

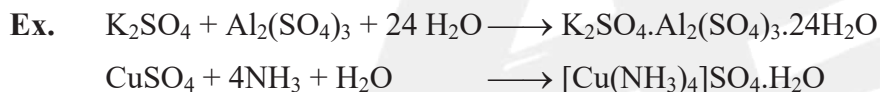
## CO-ORDINATION CHEMISTRY

## ☞ INTRODUCTION:

- (a) The concept of co-ordination compounds arises from the complex formation tendency of transition elements.
- (b) These compounds play a vital role in our lives, as chlorophyll of plants, vitamin B<sub>12</sub> and hemoglobin of animal blood are the co-ordination compounds of mg, Co and Fe respectively.
- (c) The co-ordination compounds play important role in analytical chemistry, polymerization reaction, metallurgy and refining of metals photography, water purification etc.
- (d) Co-ordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

## ☞ ADDITION COMPOUNDS :

When solutions containing two or more salts in simple molecular proportion are evaporated, crystals of new compound separate out.

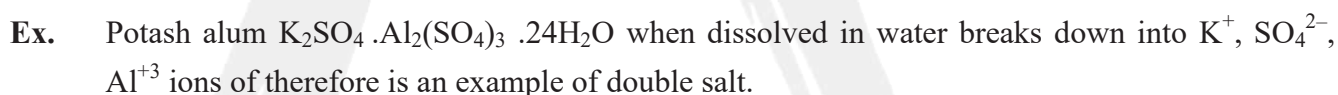


These addition compounds can be divided into two classes :

## (A) DOUBLE SALTS :

**Those which lose their identity in solution**

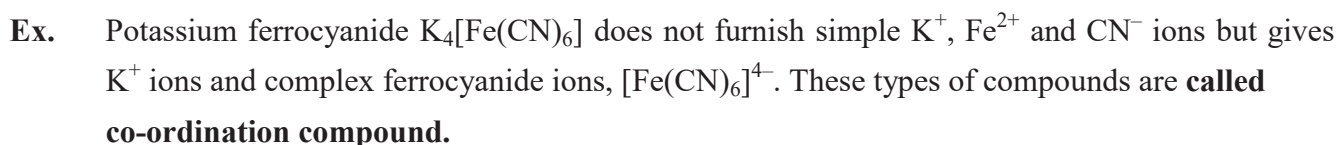
In solutions these compounds break down into simpler ions. Such addition compounds which lose their identity in solutions are called double salts.



## (B) COORDINATION COMPOUNDS:

**Those which retain their identity in solution.**

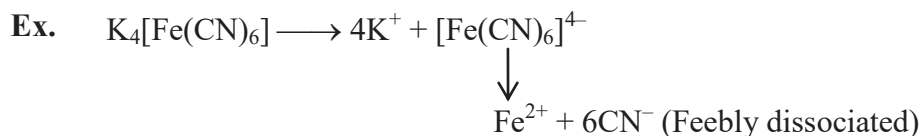
In aqueous solution, these addition compounds do not furnish all simple ions but instead give more complex ions having complicated structure.



**Complex compounds or co-ordination compounds.**

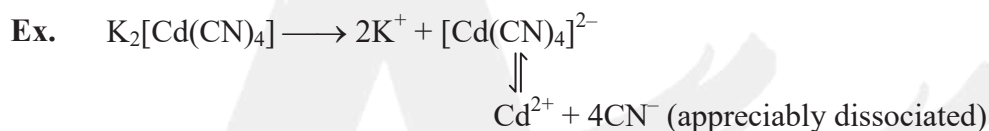
On the basis of stability of complex ion, complex ions are further divided as follows –

- (i) **Perfect complexes:** The compounds in which complex ion is fairly stable and further dissociation is not possible in solution state.



The ferrocyanide ion  $[\text{Fe}(\text{CN})_6]^{4-}$  is so insignificantly dissociated that it can be considered as practically undissociated and does not give the qualitative test of  $\text{Fe}^{2+}$  or  $\text{CN}^-$  ions.

- (ii) **Imperfect complexes:** Those complexes in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus respond to their usual qualitative test.



**Note : Homoleptic Complexes:** (Metal cation or atom surrounded by same type of ligand)



**Heteroleptic Complexes:** (Metal cation or atom surrounded by different type of ligand)

**Illustration:**

1. Study the following double salt and write the type of ions which can be tested in their aqueous solution.

**Salt**

**Ions can be tested**

- (a)  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (b)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (c)  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (d)  $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (e)  $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$

**Sol. Salt**

**Ions can be tested**

- (a)  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   $\text{K}^+$ ,  $\text{Al}^{+3}$ ,  $\text{SO}_4^{2-}$   
 (b)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   $\text{NH}_4^+$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$   
 (c)  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   $\text{K}^+$ ,  $\text{Cr}^{+3}$ ,  $\text{SO}_4^{2-}$   
 (d)  $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$   
 (e)  $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$   $\text{Al}^{+3}$ ,  $\text{OH}^-$ ,  $\text{PO}_4^{-3}$

2. Predict which among the following properties given below belong to double salt and co-ordination compounds.
- The blue colored solution prepared by  $\text{Cu}^{+2}$  (aq.) and  $\text{NH}_3(\text{NH}_4^+ \text{ aq.})$  does not show the presence of  $\text{Cu}^{+2}$  (.....)
  - Compounds which are stable in the solid state but break up into its constituents in aqueous solution (.....)
  - Aq. solution of carnallite (.....)
  - The compounds in which central metal ion form dative bonds with species surrounding it. (.....)
  - Mohrs salt (.....)
- Sol. (a) Co-ordination (b) Double salt (c) Double salt  
(d) Co-ordination (e) Double salt



