Alfred Werner

Nobel Prize in Chemistry in 1913 for his studies on the structure of coordination complexes
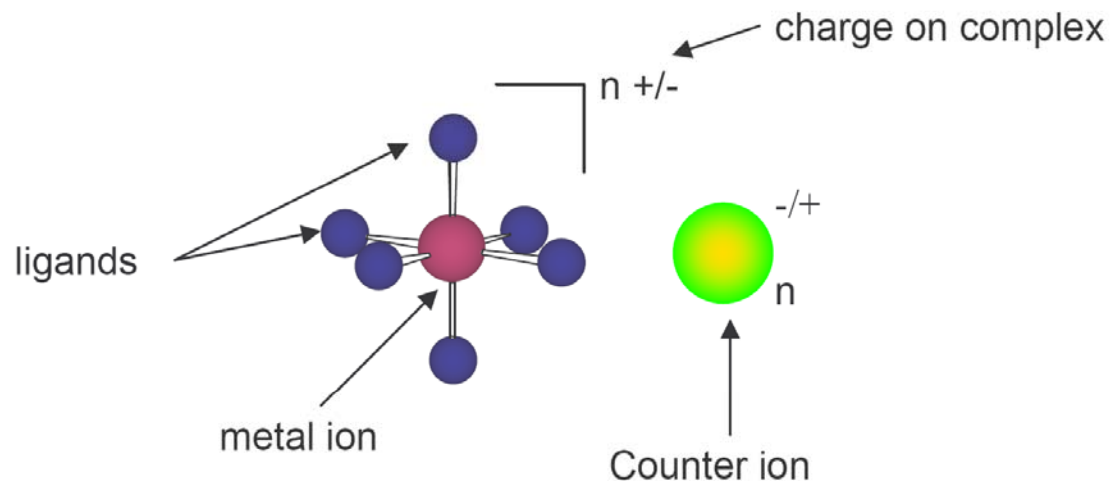
Coordination Complex

Typically consists of a complex ion and counterions (anions or cations as needed to produce a neutral compound)

$$[Co(NH_3)_5Cl]Cl_2 - [Co(NH_3)_5Cl]^{2+} \text{ and two } Cl^-; \text{ Co is in +3 oxidation state}$$

$$K_3[Fe(CN)_6] - [Fe(CN)_6]^{3-} \text{ and three } K^+; \text{ Fe is in +3 oxidation state}$$

Coordination number is the Number of bonds formed between the metal ion and the ligands in the complex ion. The most common coordination numbers are 4 and 6.

The Metal Ion

s block   **d block**   **p block**

Transition metals

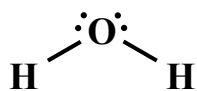|		3	4	5	6	7	8	9	10	11	12		
3	Mg											Al	
4	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	
5	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	
6	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	
7	Ra												

f block

| La | Ce | | | Tm | Yb | Lanthanides (lanthanoids) |
| Ac | Th | | | Md | No | Actinides (actinoids) |

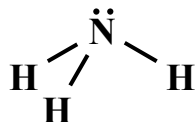# Ligands

Neutral molecules or ions having a lone electron pair that can be used to form a bond to a metal ion.

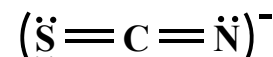## Monodentate ligand – one bond to a metal ion

water

ammonia

carbon monoxide

chloride
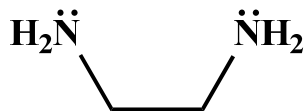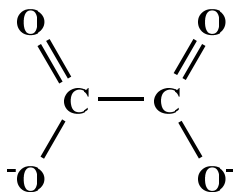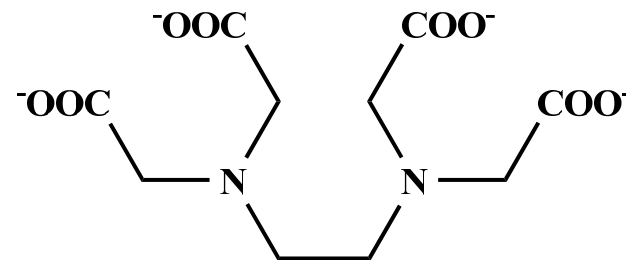
cyanide

