Unit – 5 Coordination compounds

+2 CHEMISTRY STUDY MATERIAL

It includes

- **Book back answers**
- **Knowledge based questions**
- **Book inside question**

Unit – 5 Coordination compounds

Book back

Answer the following questions:

1. Write the IUPAC names for the following complex

i)Na^2[Ni(EDTA)] – **Sodium 2 , 2' , 2'' , 2''' – (ethane diyldinitrilo)tetraacetatonickelate(II)**

ii)$[Ag(CN)_2]^-$ - **Dicyanidoargentate(I)ion**

iii)$[Co(en)_3]_2(SO_4)_3$ - **Tris(ethane 1, 2 – diamine)cobalt(III)sulphate**

iv)$[Co(ONO)(NH_3)_5]^{2+}$ - **Pentaamminenitrito-κOcobalt(III)ion**

v)$[Pt(NH_3)_2Cl(NO)_2]$ – **Diamminechloridonitro-κN platinum(II)**

2. Write the formula for the following coordination compounds.

a) potassiumhexacyanidoferrate(II) - **$K_4[Fe(CN)_6]$**

b) pentacarbonyliron(0) - **$[Fe(CO)_5]$**

c) pentaamminenitrito –_ –N-cobalt(III)ion - **$[CO(NH_3)_5(ONO)]^{2+}$**

d) hexaamminecobalt(III)sulphate – **$[CO(NH_3)_6](SO_4)_3$**

e) sodiumtetrafluoridodihydroxidochromate(III) - **$Na_3[CrF_4(OH)_2]$**

3. Arrange the following in order of increasing molar conductivity

$[Cr(NH_3)_5Cl][CoF_6]_2 < [Cr(NH_3)_3Cl_3] < Mg\,[Cr(NH_3)(Cl)_5]$

4. Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction.

$Ni[ONC(CH_3)C(CH_3)NOH]_2$ – Nickel Cis (dimethyglyoximate)$_2$

5.$[CuCl_4]^{2-}$ exists while $[CuI_4]^{2-}$ does not exist why?

In $[CuI_4]^{2-}$ Cu^{2+} is reduced to Cu^+ by I^- . So cupric iodide is converted to cuprous iodide .Therefore **$[CuI_4]^{2-}$ does not exist.**

In $[CuCl_4]^{2-}$ Cl^- cannot undergoes the above change , so it exists .

6. Calculate the ratio of $\frac{[Ag]^+}{[Ag(NH_3)_2]^+}$ in 0.2 M solution of NH_3. If the stability constant for the complex $[Ag(NH_3)_2]^+$ is 1.7×10^7

$\beta = 1.7 \times 10^7$ $[NH_3] = 0.2$ M

$Ag^+ + 2NH_3 \leftrightarrow [Ag(NH_3)_2]^+$

$$\beta = \frac{[Ag(NH_3)_2]^+]}{[Ag+][NH_3]^2}$$

$$\frac{[Ag]^+}{[Ag(NH_3)_2]^+} = \frac{1}{\beta([NH_3]^2)}$$

$$= \frac{1}{1.7\times10^7\times(0.2)^2} = 1.47 \times 10^{-5}$$

7. Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.

Biologically important coordination compounds.

- A red blood corpuscles (RBC) is composed of heme group, which is Fe^{2+} - Porphyrin complex.it plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.
- Chlorophyll, a green pigment present in green plants and algae, is a coordination complex containing Mg^{2+} as central metal ion surrounded by a modified Porphyrin ligand called corrin ring. It plays an important role in photosynthesis, by which plants converts CO_2 and water into carbohydrates and oxygen.

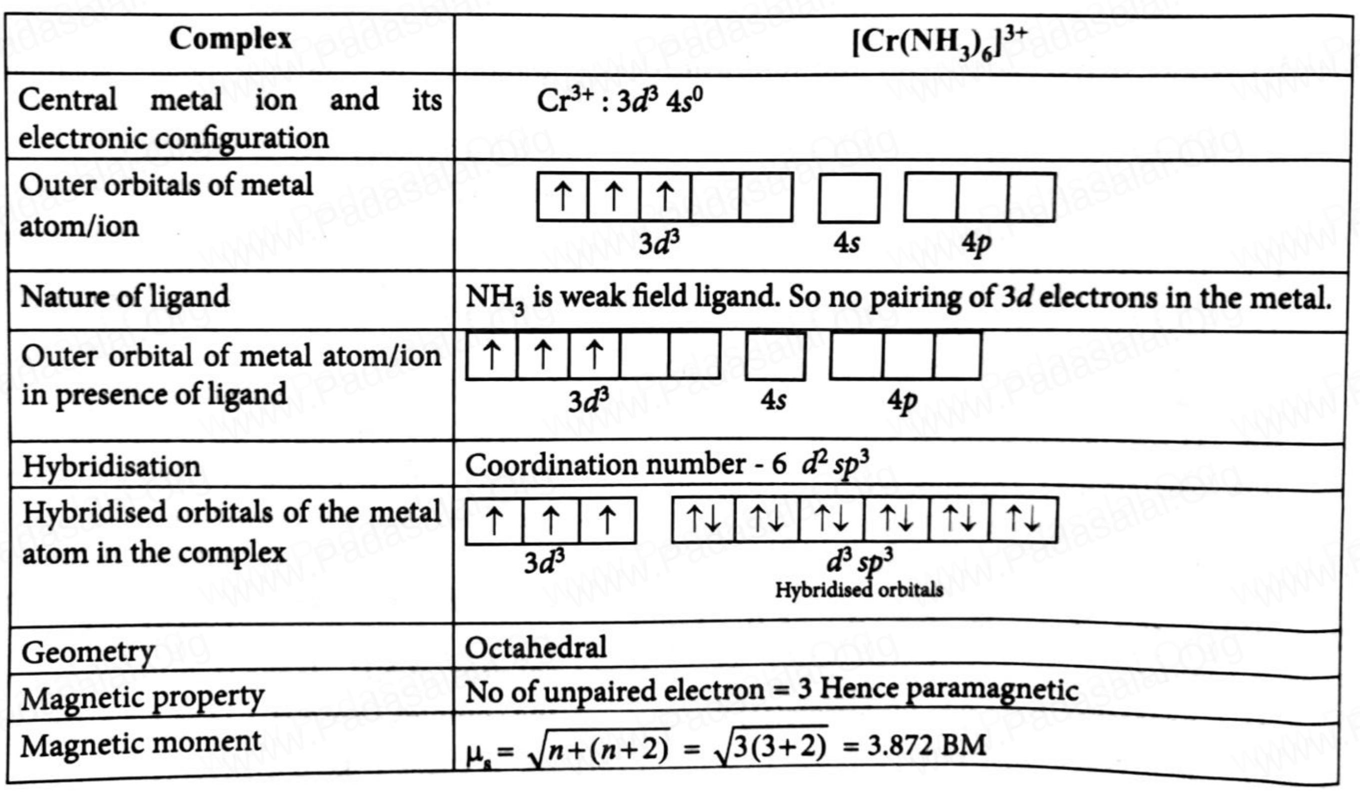
- (Vitamin B12(cyanocobalamine) is the only vitamin consist of metal ion. it is a coordination complex in which the central metal ion is Co^+ surrounded by Porphyrin like ligand.
- Many enzymes are known to be metal complexes, they regulate biological processes. For example, Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein.

Coordination compound used in medicine

(1)Ca-EDTA chelate, is used in the **treatment of lead and radioactive poisoning.** That is for removing lead and radioactive metal ions from the body.