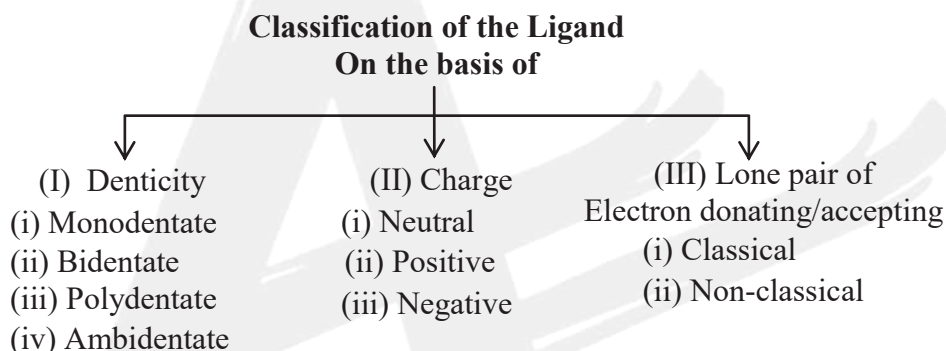
### DEFINITIONS OF TERMS USED IN CO-ORDINATION COMPOUNDS

- Co-ordination or complex compound:** Co-ordination compounds are those molecular compounds which retain their identity even when dissolved in water or any other solvent and their properties are completely different from those of the constituent ions.
- Central ion :** The cation to which one or more neutral molecules / ions are attached is called the atom / ion. Since, the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atoms of neutral molecules or ions, it must have empty orbitals of appropriate energy.
- Complex ion :** A complex ion may be defined as an electrically charged radical which is formed by the combination of a simple cation with one/more neutral molecules or one/more simple.
- Co-ordination number :** The total number of co-ordinate covalent bond is formed by central metal in complex is called the co-ordination number of the central metal ion .

Some common co-ordination numbers of important metals are as given below.

Metal	Coordination Number	Metal	Coordination Number
$\text{Cu}^+$	2, 4	$\text{Ni}^{2+}$	4, 6
$\text{Ag}^+$	2	$\text{Fe}^{2+}$	4, 6
$\text{Au}^+$	2, 4	$\text{Fe}^{3+}$	6
$\text{Hg}_2^{2+}$	2	$\text{Co}^{2+}$	4, 6
$\text{Cu}^{2+}$	4, 6	$\text{Co}^{3+}$	6
$\text{Ag}^{2+}$	4	$\text{Al}^{3+}$	6
$\text{Pt}^{2+}$	4	$\text{Sc}^{3+}$	6
$\text{Pd}^{2+}$	4	$\text{Pt}^{4+}$	6
$\text{Mg}^{2+}$	6	$\text{Pd}^{4+}$	6

- Ex.** Coordination number of the central metal ions in  
 (i)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is four (ii)  $[\text{Fe}(\text{EDTA})]^-$  is six
- (e) **Co-ordination sphere:** The part of the complex enclosed in square bracket is known as co-ordination sphere. It is actually combination of central metal and ligands.
- (f) **Ligands :**
- The ions or neutral molecules which combine with central metal ion to form complex are called ligands.
  - They act as electron pair donor (i.e. Lewis bases) though certain ligands also accept electron from central metal and such ligands are known as  $\pi$  - acid ligands.

**CLASSIFICATION OF LIGANDS:****(A) Based on charge**

- Neutral ligands :  $\text{H}_2\text{O}$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{C}_6\text{H}_6$  etc.
- Positive ligands :  $\text{NO}^+$ ,  $\text{N}_2\text{H}_5^+$
- Negative ligands :  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$

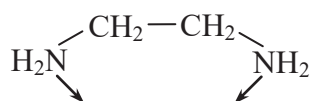
**(B) Based on DENTICITY :**

The number of electron pairs donated to central metal by ligands is known as denticity. Depending on number of electron pairs donated, these are classified in following categories.

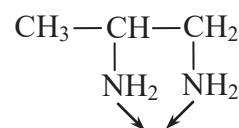
- (a) **Unidentate/monodentate ligands:** Ligands which donate one pair of electron to the central metal are called unidentate ligands.  
 $\text{X}^-$ ,  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_3$ , Pyridine,  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_3^{2-}$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{OH}^-$ ,  $\text{O}^{2-}$ ,  $(\text{C}_6\text{H}_5)_3\text{P}$  etc.

