

TEACHER ORIENTED

UNIT IX COORDINATION COMPOUNDS

(3 : MARKS)

- 1) Coordination compounds - introduction,
- 2) Ligands,
- 3) Coordination number,
- 4) Colour,
- 5) Magnetic properties and shapes,
- 6) IUPAC nomenclature of mononuclear coordination compounds.
- 7) Bonding; Isomerism,
- 8) Importance of coordination compounds
(in qualitative analysis, extraction of metals and biological systems).

STUDENT ORIENTED

COORDINATION COMPOUNDS

CONCEPT DETAIL

UNIT IX COORDINATION COMPOUNDS

(3 : MARKS)

Coordination compounds – introduction :

The compounds which contain dative bonds between metal atom and surrounding species is called co-ordination compounds.

The branch of inorganic chemistry which deals with the study of preparation properties of coordination compound is called co-ordination chemistry.

Examples- $K_4[Fe(CN)_6]$; $[Cu(NH_3)_4]SO_4$; $Ni(CO)_4$; $K_4[Fe(CN)_6]$, $[CuNH_3)_4]SO_4$

Coordination complex: A structure containing a **metal** (usually a metal ion) bonded (coordinated) to a group of surrounding **molecules or ions**. They retain their identities even when dissolved in water.

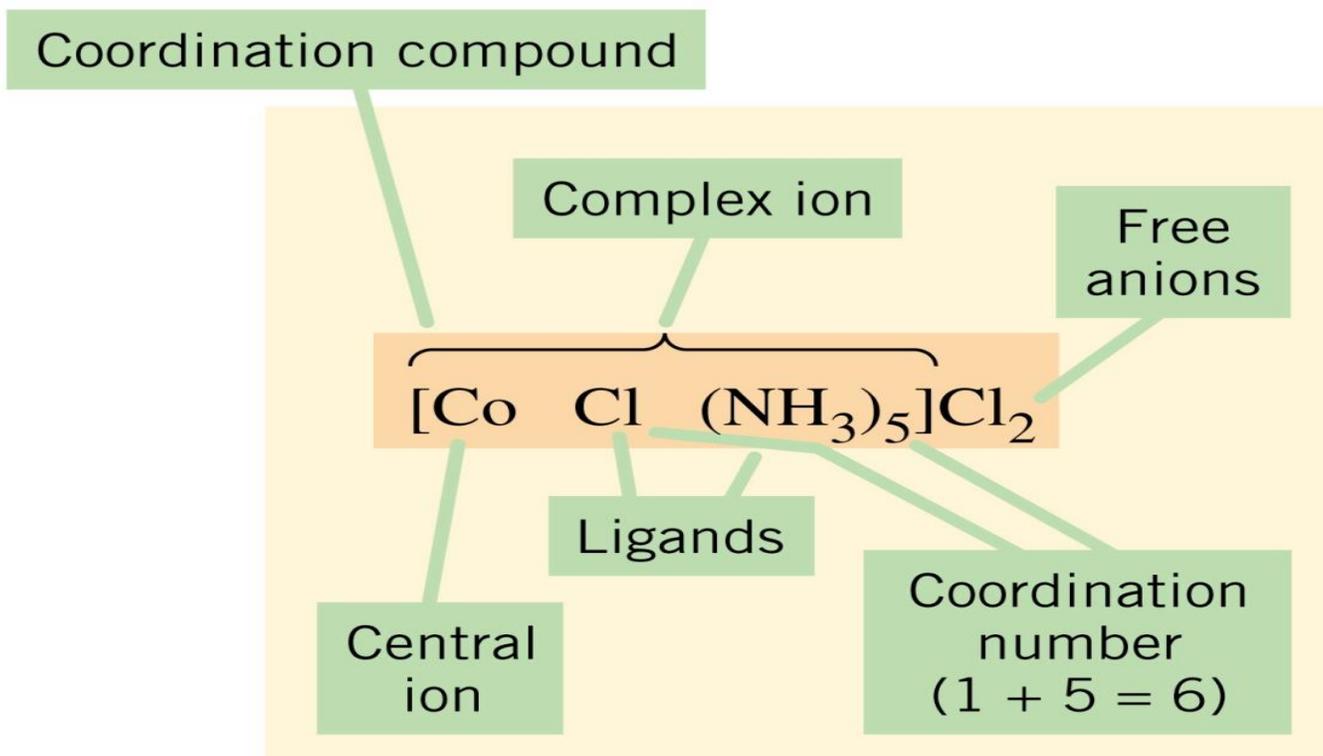
Double Salts-

The addition compounds which are stable in solid state but are broken down into individual constituents ions when dissolved in water eg: mohr's salt, potash alum etc.

