Coordination Compounds

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Types of Salts

➢Simple salt	• NaCl	Na^{+} & Cl^{-}
➢Double salt	• Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$	Fe^{+2}, NH_4^{+} & SO_4^{-2}
➢Complex salt	• $K_4[Fe(CN)_6]$	$4K^{+}$ & $[Fe(CN)_6]^{-4}$

Coordination compound / Complex compound

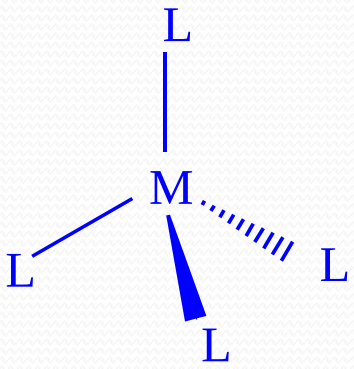
$[Fe(CN)_6]^{-3}$

- **Metal ion: (Fe^{+3})**
- Acts as a **Lewis acid** (e^- pair acceptor)

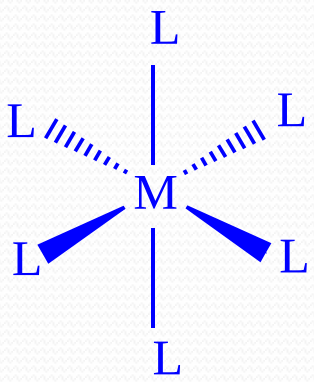
- **Ligand** or **complexing agent: (CN^-)**
- (molecule or ion with lone pair of e^- that bonds to metal ion)
- Acts as a **Lewis base** (e- pair donor)

- Coordinate covalent bond

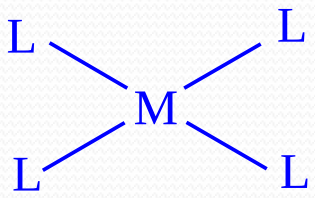
Coordination polyhedron



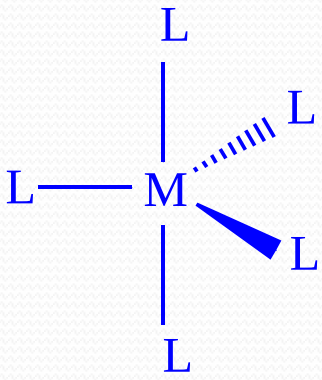
Tetrahedral



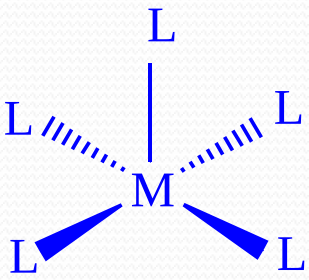
Octahedral



Square planar



Trigonal bipyramidal



Square pyramidal

Werner's theory

- **Werner** was born on December 12, 1866

- Swiss chemist
- Nobel Prize in 1913 for his work on the linkage of atoms and the coordination theory.

Werner's theory

Postulates :

- In coordination compounds metals show two types of valencies
  - Primary or ionizable valency and
  - Secondary or non-ionizable or auxiliary valency.
- The primary valences are normally ionizable and are satisfied by negative ions.
- The secondary valences are non-ionizable. 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 primary valences are non-directional.
- The secondary valencies have directional properties and directed towards a fixed position in space.

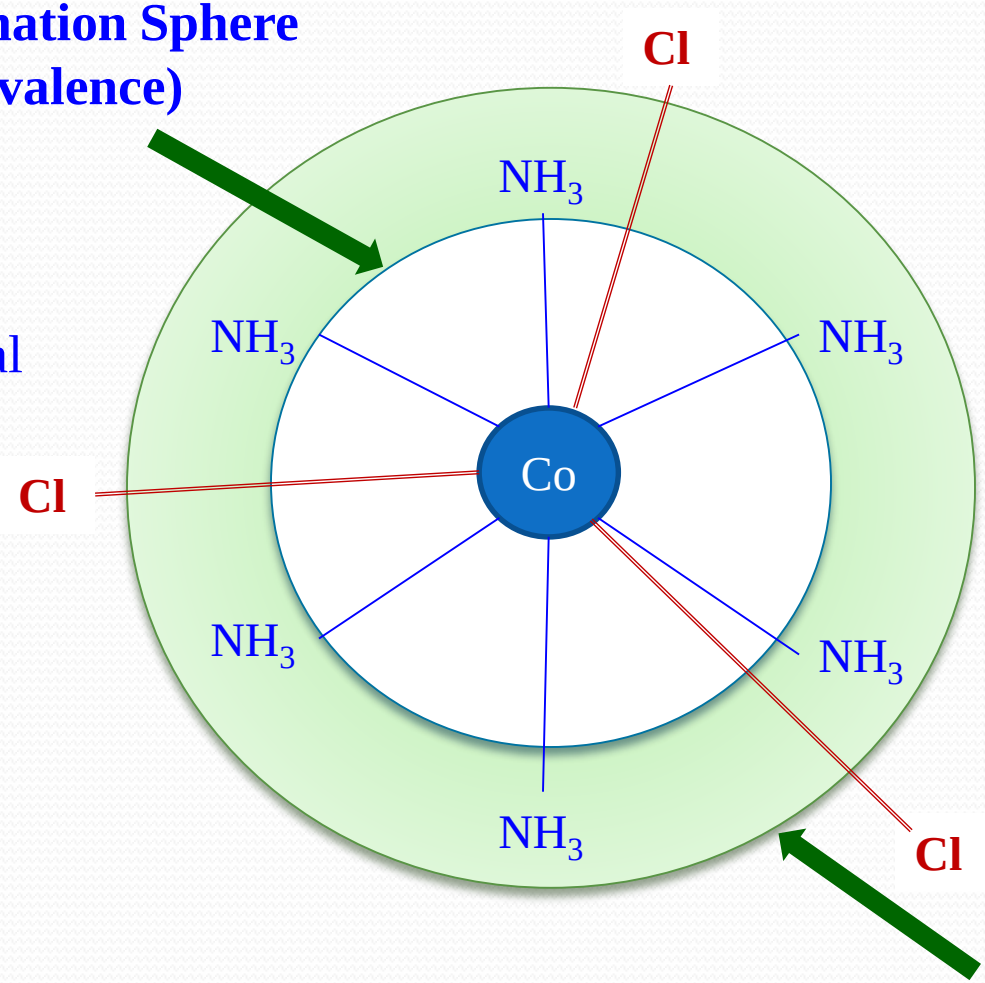
Inner or Coordination Sphere (secondary valence)

non-ionisable

- ve ions & neutral

directional

fix number (CN)



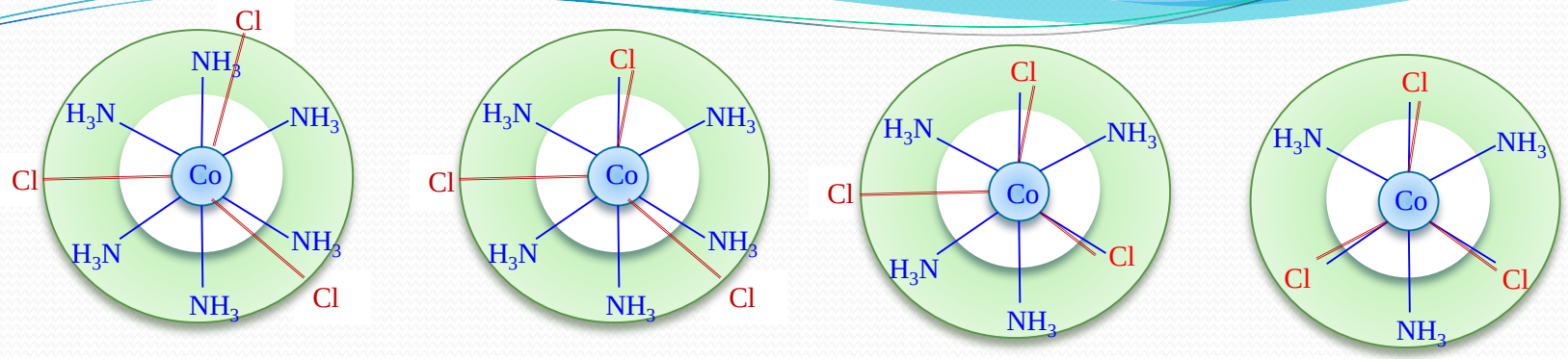
number is not fix

ionisable

- ve ions

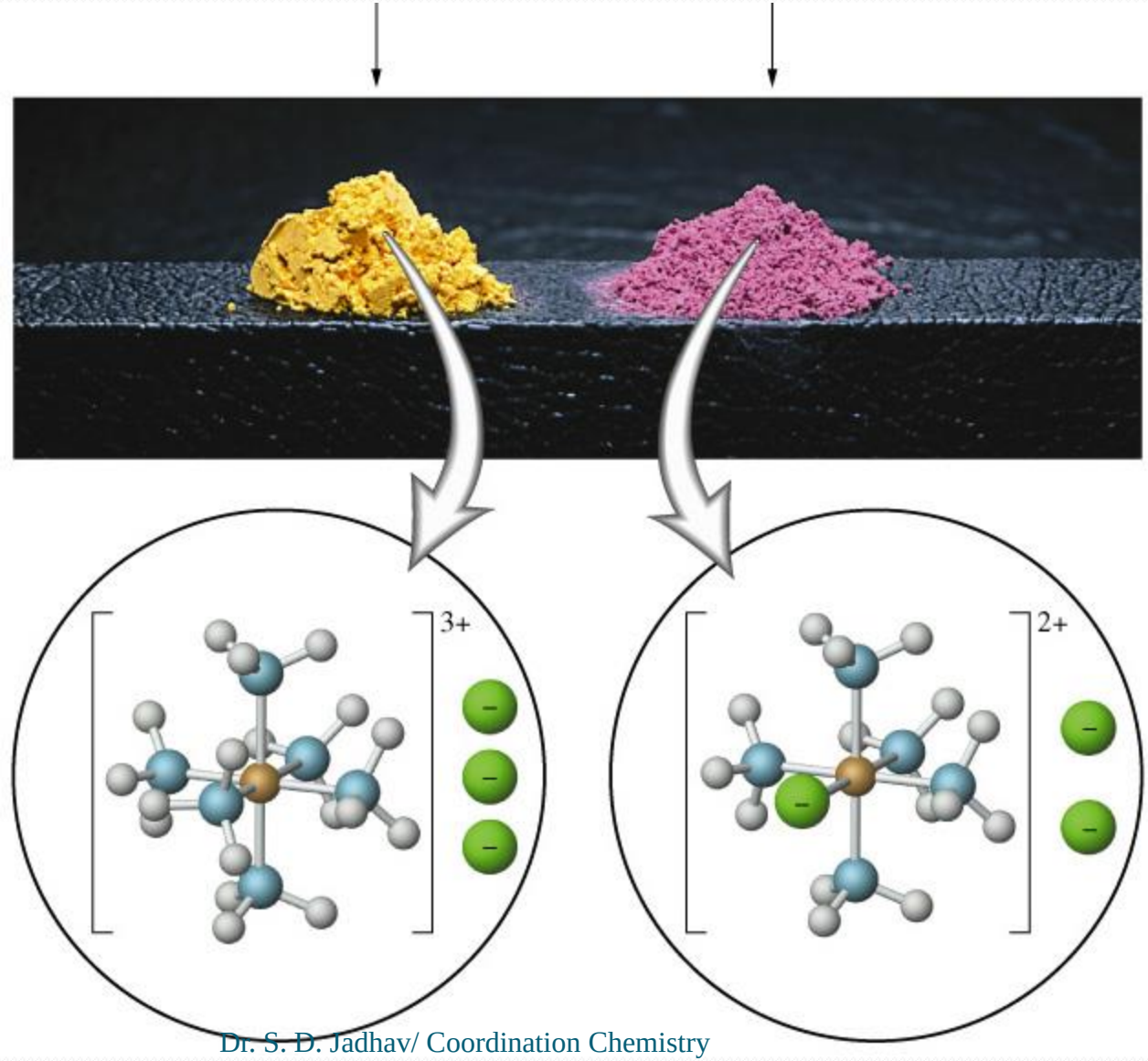
non-directional

Outer or Ionisation Sphere (primary valence)



Composition	$CoCl_3.6NH_3$	$CoCl_3.5NH_3$	$CoCl_3.4NH_3$	$CoCl_3.3NH_3$
Cl^- ions precipitated by $AgNO_3$	3	2	1	0
No. of ions / particles	4 **(+ve ion & 3Cl^- ions)**	3 **(+ve ion & 2Cl^- ions)**	2 **(+ve ion & 1Cl^- ions)**	0
Total charge	6	4	2	0
Molar Conductance	$[Co(NH_3)_6]^{+3}$ & $3Cl^-$	$[Co(NH_3)_6Cl]^{+2}$ & $2Cl^-$	$[Co(NH_3)_6Cl_2]^+$ & Cl^-	$[Co(NH_3)_3Cl_3]$
Molecular Formula	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_3Cl_3]$

$CoCl_3.6NH_3$ $CoCl_3.5NH_3$



Ligands

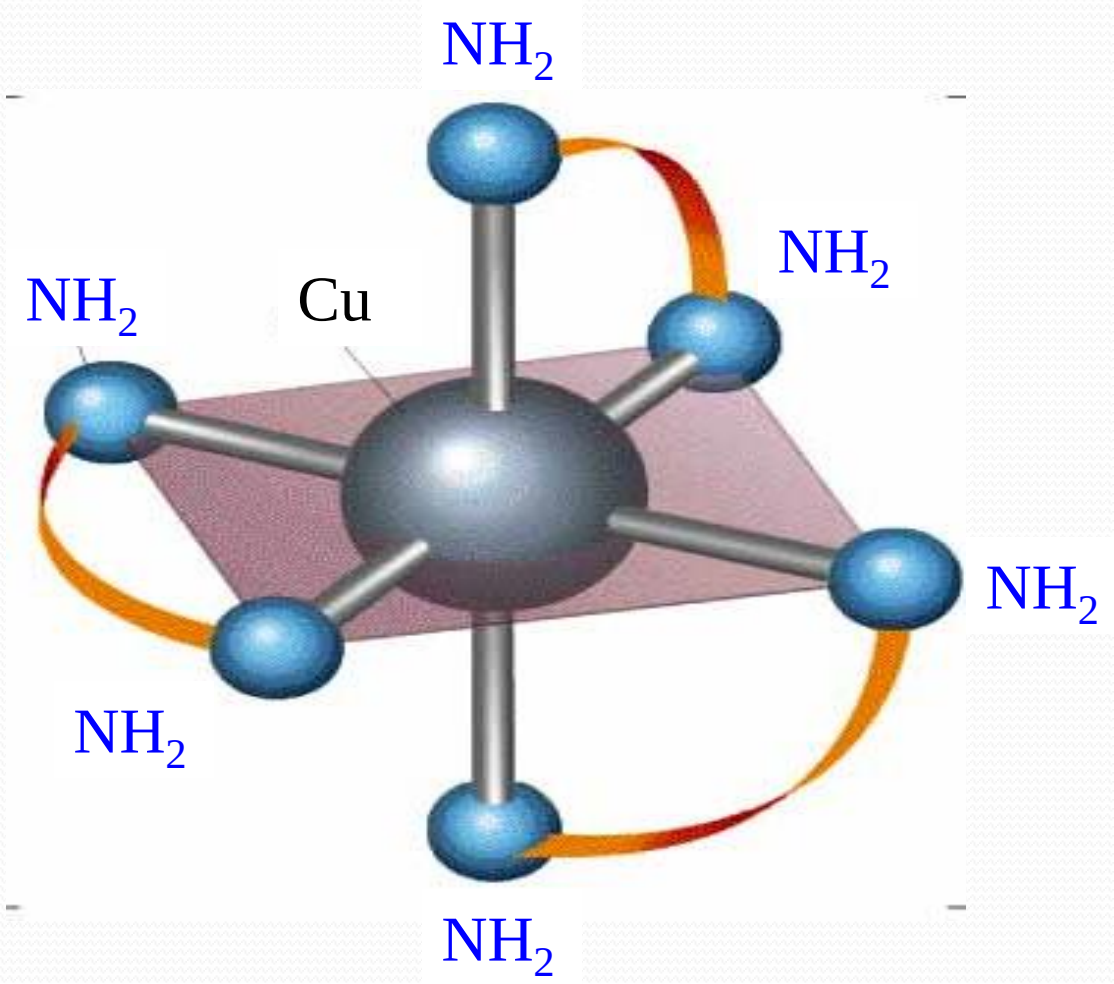
- The **molecules or ions** which are coordinated to the central metal in a coordination compound are called as Ligands.