**(b) Bidentate ligands:** Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.

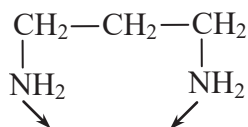
(i) en: ethylenediamine



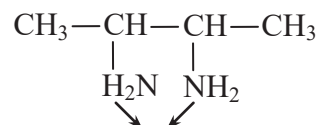
(ii) pn: propylenediamine



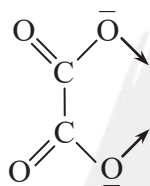
(iii) tn: trimethylenediamine



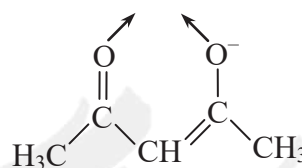
(iv) bn: butylenediamine



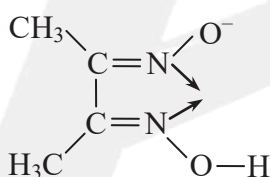
(v)  $\text{ox}^{2-}$ : oxalate



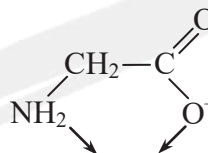
(vi)  $\text{acac}^-$ : acetylacetonate



(vii)  $\text{dmg}^-$ : dimethylglyoximate



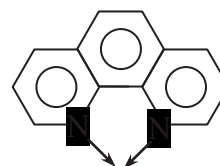
(viii)  $\text{gly}^-$ : glycinate



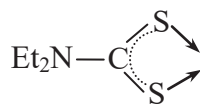
(ix) dipy: dipyridyl



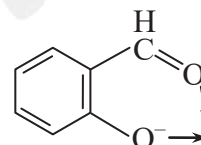
(x) o-phen: ortho-phenanthroline



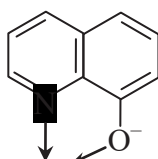
(xi) N, N'- Diethylthiocarbamate ion



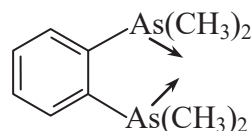
(xii) Salicylaldehyde anion



(xiii) 8-Hydroxyquinolinol ion (oxine)

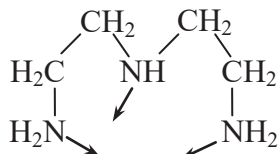


(xiv) o-Phenylenebisdimethylarsine (diarsine)

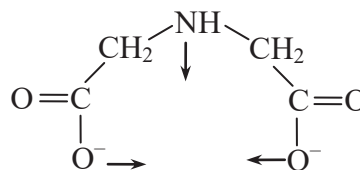


**(c) Tridentate ligands:** The ligands which donate three pairs of electrons to the central metal are called tridentate ligands. For example,

(i) dien: diethylenetriamine

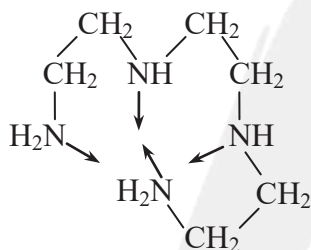


(ii) imda<sup>2-</sup>: iminodiacetate

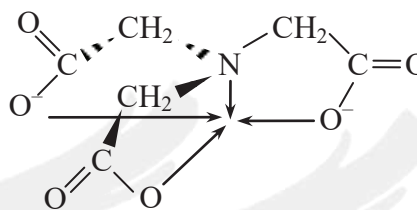


**(d) Tetradentate ligands:** Those ligands which can donate four electron pair to the central metal are known as tetradentate ligands. For example,

(i) trien: triethylenetetraamine

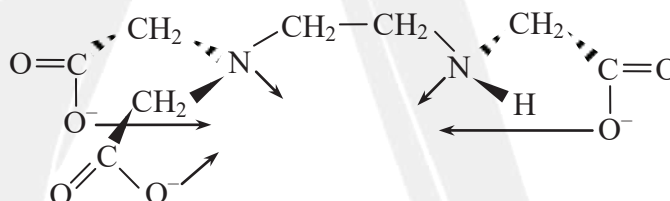


(ii) NTA<sup>3-</sup>: nitrilotriacetate



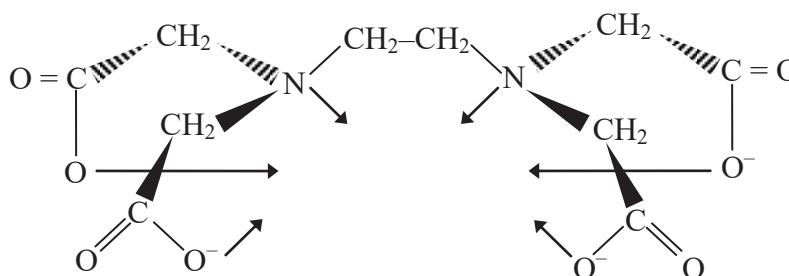
**(e) Pentadentate ligands:** Those ligands which can donate five electron pairs to the central metal are known as pentadentate ligands. For example,

EDTA<sup>3-</sup>: ethylenediamine triacetate

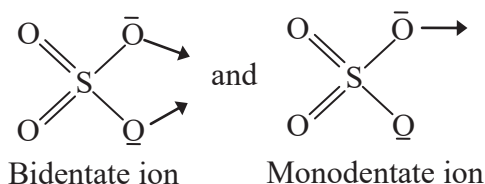


**(f) Hexadentate ligands :** Those ligands which can donate six electron pairs to the central metal are known as hexadentate ligands. For example,

EDTA<sup>4-</sup>: ethylenediamine tetracetate



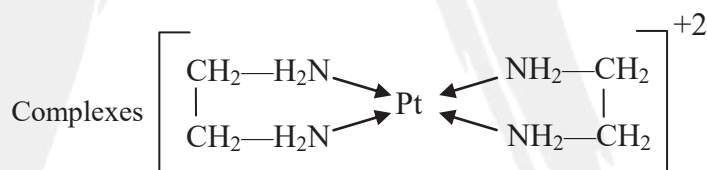
**Note : (i) Flexidentate :** A ligand which shows variable denticity is called a flexidentate ligand. For example,