(2) Cis-platin is used as **an antitumor drug in cancer treatment.**

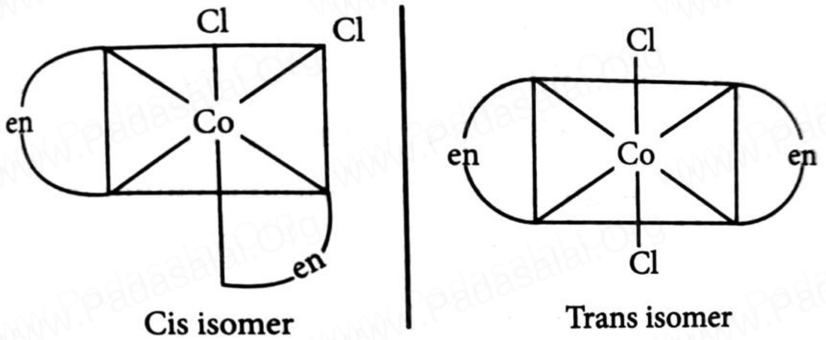
8. Based on VB theory explain why $[Cr(NH_3)_6]$ is paramagnetic, while $[Ni(CN)_4]$ is diamagnetic.



Complex	$[Cr(NH_3)_6]^{3+}$
Central metal ion and its electronic configuration	Cr^{3+} : $3d^3\ 4s^0$
Outer orbitals of metal atom/ion	↑ ↑ ↑ $3d^3$ 4s 4p
Nature of ligand	NH_3 is weak field ligand. So no pairing of 3d electrons in the metal.
Outer orbital of metal atom/ion in presence of ligand	↑ ↑ ↑ $3d^3$ 4s 4p
Hybridisation	Coordination number - 6 d^2sp^3
Hybridised orbitals of the metal atom in the complex	↑ ↑ ↑ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ $3d^3$ d^3sp^3 Hybridised orbitals
Geometry	Octahedral
Magnetic property	No of unpaired electron = 3 Hence paramagnetic
Magnetic moment	$\mu_s = \sqrt{n+(n+2)} = \sqrt{3(3+2)} = 3.872$ BM

Complex	$[Ni(CN_4)]^{4-}$
Central metal atom/ion and its outer electronic configuration	Ni^{2+} : $3d^8\ 4s^0$
Outer orbitals of metal atom/ion	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ⇅ ☐ ☐ ☐ $3d^8$ $4s^2$ $4p$
Nature of ligand	CN^- Strong field ligand causes the pairing of 3d electrons in the metal
Outer orbital of metal atom/ion in presence of ligand	↑↓ ↑↓ ↑↓ ↑↓ ☐ ☐ ☐ ☐ ☐ $3d^8$ $4s^0$ $4p^0$
Hybridisation	Coordination number - 4 Hybridisation - dsp^2
Hybridised orbitals of the metal atom in the complex	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ☐ $3d^8$ dsp^2 Hybridised orbitals $4p_z^{\ 0}$
Geometry	Square planar
Magnetic property	No of unpaired electron = 0 Hence diamagnetic
Magnetic moment	$\mu_s = \sqrt{n+(n+2)} = 0$

9. Draw all possible geometrical isomers of the complex[$Co(en)_2\ Cl_2]^+$ and identify the optically active isomer.



Cis isomer   Trans isomer

Cis$[Co\ (en)_2\ Cl_2]^+$ is optically active.

10.$[Ti\ (H_2O)_6]^{3+}$ is coloured, while $[Sc(H_2O)_6]^{3+}$ is colourless- explain.

For Ti Atomic number - 22 - Outermost electronic configuration : **$3d^2\ 4s^2$**

Ti^{3+} - Outermost electronic configuration : **$3d^1\ 4s^0$**

$[Ti\ (H_2O)_6]^{3+}$ is coloured because it contains one unpaired electron in d orbital **so d-d transition is possible**

For Sc Atomic number - 21 - Outermost electronic configuration : **$3d^1\ 4s^2$**

Sc^{3+} - Outermost electronic configuration : **$3d^0\ 4s^0$**

$[Sc(H_2O)_6]^{3+}$ is colourless because it does not contain any unpaired electron in d orbital.

11.Give an example for complex of the type [M$a_2b_2c_2$] where a, b, c are monodentate ligands and give the possible isomer

Example : [Cr(NH_3)$_2$Br$_2$]$^{-1}$

It has 7 possible isomers out of which 5 are geometrical isomer and 2 are optical isomer

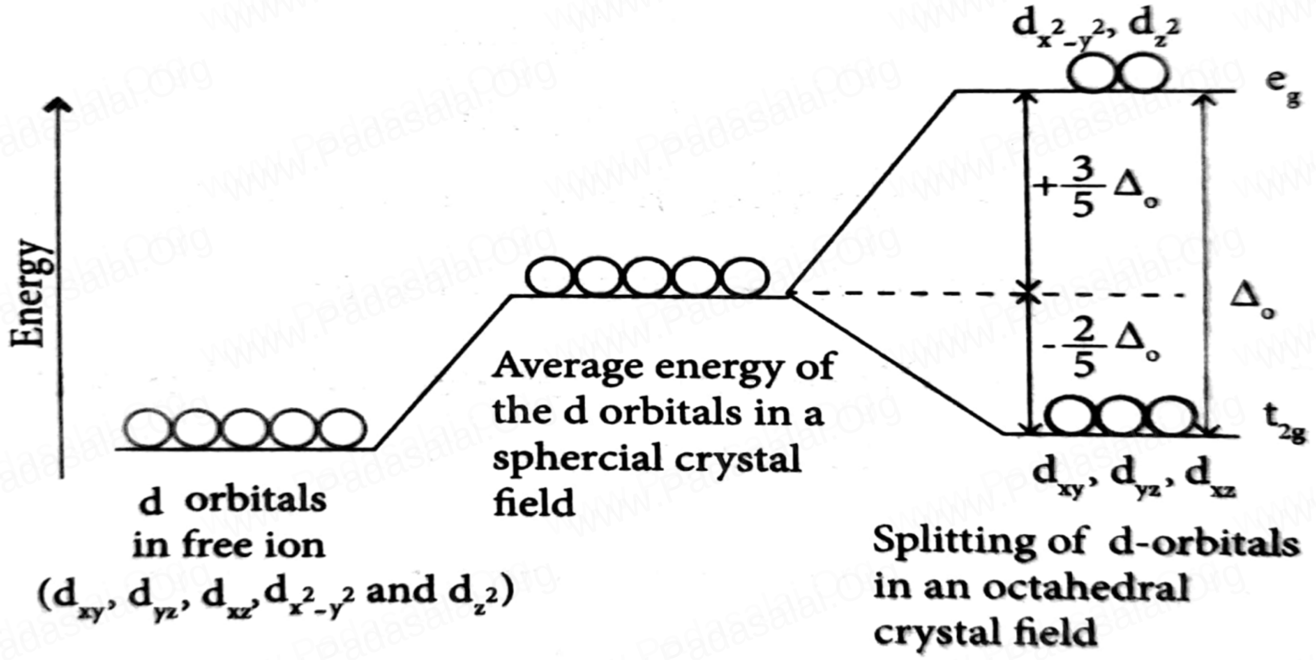
12.**Give one test to differentiate [Co (NH_3)$_5$ Cl]SO_4 and [Co(NH)$_3$ SO_4]Cl**

- Given two compounds are ionisation isomers.
- When these isomers dissolved in water , they ionise to give different ions in solution which react with differently with different reagents
- Given two compounds can be differentiated by **silver nitrate test**

Silver nitrate test

By adding silver nitrate to the solution of two compounds , **[Co (NH_3)$_5$ Cl]SO_4 will not give AgCl precipitate** as there is no Cl^- ion but **the [Co(NH)$_3$ SO_4]Cl will give one mole of AgCl precipitate** as it has one Cl^- ion.