- **Classification of Ligands**

  according to the number of donor atoms (N, O, S, X)

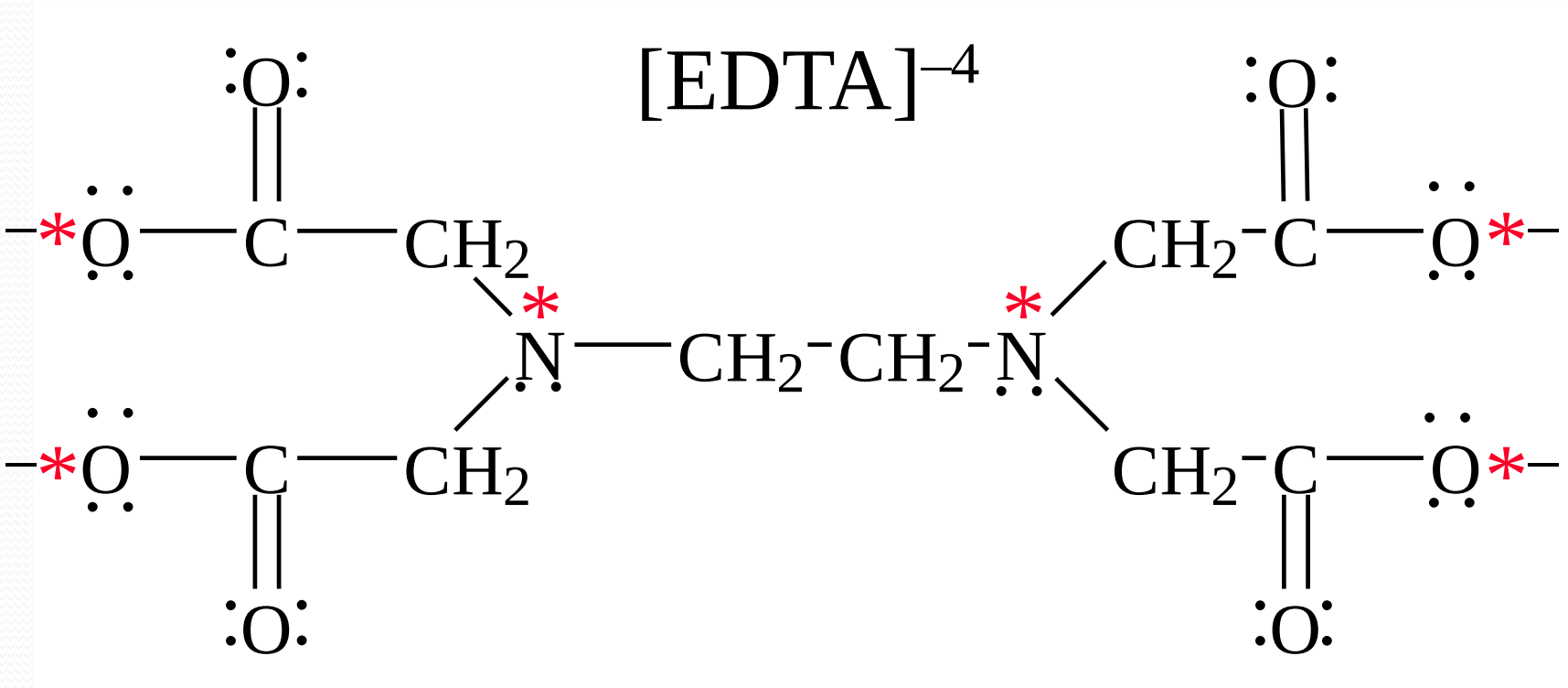
  - monodentate = 1 donor atom
  - polydentate = 2 or more donor atoms
    - bidentate = 2
    - tetradentate = 4
    - hexadentate = 6

$[Cu(en)_3]^{+2}$ (octahedral complex)

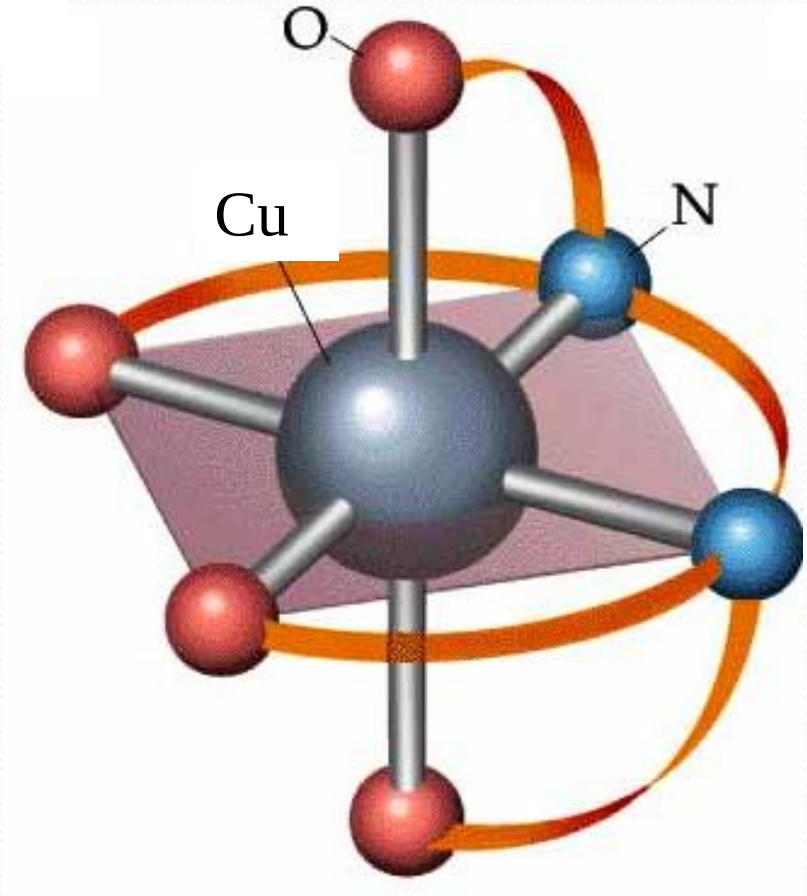


- Hexadentate

Ethylenediamminetetraacetate ion



$[Cu(EDTA)]^{-2}$ (octahedral complex)



- Ambidentate Ligands
- Ligand having 2 donor atoms

➢ **NO_2^-** (N & O)

M – NO_2

M – ONO

➢ **SCN^-** (S & N)

M – SCN

M – NCS

➢ **CN^-** (C & N)

M – CN

M – NC

Coordination number (CN)

- The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded.

Coordination number

Each metal ion has a characteristic coordination number.

Metal ion	**CN**	**Example**
Ag^{+}	2	$[Ag(NH_3)_2]^{+}$
Au^{+}, Cu^{+}	2, 4	
Zn^{+2}, Cd^{+2}, Hg^{+2}, Pt^{+2}	4	$[Cu(NH_3)_4]^{+2}$
Cu^{+2}, Ni^{+2}, Co^{+2}	4, 6	
Fe^{+3}, Co^{+3}, Cr^{+3}	6	$[Co(NH_3)_6]^{+3}$
Sn^{+4}, Pt^{+4}, Pd^{+4}	6	$[Pt(NH_3)_6]^{+4}$

Effective Atomic Number (EAN)

- Total number of electrons around the central metal ion present in the complex.
- EAN = No. of electrons on metal ion +
  No. of electrons donated by the ligands.
- EAN = Z – X + Y

  Z = at. no. of metal

  X = no. of e^-s lost

  Y = no. of e^-s donated by ligands

- Ex. $[Fe(CN)_6]^{-4}$ Fe^{+2}

  EAN = 26 – 2 +12 = 36

  At. No. of Kr = 36

EAN

Metal	Complex	Z	X	Y	EAN
Ni	$[Ni(CO)_4]$	28	0	8	36 (Kr)
Fe	$[Fe(CN)_6]^{-4}$	26	2	12	36
Co	$[Co(NH_3)_6]^{+3}$	27	3	12	36
Zn	$[Zn(NH_3)_4]^{+2}$	30	2	8	36
Pt	$[Pt(NH_3)_6]^{+4}$	78	4	12	86 (Rn)

Exceptions

Metal	Complex	Z	X	Y	EAN
Fe	$[Fe(CN)_6]^{-3}$	26	3	12	35
Cu	$[Cu(NH_3)_4]^{+2}$	29	2	8	35
Pt	$[Pt(NH_3)_4]^{+2}$	78	2	8	84

IUPAC Nomenclature

(International Union Pure and Applied Chemistry)

1. Naming complex compounds

   Cation is named first followed by anion.

   eg. $K_3[Fe(CN)_6]$ $[Co(NH_3)_4Cl_2]Cl$

2. Naming complex ions

- Complex cation

  Name ligands first and then metal ion with its oxi. no.

- Complex anion

  Name ligands first and then metal ion with suffix –ate and with its oxi. no.

3. Naming Ligands

- name ligands in alphabetical order.
- two or more number of same ligand, use prefixes di, tri, tetra, etc.
- two or more number of same chelate ligand, use prefixes bis, tris.
- Names of the anionic ligands end in – o.
- those of neutral ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO.
- cationic ligands end in –ium.

  nitrosylium for NO^+, hydrazinium for $NH_2NH_3^+$.

Ligand	Name	Ligand	Name
Br^-	bromo	CO_3^{-2}	carbonato
Cl^-	chloro	NO_2^-	nitro
CN^-	cyano	$C_2O_4^{-2}$	oxalato
OH^-	hydroxo	O^{-2}	oxo

- $K_3[Fe(CN)_6]$
  potassiumhexacyanoferrate(III)
- $K_4[Fe(CN)_6]$
  potassiumhexacyanoferrate(II)
- $[Co(NH_3)_4Cl_2]Cl$
  tetraamminedichlorocobalt(III) chloride
- $[Cu(H_2O)_2(NH_3)_2]Cl_2$
  diamminediaquacopper(II) chloride
- $[Cr(en)_3]Cl_3$
  tris(ethylenediammine)chromium(III)chloride
- $[Ni(CO)_4]$
  tetracarbonylnickel(0)

- Sodiumhexanitrocobaltate(III)

  $Na_3[Co(NO_2)_6]$
- Pentaamminechlorocobaltate(III) chloride

  $[Co(NH_3)_5Cl]Cl_2$
- Dichlorobis(ethylenedimmine)platinum(IV) nitrate

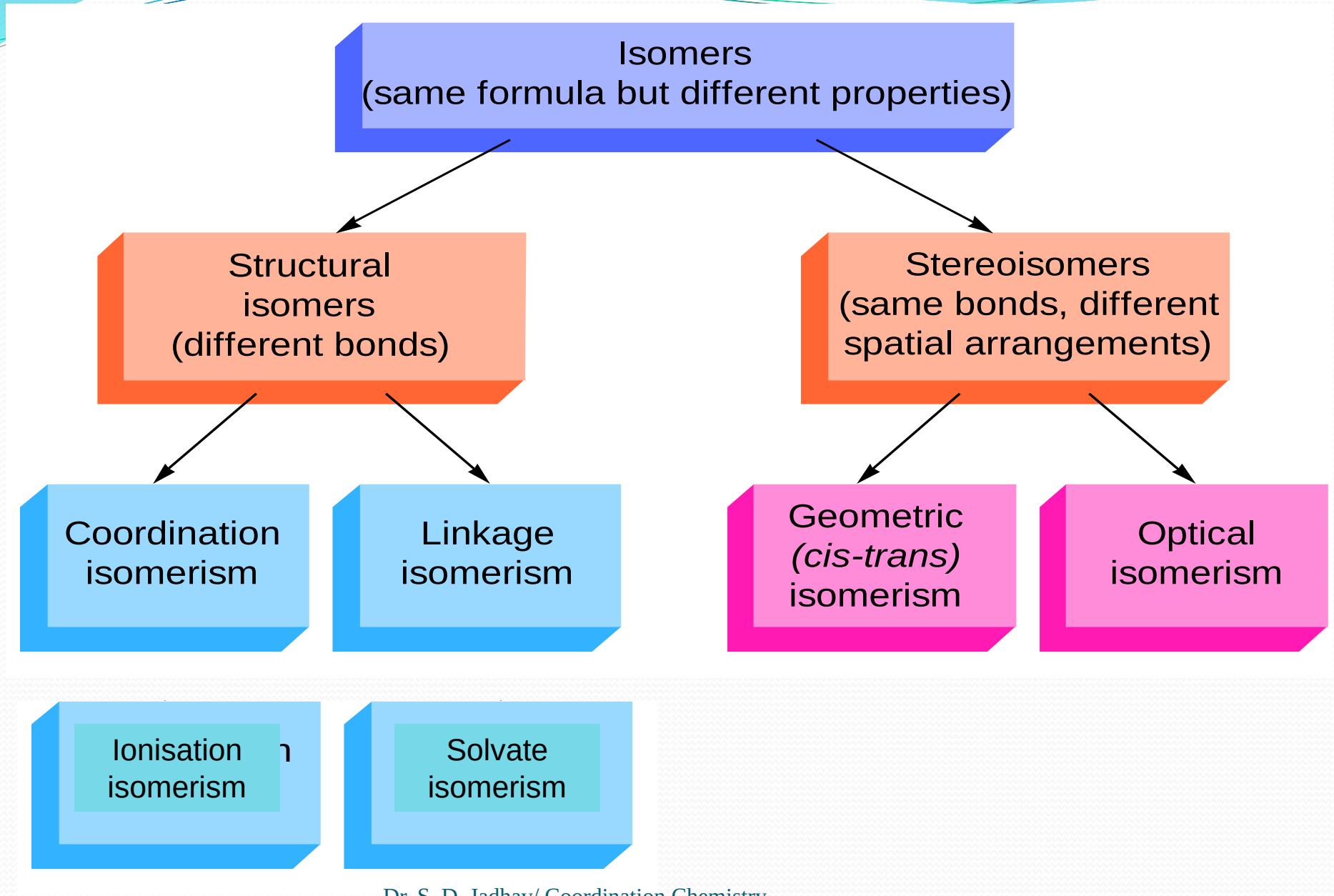
  $[Pt(en)_2Cl_2](NO_3)_2$
- Tris(ethylenediammine)nickel(III) ion

  $[Ni(en)_3]^{+3}$
- Potassiumtrioxalatoaluminate(III)

  $K_3[Al(C_2O_4)_3]$

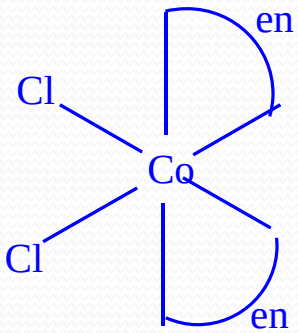
Isomerism

- Isomers are the compounds that have same chemical formula and different arrangement of atoms in space.
- The phenomenon is known as Isomerism.