- (ii)  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Br}$       and       $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Br}$   
 $\text{CO}_3^{2-}$  is bidentate                       $\text{CO}_3^{2-}$  is monodentate

**(g) Chelating ligands:**

- (i) Polydentate ligands whose structures permit the attachment of two or more donor sides to the same metal ion simultaneously, thus closing one or more rings are called chelating ligands and the compounds formed are known as chelate compounds.
- (ii) A chelate may be defined as a ring structure formed by the combination of a polydentate ligand having two or more donor atoms with a metal ion forming part of the ring.
- (iii) The process of formation of chelates is called chelation.
- (iv) Chelate complexes are more stable than ordinary complexes in which the ligand is a monodentate
- (v) This increased stability of the compound due to chelation is called the chelate effect
- (vi) In the complex ion given below, 5 membered rings are formed. So all these are called chelate



- (vii) Generally the chelate complexes with 5 or 6 membered rings are more stable.
- (viii) Out of these, 5 membered rings are very stable when they involve saturated ligands.
- On the other hand 6-membered ring structures acquire maximum stability when they involve unsaturated ligands containing conjugate double bond. This is due to the resonance effects involving metal d-orbitals and ligand p-orbital electrons.

**(h) Ambidentate ligands**

Ligands which can ligate through two different atoms present in it are called ambidentate ligands. Examples of such ligands are the  $\text{NO}_2^-$  and  $\text{SCN}^-$  ions.  $\text{NO}^-$ , The negative ion can coordinate through either the nitrogen or the oxygen atoms to a central metal atom/ion. Similarly,  $\text{SCN}^-$  ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds. There are certain ligands which have two or more donor atoms but during formation of complexes only one donor atom is attached to metal ion. Such ligands are called ambidentate ligands such as  $\text{CN}^-$ ,  $\text{CNS}^-$



**Ex. :**  $\text{CN}^-$  can coordinate through either the nitrogen or the carbon atom to central metal ion.

**(i) Flexidentate ligands :**

Ligands which sometimes do not use all the donor sites to get coordinated with central metal ion are known as flexidentate ligands.

**Ex.**  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  etc.

**Illustration : Match the Column.**

A	B
(i) Ligand contains one donor site	(a) hexadentate
(ii) Ligand contains two donor site	(b) tridentate
(iii) Ligand contain three donor site	(c) tetradentate
(iv) Ligand contain four donor site	(d) bidentate
(v) Ligand contain six donor site	(e) unidentate

**Ans.** (i) - (e); (ii) - (d); (iii) - (b); (iv) - (c); (v) - (a)

**(C) Based upon bonding interaction between the ligand and the central atom.**

**(a) Classical or simple ligand :** These ligand only donate the lone pair of electrons to the central atom.

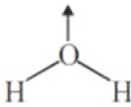
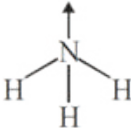
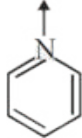
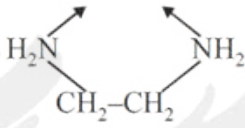
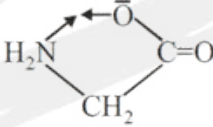
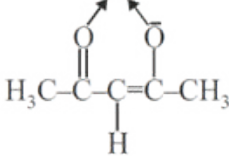
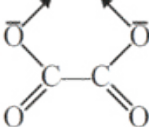
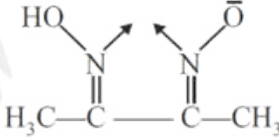
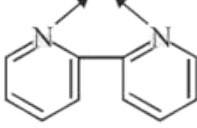
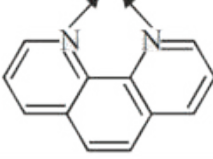
eg. :  $\text{O}^{2-}$ ,  $\text{OH}^-$ ,  $\text{F}^-$  etc.

**(b) Non classical or  $\pi$ -acid or  $\pi$ -acceptor ligand :** These ligand not only donate the lone pair of electrons to central metal but also accept the electron cloud from central atom

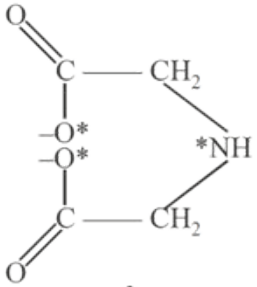
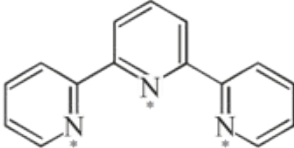
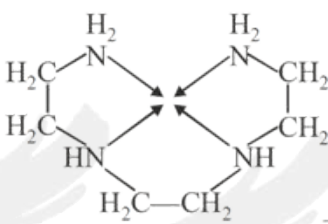
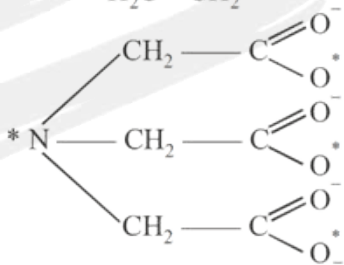
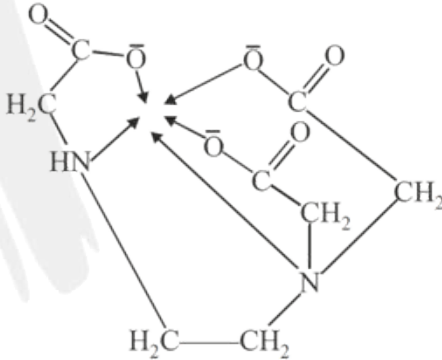
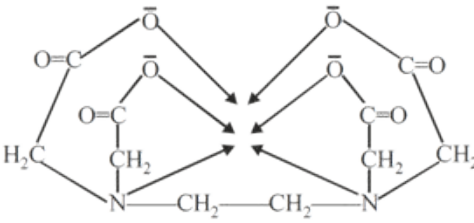
eg. :  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{NO}^+$ ,  $\text{PF}_3$ ,  $\text{PR}_3$  etc.