13.In an octahedral crystal field, draw the figure to show splitting of d orbitals.



14.What is linkage isomerism? Explain with an example.

- This type of isomers arises when an **ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.**

For example

Nitrite ion is bound to the central metal ion Co^{3+} through a nitrogen atom in one complex (i) and through oxygen atom in other complex (ii).

(i). [Co (NH_3)$_5$(NO_2)]$^{2+}$ (ii). [Co (NH_3)$_5$ ONO]$^{2+}$

15. Write briefly about the applications of coordination compounds in volumetric analysis.

- **EDTA** used in the volumetric determination of wide variety of metal ions in solution e.g zn^{2+} , Pb^{2+} , Co^{2+} etc.By careful adjustment of pH and using suitable indicators mixtures of metals can be analysed e.g; Bi^{3+} in the presence of Pb^{2+} .

- EDTA may be used as a **masking agent** to remove a metal ion which would interfere with the analysis of a second metal ion present

- Since many complexes are highly coloured they can be used as **colourimetry reagents**
  e.g: Formation of red 2 , 2' – bipyridyl and 1 , 10 – phenanthroline complexes as a test of Fe^{2+}

- **Hardness of water** due to presence of Ca^{2+} and Mg^{2+} ions is estimated by **complexometric titrations using EDTA**

16.Classify the following ligand based on the number of donor atoms.

a) NH_3 - Monodentate
b) en – **bidentate**
c) ox^{2-} - **Bidenatte**
d) triaminotriethylamine - **Polydentate**
e) pyridine – **monodentate**

17.Give the difference between double salts and coordination compounds.

S.no	**Double salts**	**Coordination compounds**
i	These are molecular compounds formed by evaporation of solution containing two or more salts in equimolar proportions	It is a compounds formed by Lewis base and Lewis acid
ii	They lose their identity and dissociates into their constituent simple ions in solutions	complex ion in coordination compound, does not lose its identity and never dissociate to give simple ions.
iii	Can easily be analysed by determining the ions present in the aqueous solution	Cannot easily be analysed by determining the ions present in the aqueous solution

iv	In double salt metal metal atom or ion exhibit **normal valency**	In this metal metal atom or ion exhibit two types of valencies – **primary and secondary valency**
v	**Mohr's salt** (Ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$)	**potassium ferrithiocynate** $K_3[Fe(SCN)_6]$.

18.Write the postulates of Werner's theory.

1. Most of the elements exhibit, two types of valence namely primary valence and secondary valence and each element tend to satisfy both the valences .

2. **Primary valence is referred as the oxidation state of the metal atom** .The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions.

3. Secondary valence is referred as the coordination number. The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these.

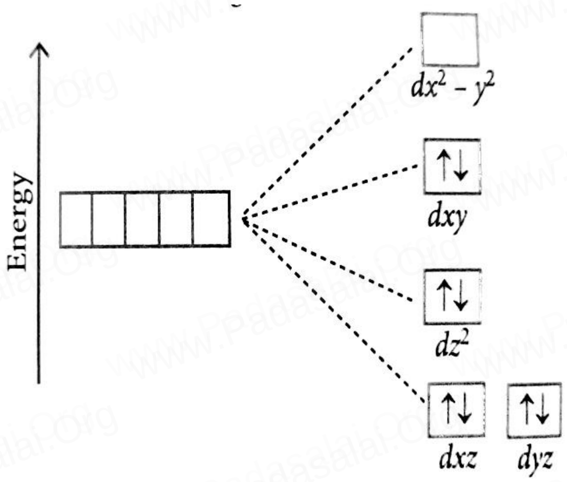
4. The primary valences are non-directional while the secondary valences are directional.

5. According to Werner, there are two spheres of attraction around a metal atom/ion in a complex. The inner sphere is known as coordination sphere and the groups present in this sphere are firmly attached to the metal. The outer sphere is called ionisation sphere. The groups present in this sphere are loosely bound to the central metal ion and hence can be separated into ions upon dissolving the complex in a suitable solvent.

19.$[Ni(CN)_4]^{2-}$ is diamagnetic , while $[NiCl_4]^{2-}$ is paramagnetic , explain using crystal field theory.

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

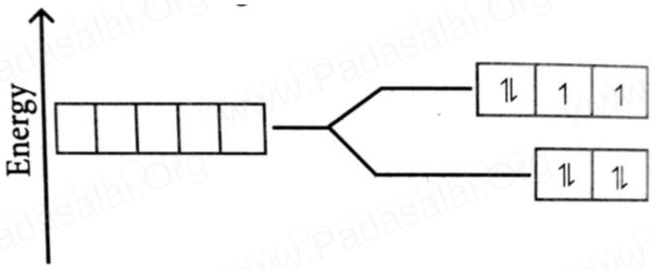
1) **It is low spin square planar complex**
2) It contains strong field ligand **CN^-**
3) Oxidation state of Ni is **+2**
4) Outer electronic configuration of Ni^{2+} ; **$3d^8 4s^0$**
5) **No unpaired electron** , so the complex is **diamagnetic** .



$[NiCl_4]^{2-}$

1) It is **high spin tetrahedral complex**
2) It contains **weak field ligand** Cl^-
3) Oxidation state of Ni is **+2**

4) Outer electronic configuration of Ni^{2+} ; **$3d^8 4s^0$**
5) It has **two unpaired electron** , so it is **paramagnetic**



20. Why tetrahedral complexes do not exhibit geometrical isomerism.

Because the relative position of unidentate ligand attached with Central metal atom are same with respect to each other.

21.**Explain optical isomerism in coordination compounds with an example.**

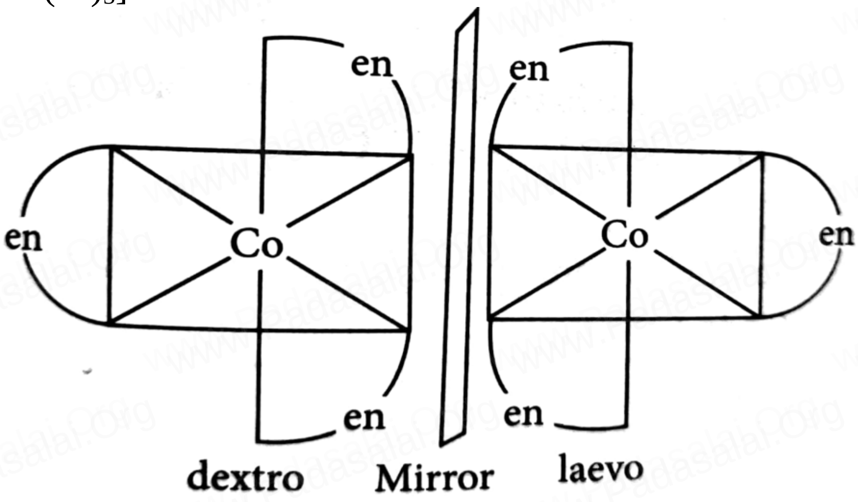
Coordination compounds which possess **chirality** exhibit optical isomerism similar to organic compounds.

The **pair of two optically active isomer**s which are **mirror images of each other** are called enantiomers.

Their solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called **'d' (dextro rotatory) and 'l' (levo rotatory) forms** respectively.