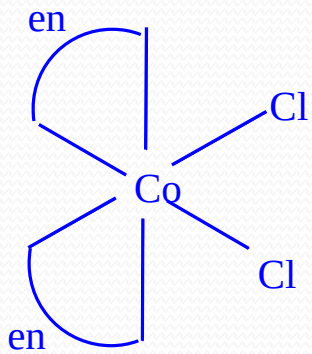

Isomers
(same formula but different properties)
Structural isomers
(different bonds)
Stereoisomers
(same bonds, different spatial arrangements)
Coordination isomerism
Linkage isomerism
Geometric
(cis-trans)
isomerism
Optical isomerism
Ionisation isomerism
Solvate isomerism

Optical isomerism

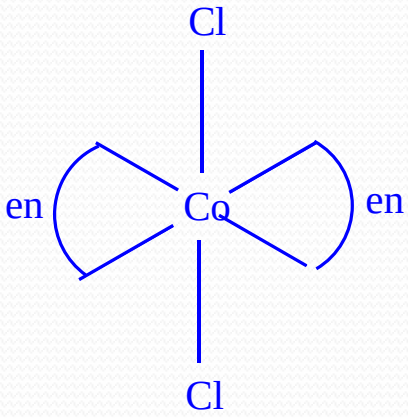
- $[Co(en)_2Cl_2]^+$
- $[M(AA)_2b_2]$



d-form

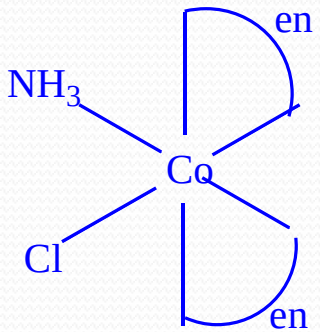


l-form



optically inactive

- $[Co(en)_2ClNH_3]^{+2}$
- $[M(AA)_2\,ab]$



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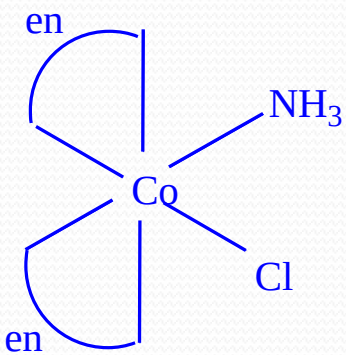

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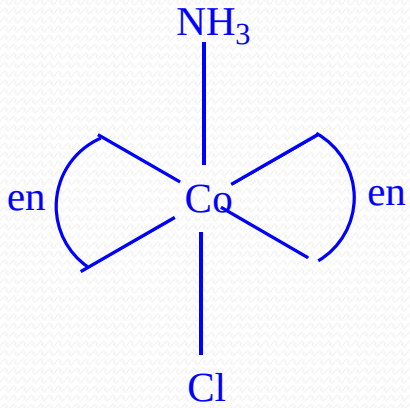
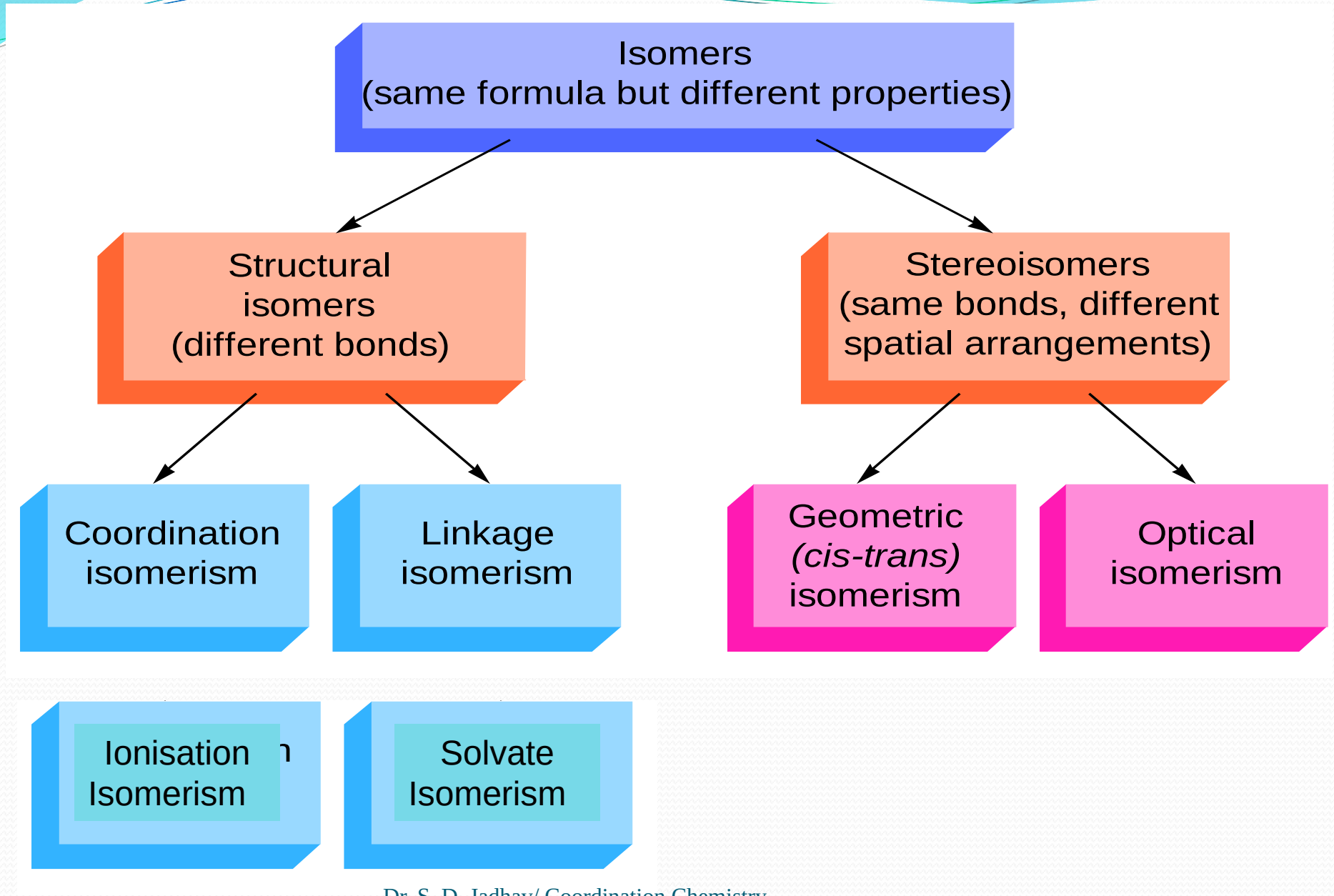


optically inactive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Structural isomers
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Coordination isomerism
Linkage isomerism
Geometric
(cis-trans)
isomerism
Optical isomerism
Ionisation Isomerism
Solvate Isomerism

Structural isomerism

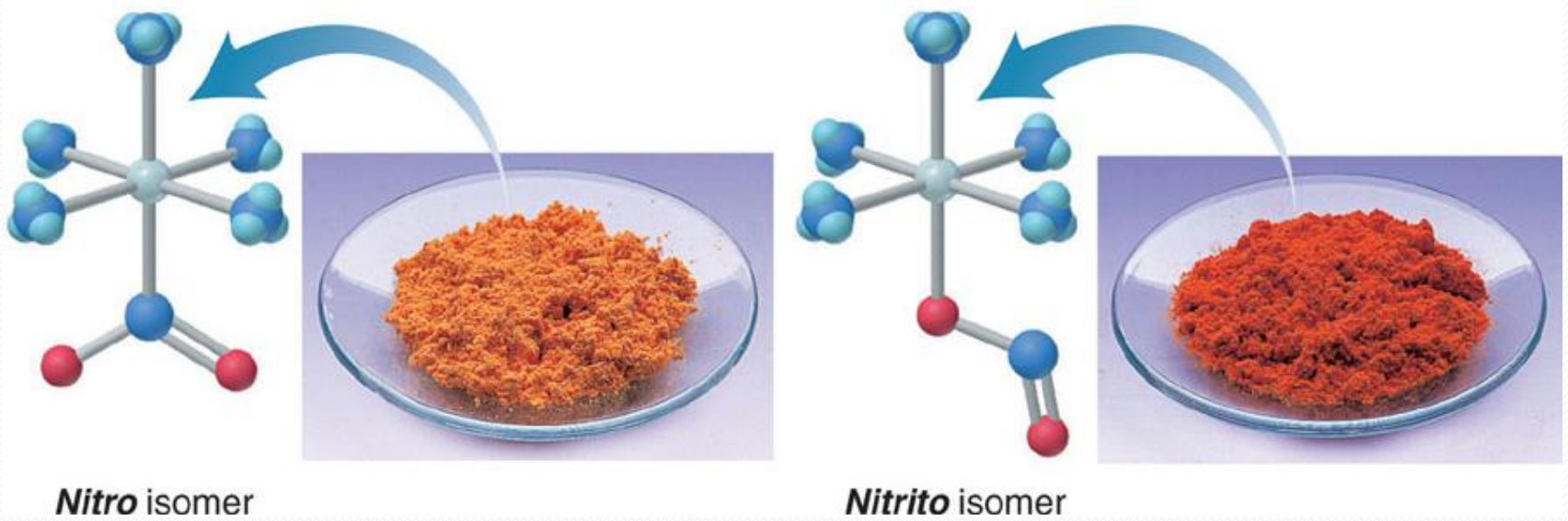
Ionisation isomerism

- $[Co(NH_3)_5SO_4]\ Br$ and $[Co(NH_3)_5Br]SO_4$
- $[Co(NH_3)_5SO_4]^{+}\ Br^{-}$ and $[Co(NH_3)_5Br]^{+2}\ SO_4^{-2}$

- $[Co(NH_3)_5SO_4]NO_3$ and $[Co(NH_3)_5NO_3]SO_4$
- $[Co(NH_3)_5SO_4]^{+}NO_3^{-}$ and $[Co(NH_3)_5NO_3]^{+2}SO_4^{-2}$

Linkage isomerism

- $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$



- cyano CN^-
- thiocyanate SCN^-

Coordination isomerism

- $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

- $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

Hydrate isomerism

- $[Cr(H_2O)_6]Cl_3$
- $[Cr(H_2O)_5Cl]Cl_2.H_2O$
- $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Complex having Co-ordination No. 6	Number of Geometrical isomers
MA_6	0
MA_5B	0
MA_4B_2	2
MA_3B_3	2
$MA_2B_2C_2$	5
MABCDEF	15

Possible number of stereoisomers for complex

Formula	Number of sterioisomers	Pairs of enantiomers
Ma_6	1	0
Ma_5b	1	0
Ma_4b_2	2	0
Ma_3b_3	2	0
Ma_4bc	2	0
Ma_3bcd	5	1
Ma_2bcde	15	6
Mabcdef	30	15
$Ma_2b_2c_2$	6	1
Ma_2b_2cd	8	2
Ma_3b_2c	3	0

Possible number of stereoisomers for complex

Formula	Number of sterioisomers	Pairs of enantiomers
M(AA)(BC)de	10	5
M(AB)(AB)cd	11	5
M(AB)(CD)ef	20	10
$M(AB)_3$	4	2
M(ABA)cde	9	3
$M(ABC)_2$	11	5
M(ABBA)cd	7	3
M(ABCBA)d	7	3
$M(AA)_3$	2	1

Valence Bond Theory (VBT)

Sailent Features:

- Central metal ion provides a definite number of vacant orbitals.
- No. of vacant orbitals provided is equal to coordination number.
- These vacant orbitals undergo hybridisation to form same number of new hybrid orbitals.
- The vacant hybrid orbitals then overlap with filled orbitals of ligand to form coordinate covalent bonds.
- The geometry of the complex depends upon the type of hybridisation.
- When the strong field ligands are involved in complex formation, then pairing of electrons takes place in metal orbitals.

Types of Hybridisation

Hybridisation	Geometry
sp	Linear
sp^2	Trigonal
sp^3	Tetrahedral
dsp^2	Square planar
dsp^3	Trigonal bipyramidal
d^2sp^3 and sp^3d^2	Octahedral
d^3sp^3	Pentagonal bipyramidal

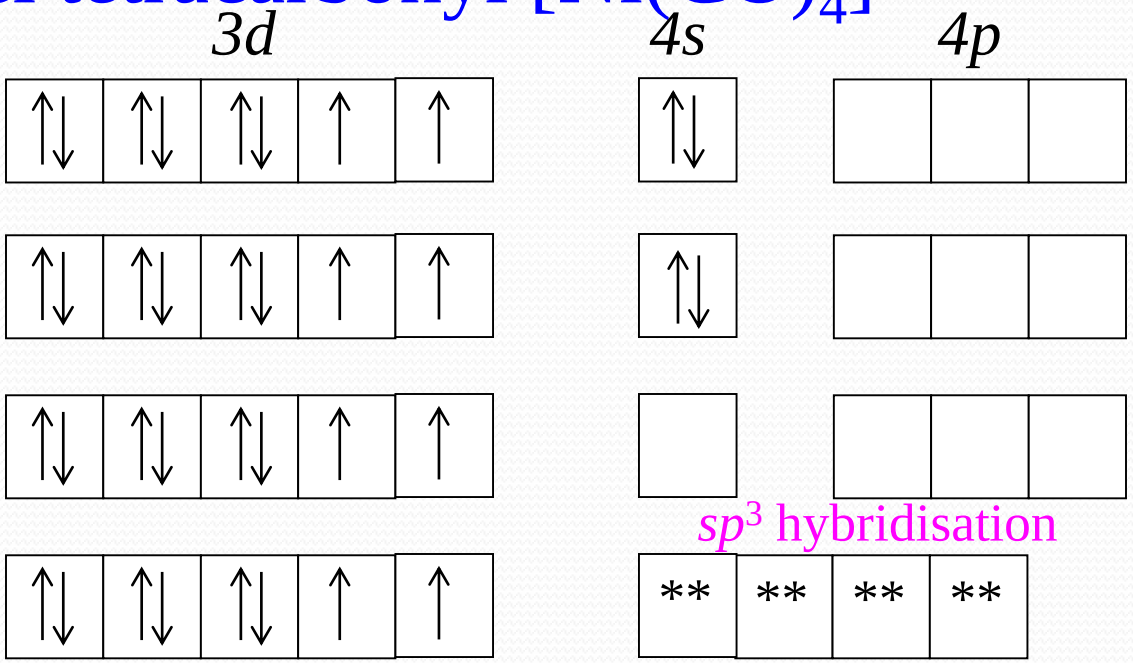
The spectrochemical series.

