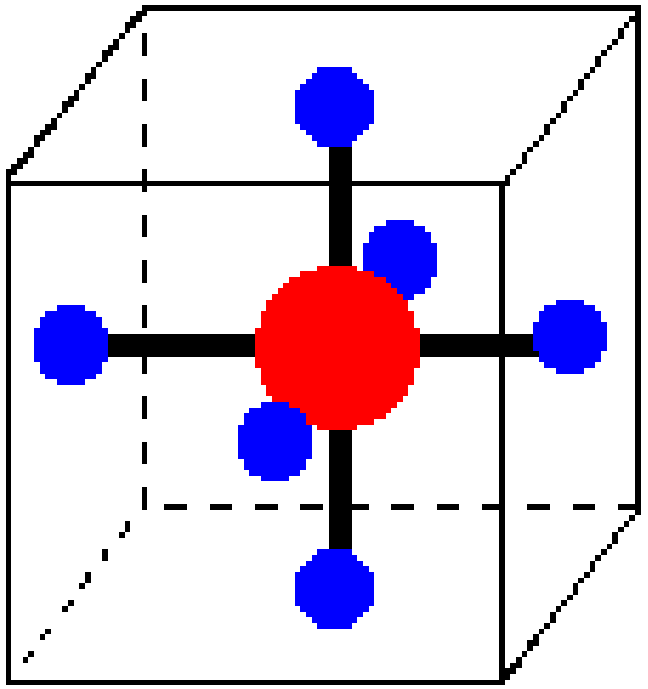
Sia il numero di coordinazione che il numero di denti deve essere noto per conoscere il numero di leganti delle specie centrale

Numeri di coordinazione e geometrie di coordinazione

Geometry		No. of ligands
Octahedral		6
Trigonal bipyramid		5
Tetrahedral		4
Square planar		4
Linear		2

Specie tipiche	Orientazione delle coppie elettroniche	Angoli di legame previsti	Esempio	Modello ball & stick
AX_2	Lineare	180°	BeF_2	
AX_3	Trigonale planare	120°	BF_3	
AX_4	Tetraedro	109.5°	CH_4	
AX_5	Bipiramide trigonale	90° 120° 180°	PF_5	
AX_6	Ottaedro	90° 180°	SF_6	

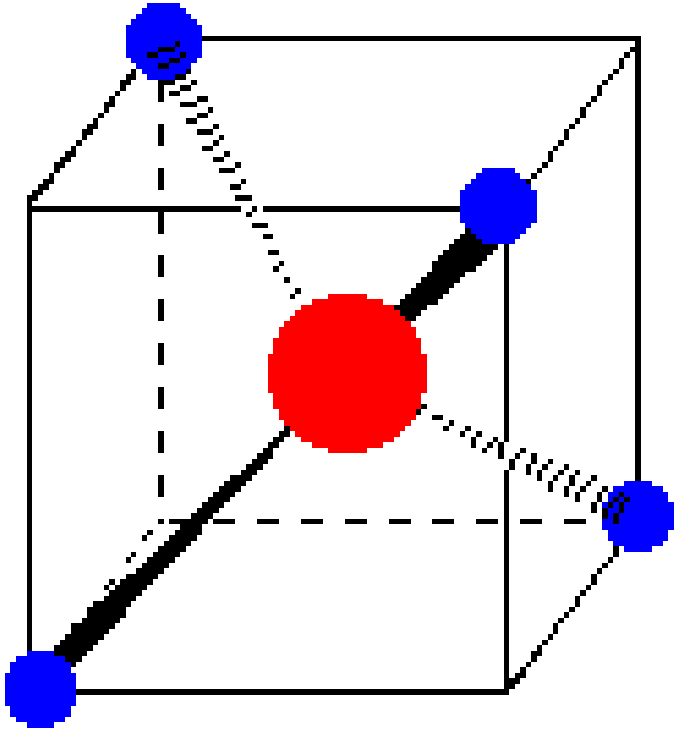
ottaedrica



Octahedral complex in a cube.

Ligands are on the centers
of the cube faces.