thiocyanate

Bi and polydentate ligand – Two or more bonds to a metal ion
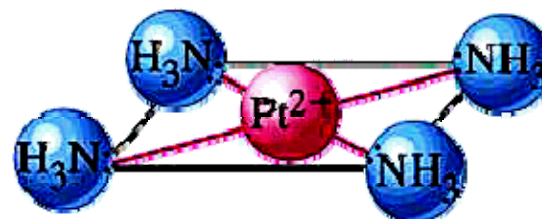
ethylenediamine (en)
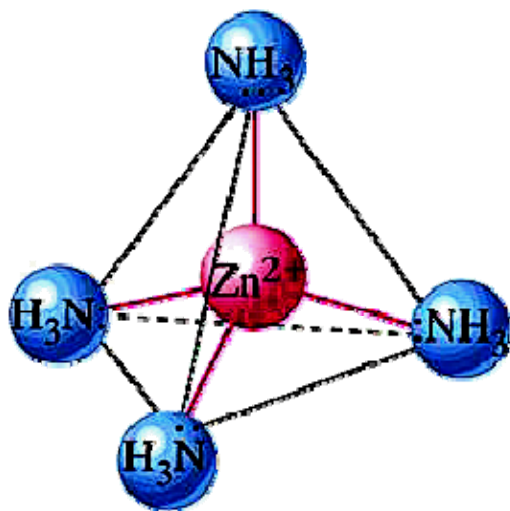
oxalate (ox)

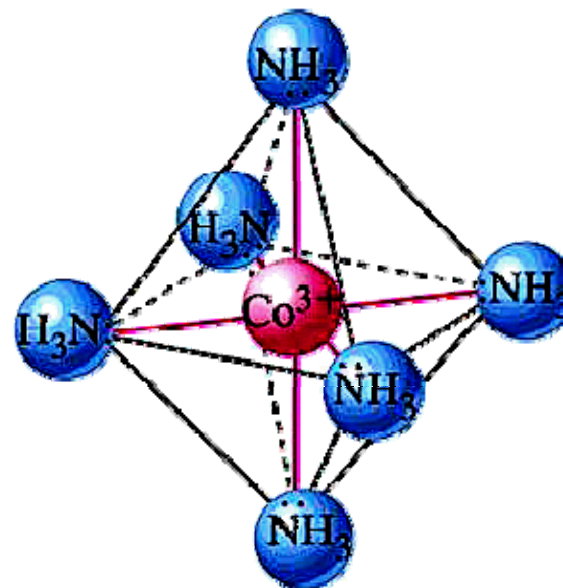ethylenediaminetetraacetate (EDTA)
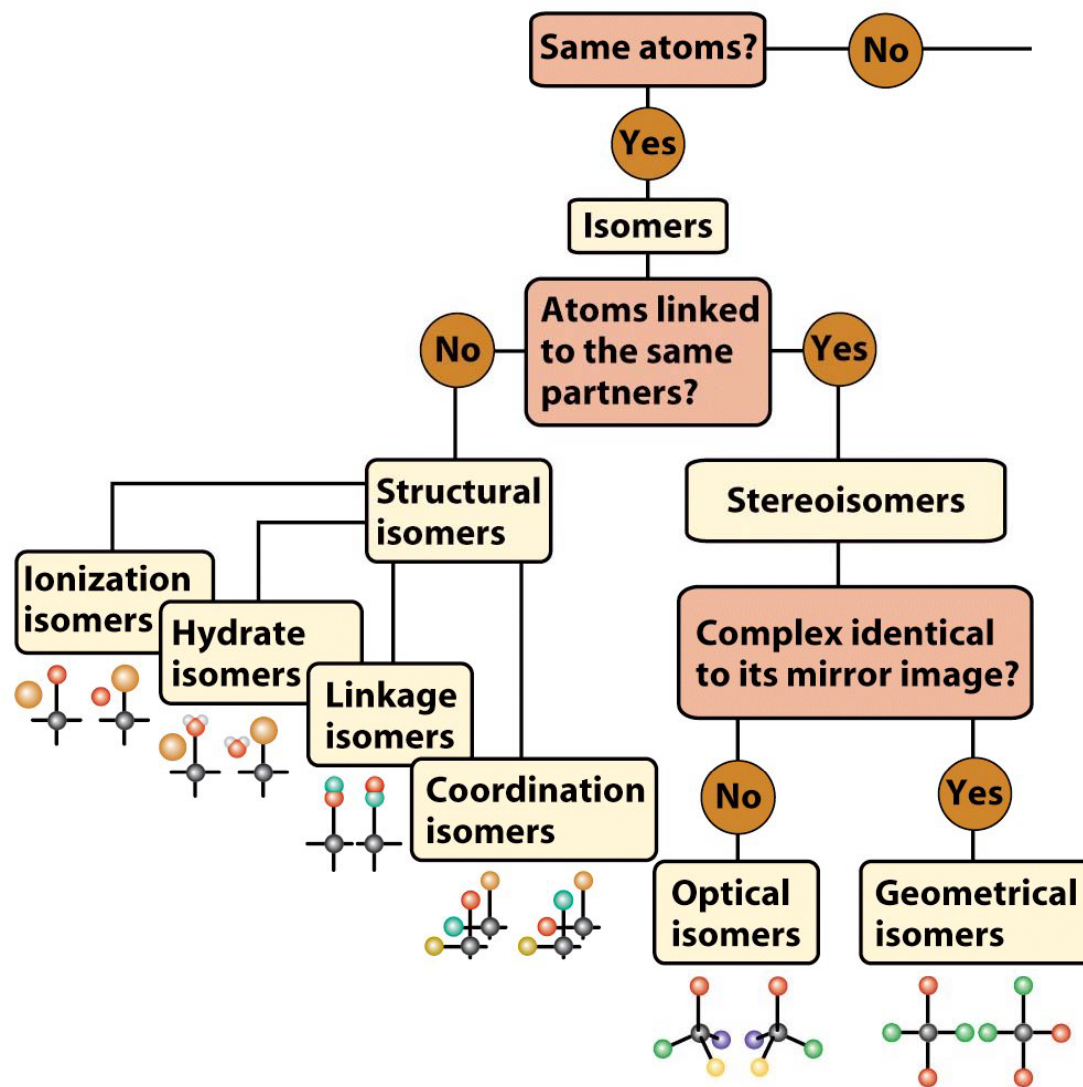
Most Common Geometries