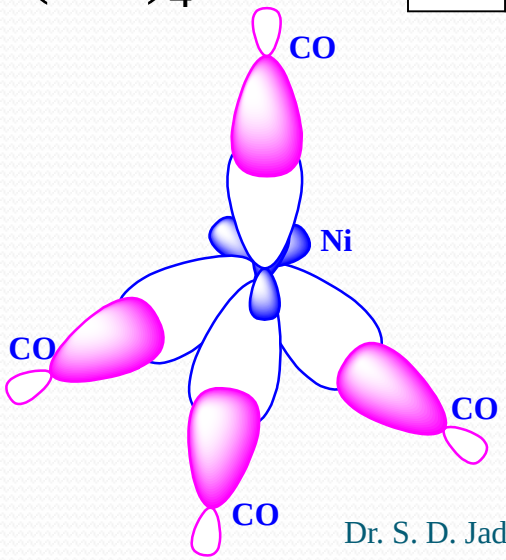
$I^- < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < en < NO_2^- < CN^- < CO$

WEAKER FIELD **STRONGER FIELD**

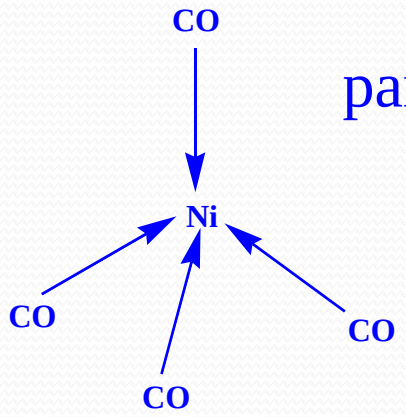
Nickel tetracarbonyl [$Ni(CO)_4$]

- Ni (Z = 28)
- Ni^0
- $Ni(CO)_4$





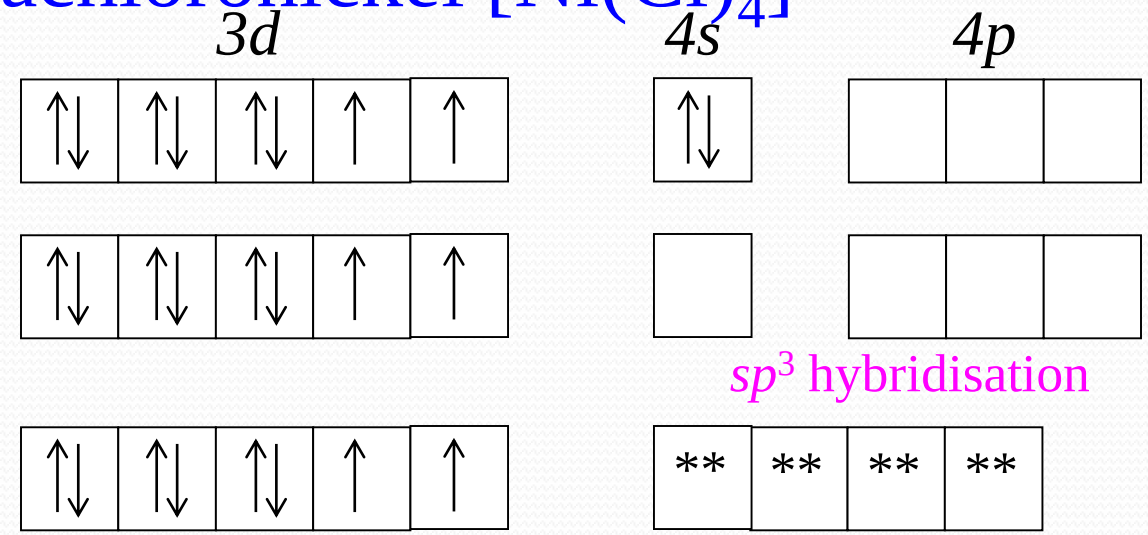
tetrahedral



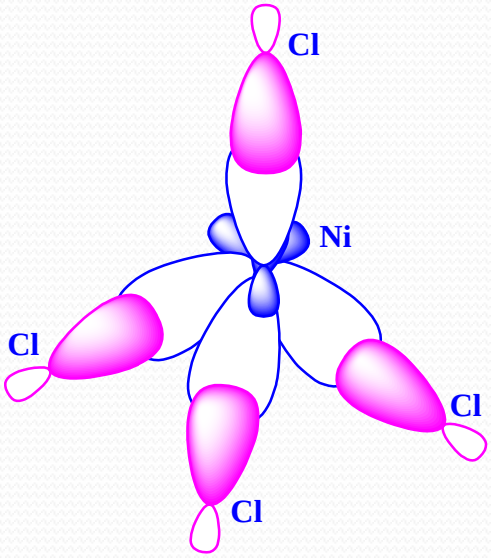
paramgnetic

Tetrachloronickel $[Ni(Cl)_4]^{-2}$

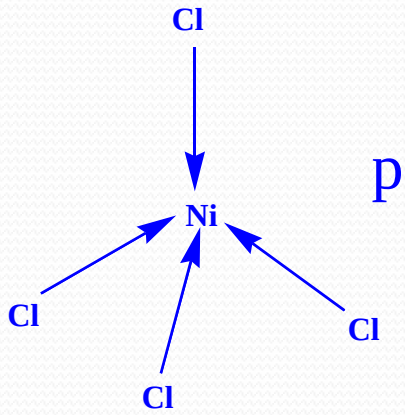
- Ni (Z = 28)
- Ni^{+2}
- $[Ni(Cl)_4]^{-2}$