Coordination or complex compounds –

The addition compounds which retain their identity in solid as well as solution state . Complex ions such as $[\text{Fe}(\text{CN})_6]^{4-}$ of $\text{K}_4[\text{Fe}(\text{CN})_6]$, do not dissociate into Fe^{2+} and CN^- ions. Some more eg: chlorophyll, hemoglobin etc.

A COMPLEX GENERALLY CONSISTS OF FOLLOWING UNITS:-



a) Central metal atom or ion –

the metal ion surrounded by number of ions or molecules.

eg:- $\text{K}_4[\text{Fe}(\text{CN})_6]$, Fe^{2+} is central metal ion.

b) Ligands –

a molecule, ion or group that coordinates to the central metal atom or ion bound in a definite geometrical arrangement in a complex . e.g.- H_2O , NH_3 , CO , CN^- etc.

Ligand (ligare is Latin, to bind): A ligand is a molecule or ion that is directly bonded to a metal ion in a coordination complex

Molecule or ion having a lone electron pair that can be used to form a bond to a metal ion

A ligand uses a **lone pair of electrons** (Lewis base) to bond to the metal ion (Lewis acid)

c) Coordination number-

The number of coordinating units/ligands around the metal ion.
The no. of ligand donor atoms to which the metal is directly bonded through sigma bonds only. It is commonly 4 or 6.

d) Coordination sphere or Coordination entity -

the square brackets enclosing the central metal ion and ligands

e) Counter ions-

the ions present outside the coordination sphere.

e.g.- K^+ in $K_4[Fe(CN)_6]$ OR $3Cl^-$ in $[Co(NH_3)_6]Cl_3$

Co-ordinate covalent bond: metal-ligand bond

Ligands may be classified as a.....

a) Monodentate/Unidentate: Ligands bound to the central metal atom/ion through a single donor atom. e.g.- Cl^- ; H_2O ; NH_3 ; NO_2^- .

b) Didentate: Ligates through two donor atoms.

e.g.- $C_2O_4^{2-}$ (ox); $H_2NCH_2CH_2NH_2$ (en)

c) Polydentate: which ligates through two or more donor atoms present in a single ligand.

e.g.- $(EDTA)^{4-}$

d) Chelating ligands: Di- or polydentate ligands that use two or more donor atoms to bind to a single metal ion to form ring- like complexes.

e.g.- (Ox); (edta)

e) Ambidentate ligand: A ligand that can ligate through two different atoms, one at a time.

e.g.- NO_2^- ; SCN^-

NAMES OF SOME COMMON LIGANDS

NEGATIVE LIGANDS	CHARGE	NEUTRAL LIGANDS	CHARGE
CN ⁻ Cyano	-1	NH ₃ Ammine	0
Cl ⁻ Chlorido	-1	H ₂ O Aqua/ aquo	0
Br ⁻ Bromido	-1	NO Nitrosyl	0
F ⁻ Fluoride	-1	CO Carbonyl	0
SO ₄ ²⁻ Sulphato	-2	PH ₃ Phosphine	0
C ₂ O ₄ ²⁻ Oxalato	-4	CH ₂ -NH ₂ CH ₂ NH ₂ (1,2-Ethane diamine)	0
NH ₂ ⁻ Amido	-1		
NH ₂ ⁻ Imido	-2		
ONO ⁻ Nitrito-O	-1		
NO ₂ ⁻ Nitro	-1		
NO ₃ ⁻ Nitrate	-1		
SCN ⁻ Thiocyanato	-1	POSITIVE LIGANDS:-	
NCS ⁻ Isothiocyanato	-1	NH ₂ -NH ₃ ⁺ Hydrazinium	+1
CH ₂ (NH ₂)COO ⁻ Glycinato	-1	NO ⁺ Nitrosonium	+1
-OH ⁻ Hydroxo	-1	NO ₂ ⁺ Nitronium	+1

COMPLEXES MAY BE CLASSIFIED AS A.....