Linear

Square planar

Tetrahedral

Octahedral

Isomerism

On finding compounds with different properties follow the chart below…

Ionization Isomerism

They form different ions in solution.

$[Cr(NH_3)_5SO_4]Br$ and $[Cr(NH_3)_5Br]SO_4$

$[PtBr(NH_3)_3]NO_2$ and $[Pt(NO_2)(NH_3)_3]Br$

Coordination Isomerism

Found in compounds in which both cations and anions are complexes, through the exchange of some ligands from the cationic part to the anionic part

$[Co(NH_3)_6] [Cr(C_2O_4)_3]$ and $[Co(C_2O_4)_3] [Cr(NH_3)_6]$

$[Zn (NH_3)_4] [CuCl_4]$ and $[ZnCl_4] [Cu(NH_3)_4]$

Hydrate Isomerism

Through the replacement of coordinated groups by water molecules

$[CrCl_2(H_2O)_4]Cl.2H_2O$ (bright-green)

$[CrCl(H_2O)_5]Cl_2.H_2O$ (grey-green)

$[Cr(H_2O)_6]Cl_3$ (violet)

Linkage Isomerism

Occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN- / NCS- and NO_2^- / ONO^-.

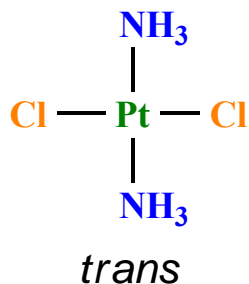$[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$
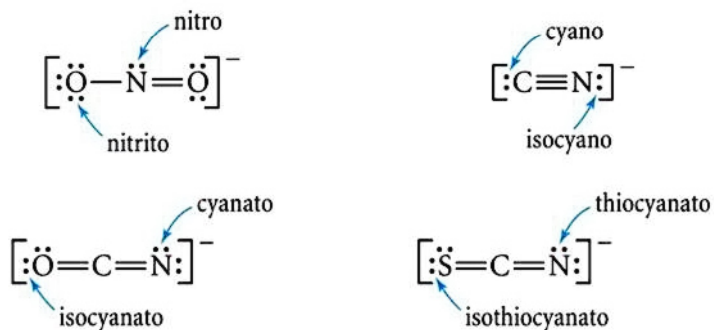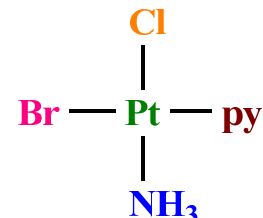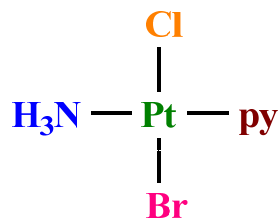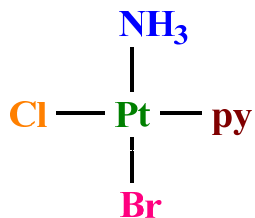

Nitro isomer

Nitrito isomer

Geometrical Isomerism

Geometrical isomerism is possible with square planar and octahedral complexes but not with tetrahedral complexes.