sp^3 hybridisation



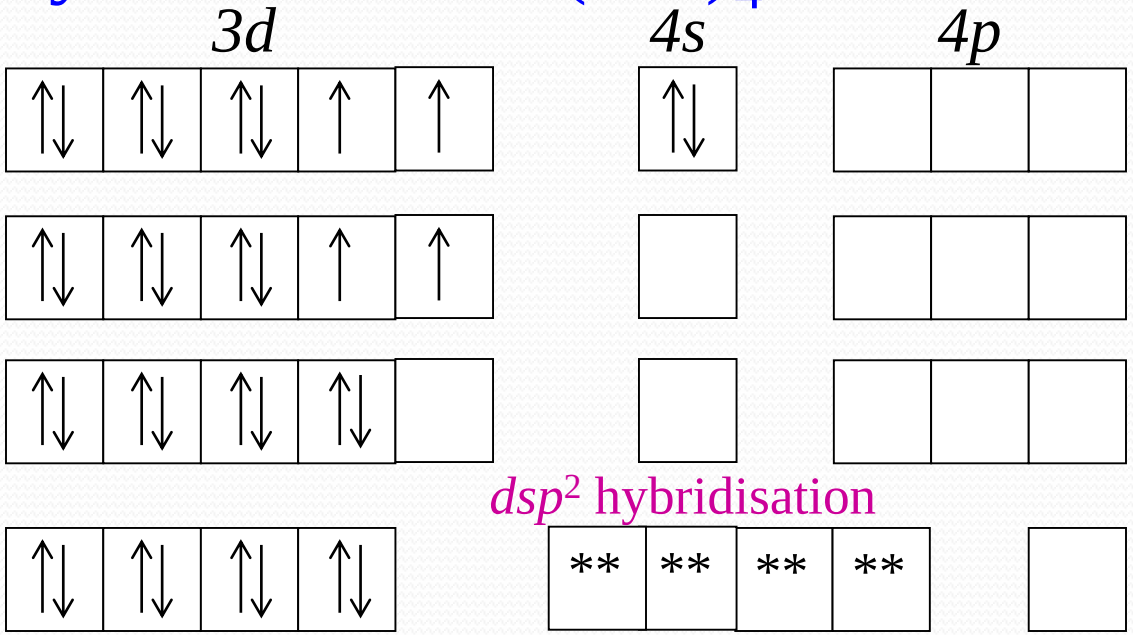
tetrahedral



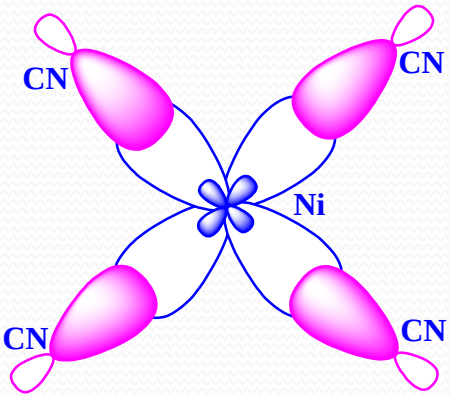
paramgnetic

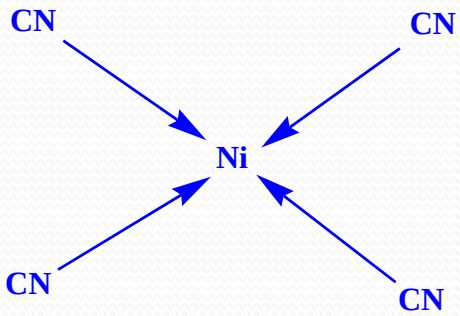
Tetracyanonickel $[Ni(CN)_4]^{-2}$

- Ni (Z = 28)
- Ni^{+2}
- $[Ni(CN)_4]^{-2}$



dsp^2 hybridisation



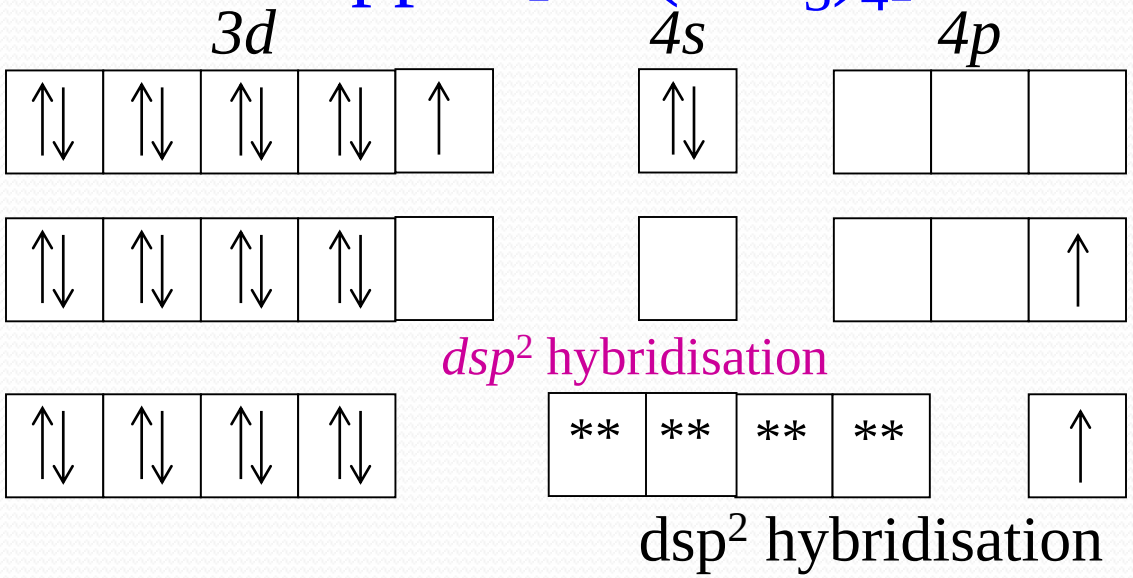


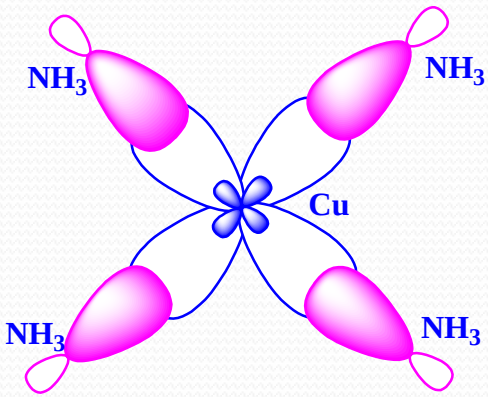
diamgnetic

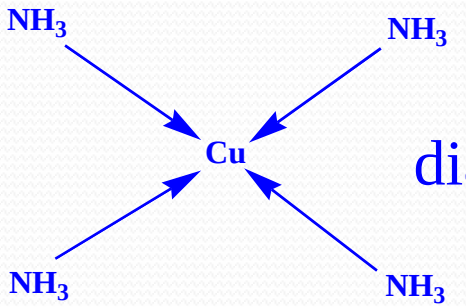
Square planar

Tetraammoniumcopper $[Cu(NH_3)_4]^{+2}$

- Cu (Z = 26)
- Cu^{+2}
- $[Cu(NH_3)_4]^{+2}$





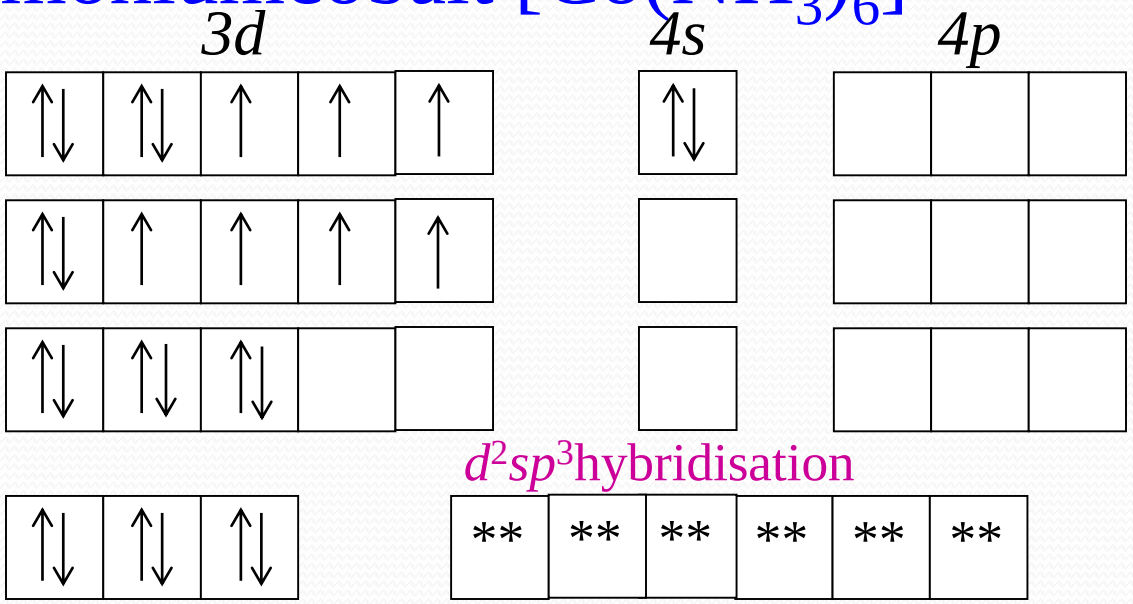


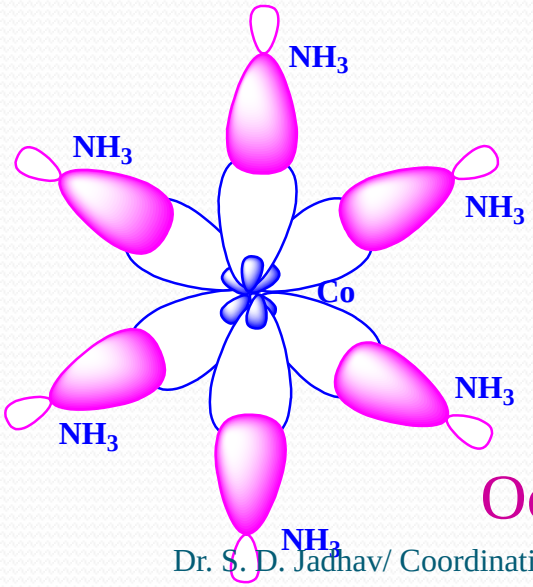
diamgnetic

Square planar

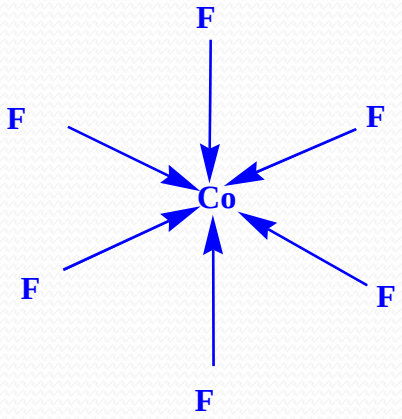
Hexaammoniumcobalt $[Co(NH_3)_6]^{+3}$

- Co (Z = 27)
- Co^{+3}
- $[Co(NH_3)_6]^{+3}$





Octahedral



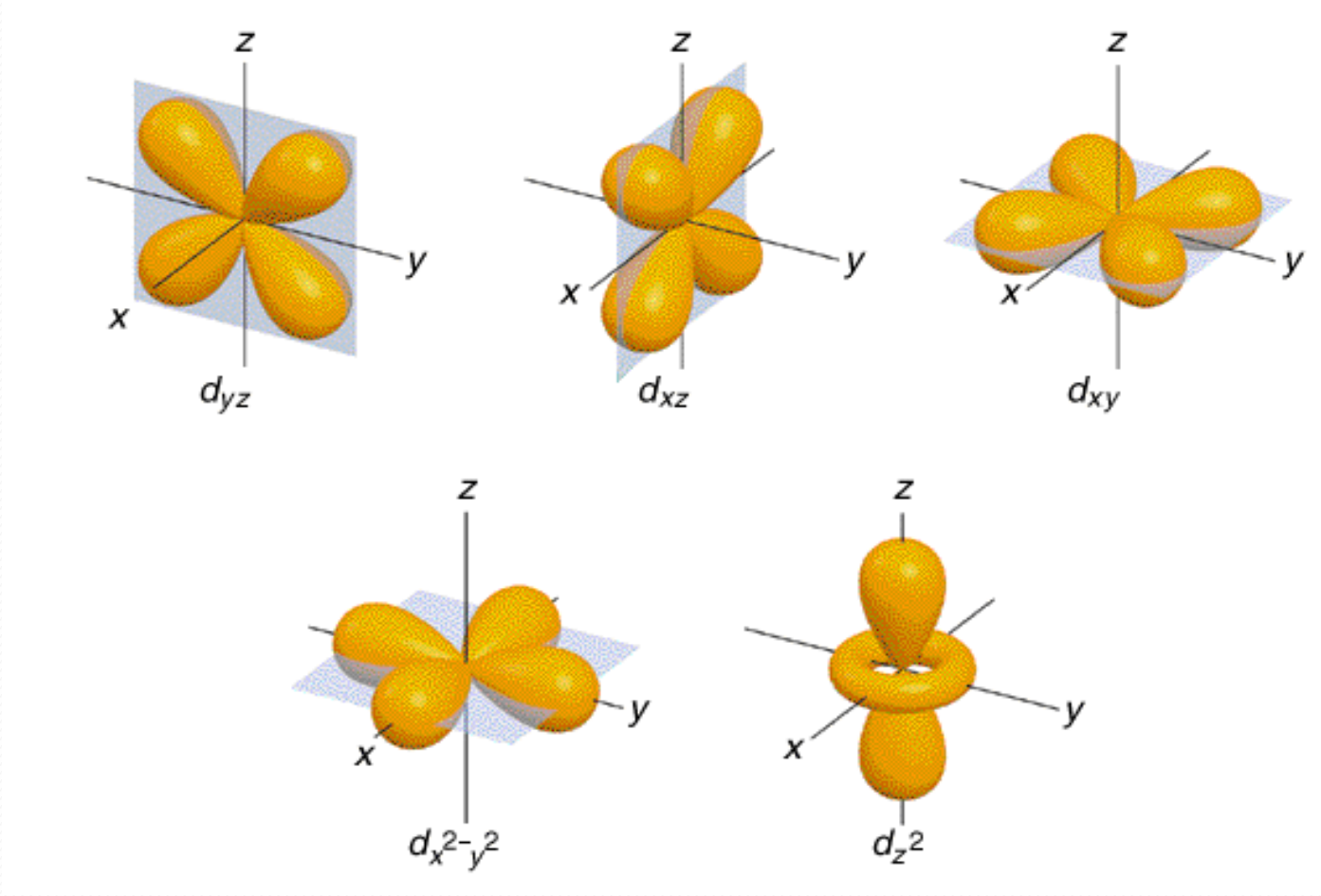
diamgnetic

Crystal Field Theory (CFT)

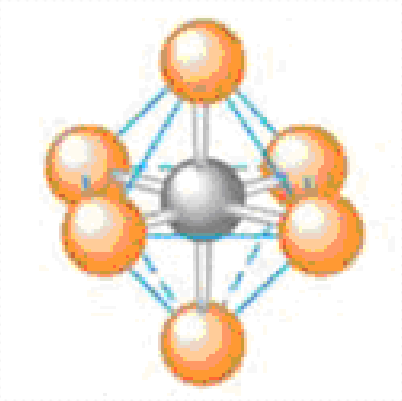
- In complex the central metal ion and ligands both act as point charges.
- The interaction between them is purely electrostatic.
- When the ligands approach the metal ion, these electrons repel each other.
- These repulsive forces destroy the degeneracy of metal d-orbitals and split them in two sets eg and t_2g.
- The electrons of metal ion then occupy the splitted d-orbitals according to Hund's rule.
- The stability of metal complex is calculated as CFSE.