HOMOLEPTIC COMPLEXES: Complexes in which a metal is bonded to only one kind of donor groups. e.g.- $[\text{Co}(\text{NH}_3)_6]^{3+}$

HETEROLEPTIC COMPLEXES: Complexes in which a metal is bonded to more than one kind of donor groups. e.g.- $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2]^+$

MAIN POSTULATES WERNER'S THEORY OF COORDINATION COMPOUNDS

- i) In coordination compounds metals show two types of linkages or valencies- Primary and Secondary.
- ii) The primary valencies are ionisable and are satisfied by negative ions.
- iii) The secondary valencies are non- ionisable and are satisfied by neutral molecules or negative ions. The secondary valence is equal to the C.N and is fixed for a metal.
- iv) The ions or groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination nos.

NAMING OF MONONUCLEAR CO-ORDINATION COMPOUNDS

The principle of additive nomenclature is followed while naming the coordination compounds. The following rules are used

- i. The cation is named first in both positively and negatively charged coordination entities.
- ii. The ligands are named in an alphabetical order before the name of the central atom/ion
- iii. The name of the anionic ligands end in -o, those of neutral and cationic ligands are the same except aqua for H_2O , ammine for NH_3 , carbonyl for CO and nitrosyl for NO . these are placed within enclosing marks .
- iv. When the prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parenthesis.

- v. Oxidation state of the metal in cation, anion, or neutral coordination entity is indicated by roman numeral in parenthesis.
- vi. If the complex ion is a cation, the metal is same as the element.
- vii. The neutral complex molecule is named similar to that of the complex cation.

SOME COMMON EXAMPLES :-

$[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ is named as: triamminetriaquachromium(III) chloride

$[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{SO}_4)_3]$: tris(ethane-1,2-diammine)cobalt(III) sulphate

ISOMERISM :- Isomers have the same molecular formula, but their atoms are arranged either in a different order (structural isomers) or spatial arrangement (stereoisomers).

(a) Stereoisomerism

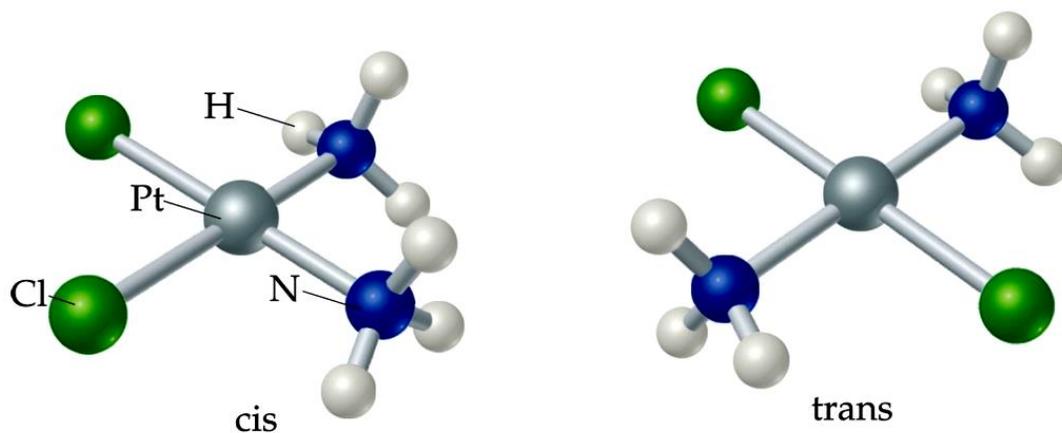
- (i) Geometrical isomerism (ii) Optical isomerism