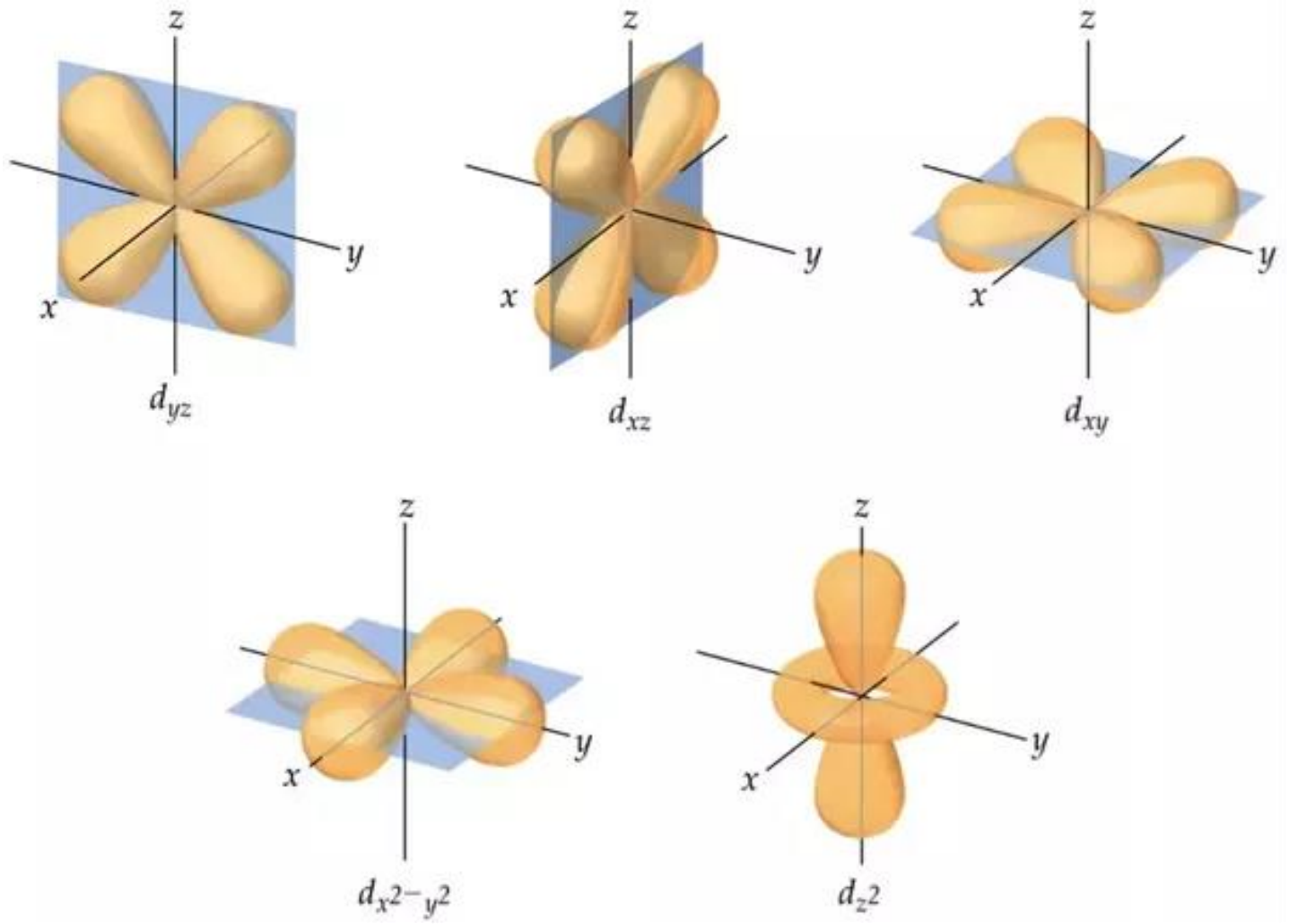
tetraedrica

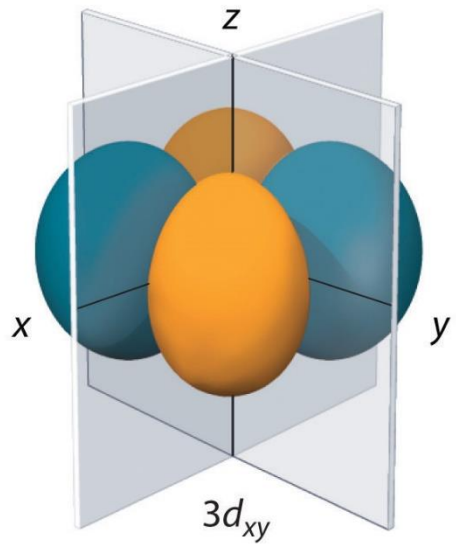


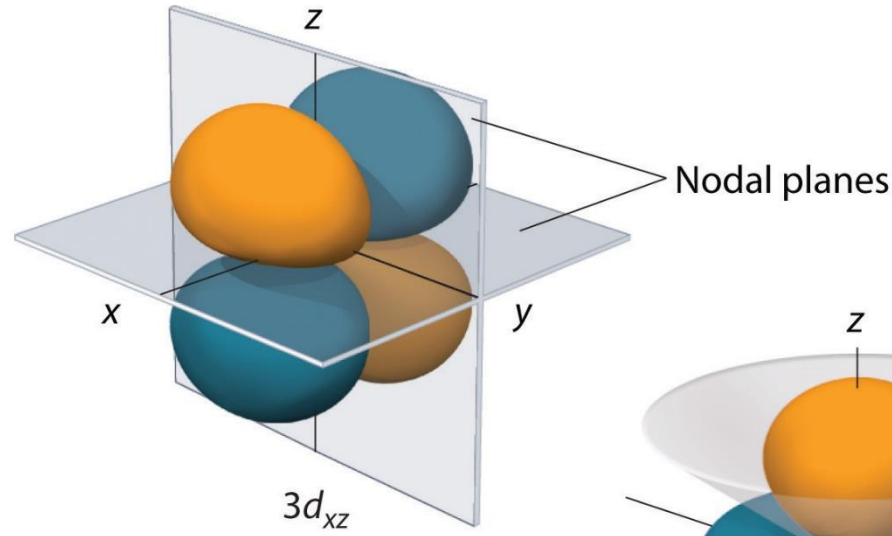
Tetrahedral complex in a cube.