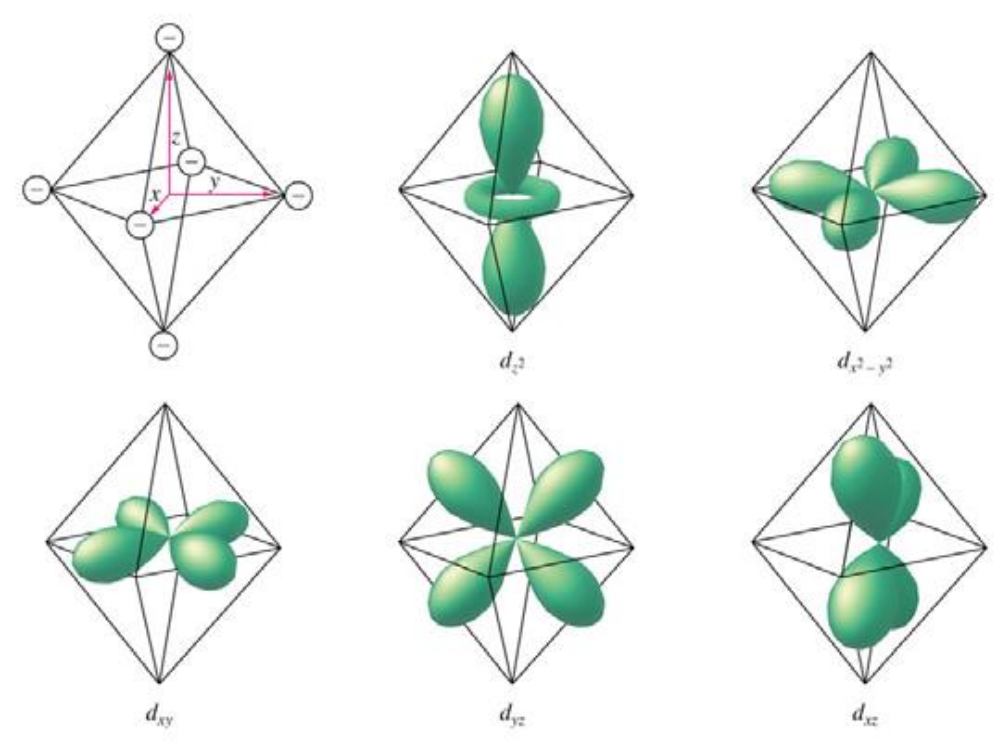
Metal d-orbitals

- t_2g set
- eg set

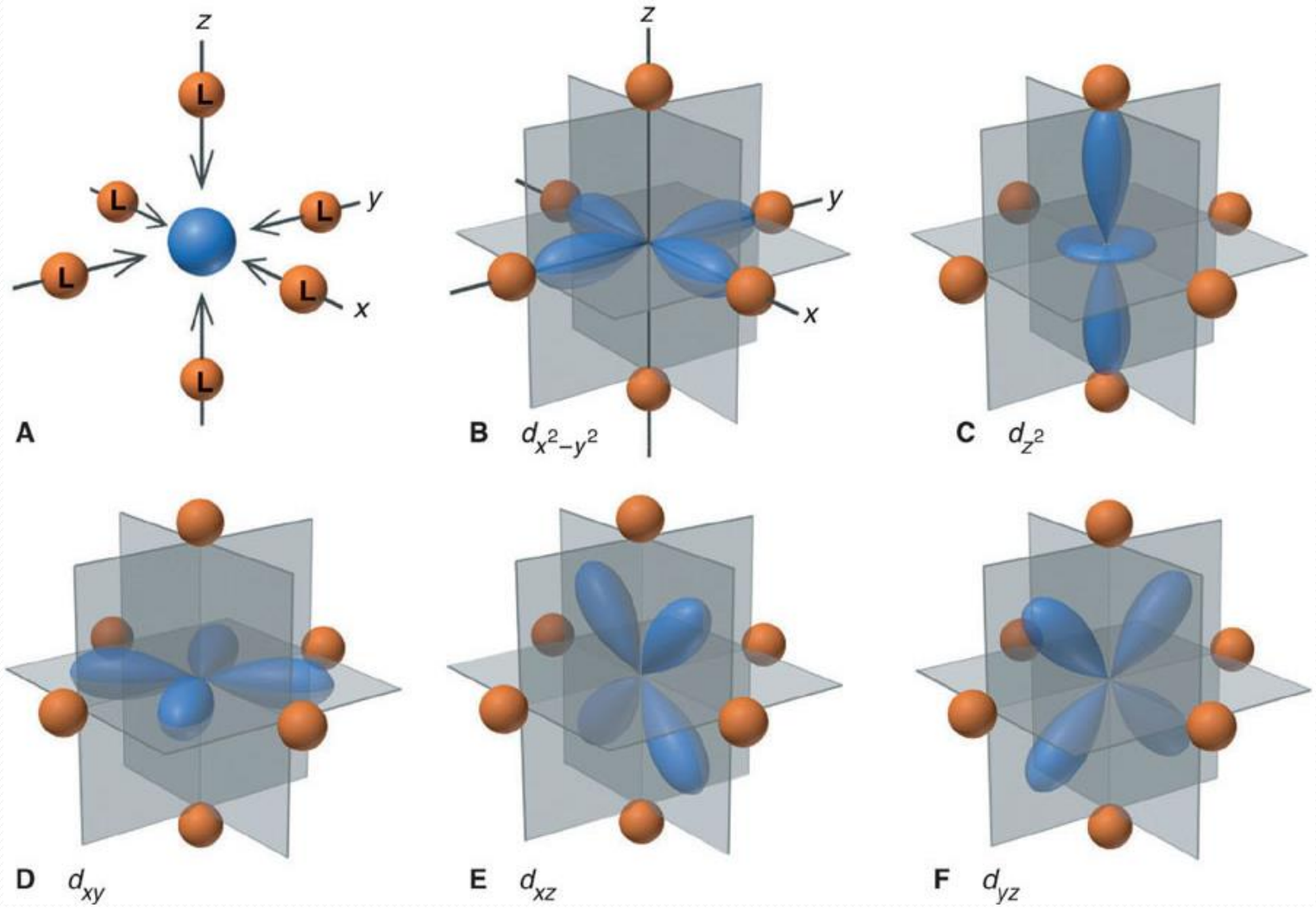


Crystal Field splitting in Octahedral Complexes

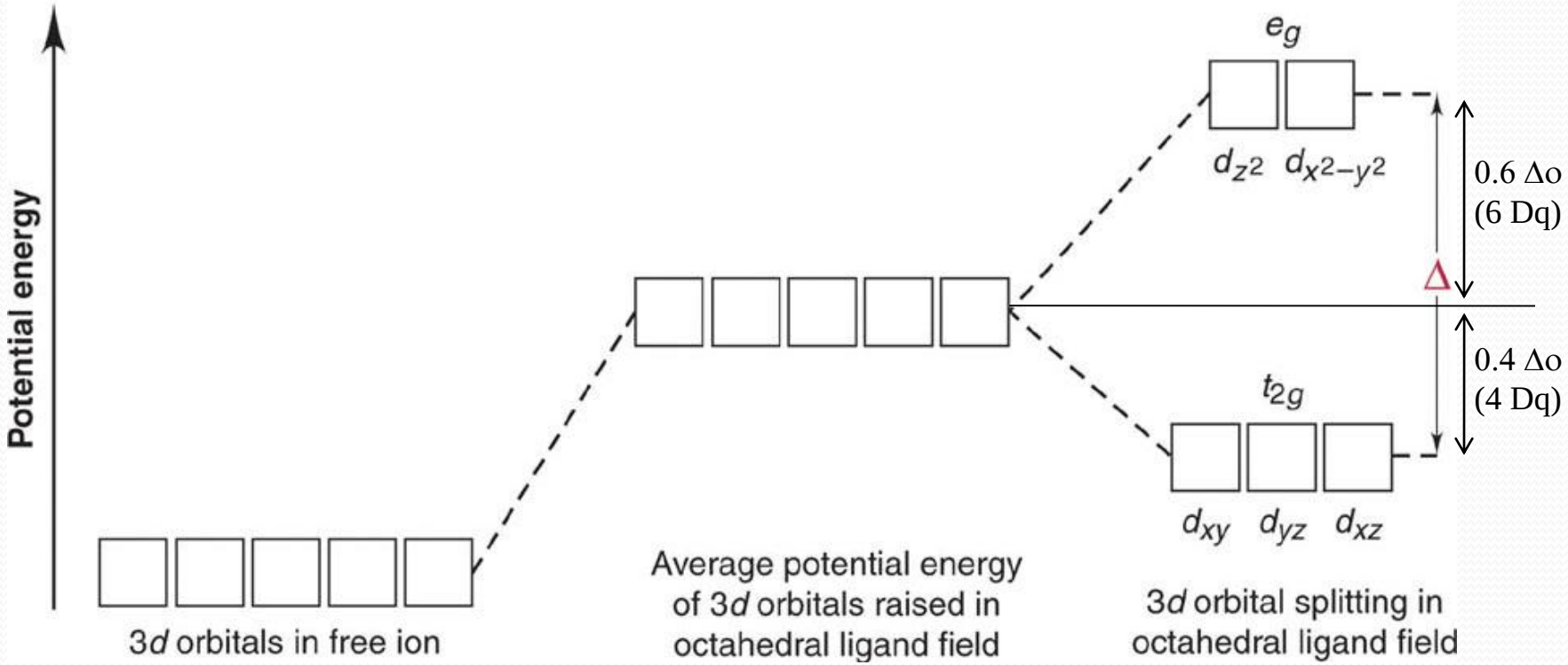




The five *d*-orbitals in an octahedral field of ligands.

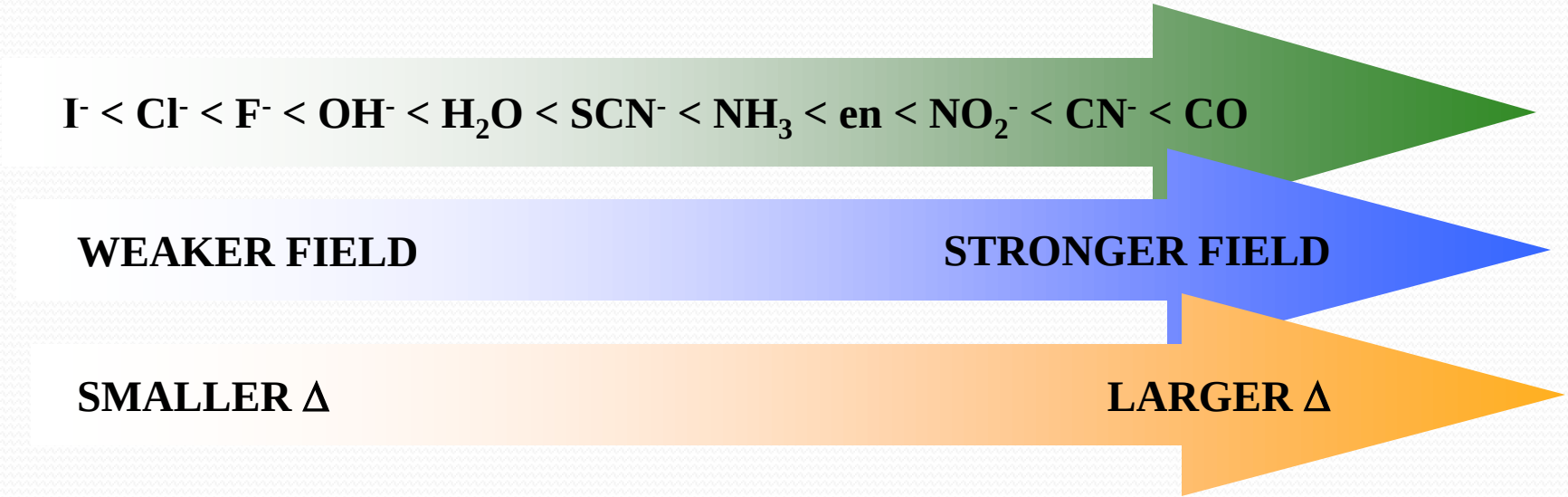


Crystal Field splitting of *d*-orbitals in octahedral complex



Δo = 10 Dq

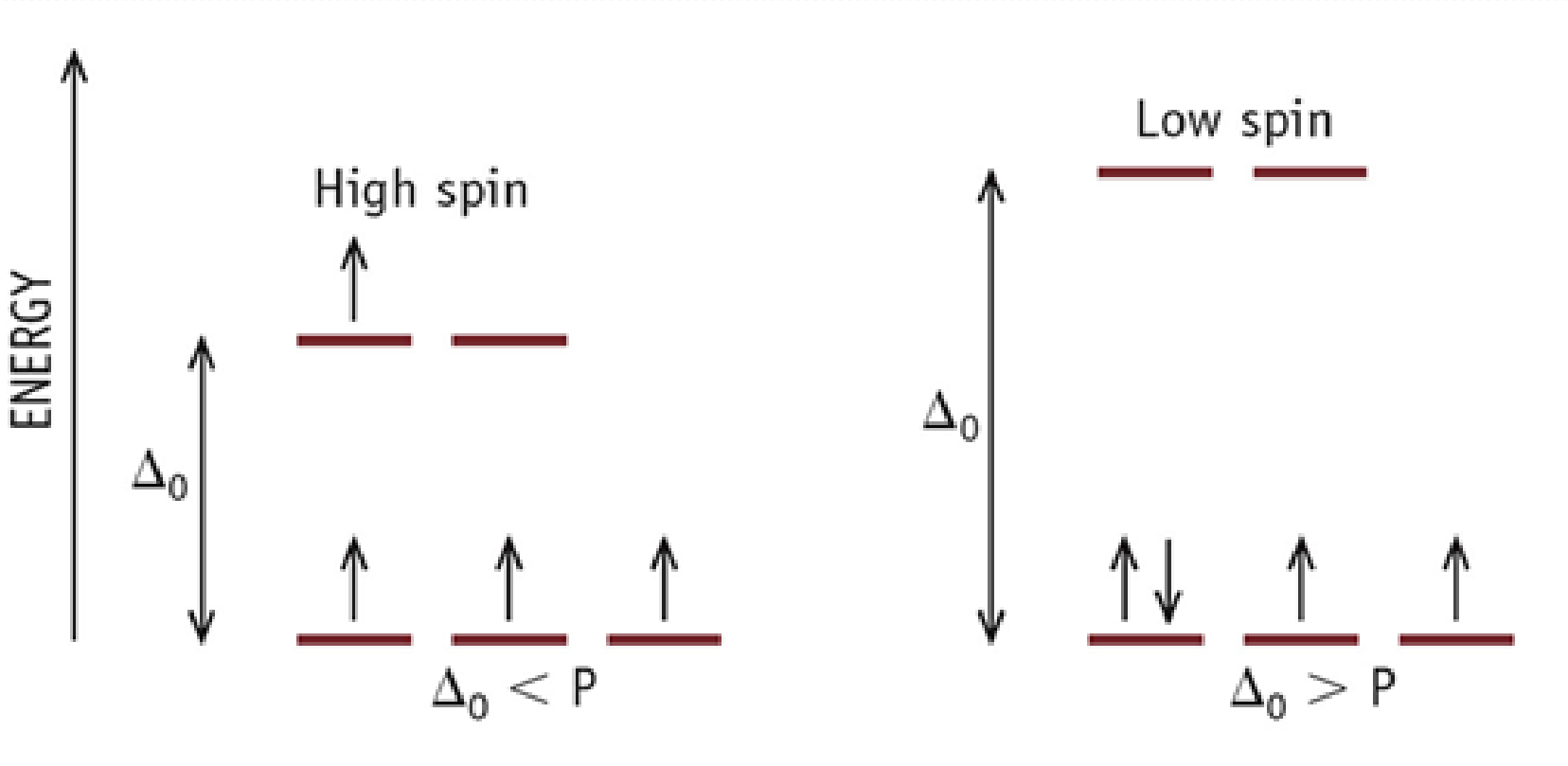
The spectrochemical series.



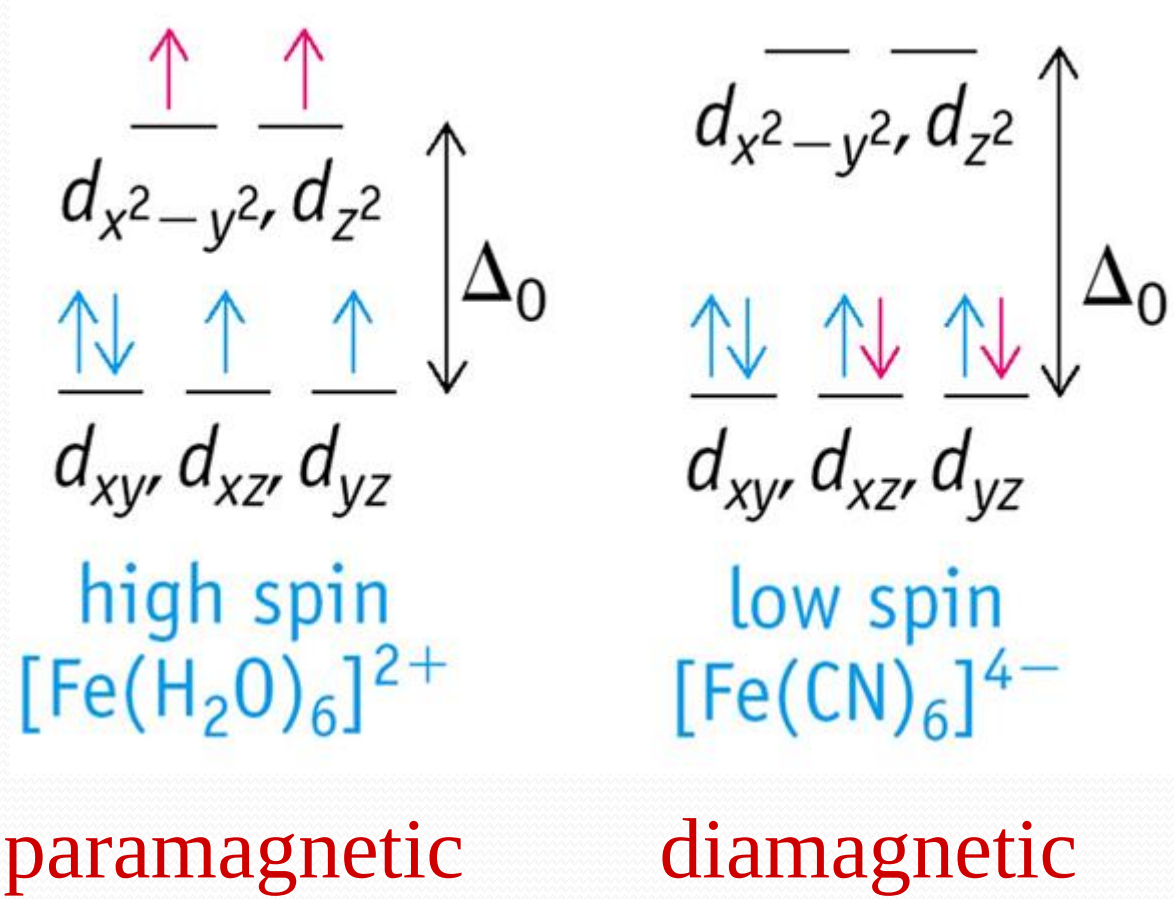
Filling of Electrons

- For 4 to 7 d electrons in octahedral complexes, there are two ways to distribute the electrons.
  - High spin — maximum number of unpaired e-
  - Low spin — minimum number of unpaired e-
- Depends on size of Δ_o and P, the pairing energy.
- P = energy required to create e- pair.

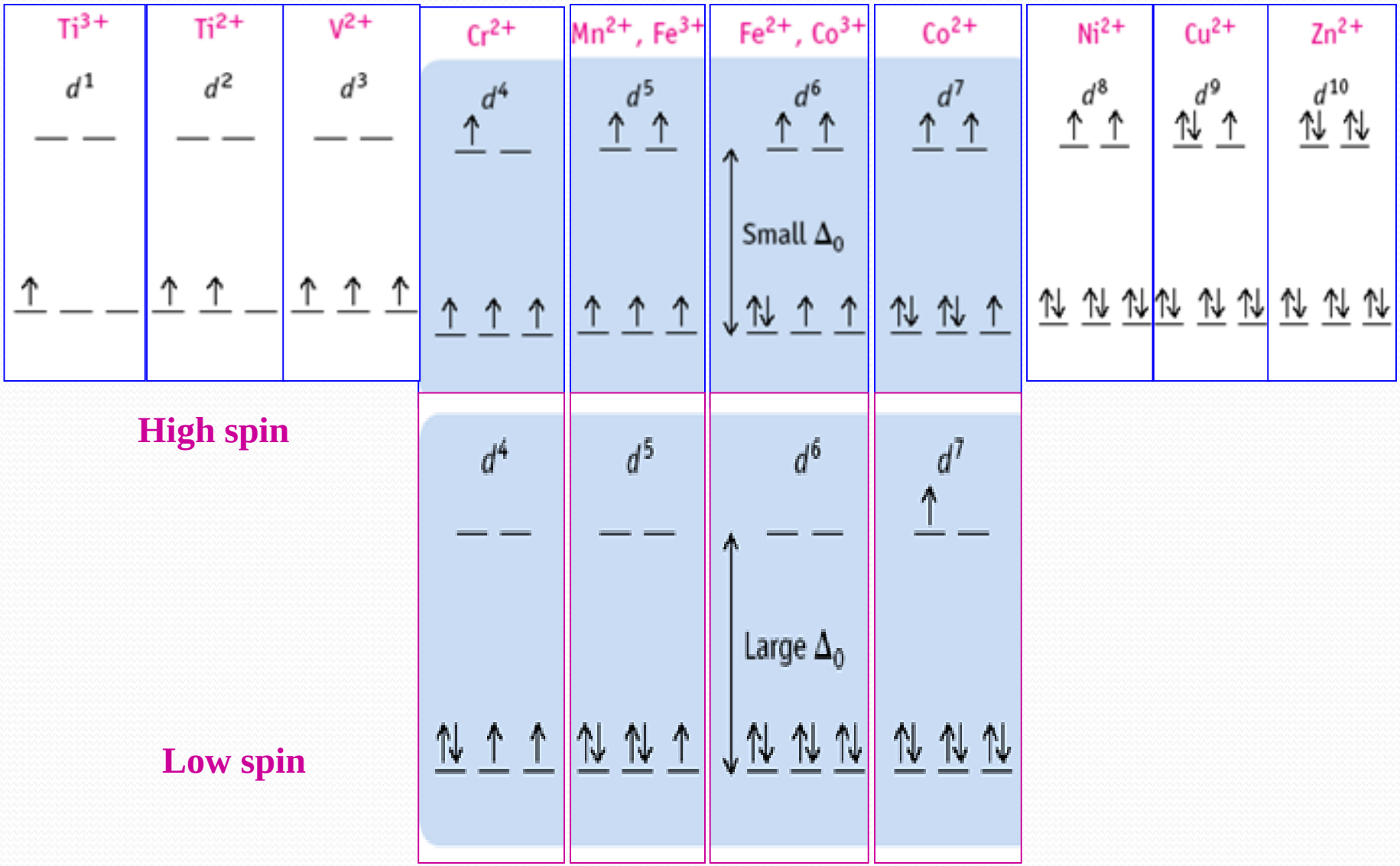
High and Low Spin Octahedral Complexes for Cr(II)