Table  
Important Ligands forming Complexes

Type of Ligand	Name of Ligand	Symbol	Structure showing only linkage sites (by $\rightarrow$ to metal ions)
Unidentate	Water	aqua	
	Ammonia	ammine	
	pyridine	py	
Bidentate	Ethylenediamine	en	
	Glycinate anion	gly	
	Acetylacetonate anion	acac	
	Oxalate anion	ox	
	Dimethylglyoximate anion	DMG	
	2,2'Dipyridyl	dipy	
	1,10 Phenanthroline	phen	

Type of Ligand	Name of Ligand	Symbol	Structure showing only linkage sites (by $\rightarrow$ to metal ions)
<b>Bidentate</b>	N,N'-Diethylthiocarbamate ion		
	Salicylaldehyde anion		
	8-Hydroxyquinolinol ion	oxine	
	o-Phenylenebisdimethylarsine	diarsine	
<b>Tridentate</b>	Diethylene triamine	dien	
	Iminodiacetate anion	ida	
	2,2',2'' Terpyridine	terpy	

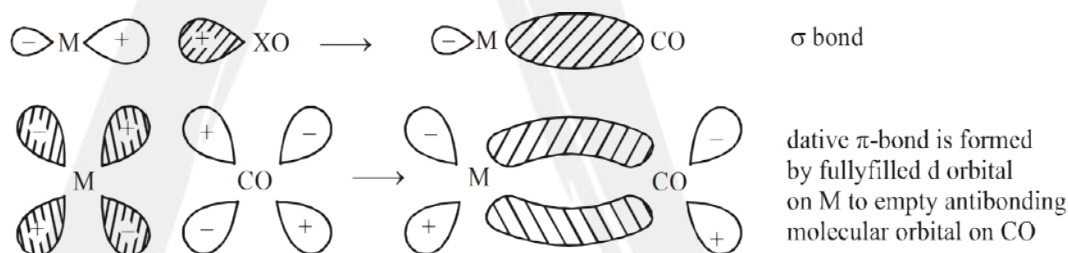
Type of Ligand	Name of Ligand	Symbol	Structure showing only linkage sites (by $\rightarrow$ to metal ions)
Tridentate	Iminodiacetato	ida	
	2,2',2''-terpyridine	terpy	
Tetradentate	Triethylene tetraamine	trien	
	Nitrilotriacetato	nta	
Pentadentate	Ethylenediamine triacetate anion	—	
Hexadentate	Ethylenediamine tetraacetate anion	EDTA	

## DO YOUR SELF – 1

- Which of the following is monodentate ligands?  
(A) en (B) dien (C) DMG (D)  $\text{OH}^-$
- Some salts although containing two different metallic elements give test for one of them in solution. Such salts are :  
(A) Complex salt (B) Double salt (C) Normal salt (D) None of these
- Which of the following is copper(I) compound?  
(A)  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  (B)  $[\text{Cu}(\text{CN})_4]^{3-}$  (C)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (D) All of these
- Diethylenetriamine is :  
(A) chelating agent (B) tridentate neutral molecule  
(C) tridentate monoanion (D) both (A) and (B)
- Some salts although containing two different metallic elements give test for one of them in solution. Such salts are :  
(A) double salts (B) complex salts (C) normal salts (D) none of these

**BONDING IN METAL CARBONYL:**

Ex.  $[\text{Fe}(\text{CO})_5]$  ;  $[\text{Ni}(\text{CO})_4]$  ;  $[\text{Cr}(\text{CO})_6]$

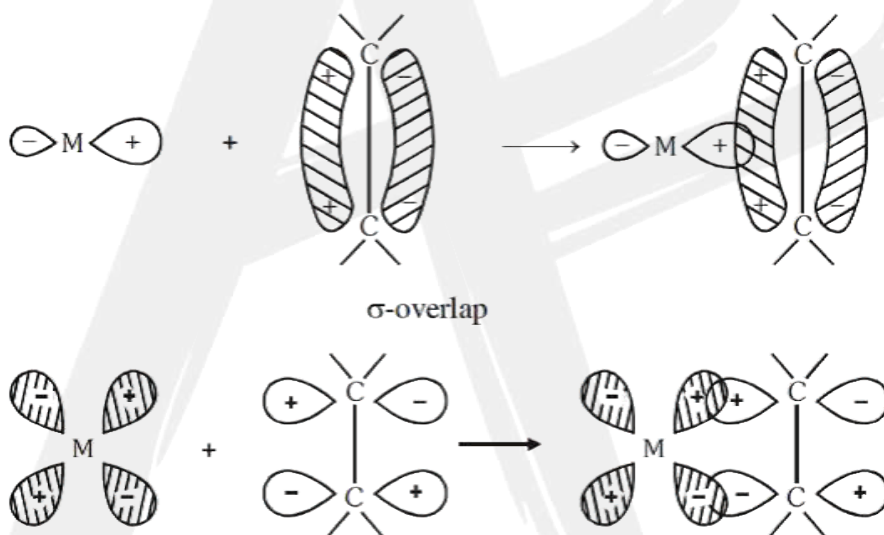


Schematic diagram of orbital overlaps in metal carbonyls.