Square planar Complexes

Ma$_2$b$_2$ – 2 isomers are possible (*cis* and *trans*)

$$Cl - \underset{\underset{NH_3}{|}}{\overset{\overset{NH_3}{|}}{Pt}} - Cl$$

trans

$$Cl - \underset{\underset{NH_3}{|}}{\overset{\overset{Cl}{|}}{Pt}} - NH_3$$

cis

Mabcd – 3 isomers are possible

$$Cl - \underset{\underset{Br}{|}}{\overset{\overset{NH_3}{|}}{Pt}} - py$$

$$H_3N - \underset{\underset{Br}{|}}{\overset{\overset{Cl}{|}}{Pt}} - py$$

$$Br - \underset{\underset{NH_3}{|}}{\overset{\overset{Cl}{|}}{Pt}} - py$$
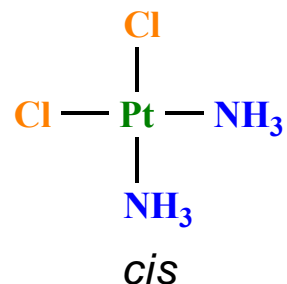
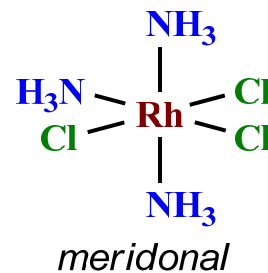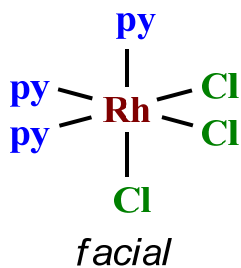# Geometrical Isomerism

Octahedral Complexes

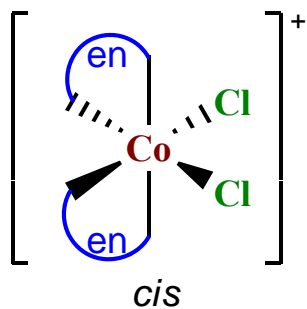**Ma_4b_2** – 2 isomers are possible (*cis* and *trans*)

trans   *cis*
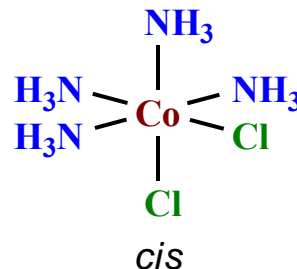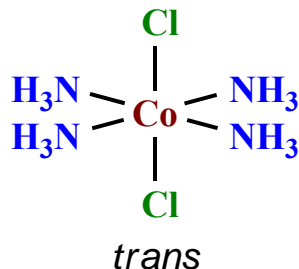
Ma_3b_3 – 2 isomers are possible (*fac* and *mer*)

facial   *meridonal*

MAA_2b_2 – 3 isomers are possible (2 *cis* and 1 *trans*)

cis   *trans*   en   is
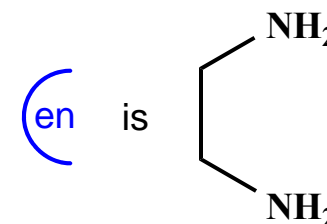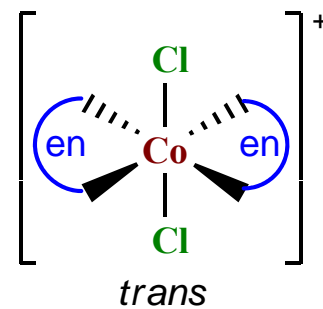
Optical Isomerism