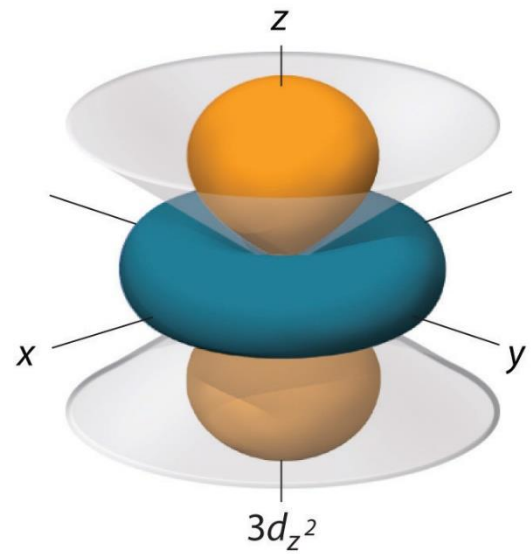
Ligands are on alternate corners
of the cube

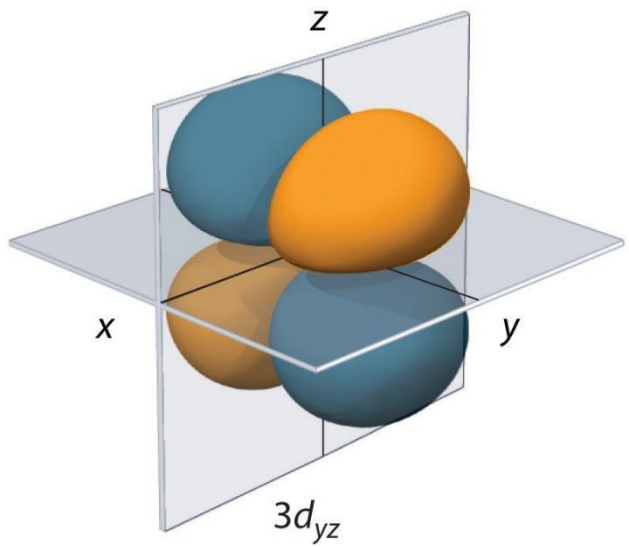
orbitali d

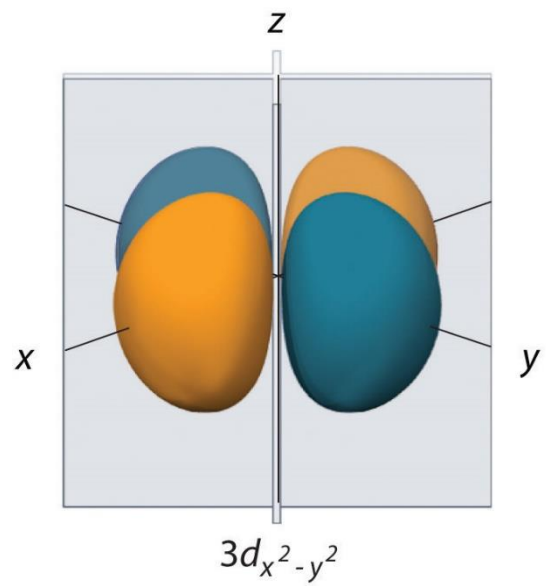



z
x
y
3d_xy


z
x
y
Nodal planes
3d_xz


z
x
y
3d_z²


z
x
y
3d_yz


z
x
y
3d_x²-y²

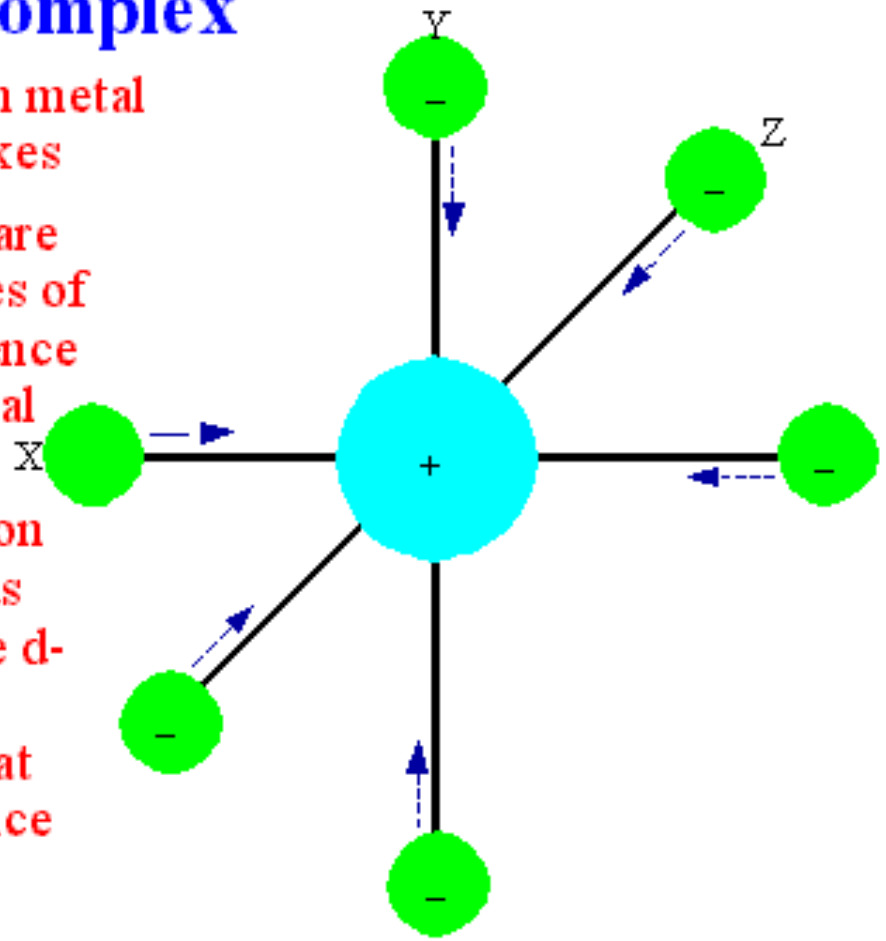
Cosa succede agli orbitali d del metalli in seguito alla coordinazione?