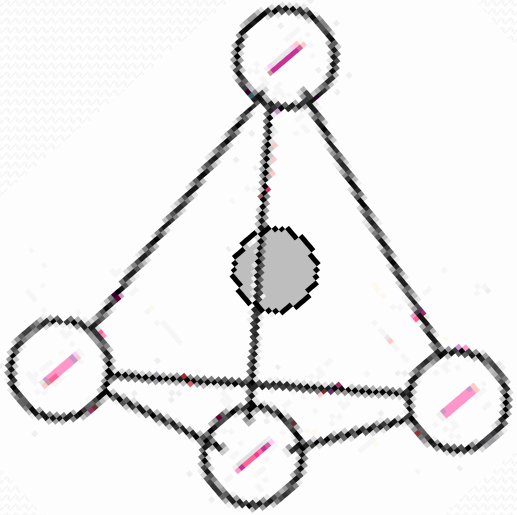
Magnetic Properties of Fe^{2+} complexes

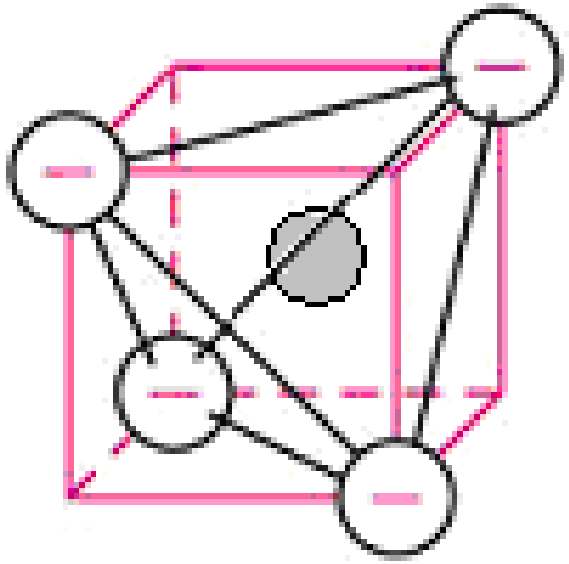


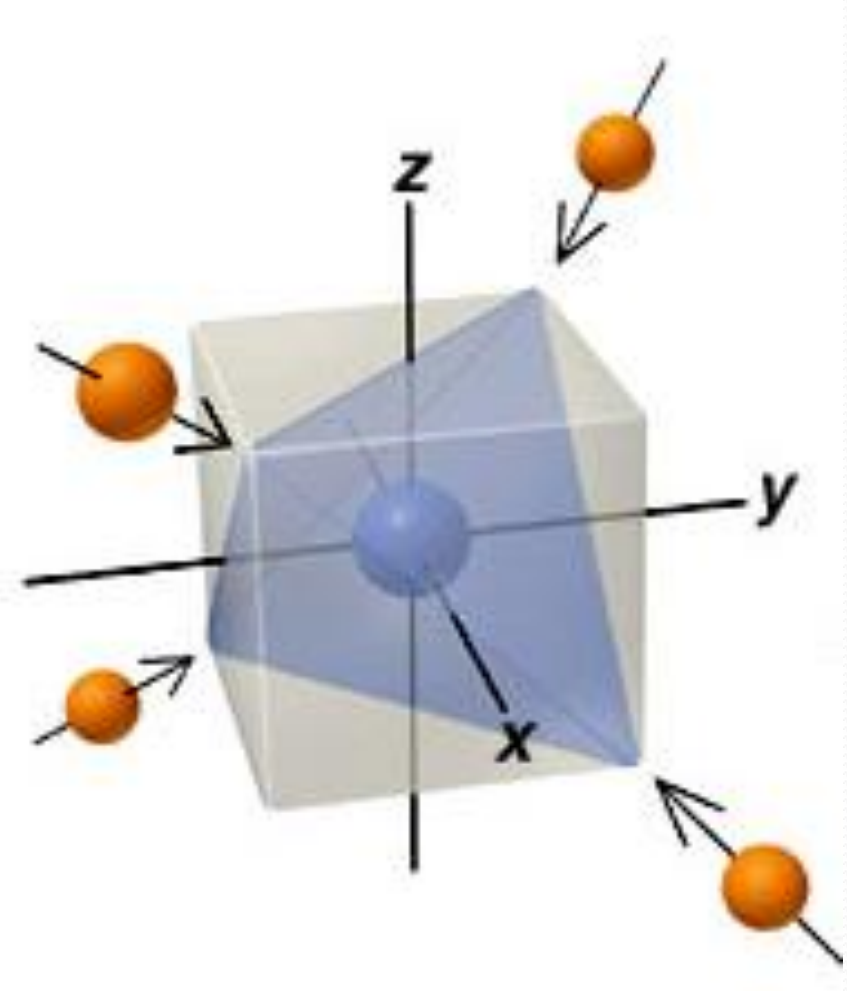
paramagnetic diamagnetic

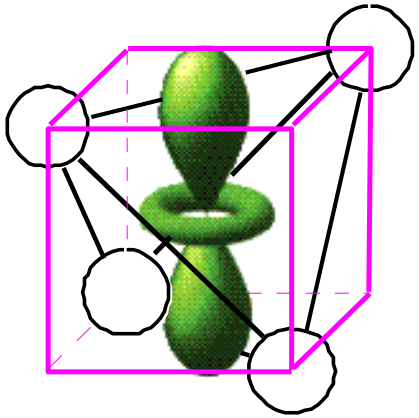

Ti3+
d1
Ti2+
d2
V2+
d3
Cr2+
d4
Mn2+, Fe3+
d5
Fe2+, Co3+
d6
Small Δ0
Co2+
d7
Ni2+
d8
Cu2+
d9
Zn2+
d10
High spin
d4
d5
d6
Large Δ0
d7
Low spin

Crystal Field splitting in Tetrahedral Complexes

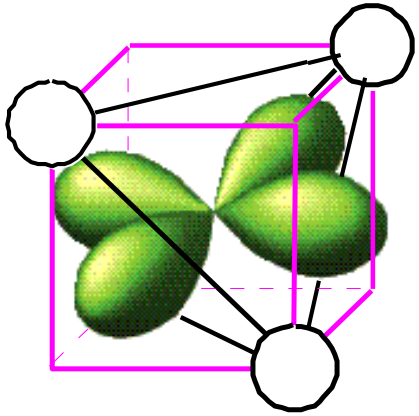




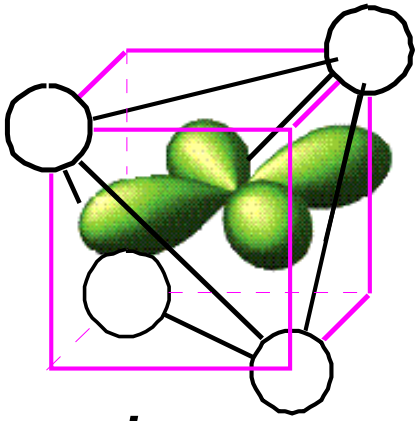

z
y
x



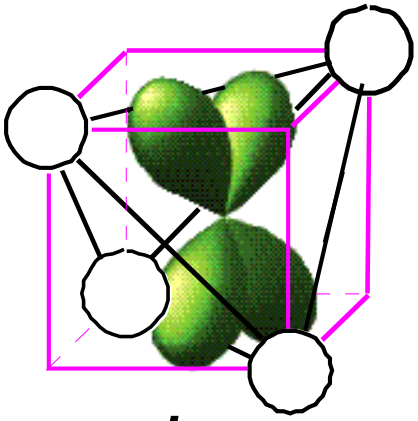
d_{z^2}



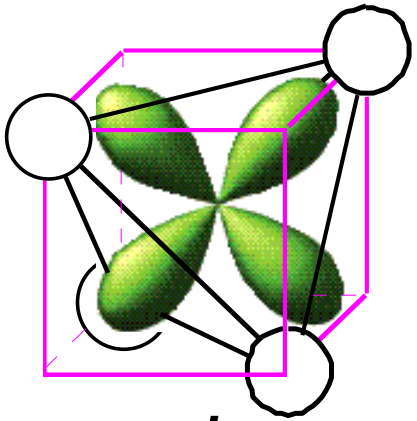
$d_{x^2-y^2}$



d_{xy}

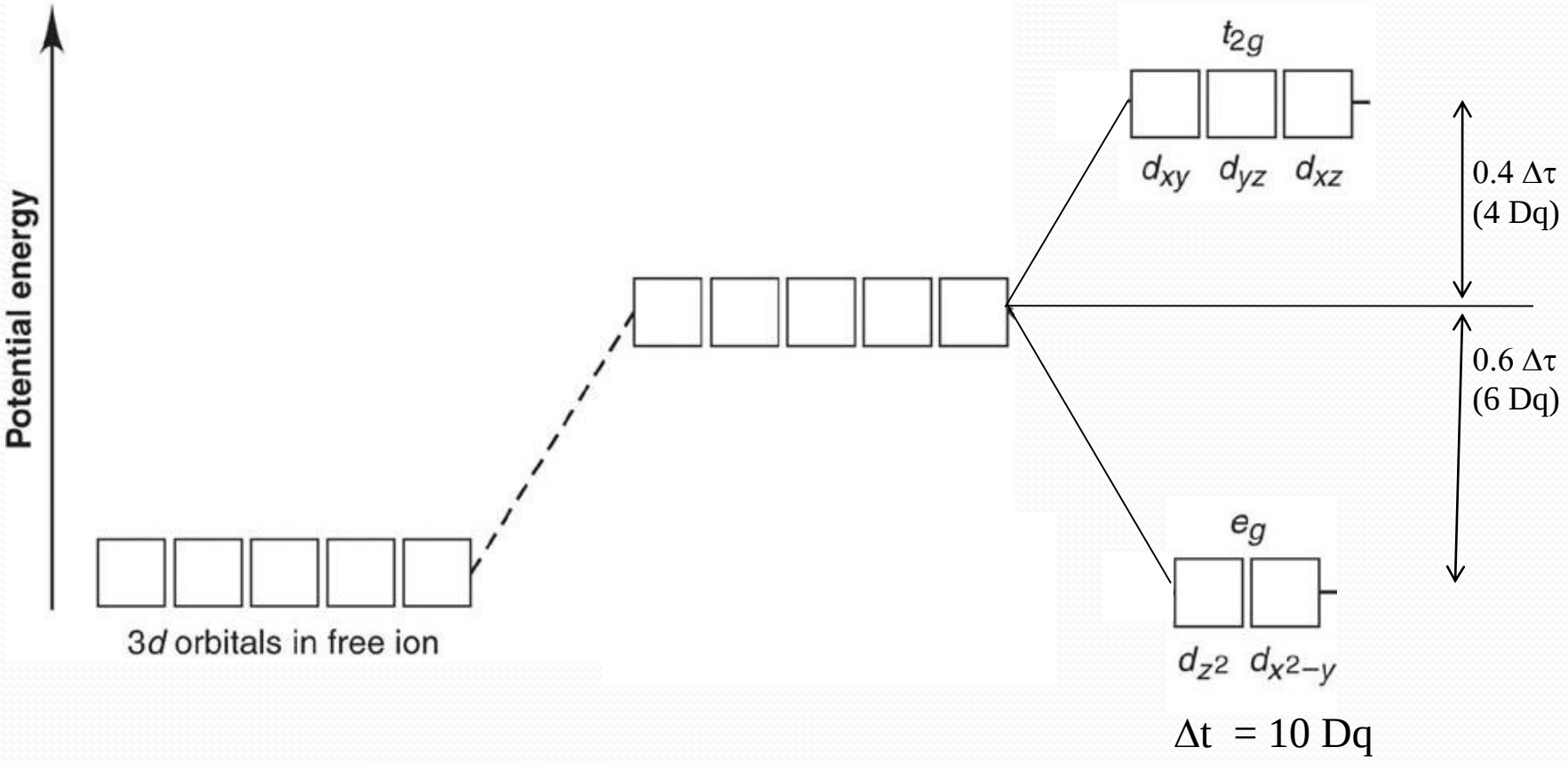


d_{xz}



d_{yz}

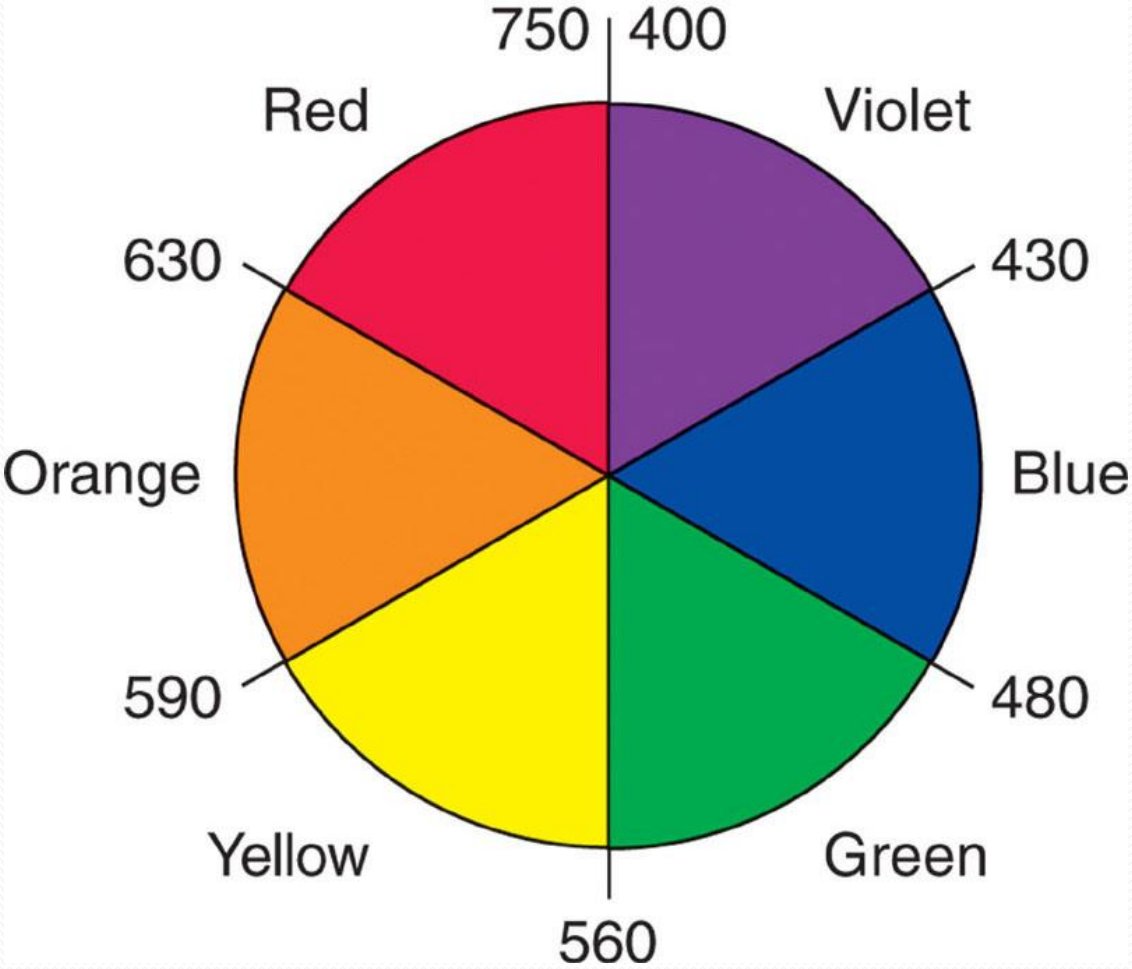
Crystal Field splitting of *d*-orbitals in tetrahedral complex