Optical isomers are related as non-superimposable mirror images and differ in the direction with which they rotate plane-polarized light. These are possible for both tetrahedral and octahedral complexes, but not square planar.
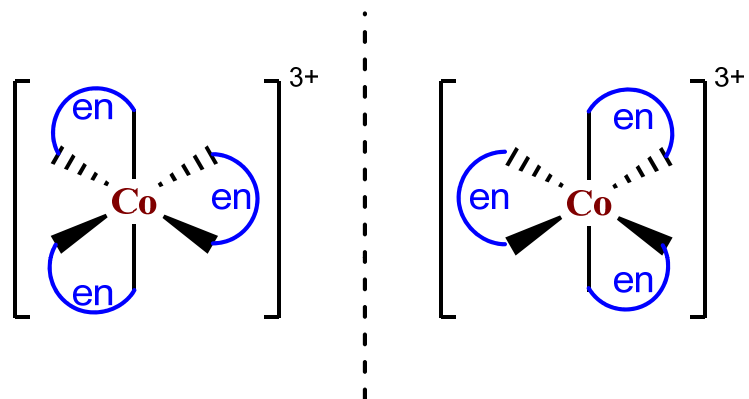
The absence of a plane of symmetry ensures optical activity in most cases

Optically active
No plane of symmetry

Optically inactive
Has a plane of symmetry

Valence Bond Theory

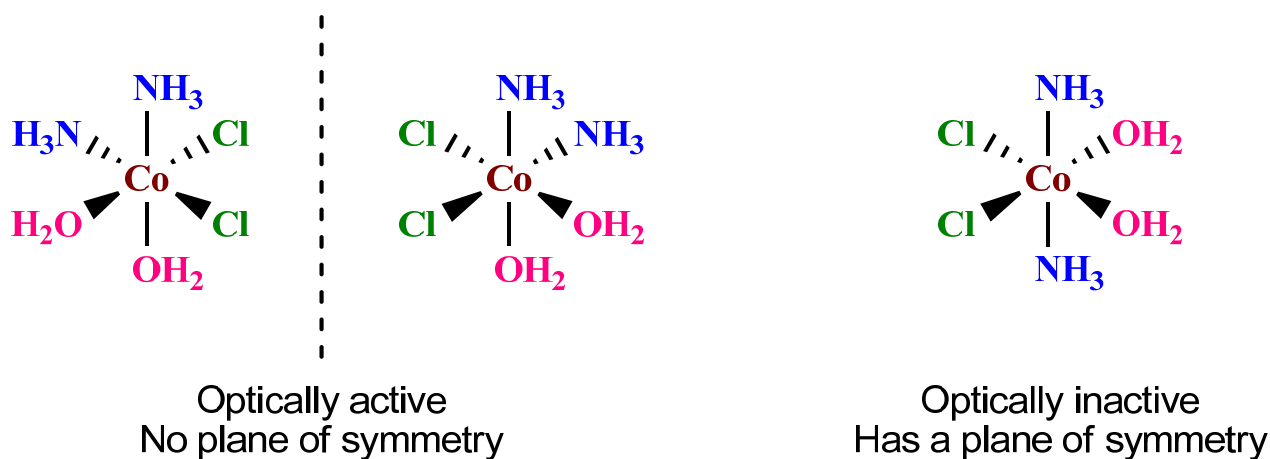The model utilizes hybridization of metal valence orbitals to account for the observed structures and magnetic properties of complexes. (n-1)d, *ns and np undergo hybridization to give* hybridized orbitals. An *empty hybrid orbital on the metal center* can accept a pair of electrons from a ligand to form a σ-bond.

Octahedral complex of Co(III) – d^6

3d	4s	4p

$$d^2sp^3$$

Pt[Cl$_4$]$^{2-}$ which is diamagnetic – d^8 square planar

5d	6s	6p

$$dsp^2$$

Ni[Cl$_4$]$^{2-}$ which is paramagnetic – d^8 tetrahedral

3d	4s	4p

$$sp^3$$

Limitations of Valence Bond Theory

- The exhibition of color by coordination complexes is not explained

- Quantitative interpretation of magnetic data is not given

- Whether a complex of coordination number 4 is square planar or tetrahedral cannot be exactly predicted

- Weak and strong ligands cannot be distinguished

- The thermodynamic and kinetic stabilities of complexes are not quantitatively interpreted

Crystal Field Theory

Proposed by Hans Bethe and van Vleck in 1929.

