



# COORDINATION COMPOUNDS

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# INTRODUCTION

The transition metals form a large number of complex compounds in which the metal atoms are bound to a number of anions or neutral molecules. In modern terminology such compounds are called coordination compounds. Chlorophyll, haemoglobin are coordination compounds of magnesium and iron. Variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Coordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

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# WERNER'S THEORY OF COORDINATION COMPOUNDS

Werner in 1898 propounded his theory of coordination compounds. The main postulates are :

- In coordination compounds metals shows two types of linkages (valences) – primary and secondary.
- The primary valences are normally ionisable and are satisfied by negative ions.
- The secondary valences are non – ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
- The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In modern formulations, such spatial arrangements are called coordination polyhedra. The species within the square bracket are coordination entities or complexes and the ions outside the square bracket are called counter ions.



## DIFFERENCE BETWEEN A DOUBLE SALT AND A COMPLEX

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However they differ in the fact that double salts such as carnallite, Mohr's salt, potash alum, dissociate into simple ions completely when dissolved in water. However, complex ions such as  $[\text{Fe}(\text{CN})_6]^{4-}$  of  $\text{K}_4\text{Fe}(\text{CN})_6$ , do not dissociate into  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions.



# DEFINITIONS OF SOME IMPORTANT TERMS PERTAINING TO COORDINATION COMPOUNDS

- ✓ Coordination entity: a coordination constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example –  $[\text{Fe}(\text{CN})_6]^{4-}$  .
- ✓ Central atom/ion: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom/ ion.
- ✓ Coordination numbers : The coordination numbers (CN) of a metal ion in a complex can be defined as number of ligand donor atoms to which the metal is directly bonded.
- ✓ Coordination Sphere : The central atom/ ion and the ligands attached to it are enclosed in square brackets and is collectively termed as the coordination sphere. The ionisable groups are written outside the bracket and are called counter ions.



✓ Ligands : The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions, small molecules, large molecules and even macromolecules.

### Classification according to the number of donor atoms.

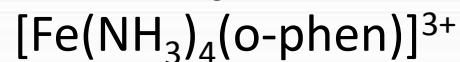
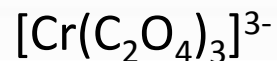
1) monodentate = 1 =  $\text{H}_2\text{O}$ ,  $\text{CN}^-$ ,  $\text{NH}_3$ ,  $\text{NO}_2^-$ ,  $\text{SCN}^-$ ,  $\text{OH}^-$ ,  $\text{X}^-$  (halides),  $\text{CO}$ ,  $\text{O}^{2-}$

Example Complexes



2) bidentate = 2 = oxalate ion =  $\text{C}_2\text{O}_4^{2-}$ , ethylenediamine (en) =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , ortho-phenanthroline (o-phen)

Example Complexes



**chelating agents**

3) polydentate = 2 or more donor atoms = ethylenediaminetetraacetate (EDTA) =  $(\text{O}_2\text{CCH}_2)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CO}_2)_2^{4-}$

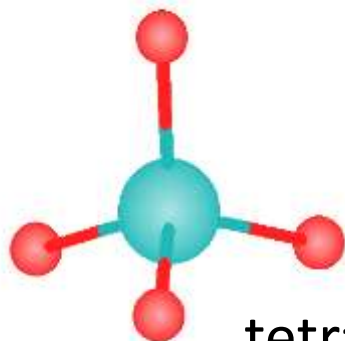
Example Complexes



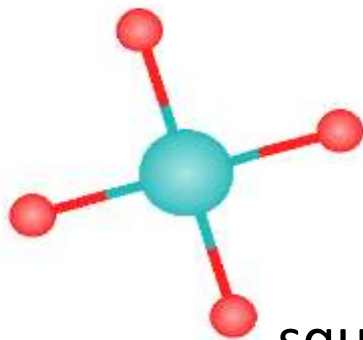
✓ **Oxidation number of central atom** : The oxidation number of central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.

✓ **Homoleptic and Heteroleptic complexes** : Complexes in which a metal is bound to only one kind of donor groups are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic.

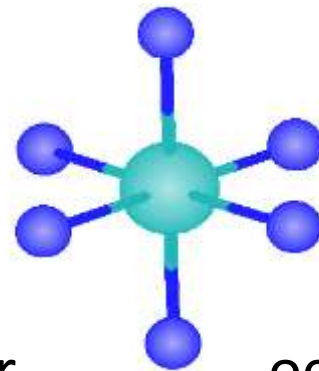
**Coordination polyhedron** : The spatial arrangement of the ligand atoms which are directly attached to the central atom/ ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and



tetrahedral



square planar



octahedral

# NOMENCLATURE OF COORDINATION COMPOUNDS

## **1. Formulas of Mononuclear Coordination Entities.**

- **The Central atom is listed first.**
- **The ligands are then listed in alphabetical order. The placement of ligands in the list does not depend on its charge.**
- **Polydentate ligands are also listed alphabetically.**
- **The formula for the entire coordination entity is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.**
- **There should be no space between ligands and the metal within a coordination sphere.**
- **When the formula of a charged coordination entity is to be written without a counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign.**
- **The charge of cation(s) is balanced by the charge of anion(s).**

# NOMENCLATURE OF COORDINATION COMPOUNDS

## 2. Formulas of Mononuclear Coordination Compounds.

- The cation is named first in both positively and negatively charged coordination entities.
- The ligands are named in an alphabetical order before the name of the central atom/ ion.
- Names of anionic ligands end in -o, those of neutral and cationic ligands are the same except aqua for  $\text{H}_2\text{O}$ , ammine for  $\text{NH}_3$ , Carbonyl for  $\text{CO}$  and Nitrosyl for  $\text{NO}$ . These are placed within enclosing marks ().
- Prefixes mono, di, tri, etc., are used to indicate the number of individual ligands in the coordination entity. When the name of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parentheses.
- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by roman numeral in parentheses.
- If the complex ion is a cation, the metal is named same as a element. If the complex is an anion, the name of the metals ends with the suffix - ate. For some metals, the Latin names are used in the complex anions, e.g. ferrate for Fe.
- The neutral complex molecule is name similar to that of the complex cation.