The octahedral complexes of type **$[M(xx)_3]^{n\pm}$, $[M(xx)AB]^{n\pm}$, $[M(xx)_2B_2]^{n\pm}$ exhibit optical isomerism.**

Eg ; $[Co(en)_3]^{3+}$



22.What are hydrate isomers? Explain with an example.

- The exchange of free solvent molecules such as water , ammonia, alcohol etc.. in the crystal lattice with a ligand in the coordination entity will give different isomers.
- These type of isomers are called solvate isomers.
- If the solvent molecule is water, then these isomers are called hydrate isomers

Eg : the complex $CrCl_3.6H_2O$ has **three hydrate isomers**

$[Cr(H_2O)_6]Cl_3$	a violet colour compound and gives three chloride ions in solution,
$[Cr(H_2O)_5Cl]Cl_2.H_2O$	a pale green colour compound and gives two chloride ions in solution and,
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	dark green colour compound and gives one chloride ion in solution

23.What is crystal field splitting energy?

It is **difference in energy between two sets of d orbitals** (t_{2g} & e_g) . It is denoted by Δ.

The magnitude of crystal field splitting energy not only depends on the ligand field but also depends on the nature of the ligand, the nature of the central metal atom/ion and the charge on it.

24. What is crystal field stabilization energy (CFSE) ?

The crystal field stabilisation energy is defined as the energy difference of electronic configurations in the ligand filed **($E_{L.F}$)** and the isotropic field/barycentre **(E_{iso}).**

$$CFSE\ (\Delta E_o) = \{E_{LF}\} - \{E_{iso}\}$$

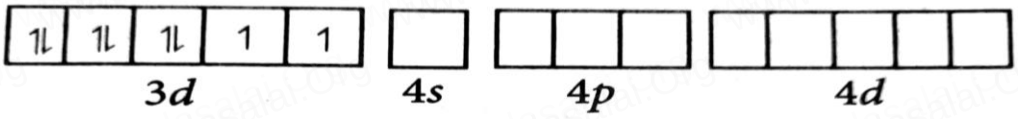
$$= \{[n_{t_{2g}}(-0.4)+n_{e_g}(0.6)]\ \Delta_o + n_p P\} - \{n'_p\ P\}$$

Here, $n_{t_{2g}}$ is the number of electrons in t_{2g} orbitals; n_{e_g} is number of electrons in e_g orbitals; n_p is number of electron pairs in the ligand field; & n'_p is the number of electron pairs in the isotropic field (barycentre).

25. A solution of $[Ni(H_2O)_6]^{2+}$ is green , whereas a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain

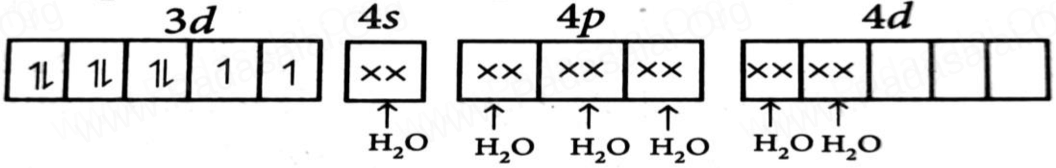
$[Ni(H_2O)_6]^{2+}$

Ni^{2+} ion $3d^8 4s^0$



Ni in $[Ni(H_2O)_6]^{2+}$

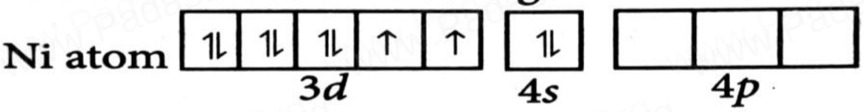
H_2O is a weak field ligand so pairing does occur.

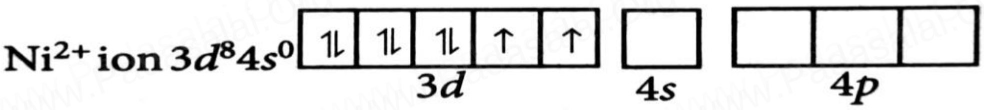


Since d orbital contains two unpaired electron so d-d transition is possible which leads to coloured.

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

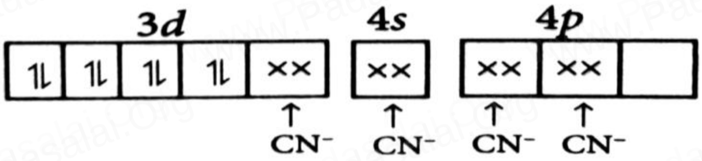
The outer electronic configuration of Ni is $3d^8 4s^2$





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

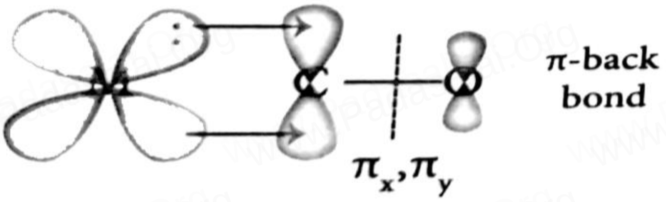
CN^- is a strong field ligand so pairing occurs.

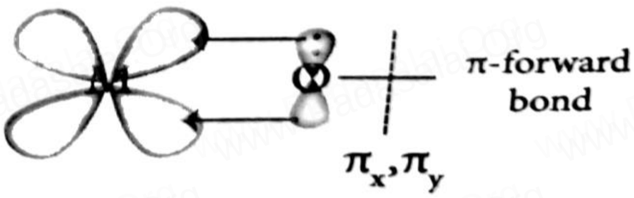


Since d orbital does not contains any unpaired electron , so it is colourless

26.Discuss briefly the nature of bonding in metal carbonyls.

- In metal carbonyls, the bond between metal atom and the carbonyl ligand consists of two components.
- The first component is an electron pair donation from the carbon atom of carbonyl ligand into a vacant d-orbital of central metal atom.
- This electron pair donation forms M_← CO sigma bond.
- This sigma bond formation increases the electron density in metal d orbitals and makes the metal electron rich.
- In order to compensate for this increased electron density, a filled metal d-orbital interacts with the empty π^* orbital on the carbonyl Ligand and transfers the added electron density back to the ligand. This second component is called π-back bonding . Thus in metal carbonyls, electron density moves from ligand to metal through sigma bonding and from metal to ligand through pi bonding, this synergic effect accounts for strong M ← CO bond in metal carbonyls.





27. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution copper sulphate?

The coordination entity formed when excess of liquid ammonia is added to an aqueous solution copper sulphate is **$[Cu(NH_3)_4]SO_4$ - Tetraamminecopper(II)Sulphate**

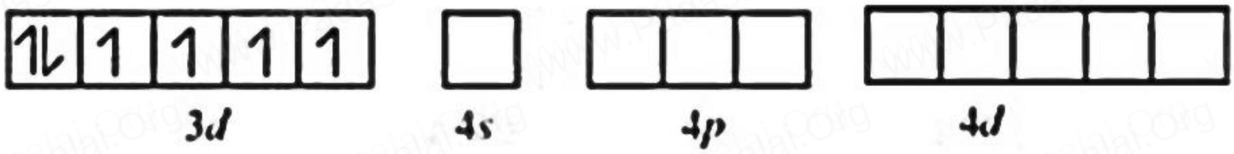
28. On the basis of VB theory explain the nature of bonding in $[Co(C_2O_4)_3]^{3-}$

$[Co(C_2O_4)_3]^{3-}$

Outer electronic configuration : $3d^7 4s^2$

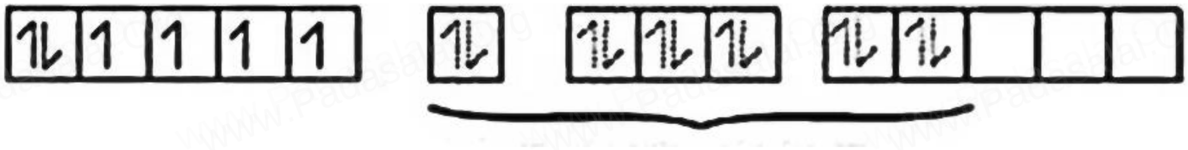
Oxidation state of Co in given complex is **+3**

Co^{+3}



Oxalate is weak field ligand .Therefore no pairing of orbitals occurs.