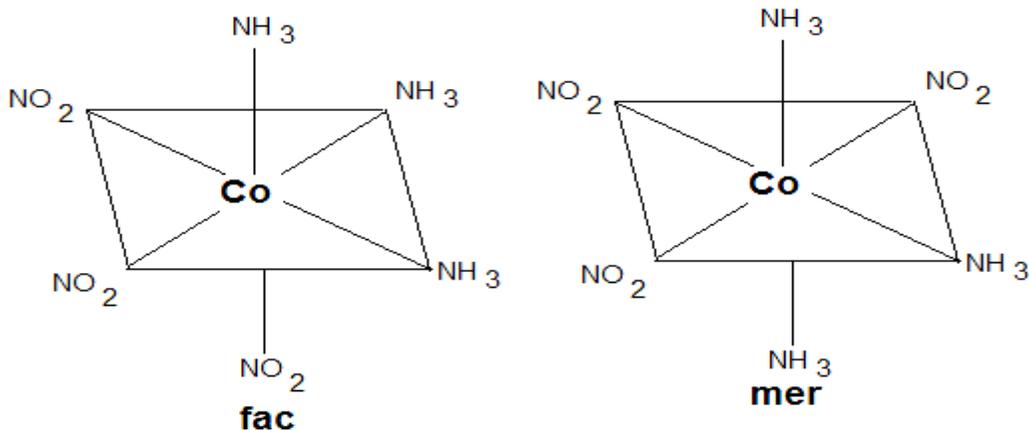
(b) Structural isomerism

- (i) Linkage isomerism (ii) Coordination isomerism
- (iii) Ionisation isomerism (iv) Solvate isomerism

(i) Geometrical isomerism:-

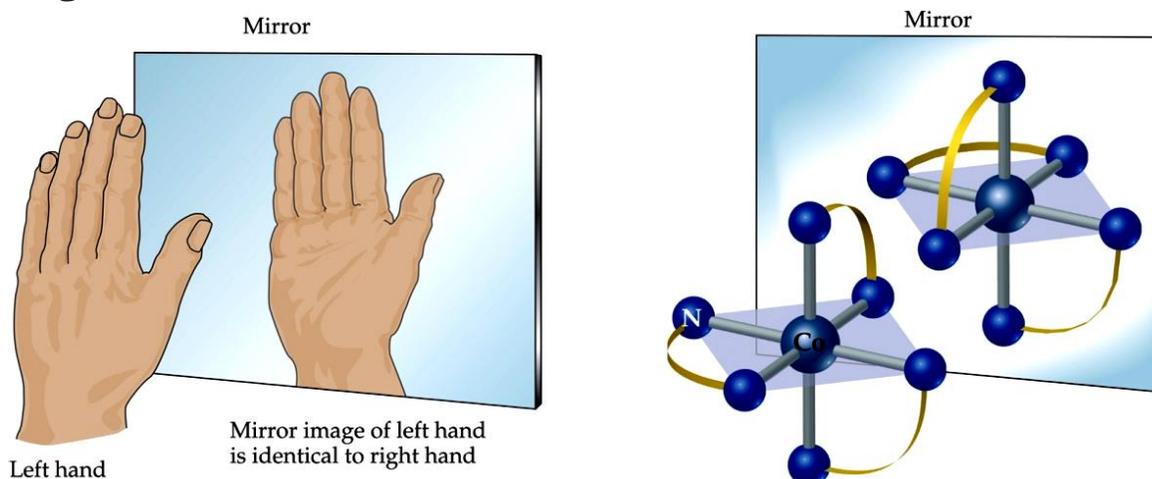
It arises in heteroleptic complexes due to different possible geometrical arrangements of ligands.





(ii) Optical isomerism :

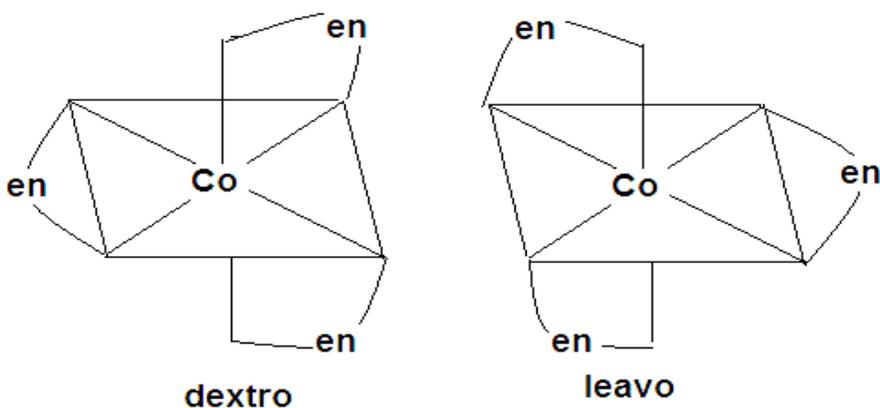
Optical isomers are those isomers which are non superimposable mirror images.



OPTICAL ISOMERISM:

Optical isomers (**enantiomers**) are mirror images which cannot be superimposed on one another.

The molecules or ions which cannot be superimposed are called **chiral**.