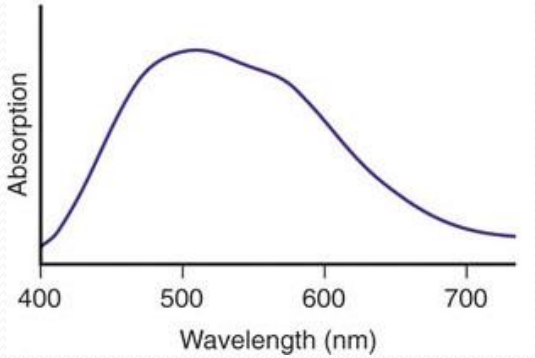
$\Delta t = 10\ Dq$

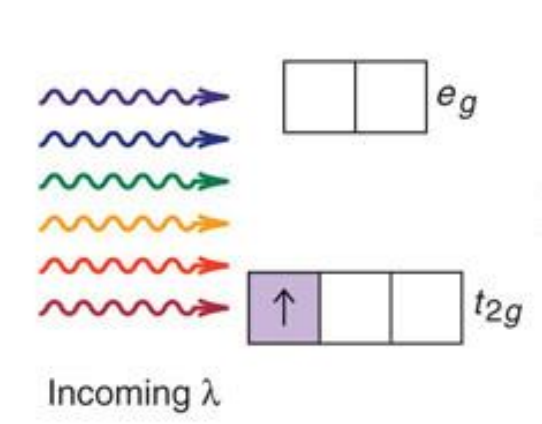
Colours in Coordination Compounds

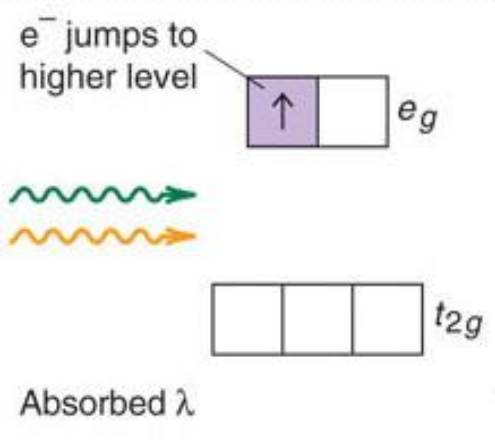

$[V(H_2O)_6]^{2+}$
$[V(H_2O)_6]^{3+}$
$[Cr(NH_3)_6]^{3+}$
$[Cr(NH_3)_5Cl]^{2+s}$

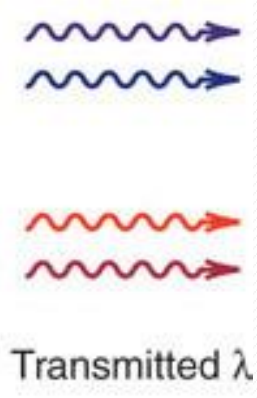

750
400
Red
Violet
630
430
Orange
Blue
590
480
Yellow
Green
560

The color of $[Ti(H_2O)_6]^{3+}$









Metal complexes and color

$[Cu(H_2O)_4]SO_4$ $[Cu(NH_3)_4]SO_4$

Addition of NH_3 ligand to $Cu(H_2O)_4$ changes its color

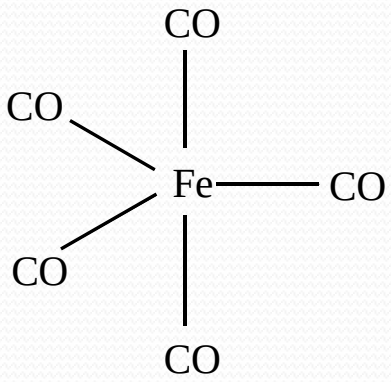
Limitations of CFT

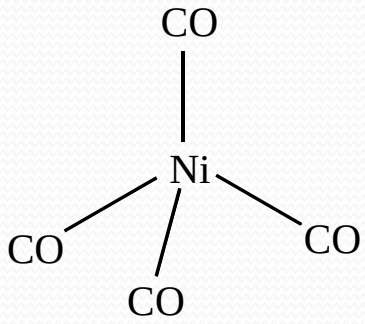
- CFT explains only metal d-orbitals and not s and p- orbitals.
- CFT does not explains pi-bonding in complexes.
- In spectrochemical series, water is stronger ligand than OH^-. CFT does not explains this.
- According to CFT, M-L bond is ionic. CFT could not explain covalent nature of M-L bond.

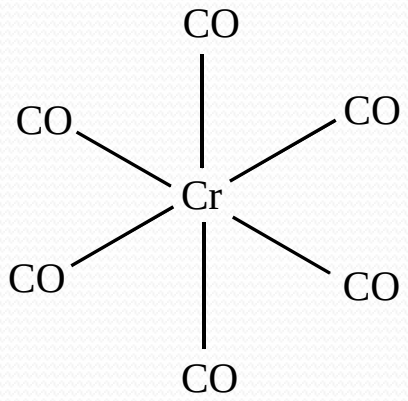
Superiorities of CFT

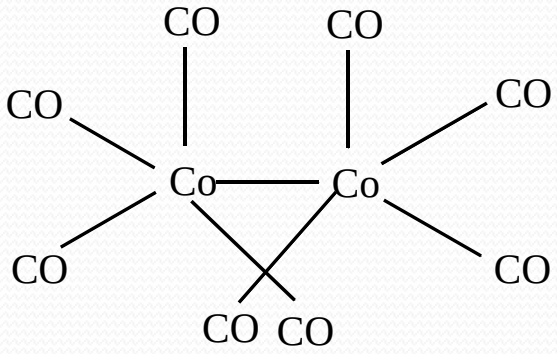
- CFT explains magnetic properties of the complexes.
- CFT can quantitatively measure the stability of the complex.
- CFT explains kinetic and thermodynamic properties of complexes.
- CFT can explain the colour of complexes.

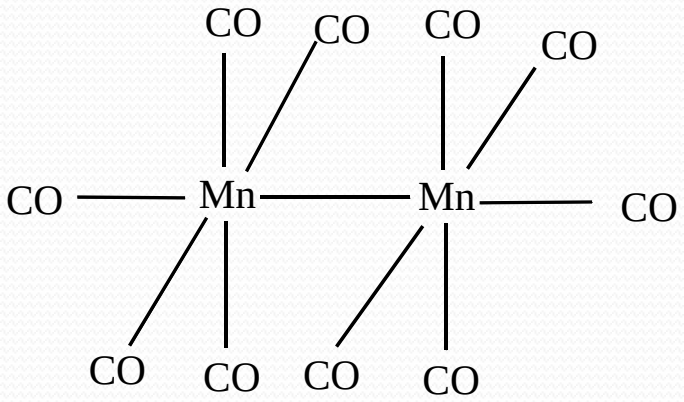
Metal Carbonyls



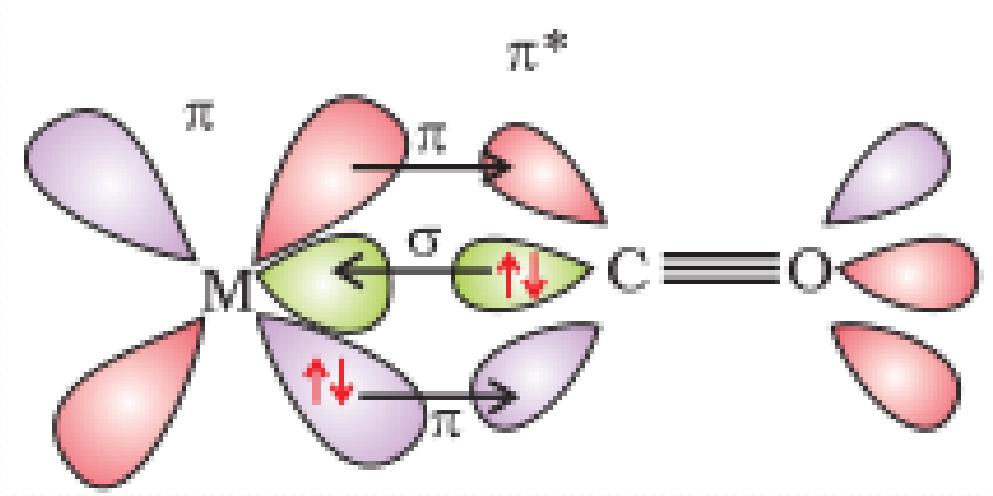




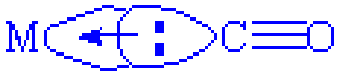




Metal Carbonyl



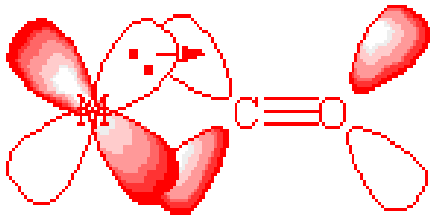
σ bond:



empty d-orbital

filled σ-orbital

π backbond:



filled d-orbital

empty π*-orbital

Stability of coordination compounds

- $M + 4L \longrightarrow ML_4$

  the larger the stability constant, the higher the proportion of ML_4 that exists in solution.

- We can write four stability constants as follows:

  $M + L \longrightarrow ML$ $\quad K_1 = [ML]/[M][L]$

  $ML + L \longrightarrow ML_2$ $\quad K_2 = [ML_2]/[ML][L]$

  $ML_2 + L \longrightarrow ML_3$ $\quad K_3 = [ML3]/[ML2][L]$

  $ML_3 + L \longrightarrow ML_4$ $\quad K_4 = [ML4]/[ML3][L]$

  where K_1, K_2, etc., are referred to as stepwise stability constants.

- Alternatively, we can write the overall stability constant thus:

  $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$

Stability & Factors affecting stability

- $M + nL \longrightarrow ML_n$
- overall stability constant
- $\beta n = K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots K_n$

- Factors affecting stability
- Charge density of complexes –

  Higner the magnitude of charge and smaller the size of the ion, more is the charge density on the metal ion and greater is the stability of the complex.

  $Cu^{+2} > Ni^{+2} > Co^{+2} > Fe^{+2} > Mn^{+2} > Cd^{+2}$

- Nature of Ligands –

  Greater the basic strength of ligand, greater is the stability of complex.

  K for $[Ag(CN)_2]^{-2} = 5.5 \times 10^{18}$

  K for $[Ag(NH_3)_2]^{+2} = 1.6 \times 10^{7}$

Applications

- Coordination compounds find use in many qualitative and quantitative chemical analysis.
- Hardness of water is estimated by simple titration with Na_2EDTA.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation.
- Purification of metals can be achieved through formation of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.
- Coordination compounds are of great importance in biological systems. Chlorophyll, is a coordination compound of magnesium.
  Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron.
- Coordination compounds are used as catalysts for many industrial processes.
- There is growing interest in the use of chelate therapy in medicinal chemistry. Excess of copper and iron are removed by the chelating ligands. EDTA is used in the treatment of lead poisoning.

- 2014

46. Which of the following complexes has lowest molar conductance ?

A) $CoCl_3 . 3NH_3$ B) $CoCl_3 . 4NH_3$

C) $CoCl_3 . 5NH_3$ D) $CoCl_3 . 6NH_3$

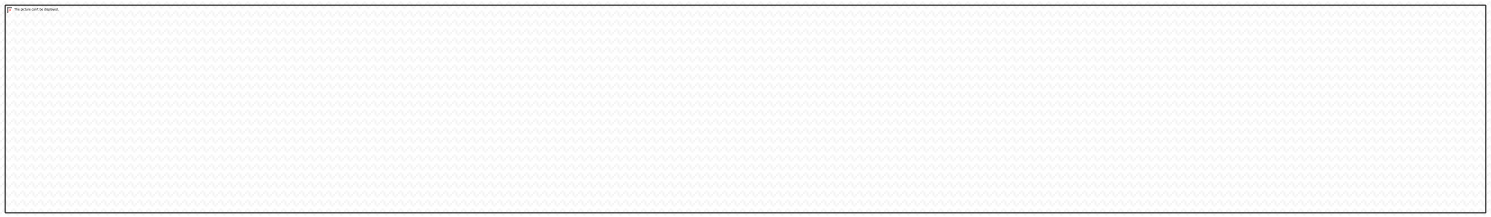
87. Select the diamagnetic complex ion amongst the following complexes

(Atomic No. Fe = 26, Co = 27)

A) $K_3[Fe(CN)_6]$ B) $[Co(NH_3)_6]Cl_3$

C) $K_3[FeF_6]$ D) $K_3[CoF_6]$

- 2015



57. $[Cr(NH_3)_6]$ $[Cr(SCN)_6]$ and $[Cr(NH_3)_2 (SCN)_4]$ $[Cr (NH_3)_4 (SCN)_2]$ are the examples of what type of isomerism ?

A) Ionisation isomerism B) Linkage isomerism

C) Coordination isomerism D) Solvate isomerism

THANK YOU