# Isomerism in coordination compounds

- Isomers

compounds that have the same composition but a different arrangement of atoms

- Major Types

  - STEREISOISOMERS

    - 1) Geometrical isomerism

    - 2) Optical isomerism

  - STRUCTURAL ISOMERS

    - 1) Linkage isomerism

    - 2) Coordination isomerism

    - 3) Ionisation isomerism

    - 4) Solvate isomerism



# STEREISOISOMERS

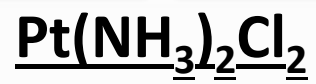
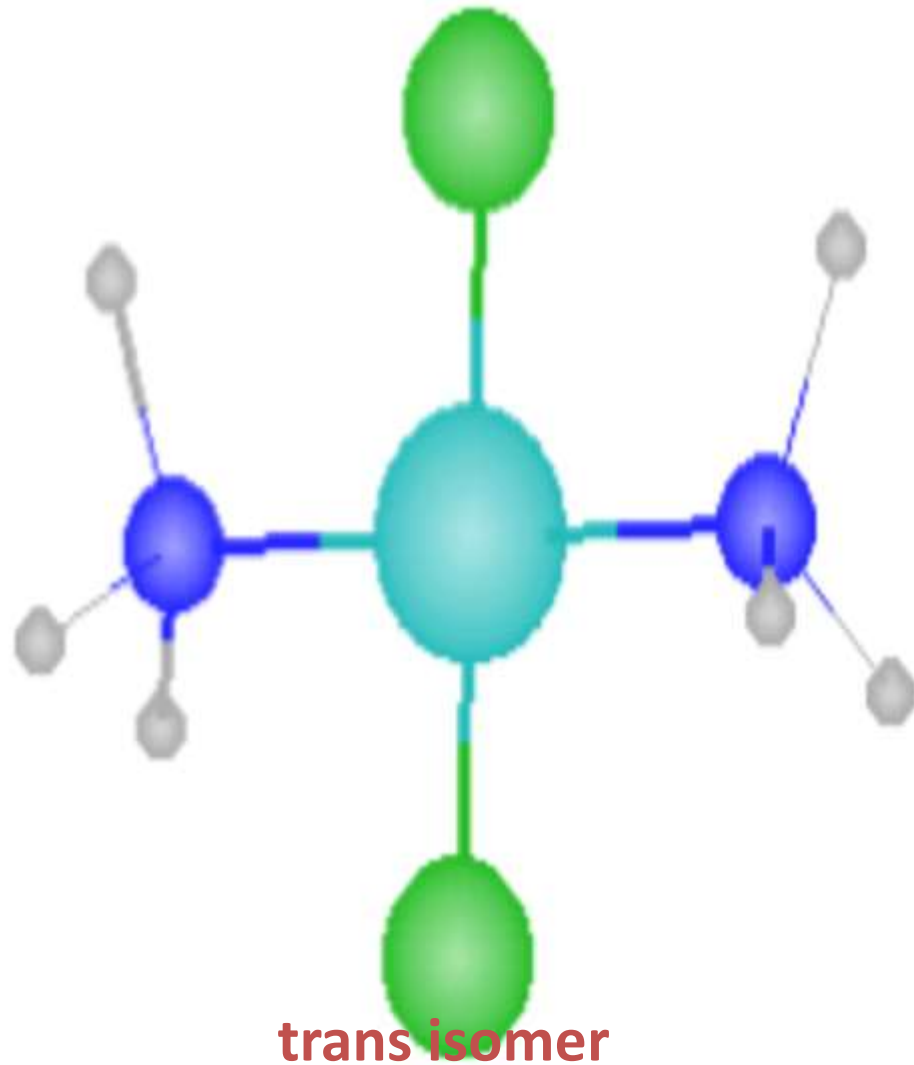
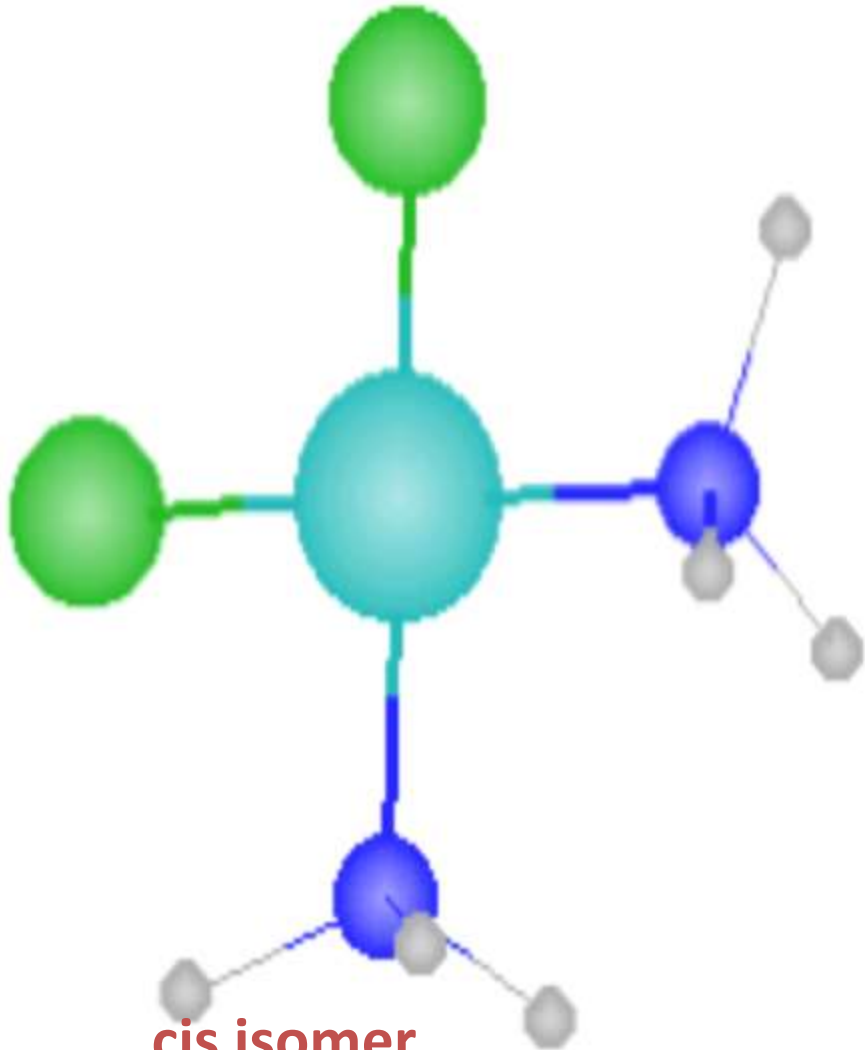
Isomers that have the same bonds, but different spatial arrangements.

## 1. Geometric isomers

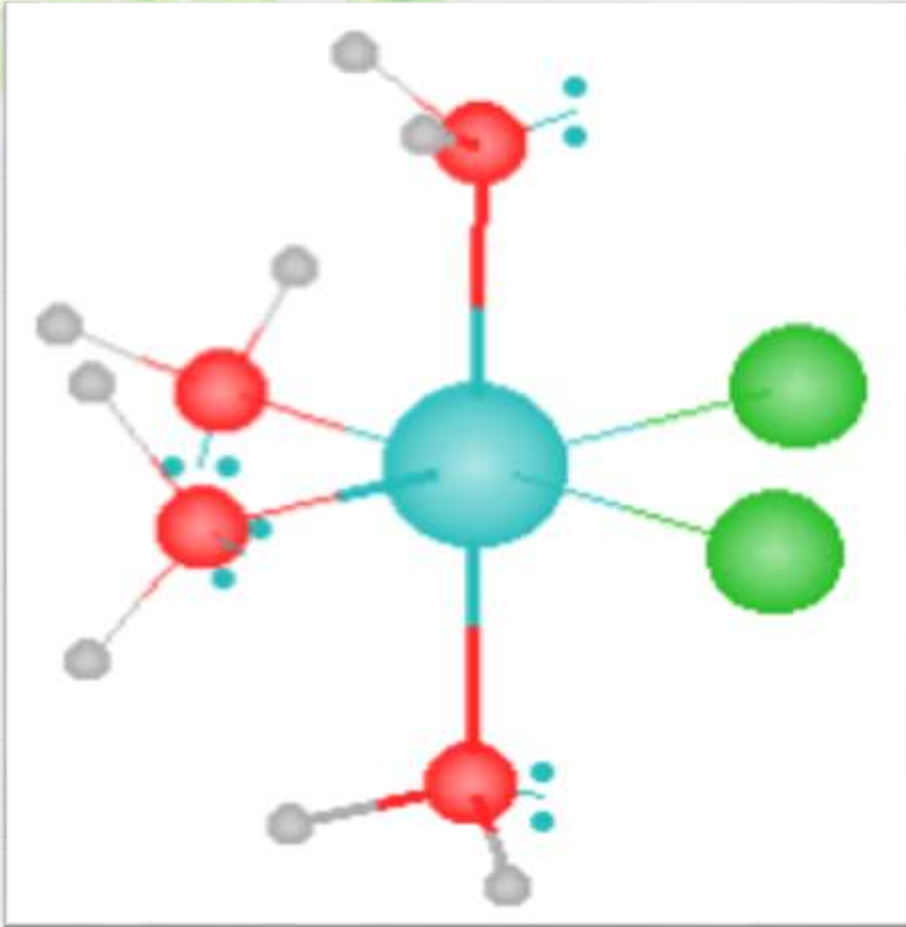
Differ in the spatial arrangements of the ligands, have different chemical/physical properties different colors, melting points, polarities, solubilities, reactivities, etc.