- The metal-carbon bond in metal carbonyls may be represented as the donation of an electron pair from carbon to vacant orbital of metal & form  $\sigma$  bond ( $\text{M} \leftarrow \text{CO}$ ).
- A second bond is formed by back bonding sometimes called dative  $\pi$ -bonding. This bond formation take place from sideways overlap of a filled orbital on the metal with the empty antibonding  $\pi^*p_y/\pi^*p_z$  (if x-axis is molecular axis) molecular orbital of the carbon monoxide, thus forming a  $\text{M} \longrightarrow \text{CO}$ . bond ( $d\pi\text{-}p\pi$  back bond).

- (c) The filling or partial filling, of the antibonding orbital on CO reduces the bond order of C–O bond from the triple bond in CO towards a double bond. This shown by the increase in C–O bond length from 1.128 Å in CO to about 1.15 Å in many carbonyls.
- (d) Since CO accept the back donated electron from the metal atom in to its vacant  $\pi^*$  orbital, CO is called  $\pi$ -acid or  $\pi$ -acceptor ligand or  $\pi$ -bonding ligand.
- (e) Other  $\pi$ -acid ligands are  $\text{CN}^-$ ,  $\text{RCN}$ ,  $\text{NO}^+$ ,  $\text{PF}_3$ ,  $\text{PPh}_3$  etc.
- **Bonding in  $\pi$ -bonded organo metallic compound.**

Like zeise's salt  $\text{K}[\text{PtCl}_3(\pi\text{-C}_2\text{H}_4)]$ , the bonding of alkenes to a transition metal to form complexes has two metal atom. First, the  $\pi$ -electron density of the alkene overlaps with a  $\sigma$ -type vacant orbital of the metal atom. Second is the  $\pi$  back bond formed by the flow of electron density from a filled d-orbital on the metal into the vacant  $\pi^*$ - antibonding molecular orbital on the alkene molecule as shown below:



### IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The main rules of naming of complexes are –

- (a) Like simple salts, the positive part of the coordination compound is named first.  
**Ex.**  $\text{K}_4[\text{Fe}(\text{CN})_6]$  the naming of this complex starts with potassium.  
 $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  the naming of this complex starts with name of complex ion.
- (b) Naming of coordination sphere :- The names of ligands along with their numerical prefixes (to represent their no) are written first, followed by the name of central metal.
- (c) The ligands can be neutral, anionic or cationic.

- (i) The neutral ligands are named as the molecule Ex.  $(C_5H_5N)$  pyridine,  $(C_6H_5)_3P$  Triphenyl phosphine,  $(H_2N-CH_2-CH_2-NH_2)$  ethylene diamine.  
The neutral ligands which are not named as the molecule are CO carbonyl, NO nitrosyl,  $H_2O$  Aqua,  $NH_3$  ammine.
- (ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol	Name as ligand	Symbol	Name as ligand
$Cl^-$	Chloro/Chlorido	$N^{3-}$	Nitrido
$Br^-$	Bromo/Bromido	$O_2^{2-}$	Peroxo/Peroxido
$CN^-$	Cyano/Cyanido	$O_2H^-$	Perhydroxo/Perhydroxido
$O^{2-}$	Oxo/Oxido	$S^{2-}$	Sulphido
$OH^-$	Hydroxo/Hydroxido	$NH^{2-}$	Imido
$H^-$	Hydrido/Hydrido	$NH_2^-$	Amido

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing the ending 'e' with 'o' as follows.

Symbol	Name as ligand	Symbol	Name as ligand
$CO_3^{2-}$	Carbonato	$SO_3^{2-}$	Sulphito
$C_2O_4^{2-}$	Oxalato	$CH_3COO^-$	Acetato
$SO_4^{2-}$	Sulphato	$ONO^-$	(bonded through oxygen) nitrito
$NO_3^-$	Nitrato	$NO_2^-$	(bonded through nitrogen) nitro/nitrito-N
$S_2O_3^{2-}$	Thiosulphato		

- (iii) Positive ligands naming ends in 'ium'  $NH_2-NH_3^+$  Hydrazinium,  $NO_2^+$  nitronium,  $NO^+$  nitrosonium/nitrosylium.
- (d) If ligands are present more than once, then their number is indicated by prefixes like di, tri, tetra etc.
- (e) If words like di, tri, tetra are already used in the naming of ligand, or if it is polydentate ligand or organic ligand, the prefixes bis-, tris-, tetrakis-, pentakis- etc. are used to specify their number.  
**Example :**  $[Pt(en)_2Cl_2]Cl_2$  : Dichlorobis(ethylenediamine)platinum(IV) chloride.
- (f) When more than one type of ligands are present in the complex, then the ligands are named in the alphabetical order.

- (g) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is.

If the complex provides anionic complex ion then the name of central metal ion ends with 'ate'

**Example :**  $(\text{NH}_4)_2[\text{CuCl}_4]$  : Ammonium tetrachlorocuprate(II)

- (h) After the naming of central metal ion, anion which is in the outer sphere is to be named.