Co^{3+} in **$[Co(C_2O_4)_3]^{3-}$**



sp^3d^2 Hybridization (Six electron pair from the 3 oxalate ions which is bidentate ligand

Geometry is **Octahedral**

29.What are the limitations of VB theory?

1.It does not **explain the colour of the complex**

2. It considers **only the spin only magnetic moments** and does not consider the other components of magnetic moments.

3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal. For example, $[Fe(CN)_6]^{4-}$ is diamagnetic (low spin) whereas $[FeF_6]^{4-}$ is paramagnetic (high spin).

30.Write the oxidation state, coordination number , nature of ligand, magnetic property and electronic configuration in octahedral crystal field for the complex $K_4[Mn(CN)_6]$

i.	**oxidation state**	$4 + x + 6(-1) = 0$ $x = +2$
ii	**coordination number ,**	6
iii	**nature of ligand,**	Negative ligand (strong ligand)
iv.	**magnetic property**	Paramagnetic
v.	**electronic configuration**	d^5 ; t_{2g}^5

Knowledge based questions

1.$[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solution.Why?

- The colour of particular compound depends on the **magnitude of crystal field splitting energy (CFSE) Δ.**
- CFSE depends on the nature of the ligand.
- $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solution because of difference in CFSE.
- CN^- is a strong field ligand having higher CFSE value compared to CFSE value of H_2O .
- This means that absorption of energy for the intra d-d transition also differs .
- Hence the transmitted colour differs.

2.Give the oxidation state , d – orbital occupation of central metal ion in the following

i).$K_3[Co(C_2O_4)_3]$

Central metal ion : Co

Oxidation state : $x - 6 = -3$

$x = +3$

d – orbital occupation of Co^{3+} : $t_{2g}^6\ e_g^0$

ii)cis – $[Cr(en)_2Cl_2]$

Central metal ion : Co

Oxidation state : $x + 2(0) + 2(-1) = +1$

$x = +3$

d – orbital occupation of Cr^{3+} : t_{2g}^3

3.Among the following ions which one has highest magnetic moment values
(i)$[Cr(H_2O)_6]^{3+}$ ii)$[Fe(H_2O)_6]^{2+}$ iii)$[Zn(H_2O)_6]^{2+}$

(i)$[Cr(H_2O)_6]^{3+}$
No of unpaired electron in (i)$[Cr(H_2O)_6]^{3+}$ is 3
μ = $\sqrt{n(n+2)}$
= $\sqrt{15}$ = **3.87B.M**

ii)$[Fe(H_2O)_6]^{2+}$
n = 4
μ = $\sqrt{n(n+2)}$
= $\sqrt{24}$ = **4.89 B.M**

iii)$[Zn(H_2O)_6]^{2}$
n = 0
μ = 0
Hence **$[Fe(H_2O)_6]^{2+}$ has highest magnetic moment values**

4.What will be the correct order for the wavelength of absorption in the visible region for the following $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$

- The central metal ion is same in all three complexes
- Therefore absorption in the visible region depends on the ligands.
- The order in which the CFSE value of the ligands increase in the spectrochemical series is as follows **$H_2O < NH_3 < NO_2$**
- Thus the amount of CFSE observed will be in the order $\Delta_0(H_2O) < \Delta_0(NH_3) < \Delta_0(NO_2)$

Hence the wavelength of absorption in the visible region in the order of
$Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$

5. Which of the following cannot act as ligand H_2O , NH_3 , CH_4 give reason
CH_4 – Does not contain lone pair of electrons

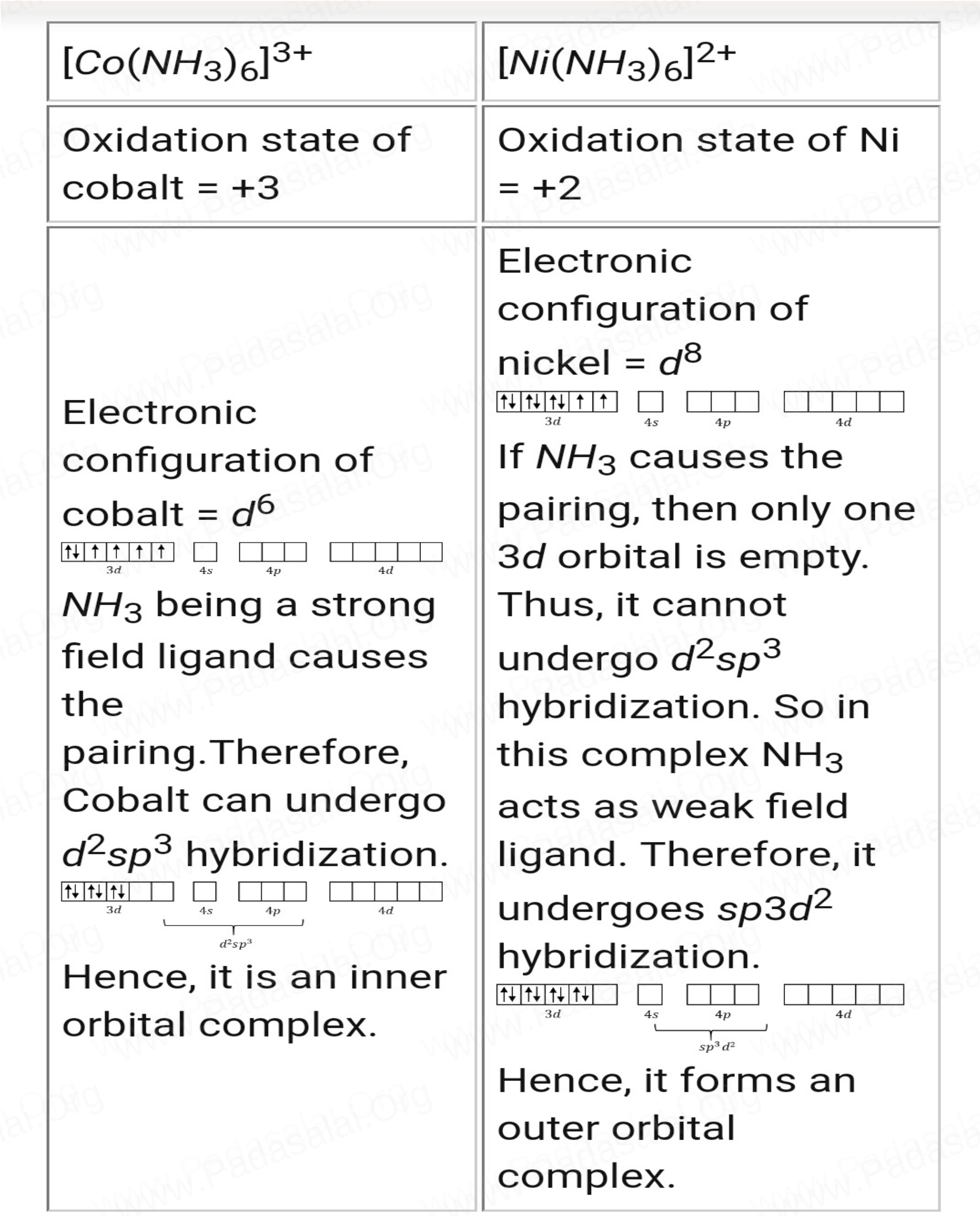
6.What do you meant by degenerate orbital?
d orbitals having same energy are called degenerate orbitals

7.WhyMetal carbonyls are much more stable than normal complexes

1) **The metal – carbon bonds in metal carbonyls** have both σ& π characters.
2) A carbonyl carbon donates a lone pair of electrons to the vacant orbital of metal .
3) A π bond is formed by a donation of a pair of electrons from the filled metal d orbital into the vacant anti bonding π* orbital .
4) The σ bond strengthens the π – bonds and vice-versa.
5) Thus a synergic effect is created due to this metal – ligand bonding .