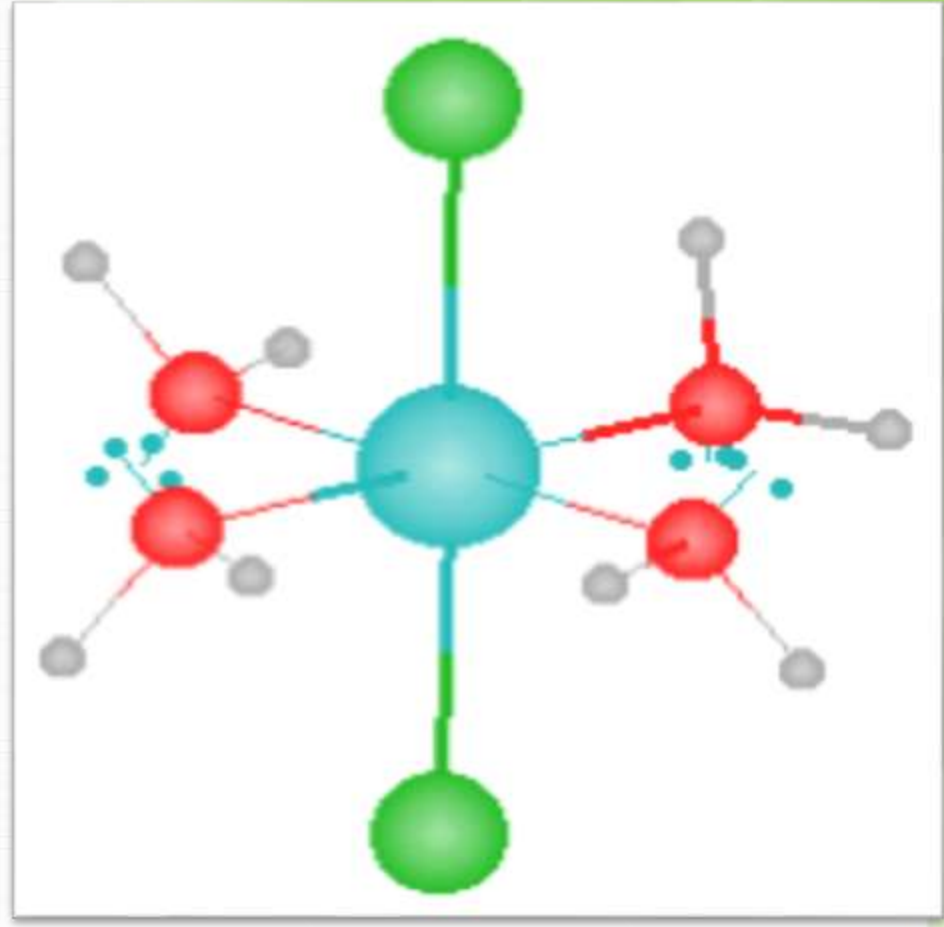
# Example



# Example



cis isomer



trans isomer



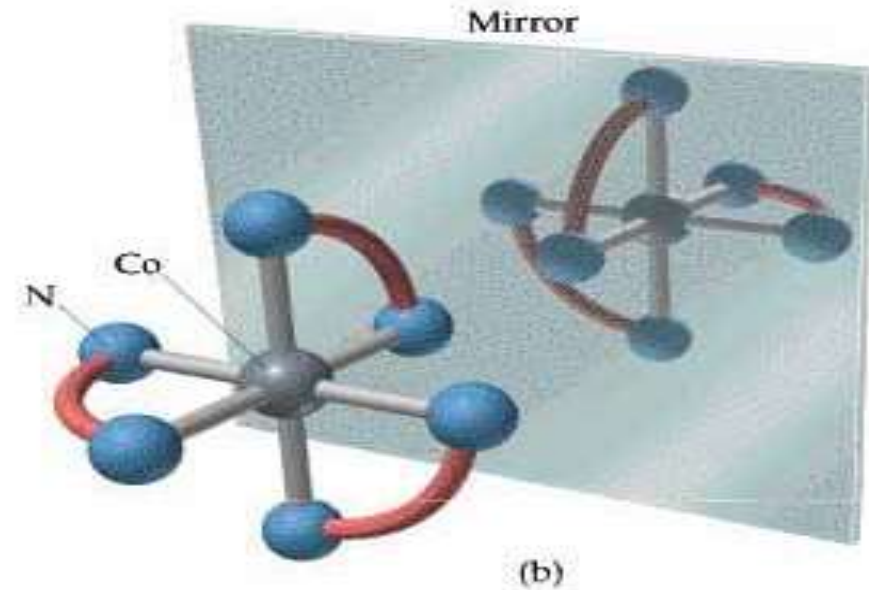
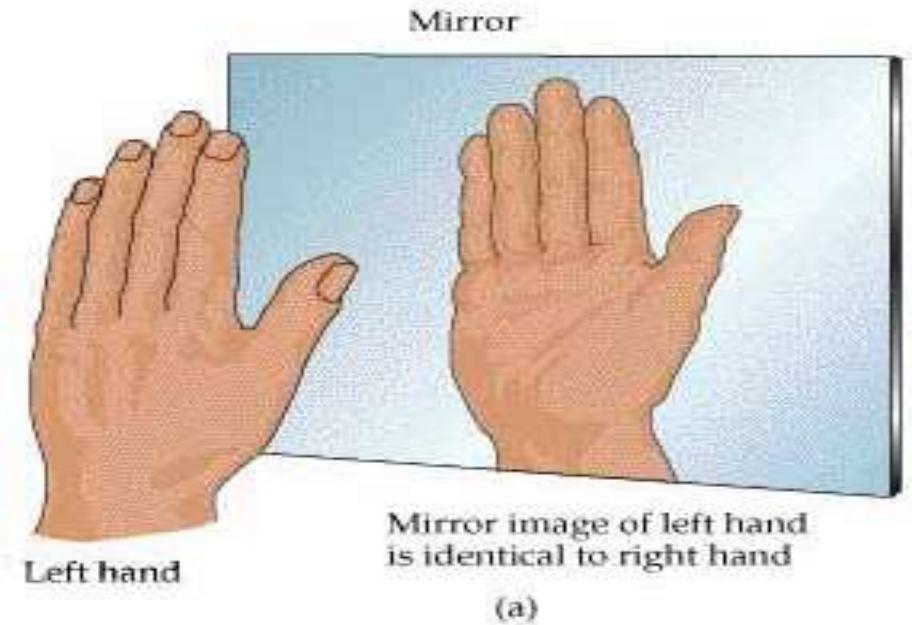
## 2) Optical isomers

isomers that are nonsuperimposable mirror images

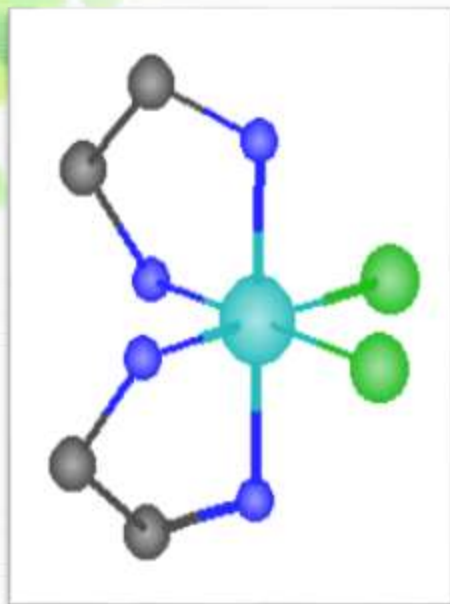
-said to be “chiral” (handed)