STRUCTURAL ISOMERISM –

This type of isomerism arises due to the difference in structures of coordination compounds. Structural isomerism, or constitutional isomerism, is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

A. IONISATION ISOMERISM: This form of 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: $[\text{Co}(\text{NH}_3)_5\text{Br}] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5 \text{SO}_4] \text{Br}$

B. LINKAGE ISOMERISM:

Arises due to the presence of ambidentate ligand

In the isomerism, a ligand can form linkage with metal through different atoms.

Example: $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$

C. COORDINATION ISOMERISM:

Arises due to the interchange of ligands between cationic and anionic entities of different metal ions

Example: $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$

D. SOLVATE ISOMERISM (Hydrate isomerism when solvent is water):

Arises depending upon whether a solvent molecule is directly bonded to the metal ion or is present as a free solvent molecule.

Example: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{CrCl}_2(\text{H}_2\text{O})_4] \text{Cl}_2 \cdot 2\text{H}_2\text{O}$

VALENCE BOND THEORY:

1. Central metal uses, p, d orbitals for hybridization depending upon the total no of ligands.
2. The hybridized orbitals are allowed to overlap with ligands orbitals
3. High spin or low spin complexes are formed depending upon whether inner or outer orbitals are used .

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

Inner-orbital or low spin or spin-paired complexes: Complexes that use inner d - orbitals in hybridisation, e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$

Outer-orbital or high spin or spin-free complexes: Complexes that use outer d - orbitals in hybridisation, e.g., $[\text{CoF}_6]^{3-}$

LIMITATIONS OF VALENCE BOND THEORY:

1. A number of assumptions are involved.
2. Quantitative interpretation of magnetic data is not given.
3. The exhibition of colour by coordination compounds is not explained.
4. The thermodynamic or kinetic stabilities of coordination compounds are not quantitatively interpreted.
5. Whether a complex of coordination number 4 is tetrahedral or square planar cannot be exactly predicted.
6. Weak and strong ligands cannot be distinguished.

MAGNETIC PROPERTIES OF COORDINATION COMPOUNDS:

A coordination compound is paramagnetic in nature if it has unpaired electrons and diamagnetic if all the electrons in the coordination compound are paired.