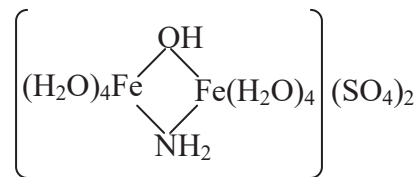
The naming of some of the complexes is done as follows – (as per IUPAC)

Complex Compounds		IUPAC Name
(i)	$\text{K}_4[\text{Fe}(\text{CN})_6]$ (anionic complex) So suffix 'ate' is added with metal name	Potassium hexacyanidoferrate(II)
(ii)	$\text{K}_2[\text{PtCl}_6]$	Potassium hexachloridoplatinate(IV)
(iii)	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (Cationic complex) So metal name will be written without any suffix	Hexamminecobalt(III) chloride
(iv)	$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	Tetraaquadichloridochromium(III) chloride
(v)	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	Diamminetetrachloridoplatinum(IV)
(vi)	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (Neutral complex) So no suffix is used with name of metal ion	Triamminetrichloridocobalt(III)
(vii)	$\text{K}_3[\text{Co}(\text{NO}_2)_6]$	Potassium hexanitrocobaltate(III)
(viii)	$\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Sodium pentacyanidonitrosoniumferrate(II)
(ix)	$[\text{NiCl}_4]^{-2}$	Tetrachloridonickelate(II) ion
(x)	$[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{+2}$	Pentamminechloridoruthenium(III) ion
(xi)	$[\text{Fe}(\text{en})_3]\text{Cl}_3$	Tris-(ethylenediamine)iron(III) chloride
(xii)	$[\text{Ni}(\text{Gly})_2]$	Bis-(glycinato)nickel(II)



- (i) If a complex ion has two metal atoms then it is termed polynuclear. The ligand which connects the two metal ions is called as **Bridging ligand or Bridge group**.

A prefix of Greek letter  $\mu$ , is repeated before the name of each different kind of bridging group.



Tetraaquairon(III)- $\mu$ -amido- $\mu$ -hydroxidotetraaquairon(III) sulphate

**Illustration:** Write the systematic names of the following co-ordination entities and compounds:

- (i)  $[\text{CoCl}_2(\text{NH}_3)_3]^+$  (ii)  $[\text{CrCl}_3(\text{NH}_3)_3]$  (iii)  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$  (iv)  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 (v)  $[\text{PtCl}(\text{NH}_3)_5]\text{Cl}_3$

**Solution :** (i) triaamminedichloridocobalt(III) (ii) triamminetrichloridochromium(II)  
 (iii) potassium trioxalatochromate(III) (iv) potassium hexacyanidoferrate(II)  
 (v) pentaamminechloridoplatinum(IV) chloride

### DO YOUR SELF – 2

- The formula of the complex tris-(ethylenediamine)cobalt(III) sulphate is  
 (A)  $[\text{Co}(\text{en})_2\text{SO}_4]$  (B)  $[\text{Co}(\text{en})_3\text{SO}_4]$  (C)  $[\text{Co}(\text{en})_3]_2\text{SO}_4$  (D)  $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$
- The IUPAC name of  $[\text{Ni}(\text{CO})_4]$  is  
 (A) tetracarbonylnickelate(0) (B) tetracarbonylnickelate(II)  
 (C) tetracarbonylnickel(0) (D) tetracarbonylnickel(II)
- The complex  $\text{Hg}[\text{Co}(\text{CNS})_4]$  is correctly named as :  
 (A) mercury(II) tetrathiocyanatocobaltate(II)  
 (B) mercury(II) cobalttetrasulphocyano(II)  
 (C) mercury(II) tetrasulphocyanidecobaltate(II)  
 (D) mercury(II) sulphocyanatocobalt(II)
- The hypothetical complex triamminediaquachloridocobalt(III) chloride can be represented as  
 (A)  $[\text{CoCl}(\text{NH}_3)_3(\text{H}_2\text{O})_2]$  (B)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}_3]$   
 (C)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}_2$  (D)  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$
- The correct IUPAC name of the complex  $\text{Fe}(\pi\text{-C}_5\text{H}_5)_2$  is  
 (A) cyclopentadienyliron (II) (B) bis-( $\eta^5$ -cyclopentadienyl)iron(II)  
 (C) dicyclopentadiencyferrate (II) (D) ferrocene



## ☞ SOME IMPORTANT COMPOUNDS WITH THEIR COMMON NAME :

1. **Switzer Reagent:**  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
2. **Nessler's Reagent:**  $\text{K}_2[\text{HgI}_4] + \text{KOH}$
3. **Cisplatin:**  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
4. **Brown Ring Complex:**  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}^+] \text{SO}_4^-$
5. **Sodium Nitro Prusside:**  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}^+]$
6. **Wilkinson Catalyst:**  $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$
7. **Vaska's Complex:**  $[\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$
8. **Magnus Green Salt:**  $[\text{Pt}(\text{NH}_3)_4]^{+2} [\text{PtCl}_4]^{-2}$
9. **Collman's Reagent:**  $\text{Na}_2[\text{Fe}(\text{CO})_4]^{-2}$
10. **Prussian Blue and Turnbull's blue :** Prussian Blue and Turnbull's blue is the same substance made from different reagents.  

$$\text{Fe}^{3+} + [\text{Fe}^{2+}(\text{CN})_6]^{4-} \longrightarrow \text{Fe}^{3+}_4[\text{Fe}^{2+}(\text{CN})_6]_3 \text{ (Prussian Blue)}$$

$$\text{Fe}^{2+} + [\text{Fe}^{3+}(\text{CN})_6]^{3-} \longrightarrow \text{Fe}^{3+}_4[\text{Fe}^{2+}(\text{CN})_6]_3 \text{ (Turnbull's Blue)}$$

## ☞ FORMATION OF CO-ORDINATION COMPOUNDS

It can be explained by number of theories.