-referred to as enantiomers

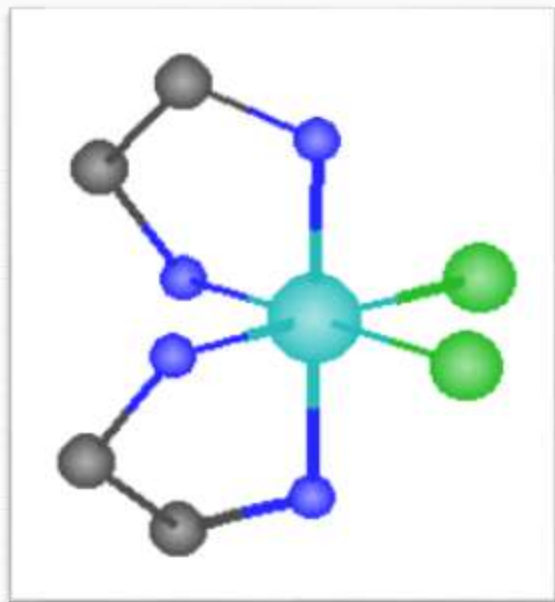
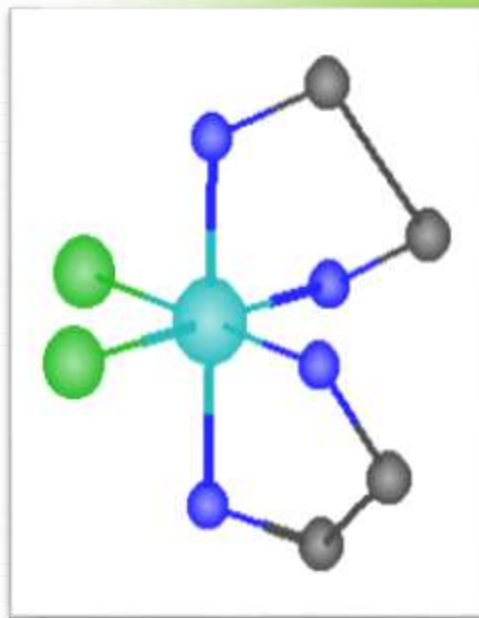
A substance is “chiral” if it does not have a “plane of symmetry”



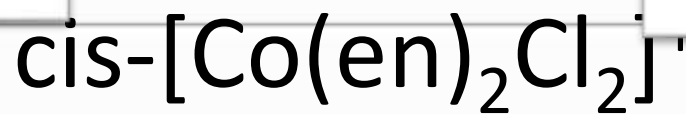
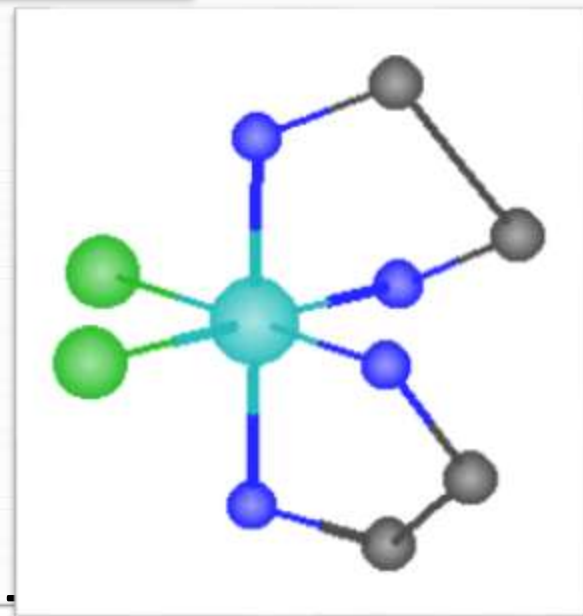
# Example 1



mirror plane



Enantiomers  
(Non – superimposable)



# Properties of Optical Isomers

- Enantiomers

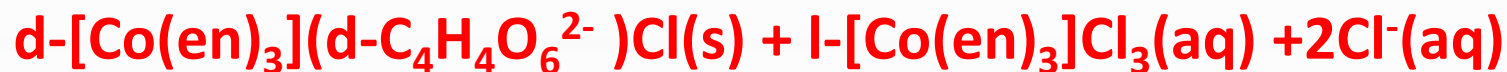
- possess many identical properties

- solubility, melting point, boiling point, color, chemical reactivity (with nonchiral reagents).

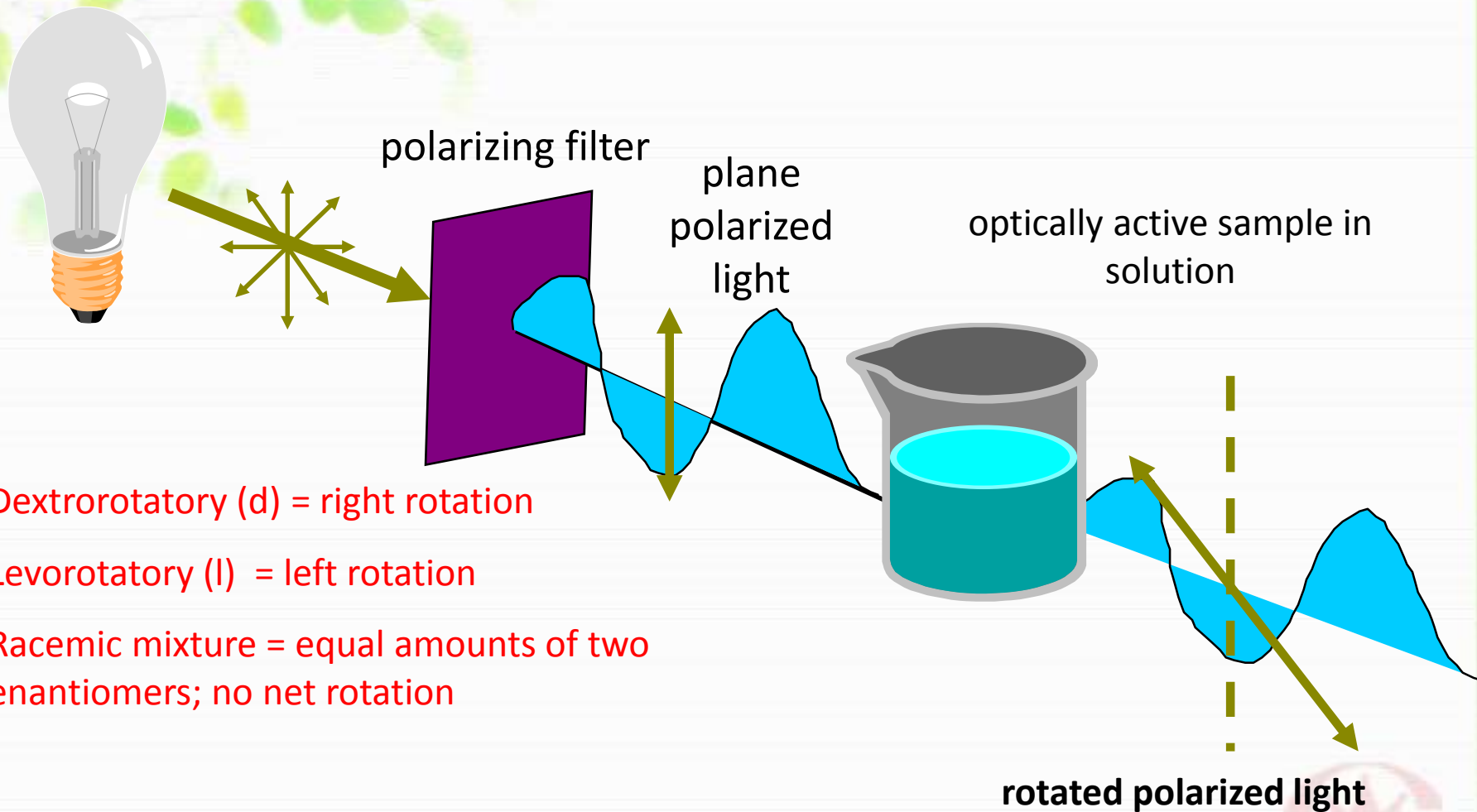
- different in:

- reactivity with “chiral” reagents

Example



# •interactions with plane polarized light



# Structural Isomers

Isomers that have different bonds

## 1) Coordination isomers

Arises from interchange of ligands between cationic and anionic entities of different metal ions present in a complex

### Example



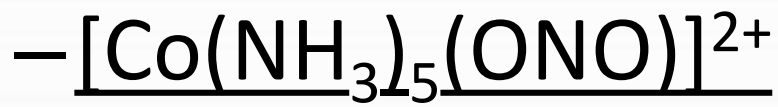
- Consider ionization in water



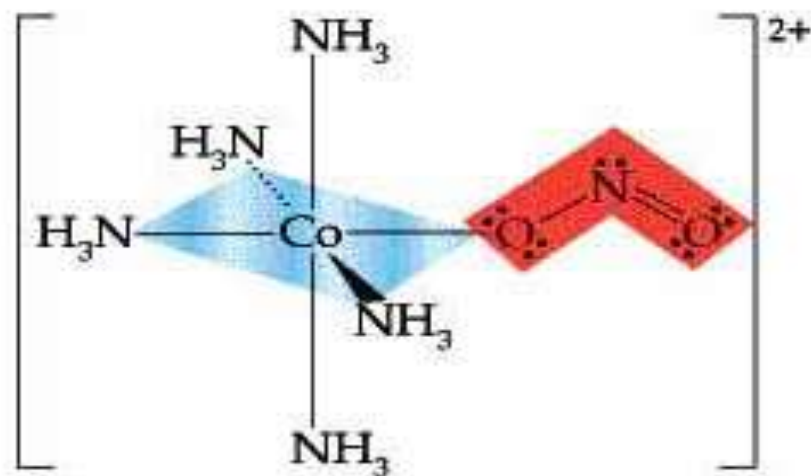
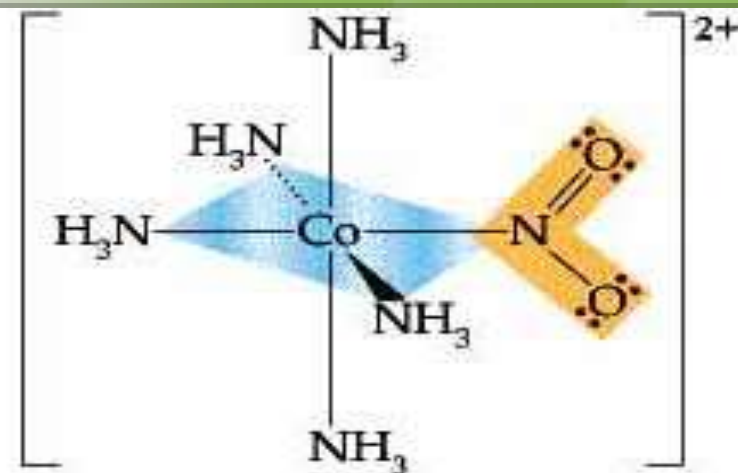
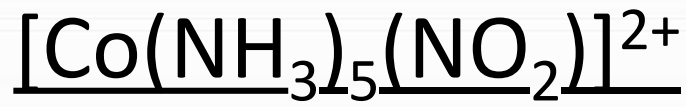
## 2) Linkage isomers

– differ in the atom of a ligand bonded to the metal in the complex

### • Example



vs.



### 3) Ionisation Isomerism

-Arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

#### -Example

ionisation isomers  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ .

### 4) Solvate Isomerism

-also known as 'hydrate isomerism in case water is involved as solvent

-similar to ionisation isomerism, differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice.

#### -Example

aqua complex  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) and its solvate isomer  $[\text{Cr}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (grey green).

# VALENCE BOND THEORY

According to this theory, the metal atom/ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of definite geometry such as octahedral, tetrahedral, square planar. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

Coordination Number	Type of Hybridisation	Distribution of hybrid orbitals in space
4	$sp^3$	Tetrahedral
4	$dsp^2$	Square planar
5	$sp^3d$	Trigonal bipyramidal
6	$sp^3d^2$	Octahedral
6	$d^2sp^3$	Octahedral

# LIMITATIONS OF VALENCE BOND THEORY

- a) Involves a number of assumptions.
- b) Does not give quantitative interpretation of magnetic data.
- c) Does not explain the colour exhibited by coordination compounds.
- d) Does not give quantitative interpretation of thermodynamic or kinetic stabilities of coordination compounds.
- e) Does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate compounds.
- f) Does not distinguish between weak and strong ligands.

# Crystal Field Theory

- ✓ Electrostatic model for bonding in transition metal complexes.
  - Accounts for observed properties of transition metal complexes.
- ✓ Focuses on d-orbitals
- ✓ Ligands = point charges in case of anions or dipoles in case of neutral molecules.
- ✓ Assumes metal ligand bond to be ionic.



## ✓ Electrostatic Interactions

➤ (+) metal ion attracted to (-) ligands (anion or dipole)

- provides stability

➤ lone pair e<sup>-</sup>'s on ligands repulsed by e<sup>-</sup>'s in metal d orbitals

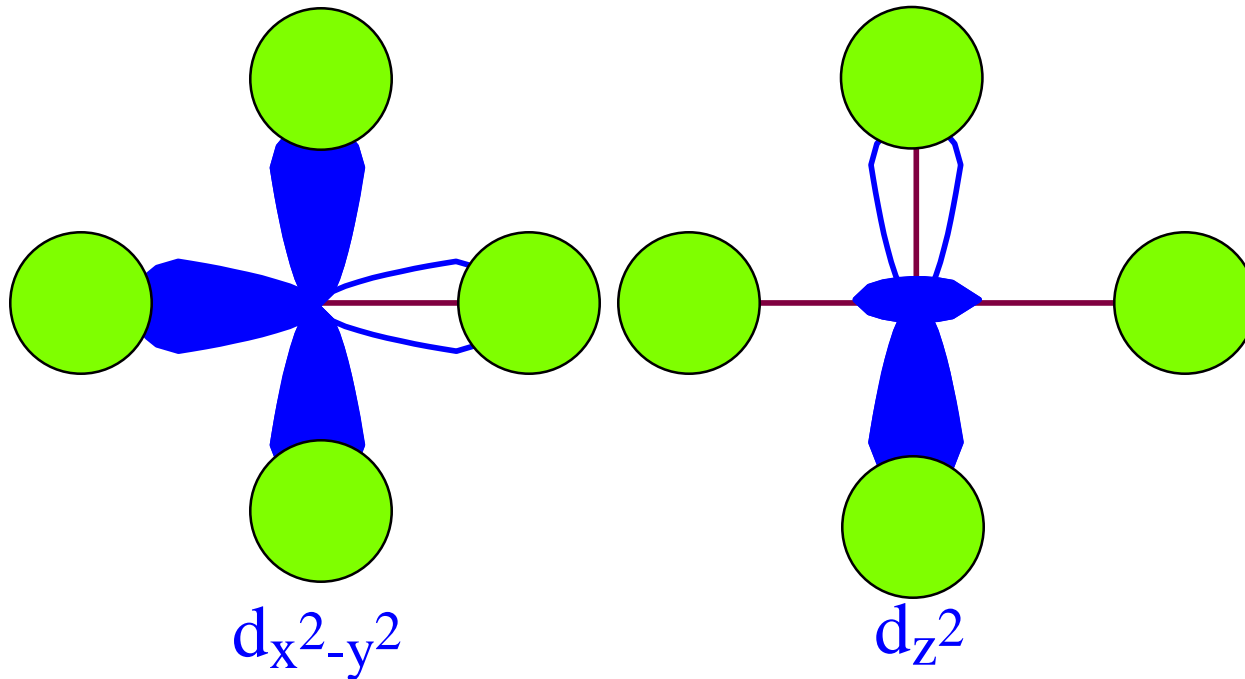
- interaction called crystal field

- influences d orbital energies

(not all d orbitals influenced the same way)