Teoria del campo cristallino

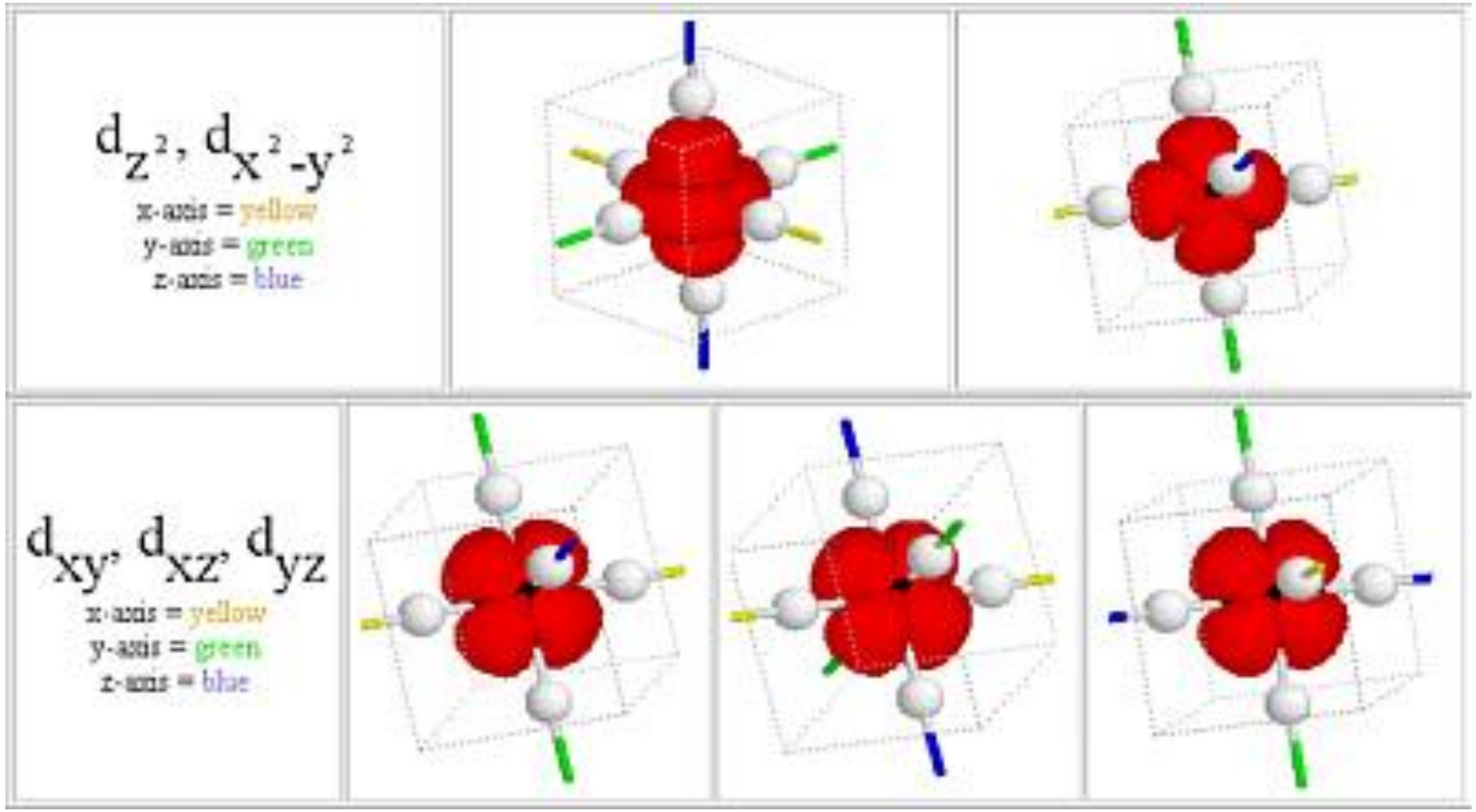
Octahedral Complex

1) Ligands approach metal ion along X, Y, Z axes

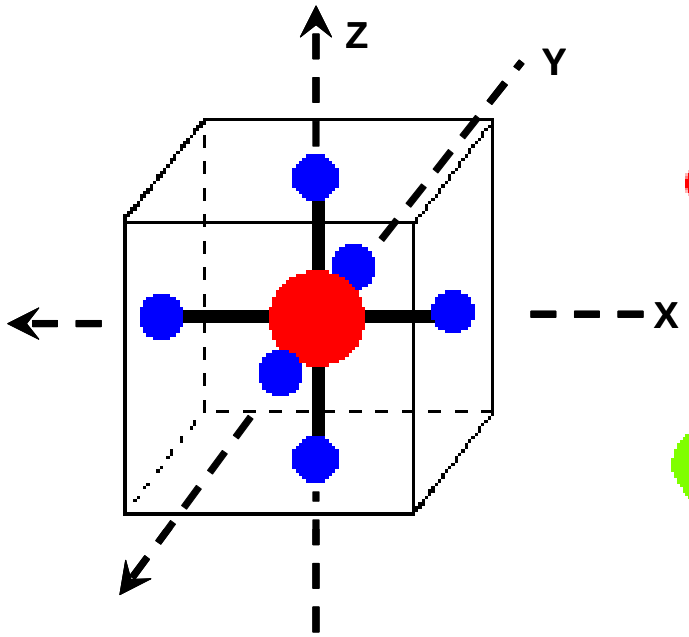
2) e⁻'s in d-orbitals are repulsed by - charges of ligands and experience increases in potential energy. Degree of electrostatic repulsion experienced depends on orientation of the d-orbitals. d-orbitals with lobes directed at the ligands experience more repulsion.