The assumptions of the crystal field theory are as follow:

- The interaction between the metal ion and the ligand is assumed to be purely electrostatic (ionic) in nature.
- The ligands are treated as point charges. CFT does not allow for any overlap between the metal orbitals and the ligand orbitals.
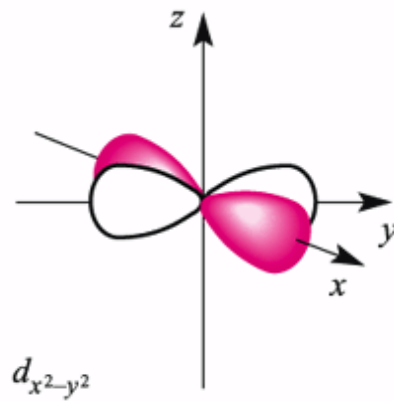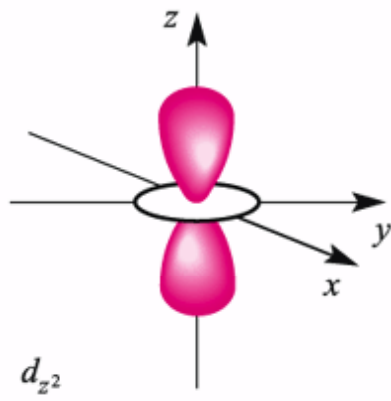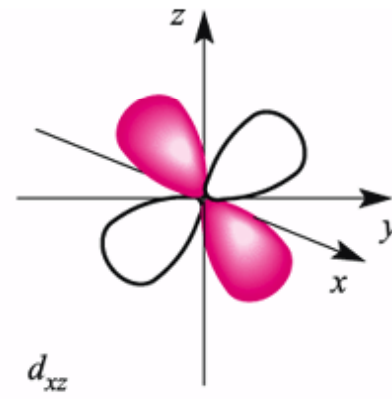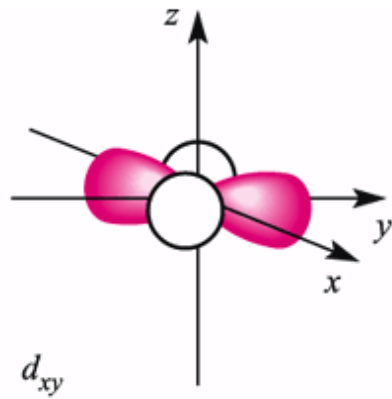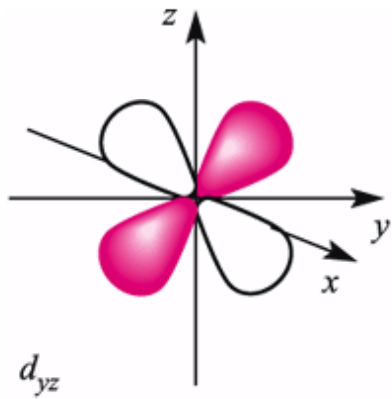
Consequences

Metal ions are attracted to the electron pairs in ligands

The lone pair of electrons in the ligands repel the electrons present in the d orbitals