# Crystal Field Theory

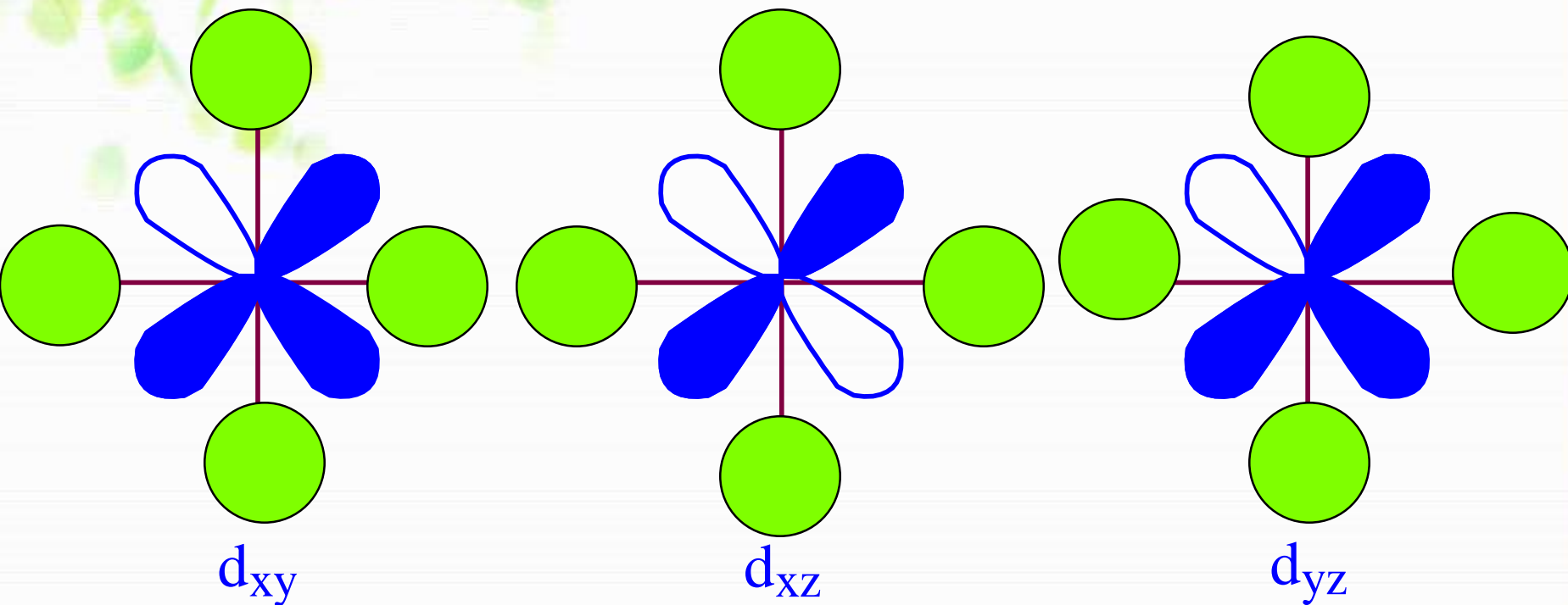


Lobes directed at ligands

greater electrostatic repulsion = higher potential energy



# Crystal Field Theory



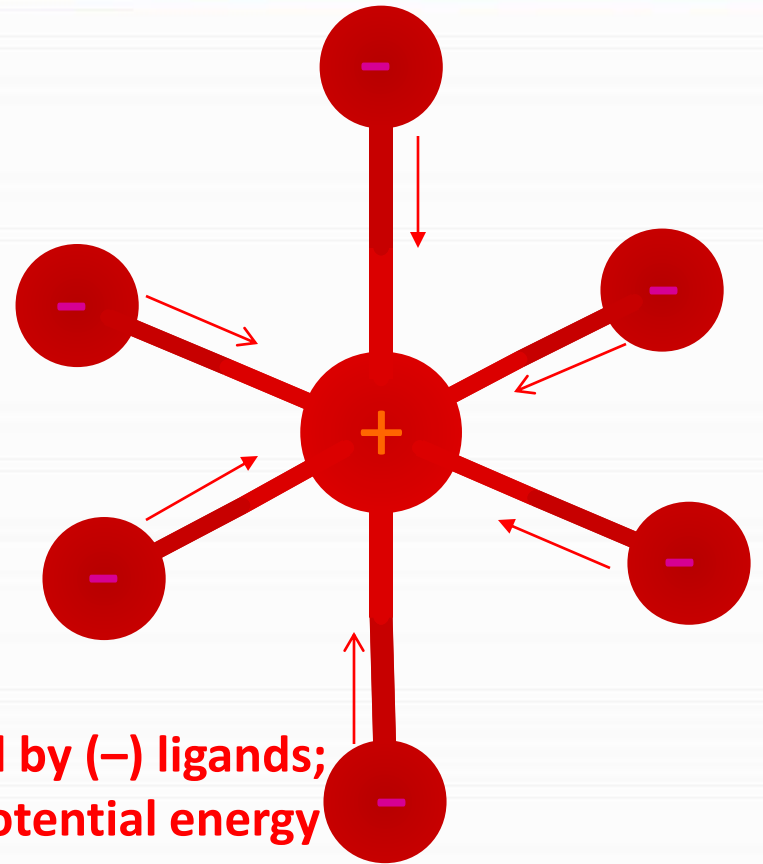
Lobes directed between ligands

less electrostatic repulsion = lower potential energy



# Octahedral Crystal Field

(-) Ligands attracted to (+) metal ion;  
provides stability

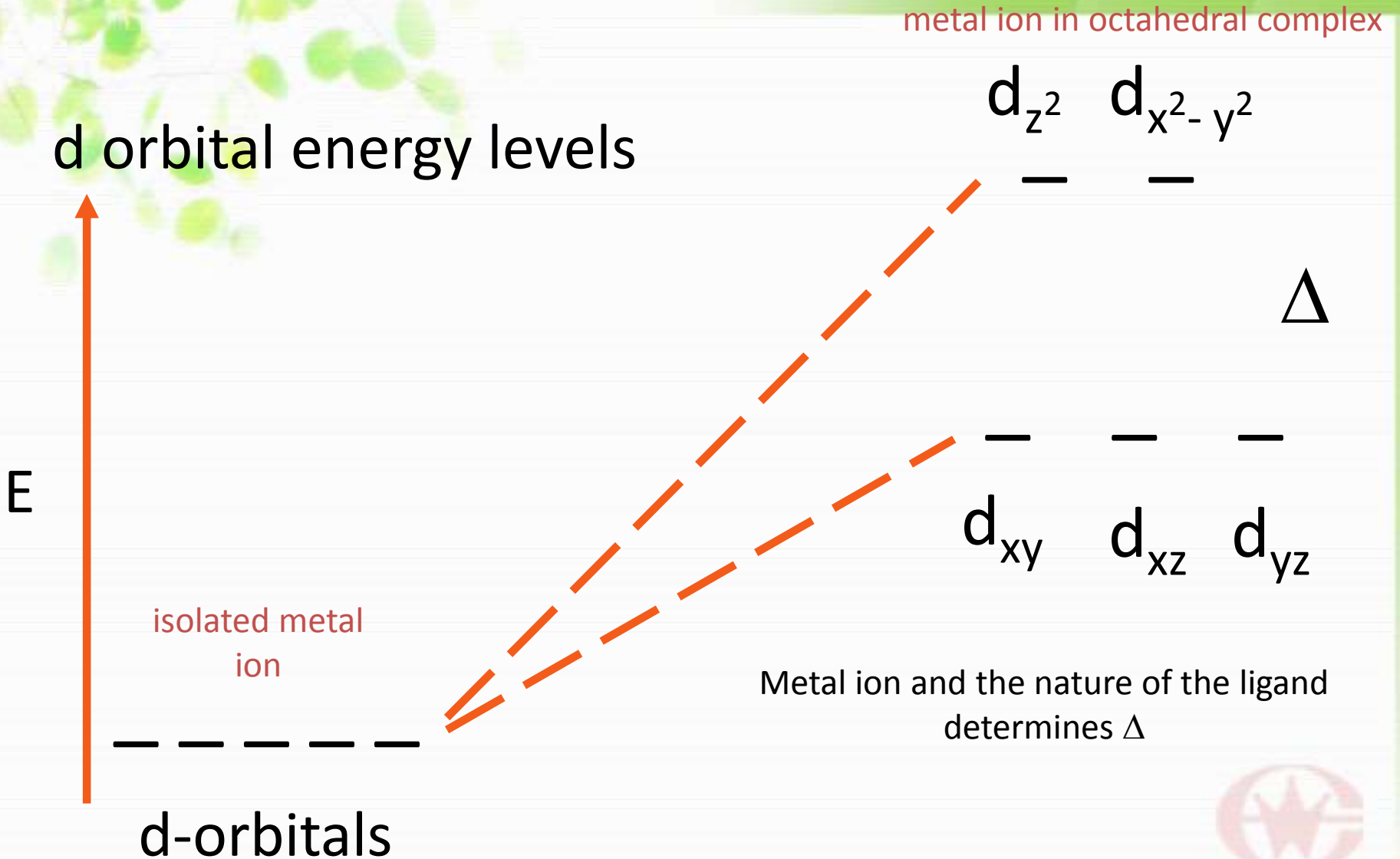


d orbital e<sup>-</sup>'s repulsed by (-) ligands;  
increases d orbital potential energy