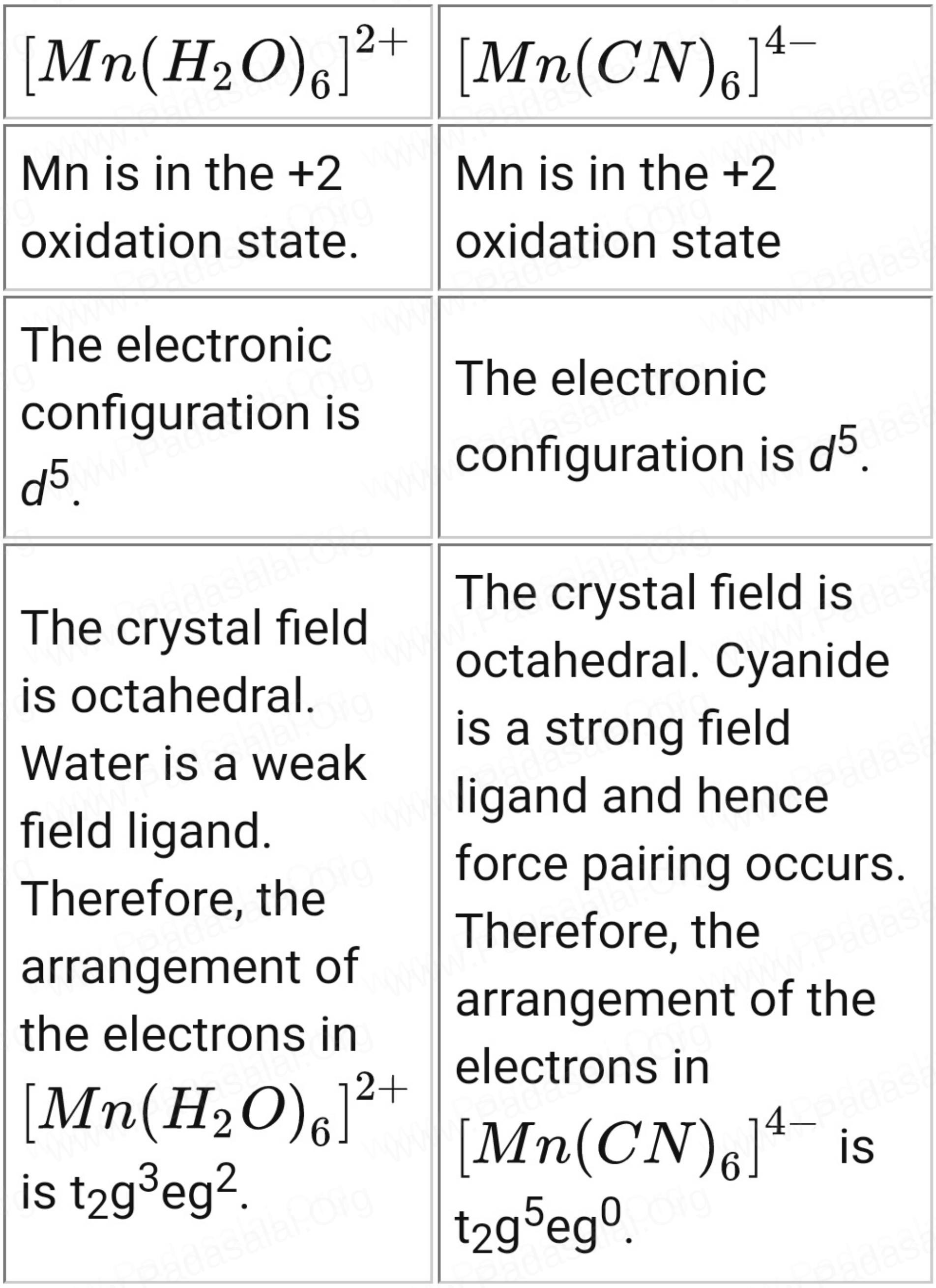
6) This synergic effect strengthens the bond between CO and metal

8.Explain $[Co(NH_3)]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex



$[Co(NH_3)_6]^{3+}$	$[Ni(NH_3)_6]^{2+}$
Oxidation state of cobalt = +3	Oxidation state of Ni = +2
Electronic configuration of cobalt = d^6 NH_3 being a strong field ligand causes the pairing.Therefore, Cobalt can undergo d^2sp^3 hybridization. Hence, it is an inner orbital complex.	Electronic configuration of nickel = d^8 If NH_3 causes the pairing, then only one $3d$ orbital is empty. Thus, it cannot undergo d^2sp^3 hybridization. So in this complex NH_3 acts as weak field ligand. Therefore, it undergoes $sp3d^2$ hybridization. Hence, it forms an outer orbital complex.

9.The hexaaquomanganese (II)ion contains five unpaired electron , while the hexacyanoion contains only one unpaired electron .Explain using Crystal field theory



$[Mn(H_2O)_6]^{2+}$	$[Mn(CN)_6]^{4-}$
Mn is in the +2 oxidation state.	Mn is in the +2 oxidation state
The electronic configuration is d^5.	The electronic configuration is d^5.
The crystal field is octahedral. Water is a weak field ligand. Therefore, the arrangement of the electrons in $[Mn(H_2O)_6]^{2+}$ is $t_{2}g^{3}eg^{2}$.	The crystal field is octahedral. Cyanide is a strong field ligand and hence force pairing occurs. Therefore, the arrangement of the electrons in $[Mn(CN)_6]^{4-}$ is $t_{2}g^{5}eg^{0}$.

Hence
hexaaquomanganese (II)ion contains five unpaired electron , while the hexacyanoion contains only one unpaired electron

Book inside questions

Two marks

1.What are the Limitations of Werner's theory:

Even though, Werner's theory was able to explain a number of properties of coordination compounds, it does not **explain their colour and the magnetic properties**.

2.Define Coordination entity

Coordination entity is an ion or a neutral molecule, composed of a central atom, usually a metal and the array of other atoms or groups of atoms (ligands) that are attached to it. In the formula, the coordination entity is enclosed in square brackets.

For example : In nickel tetracarbonyl, **the coordination entity is [Ni(CO)$_4$]**

3.Define central metal atom/ ion

The central atom/ion is the one that occupies the central position in a coordination entity and binds other atoms or groups of atoms (ligands) to itself, through a coordinate covalent bond.

In **[Ni(CO)$_4$] central metal atom is Nickel**

4.Define Ligands

The ligands are the atoms or groups of atoms bound to the central atom/ion. The atom in a ligand that is bound directly to the central metal atom is known as a donor atom.