$$\mu = \sqrt{n(n+2)}$$

where

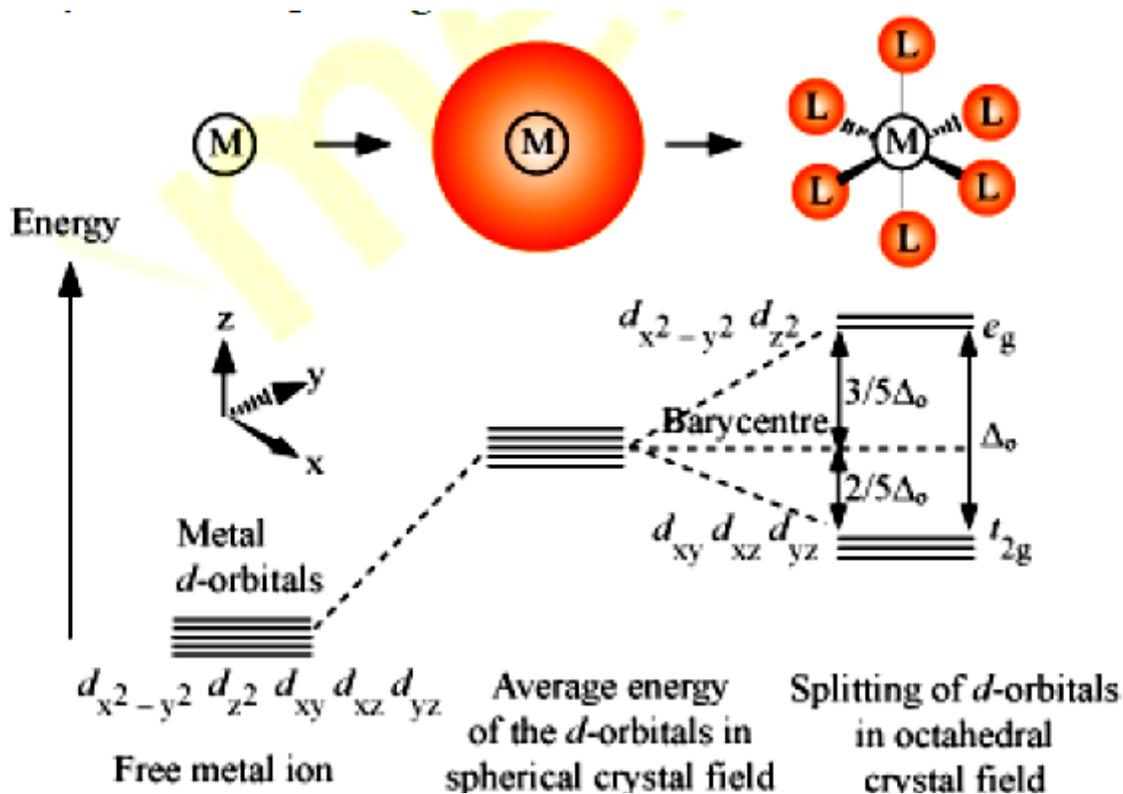
μ is Magnetic moment

n is number of unpaired electrons.

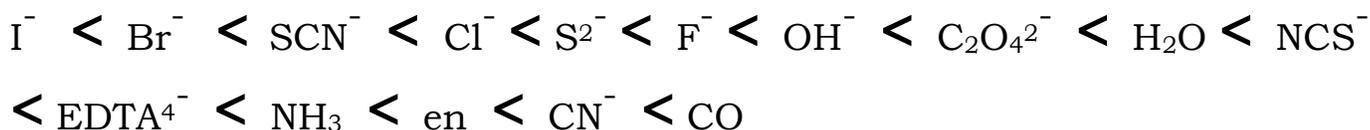
CRYSTAL-FIELD THEORY:

[Crystal-field splitting is the splitting of the degenerate energy levels due to the presence of ligands.]

Crystal-field splitting in octahedral coordination entities:



SPECTROCHEMICAL SERIES:

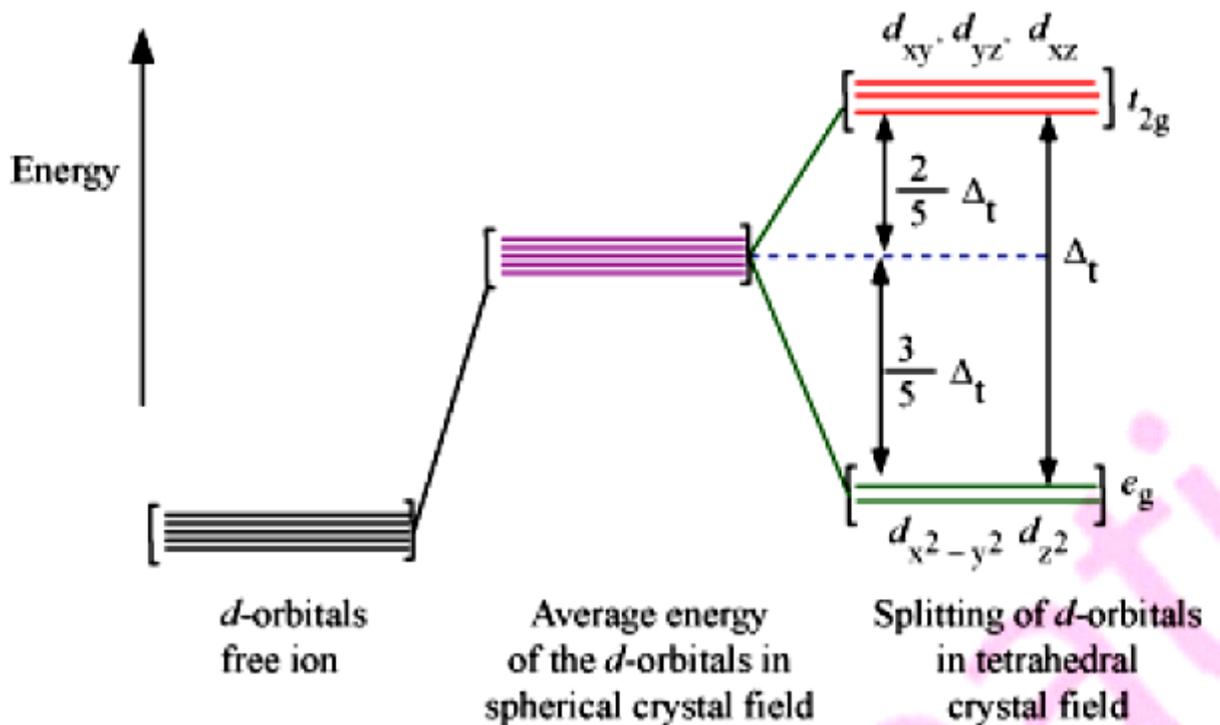


WEAK-FIELD LIGANDS:- Ligands for which Δ_o (crystal-field splitting) $< P$ (pairing energy) are called weak-field ligands, and form high-spin complexes.