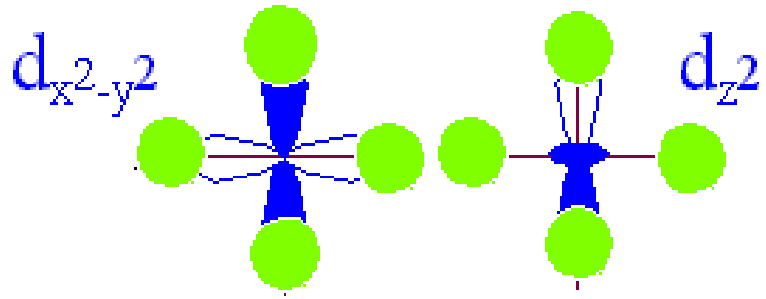


d-orbital orientations

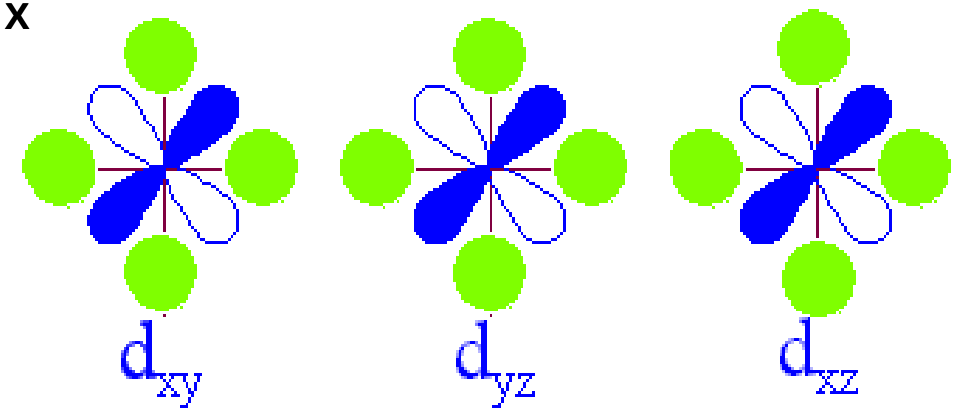


Different effect of ligands



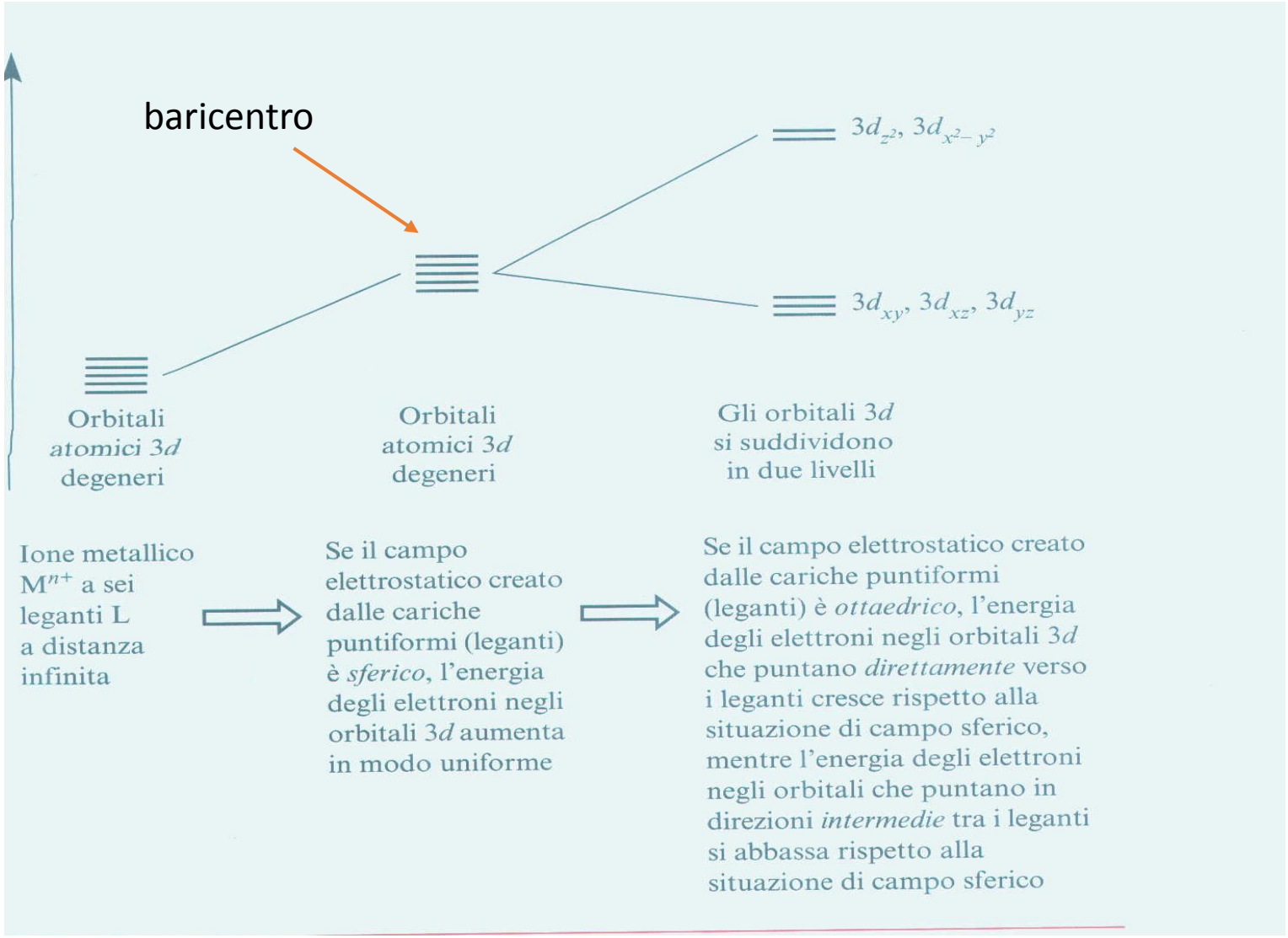


experience greater electrostatic repulsion
(higher potential energy)



experience less electrostatic repulsion
(lower potential energy)