These interactions are called crystal field

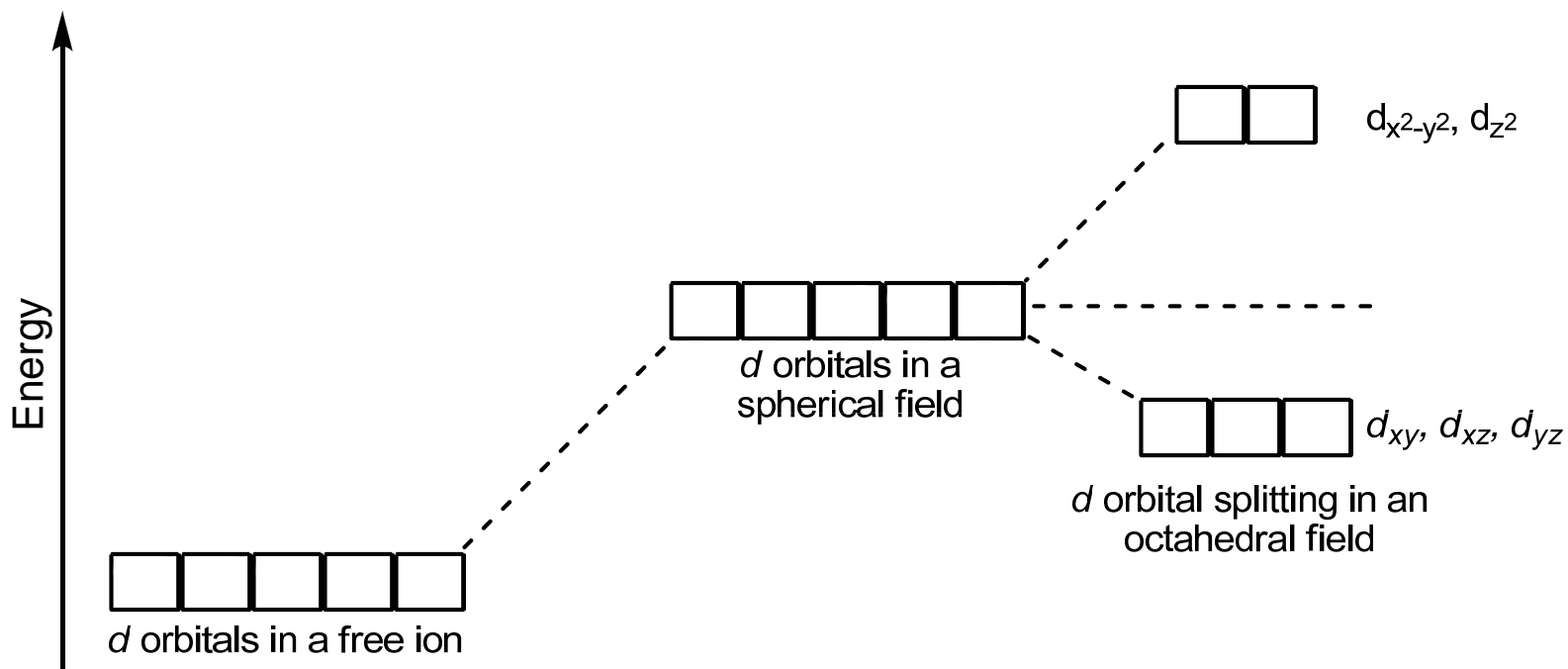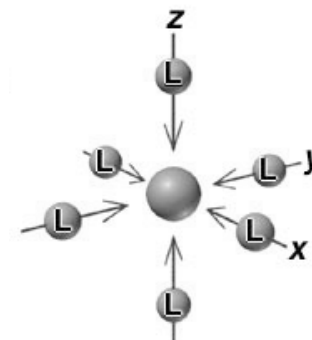Such interactions affect the energy of the d orbitals but not uniformly

d orbitals

Octahedral Field

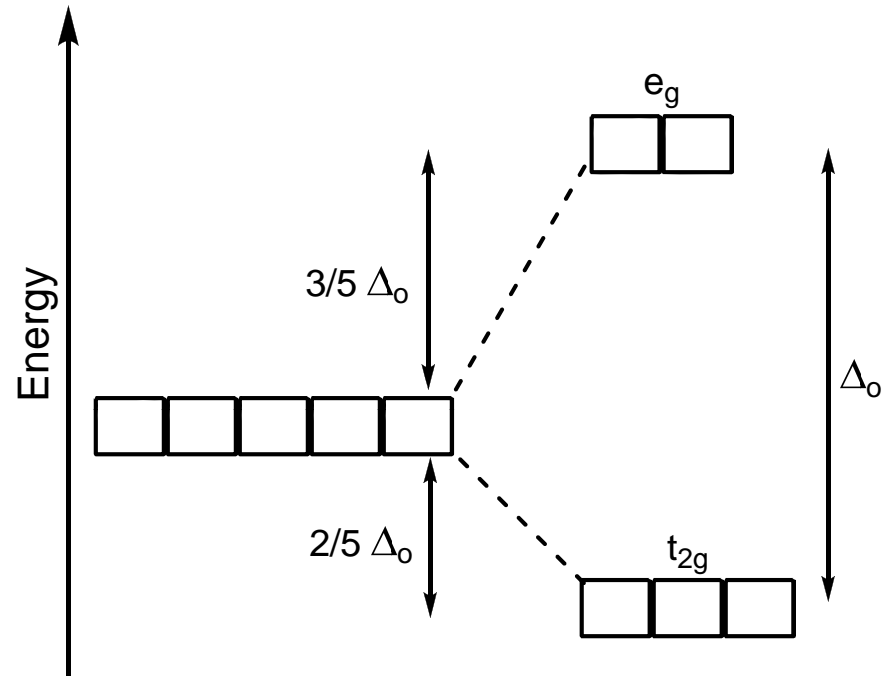The corners of octahedron are assumed to be placed on the axes.