In $K_4[Fe(CN)_6]$ the ligand is CN^- ion

5. Define **Coordination sphere**

The complex ion of the coordination compound containing the central metal atom/ion and the ligands attached to it, is collectively called coordination sphere and are usually enclosed in square brackets with the net charge. The other ionisable ions, are written outside the bracket are called counter ions.

For example [Ni(CO)$_4$]

6. Define Coordination polyhedron

The three dimensional spacial arrangement of ligand atoms/ions that are directly attached to the central atom is known as the coordination polyhedron (or polygon). For example, in $K_4[Fe(CN)_6]$, the coordination polyhedron is **octahedral.**

7.Define Coordination number:

The number of ligand donor atoms bonded to a central metal ion in a complex is called the coordination number of the metal. In other words, the coordination number is equal to the number of σ-bonds between ligands and the central atom.

For example

In $K_4[Fe(CN)_6]$ the coordination number of Fe^{2+} is 6.

8. Evaluate yourself 2: In the complex, $[Pt(NO_2)(H_2O)(NH_3)_2]Br$, identify the following

i. Central metal atom/ion - Pt
ii. Ligand(s) and their types - NO_2 – Negative ligand H_2O- Neutral ligand NH_3 – Neutral ligand
iii. Coordination entity - $[Pt(NO_2)(H_2O)(NH_3)_2]Br$
iv. Oxidation number of the central metal ion - +2
v. Coordination number - 6

9. What are Structural isomers and its types

The coordination compounds with same formula, but have different connections among their constituent atoms are called structural isomers or constitutional isomers

Types of Structural isomers

Ionisation somerism
Hydration isomerism
Linkage isomerism
Coordination isomerism

10.What are Stereo isomers and its types

The stereoisomers of a coordination compound have the same chemical formula and connectivity between the central metal atom and the ligands. But they differ in the spatial arrangement of ligands in three dimensional space.
Two types are **geometrical isomers and optical isomers.**

11. What are Metallic carbonyls ?

Metal carbonyls are the transition metal complexes of carbon monoxide, containing Metal- Carbon bond. In these complexes CO molecule acts as a neutral ligand.

Long answers

1.Explain about Types of complexes:

The coordination compounds can be classified into the following types based on (i) the net charge of the complex ion, (ii) kinds of ligands present in the coordination entity.

Classification based on the net charge on the complex:

A coordination compound in which the complex ion

i. carries a net **positive charge** is called a **cationic complex**. Examples: $[Ag(NH_3)_2]^+$

ii. carries a net **negative charge** is called an **anionic complex.** Examples: $[Ag(CN)_2]^-$

iii. bears **no net charge**, is called a **neutral complex.** Examples: $[Ni(CO)_4]$

Classification based on kinds of ligands present in the coordination entity

A coordination compound in which

i. the central metal ion/atom is coordinated to **only one kind of ligands** is called a **homoleptic complex.** Examples: $[Co(NH_3)_6]^{3+}$

ii. the central metal ion/atom is coordinated to more than one kind of ligands is called a heteroleptic complex. Example, $[Co(NH^3)^5Cl]^{2+}$

2. Explain about Coordination isomers

This type of isomers arises in the coordination compounds having both the cation and anion as complex ions. The interchange of one or more ligands between the cationic and the anionic coordination entities result in different isomers.

For example, in the coordination compound, $[Co(NH_3)_6][Cr(CN)_6]$ the ligands ammonia and cyanide were bound respectively to cobalt and chromium while in its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$ they are reversed.

3.What are the Main assumptions of Valence bond theory (VBT)

1. The ligand → metal bond in a coordination complex is covalent in nature. It is formed by sharing of electrons (provided by the ligands) between the central metal atom and the ligand.

2. Each ligand should **have at least one filled orbital** containing a lone pair of electrons.

3. In order to accommodate the electron pairs donated by the ligands, **the central metal ion present in a complex provides required number (coordination number) of vacant orbitals**.

4. These **vacant orbitals of central metal atom undergo hybridisation,** the process of mixing of atomic orbitals of comparable energy to form equal number of new orbitals called hybridised orbitals with same energy.

5. The vacant hybridised orbitals of the central metal ion, linearly overlap with filled orbitals of the ligands to form coordinate covalent sigma bonds between the metal and the ligand.

6. The **hybridised orbitals are directional** and their orientation in space gives a definite geometry to the complex ion.

7. In the octahedral complexes, if the (n-1) d orbitals are involved in hybridisation, then they are called inner orbital complexes or low spin complexes or spin paired complexes. If the nd orbitals are involved in hybridisation, then such complexes are called outer orbital or high spin or spin free complexes. Here n represents the principle quantum number of the outermost shell.

8. The complexes containing a central meal atom with unpaired electron(s) are paramagnetic. If all the electrons are paired, then the complexes will be diamagnetic.

9. Ligands such as CO, CN^-, en, and NH_3 present in the complexes cause pairing of electrons present in the central metal atom. Such ligands are called strong field ligands.
10**. Greater the overlapping** between the ligand orbitals and the hybridised metal orbital, **greater is the bond strength**.

3.Explain the Classification of metallic carbonyls

Generally metal carbonyls are classified in two different ways as described below.

(i) Classification based on the number of metal atoms present.

Depending upon the number of metal atoms present in a given metallic carbonyl, they are classified as follows.

a. Mononuclear carbonyls

These compounds contain only one metal atom, and have comparatively simple structures For example, $[Ni(CO)_4]$ - nickel tetracarbonyl is tetrahedral

b. Poly nuclear carbonyls

Metallic carbonyls containing two or more metal atoms are called poly nuclear carbonyls. Poly nuclear metal carbonyls may be Homonuclear $[Co(CO)_8]$ or Hetero nuclear $[MnCo(CO)_9]$

(ii) Classification based on the structure:

The structures of the binuclear metal carbonyls involve either metal–metal bonds or bridging CO groups, or both. The carbonyl ligands that are attached to only one metal atom are referred to as **terminal** carbonyl groups, whereas those attached to two metal atoms simultaneously are called *bridging* carbonyls. Depending upon the structures of the structure of the metal carbonyl they are classified as follows.

a. Non-bridged metal carbonyls:

These metal carbonyls do not contain any bridging carbonyl ligands. They may be of two types.

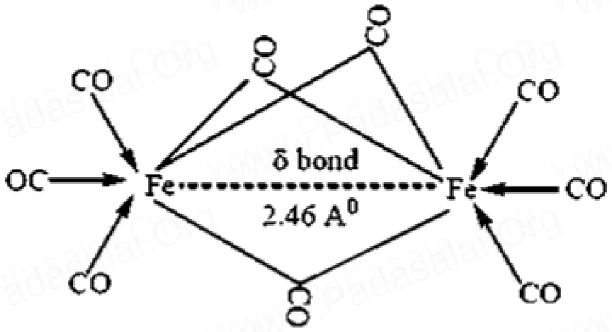
(i) Non- bridged metal carbonyls which contain only terminal carbonyls. Example ; $[Ni(CO)_4]$

(ii) Non- bridged metal carbonyls which contain terminal carbonyls as well as Metal-Metal bonds. For examples,The structure of $Mn_2(CO)_{10}$ actually involve only a metal–metal bond, so the formula is more correctly represented as $(CO)_5Mn-Mn(CO)_5$.