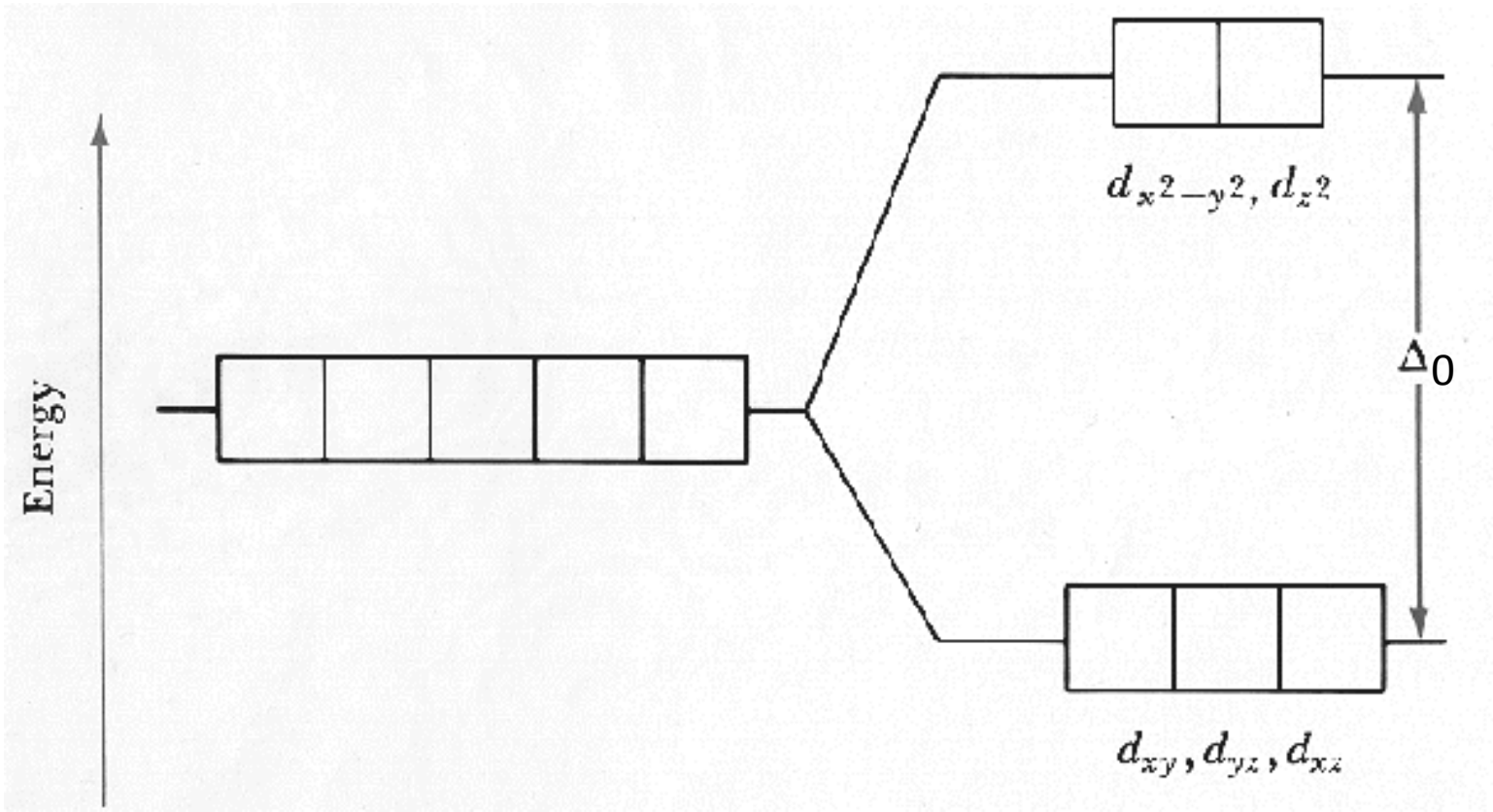
Rimozione della degenerazione

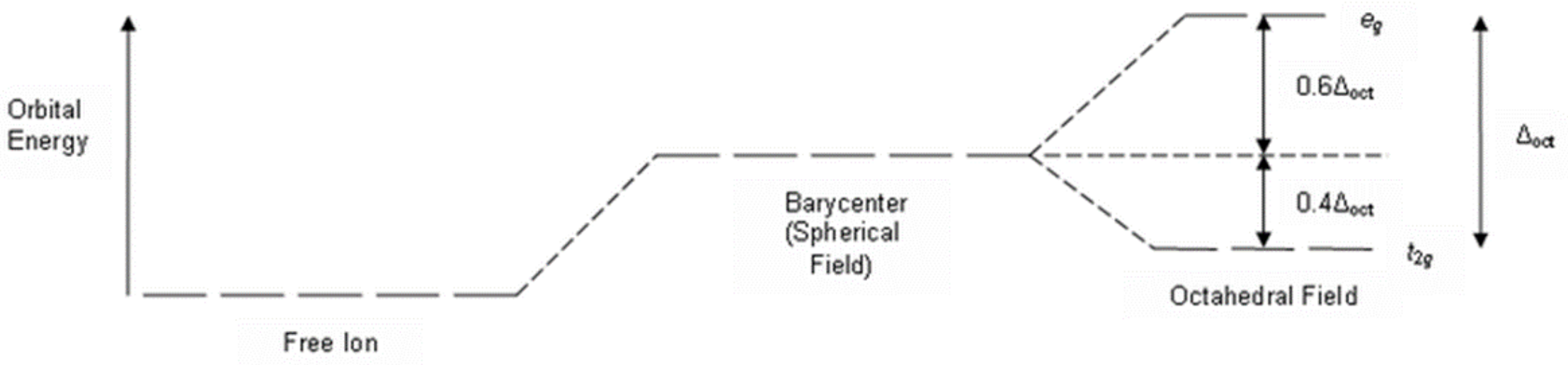


Rimozione della degenerazione

In un campo ottaedrico d_{xz} and d_{yz} si comportano analogamente a d_{xy} mentre dz^2 a dx^2-y^2

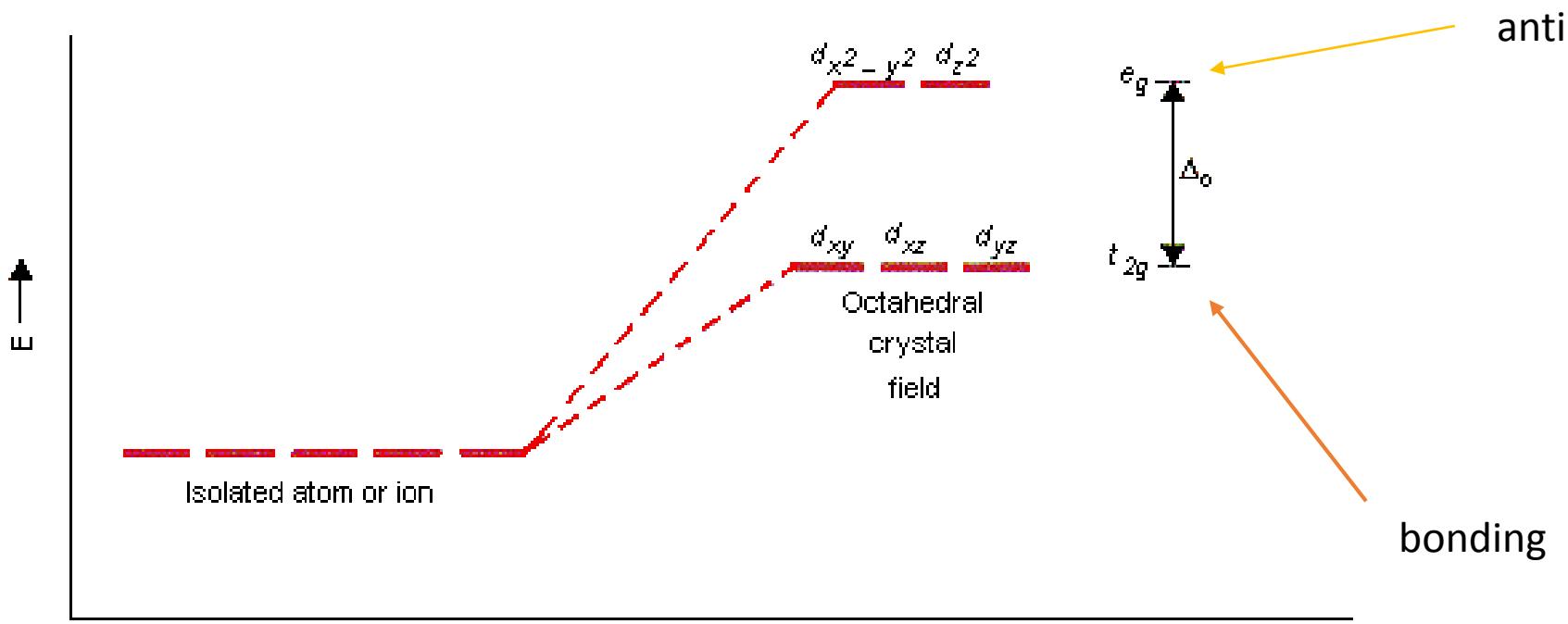
Gli orbitali d sono pertanto divisi in due gruppi, di differente energia





g (invariante) : centrosimmetrico