The ligands approach along the axes and occupy the corners

Electrons in the d orbitals lying along the axes are repelled the most, while those lying in between the axes are less repelled

Energy

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

d orbitals in a spherical field

d_{xy}, d_{xz}, d_{yz}

d orbital splitting in an octahedral field

d orbitals in a free ion

Crystal Field Splitting in an Octahedral Field

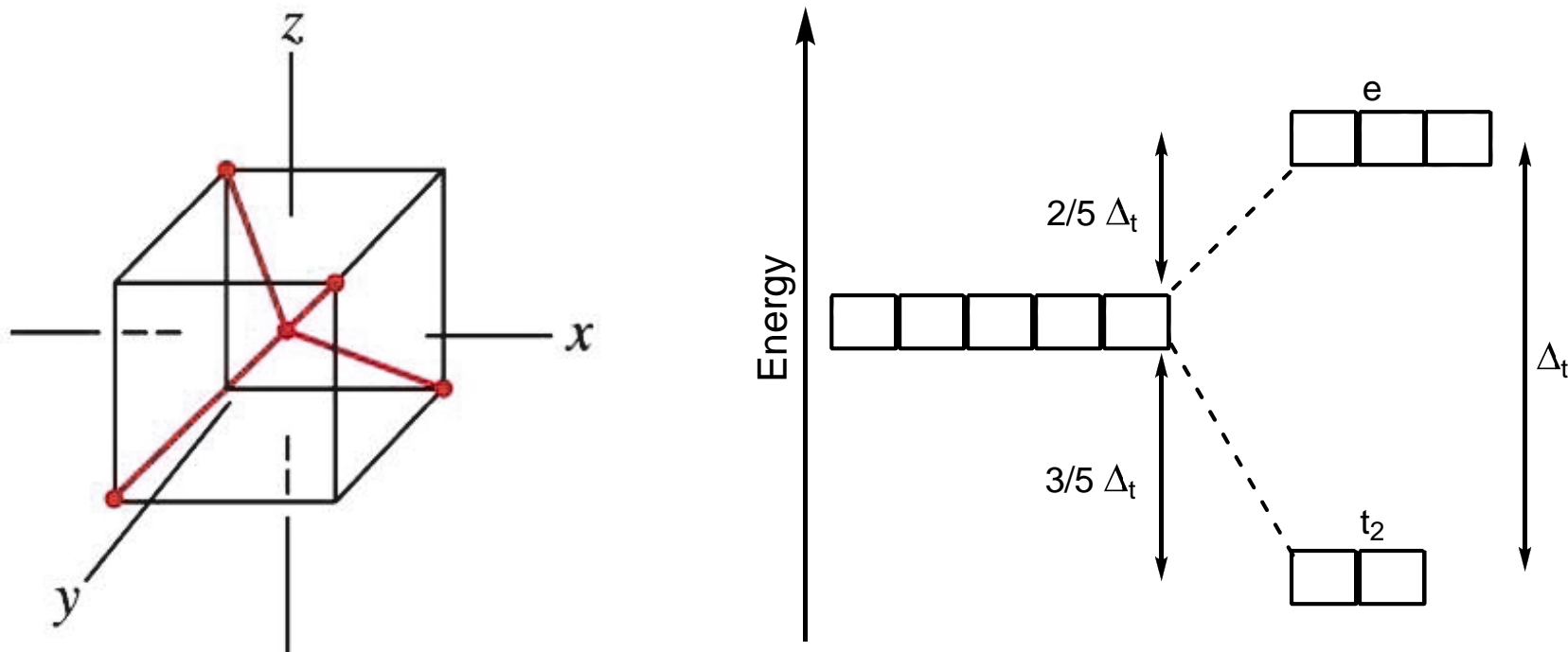
The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$) are labeled as e_g and the lower energy set is labeled as t_{2g}. These notations are based on the symmetry of the orbitals.

The energy separation between the two levels is denoted by Δ_o or 10 Dq.

To maintain the average energy, the e_g orbitals need to be repelled by an amount of 0.6 Δo and the t_{2g} orbitals to be stabilized to the extent of 0.4 Δo.

Tetrahedral Field

The higher energy set of orbitals (d_{xz}, d_{yz}, d_{xy}) are 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 $\Delta_t = 4/9 \, \Delta_o$