STRONG-FIELD LIGANDS:- Ligands for which Δ_o (crystal-field splitting) $> P$ (pairing energy), are called strong-field ligands, and form low-spin complexes.

Crystal-field splitting in tetrahedral coordination entities:

$$\Delta_t = (4/9) \Delta_o$$



COLOUR IN COORDINATION COMPOUNDS:

The colour of the coordination compounds is attributed to $d-d$ transition of electrons.

LIMITATIONS OF THE CRYSTAL-FIELD THEORY:

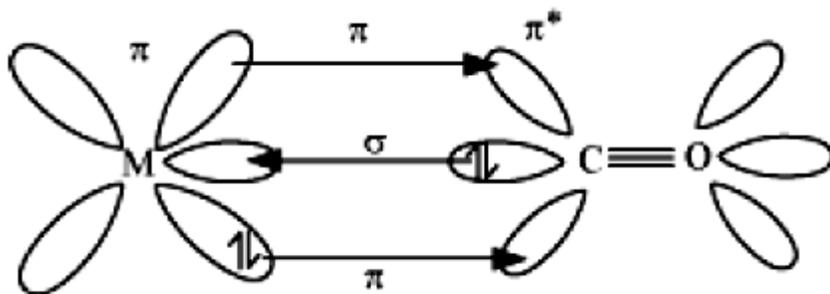
Anionic ligands are assumed to exert the greatest splitting effect. But the anionic ligands are found at the lower end of the spectrochemical series. Crystal-field theory does not take into account the covalent character of bonding between ligand and the central metal atom.

BONDING IN METAL CARBONYLS:

Metal carbonyls are homoleptic complexes in which carbon monoxide (CO) acts as the ligand. For example: $\text{Ni}(\text{CO})_4$

The metal – carbon bond in metal carbonyls possesses both σ and π characters. The metal-carbon bond in metal carbonyls possess both s and p character. The M–C σ bond is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

SYNERGIC BONDING –



STABILITY OF COORDINATION COMPOUNDS:

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \dots K_n$$

Where,

β → Overall stability constant

K → Stepwise stability constant

APPLICATIONS OF COORDINATION COMPOUNDS:

- A) Analytical chemistry – Transition metal ions may be estimated by adding reagents to a metal ion solution to form insoluble precipitate of metal- ligand complex. E.g- Ni^{2+} is estimated using dimethylglyoxime.
- B) Metallurgy – Au and Ag are extracted by forming cyanide complex and then adding Zn as reducing agent.
- C) Biological processes—chlorophyll contains Mg used in photosynthesis ,vitamin= contains cobalt is used to prevent anaemia.
- D) EDTA is used in the treatment of lead poisoning
- E) EDTA is used in softening of hard water
- F) Cis-platin is used in the treatment of cancer.

INSTANT DIAGNOSTIC QUESTIONS

Name one complex which is used in medicine.

What is the solution in which photographic film is washed?

LEVELWISE ASSIGNMENTS

LEVEL I : SLOW BLOOMERS

- 1)write the IUPAC name of $[\text{Co}(\text{en})_2(\text{ONO})\text{Cl}]\text{Cl}$
- 2) which of two is more stable $\text{K}_4[\text{Fe}(\text{CN})_6]$ or $\text{K}_3[\text{Fe}(\text{CN})_6]$ and why?
- 3) NH_3 has strong ligand but NH_4^+ is not why?

LEVEL II : AVERAGE

- 1)Give one example of hexadentate ligand. Give its use.
- 2). $[\text{Ti}(\text{H}_2\text{O})]^{3+}$ is colored but $[\text{Sc}(\text{H}_2\text{O})]^{3+}$ is colorless why?
5. Write the formula of following:
 - a) Ferric hexacyanoferrate(II)
 - b) Sodium tetrafluorido oxochromate(IV)

LEVEL III : BRIGHT LEARNERS

1. Using valence bond approach predict the shape and magnetic character of $[\text{Ni}(\text{CN})_4]^{2-}$.
- 2.(a) Name one complex which is used in medicine.
3. $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why?
4. Square planar complexes with coordination number 4. Show geometrical isomerism whereas tetrahedral complexes do not. Why?

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