u (variante) : anticentrosimmetrico
e: doppiamente degenere
t: 3 volte degenere

"1" or "2" considerano la simmetria (1) o la anti-simmetria (2) a seguito della rotazione intorno ad una asse binario C2

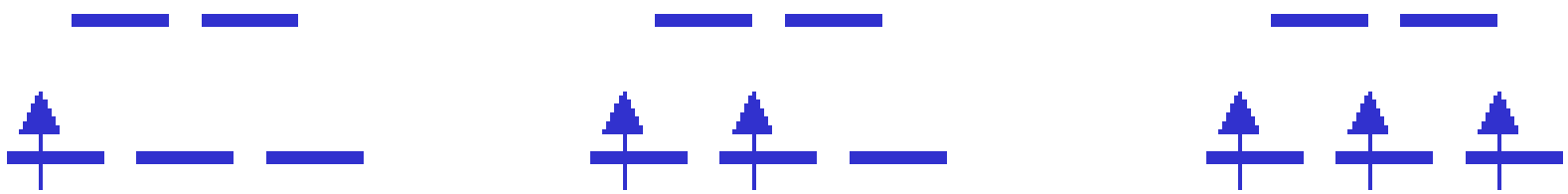


The d_{xy}, d_{xz}, and d_{yz} orbitals are collectively called the "t_{2g}" orbitals, whereas the dz^2 and dx^2-y^2 orbitals are called the "e_g" orbitals.