ligands approach along x, y, z axes

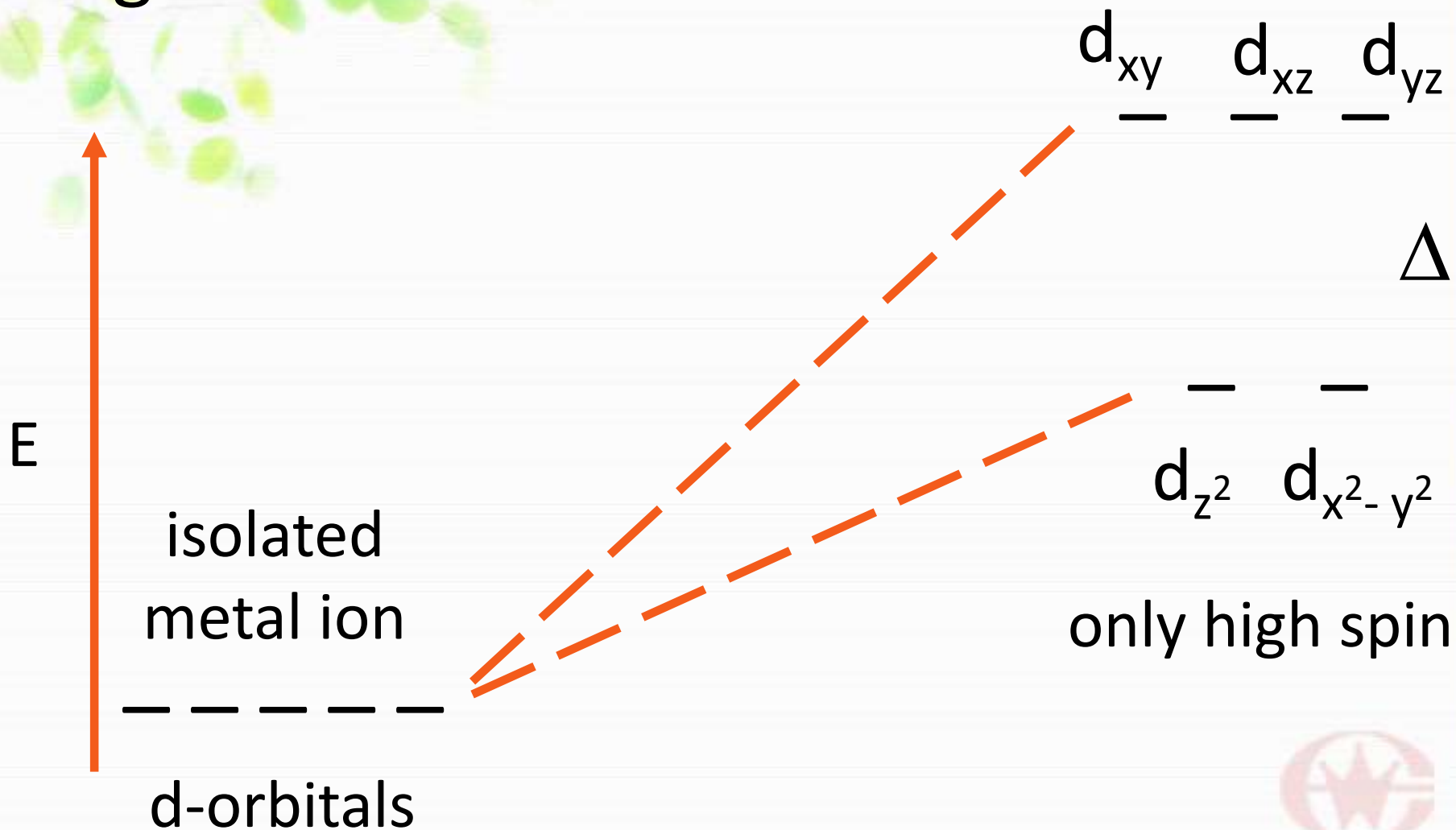


# Octahedral Crystal Field



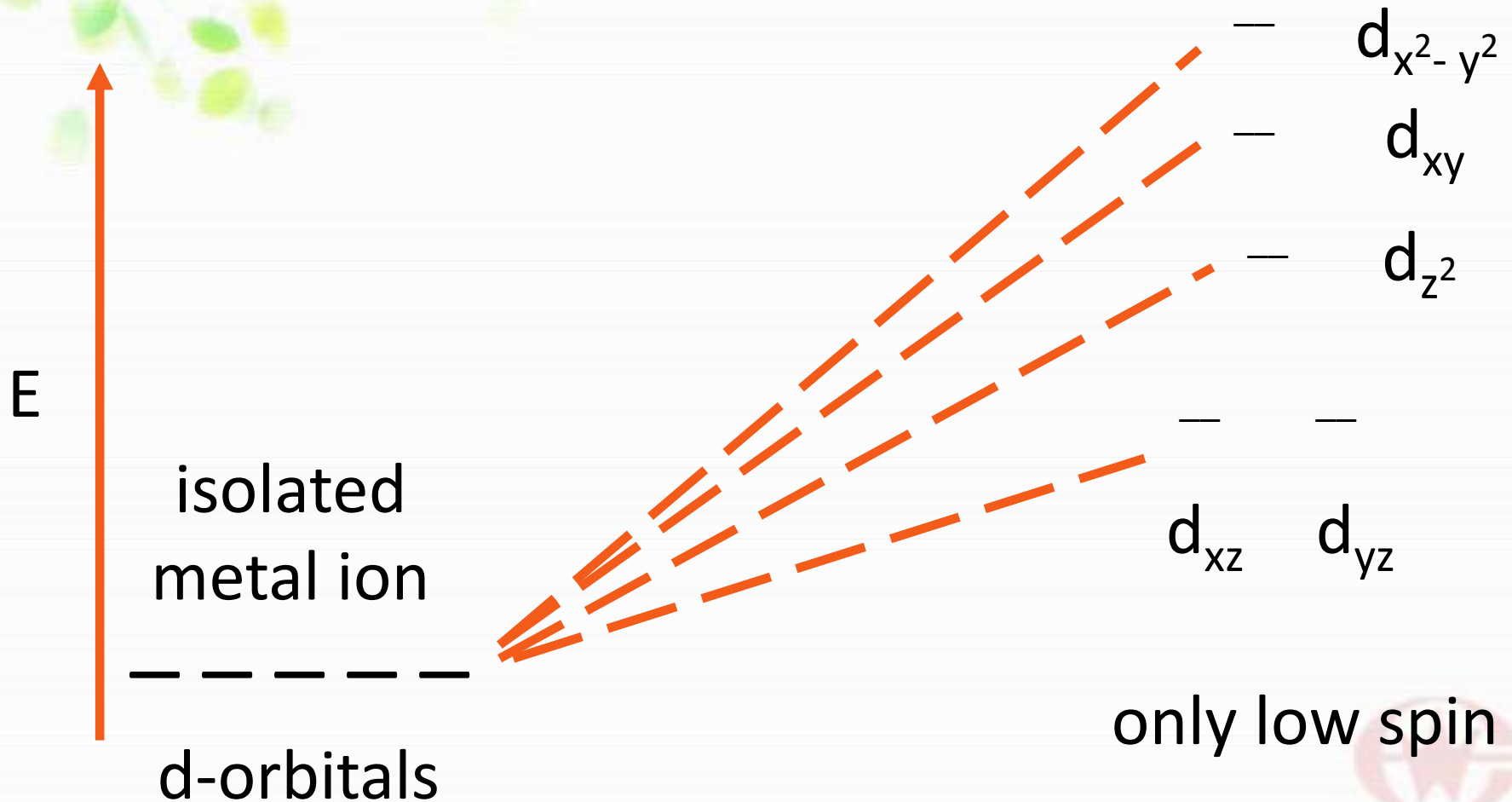
# d-orbital energy level diagram

metal ion in tetrahedral complex



# d-orbital energy level diagram

metal ion in square planar complex



# Colors of transition metal complexes

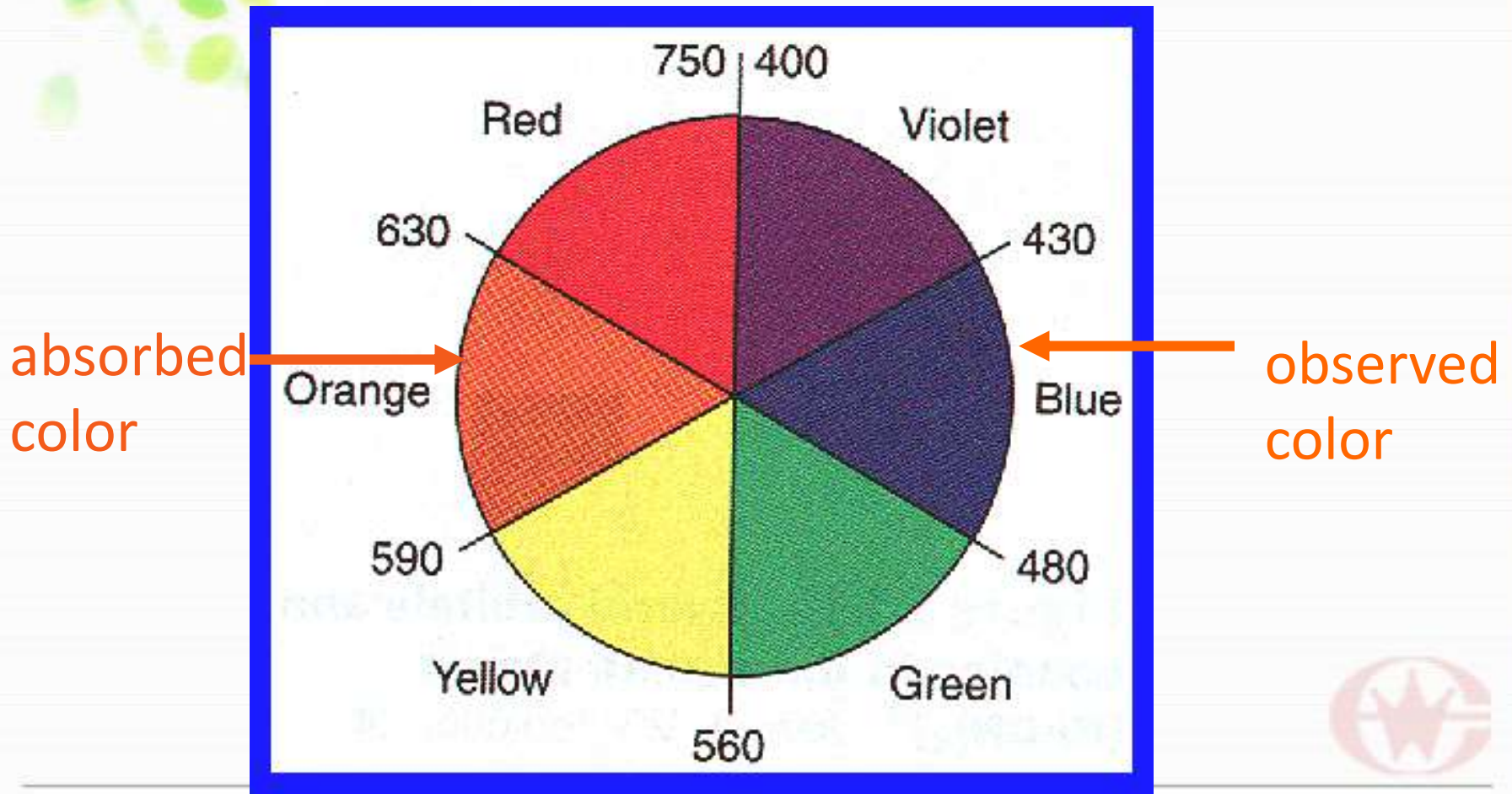
- 1) A complex must have partially filled d subshell on metal to exhibit color
- 2) A complex with 0 or 10 d e<sup>-</sup>s is colorless
- 3) Compounds/complexes that have color absorb specific wavelengths of visible light (400 – 700 nm)
- 4) Absorption of UV-visible radiation by atom, ion, or molecule:
  - Occurs only if radiation has the energy needed to raise an e<sup>-</sup> from its ground state to an excited state i.e., from lower to higher energy orbital

light energy absorbed = energy difference between the ground state and excited state



5)wavelengths not absorbed are transmitted

6)color observed = complementary color of color absorbed



## 7) Different complexes exhibit different colors because:

- color of light absorbed depends on  $\Delta$ 
  - larger  $\Delta$  = higher energy light absorbed
    - Shorter wavelengths
  - smaller  $\Delta$  = lower energy light absorbed
    - Longer wavelengths
- magnitude of  $\Delta$  depends on:
  - ligand(s)
  - Metal

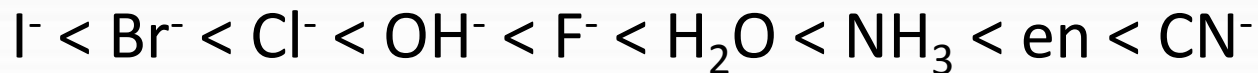


# Spectrochemical Series

Smallest  $\Delta$

$\Delta$  increases

Largest  $\Delta$



weak field

strong field



# Limitations of crystal field theory

- From the assumptions that ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect but the anionic ligands are actually found at the low end of spectrochemical series.
- Further it does not take into account the covalent character of bonding between the ligand and the central atom.





THANK YOU