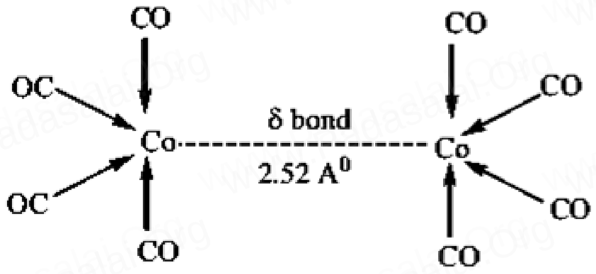
b. Bridged carbonyls:

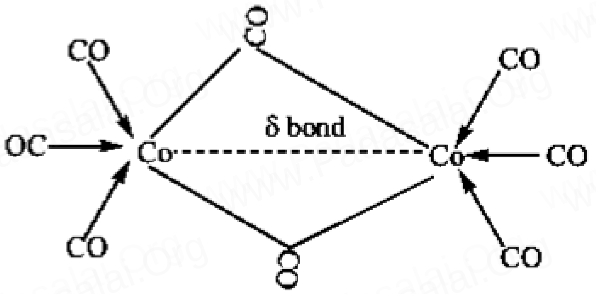
These metal carbonyls contain one or more bridging carbonyl ligands along with terminal carbonyl ligands and one or more Metal-Metal bonds.

(i) The structure of $Fe_2(CO)_9$, di-ironennea carbonyl molecule consists of three bridging CO ligands, six terminal CO groups and single Fe-Fe Δ bond formed by weak coupling of the unpaired electrons present in two 3d orbitals of two Fe atoms. This bond is represented by dotted line and is called as fractional single bond.



(ii) For dicobaltoctacarbonyl$Co_2(CO)_8$two isomers are possible. The one has a metal–metal bond between the cobalt atoms, and the other has two bridging CO ligands and a metal–metal bond.





4.Discuss briefly giving an example in each case the role of coordination compounds in i)Extraction/metallurgy of metals ii)General uses

i)Extraction/metallurgy of metals

1. Coordination complexes are used in the **extraction of silver and gold from their ores by forming soluble cyano complex.** These cyano complexes are reduced by zinc to yield metals. This process is called as Mac-Arthur –Forrest cyanide process.

2. Purification of Nickel by Mond’s process involves formation **$[Ni(CO)_4]$, which Yields 99.5% pure Nickel on decomposition. – Refining**

For estimation

Some metal ions are estimated more accurately by complex formation. For example, Ni^{2+} ions present in Nickel chloride solution is estimated accurately for forming an insoluble complex called $[Ni(DMG)_2]$

Industrial use

1. **Phthalo blue –** a bright blue pigment is a complex of Copper (II) ion and it is used in **printing ink and in the packaging industry**.

2. EDTA is used as a chelating ligand for the separation of lanthanides,in **softening of hard water** and also in **removing lead poisoning.**

Catalyst

Many of the complexes are used as catalysts in organic and inorganic reactions. For example,

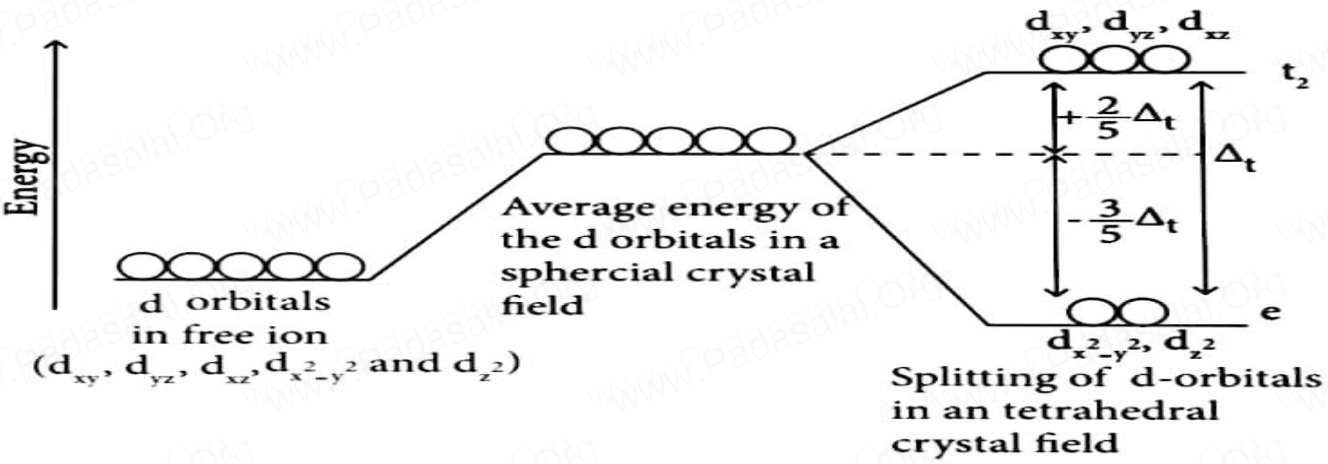
(i) **Wilkinson's catalyst –** $[(PPh_3)_3 RhCl]$ is used for **hydrogenation of alkenes.**

(ii) **Ziegler-Natta catalyst -** $TiCl + Al(C_2H_5)_3$ is used in the **polymerization of ethene.**

Photography

In photography, when the developed film is washed with sodium thio sulphatesolution (hypo), the negative film gets fixed. Undecomposed AgBr forms a soluble complex called **sodiumthiosulphatoargentate(I)** which can be easily removed by washing the film with water.

5. In an tetrahedral crystal field, draw the figure to show splitting of d orbitals.



6.What is spectrochemical series ?.Explain the difference between a weak field ligand and strong field ligand

- It is the arrangement of common ligands in the increasing order of their crystal field splitting energy (CFSE) values.

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- \approx urea < ox^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$$

- The ligand present on the R.H.S of the series are strong field ligands while that on the L.H.S are weak field ligand.
- Strong field ligand causes higher splitting in the d orbitals than weak field ligands

7.How does Δ_0 (CFSE) decide actual configuration of d orbitals in coordination entity?

- The degenerate d-orbitals (in a spherical environment) split into two levels t_{2g} & e_g in the presence of ligands.

- The splitting of degenerate levels due to presence of ligands is called Crystal field splitting and energy difference between these two levels is called CFSE **(Δ_0)**
- After splitting , filling of electrons takes place.
- After 1 electron (each) has been filled in three t_{2g} orbital , the filling of fourth electrons takes place in two ways .
- It can enter either the e_g orbital **(giving rise to t^3_{2g} e^1_g)** or pairing of electron can take place in the t_{2g} orbital **(giving rise to t^4_{2g} e^0_g)**
- If the Δ_0 value is less than pairing energy , then the electrons enter the g orbital
- If the Δ_0 is greater than the pairing energy , then the electrons enters the t_{2g} orbital

8.What is meant by stability of a coordination of compound in solution? State the factors which govern stability of complexes

The stability of a coordination complex is a measure of its resistance to the replacement of one ligand by another. The stability of a complex refers to the degree of association between two species involved in an equilibrium.

$[M] + [L] \leftrightarrow [ML]$

$\beta = \frac{[ML]}{[M][L]}$

Therefore the greater the value of stability constant greater is the stability of the complex.

Stability can be of two types

Thermodynamic stability

Thermodynamic stability of a coordination complex refers to the free energy change (ΔG) of a complex formation reaction.

Kinetic stability

Kinetic stability of a coordination complex refers to the ligand substitution. In some cases, complexes can undergo rapid ligand substitution; such complexes are called labile complexes. However, some complexes undergo ligand substitution very slowly (or sometimes no substitution), such complexes are called inert complexes.

Factors which govern stability of complexes

- **Charge on the central metal ion**

The greater the charge on the central metal ion , greater is the stability of the complex

- **Basic nature of the ligand**

A more basic ligand will form more stable complex

- **Presence of chelate rings**

Chelation increases the stability of complexes