The octahedral splitting energy is the energy difference between the t_{2g} and e_g orbitals.

In an octahedral field, the t_{2g} orbitals are stabilized by 2/5 Δ_0, and the e_g orbitals are destabilized by 3/5 Δ_0

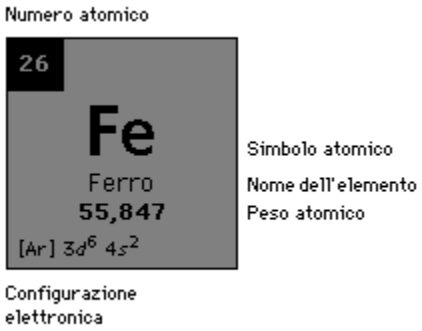
With the above diagram in mind, one can therefore assign "*electronic configurations*" for various octahedral complexes:



Ti^{3+} V^{3+} Cr^{3+}

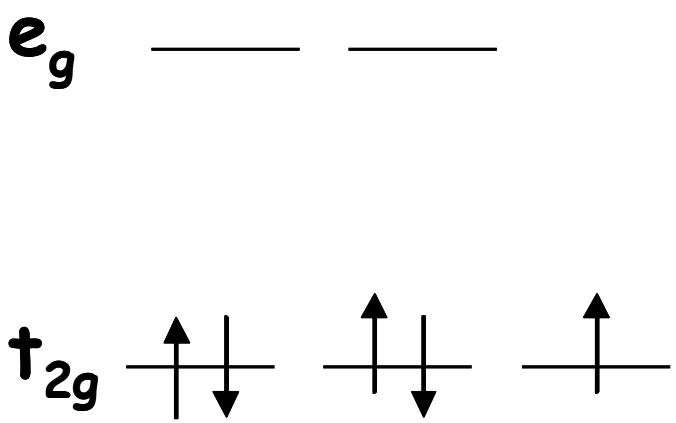
It is straightforward as long as the number of *d* electrons is less than or equal to 3 (or greater than or equal to 8).

With 4 to 7 *d* electrons, two options are possible for octahedral complexes.

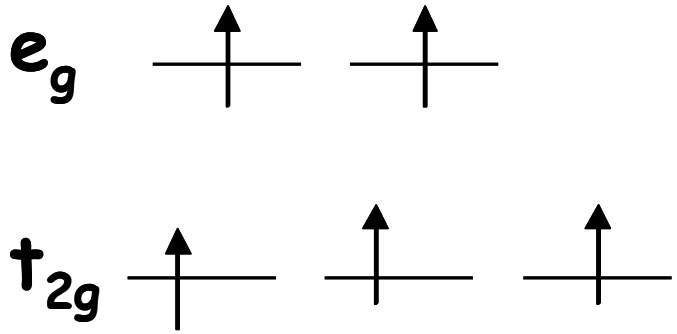


octahedral
Fe^{3+} (d5)

Low spin

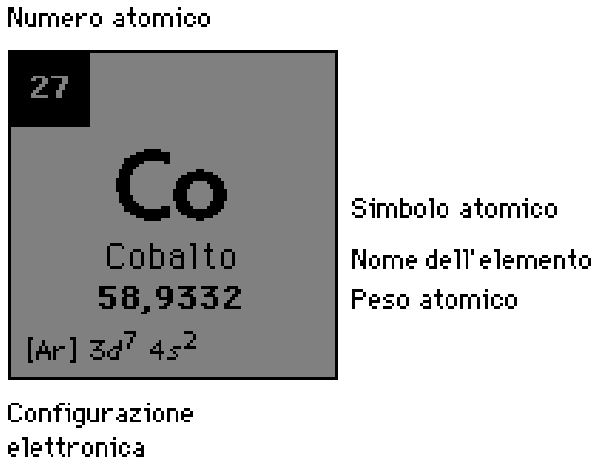


High spin



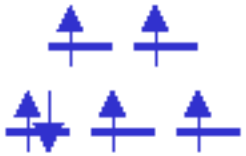
Effect of different ligands on the electronic configuration:

the example of Co(III)



$Co^{3+}(d^6)$

High Spin vs. Low Spin



$[CoF_6]^{3-}$

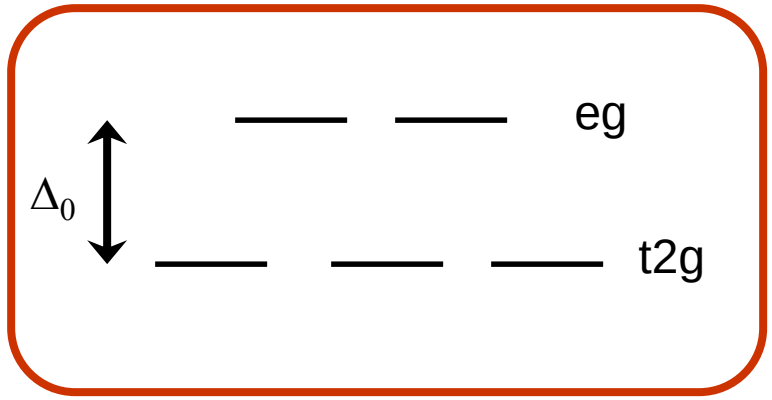
$[Co(NH_3)_6]^{3+}$

La serie spettrochimica

$Cl^- < F^- < H_2O < NH_3 <$ ethylenediamine (en) $< NO_2^- < CN^-, CO$

Campo Debole **Campo Forte**

Relativamente piccolo Δ_0



Relativamente grande Δ_0