- (A) Werner's co-ordination theory
- (B) Sidgwick theory or Effective Atomic Number Theory (EAN)
- (C) Valence bond theory
- (D) Crystal field theory

**(A) WERNER'S CO-ORDINATION THEORY :**

Werner's co-ordination theory was the first attempt to explain the bonding in co-ordination compounds. The main postulates of this theory are :

- (a) Metals possess two types of valencies - Primary valency and secondary valency.
- (b) Primary valencies are ionisable and are exhibited by a metal in the formation of its simple salts such as  $\text{CoCl}_3$ ,  $\text{CuSO}_4$  and  $\text{AgCl}$ . In these salts the primary valencies of Co, Cu and Ag are 3, 2, 1 respectively. Now-a-days primary valencies are referred to as oxidation state of their metal ion.
- (c) Secondary valencies are non-ionisable and are exhibited by a metal in the formation of its complex ions such as  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ag}(\text{NH}_3)_2]^+$ . In these complex, the secondary valencies of  $\text{Co}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$  are 6, 4 and 2 respectively. These are referred to as co-ordination number (C.N.) of the metal cation.
- (d) Primary linkages (valencies) are satisfied by negative ions while secondary valencies are satisfied by neutral molecules, negative ions.
- (e) Every metal atom or ion has a fixed number of secondary valencies. In other words, the co-ordination number of the metal atom is usually fixed.
- (f) Every metal has tendency to satisfy both its primary and secondary valencies.
- (g) The ligands satisfying secondary valency are always directed towards fixed positions in space about the central metal atom or ion. Thus, the co-ordination compounds have a definite geometry. Werner deduced that in  $\text{CoCl}_3 \cdot 5\text{NH}_3$  only two of the three chlorine atoms are ionic and 5  $\text{NH}_3$  and one Cl form co-ordinate bonds to  $\text{Co}^{3+}$  ion.

Formula of some cobalt complexes.

Example :

	Old	New	No. of $\text{Cl}^-$ ions precipitated	Total No. of ions
(i)	$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	3	4
(ii)	$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	2	3
(iii)	$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	1	2

Complex	Modern formula	No. of $\text{Cl}^-$ ions precipitated	Total No. of ions
$\text{PtCl}_4 \cdot 6\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	4	5
$\text{PtCl}_4 \cdot 5\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$	3	4
$\text{PtCl}_4 \cdot 4\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$	2	3
$\text{PtCl}_4 \cdot 3\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	1	2
$\text{PtCl}_4 \cdot 2\text{NH}_3$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	0	0 (non-electrolyte)

▪ WERNER'S REPRESENTATION OF COMPLEXES

(i)	$\text{Fe}(\text{NH}_3)_6\text{Cl}_3$		$[\text{Fe}(\text{NH}_3)_6]\text{Cl}_3$ Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.
(ii)	$\text{Fe}(\text{NH}_3)_5\text{Cl}_3$		$[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ In this complex two 'Cl' group act as primary valency and one of the 'Cl' acts as secondary valency also.
(iii)	$\text{Fe}(\text{NH}_3)_4\text{Cl}_3$		$[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ In this complex one 'Cl' group act as primary valency and two of the 'Cl' groups act as secondary valency also.

**(B) SIDGWICK THEORY OR EFFECTIVE ATOMIC NUMBER CONCEPT (EAN)**

Sidgwick proposed effective atomic number theory to explain the stability of the complexes. Total number of electrons on central metal including those transferred from ligands is known as EAN. The EAN generally coincides with the atomic number of next inert gas except in some cases.

EAN can be calculated by the following relation :

**EAN = (atomic number of the metal – oxidation state of central metal) + number of electrons gained from the donor atoms of the ligands.**

**Example :** Effective atomic number of the metal atom in the following:

(a)  $K_3[Cr(C_2O_4)_3]$  is 33

(b)  $K_4[Fe(CN)_6]$  is 36

**Illustration:** When  $AgNO_3$  is added to a solution of  $Co(NH_3)_5Cl_3$ , the precipitate of  $AgCl$  shows two ionisable chloride ions. This means -

- (A) Two chlorine atom satisfy primary valency and one chlorine atom satisfy primary valency as well as secondary valency.
- (B) One chlorine atom satisfies primary valency.
- (C) Two chlorine atoms satisfy secondary valency.
- (D) Three chlorine atoms satisfy secondary valency.

**Ans.** (A)

**Sol.**  $[Co(NH_3)_5Cl]Cl_2 \longrightarrow$  These two Cl Show PV  
 $\downarrow$   
 These one Cl show PV as well SV

Complex	Metal (Oxidation State)	Atomic Number or Metal	Coordination number	Effective atomic number (E-A.N.)
$K_4[Fe(CN)_6]$	+2	26	6	$(26-2) + (6 \times 2) = 36$ [Kr]
$[Cu(NH_3)_4]SO_4$	+2	29	4	$(29-2) + (4 \times 2) = 35$
$[Co(CH_3)_6]Cl_3$	+3	27	6	$(27-3) + (6 \times 2) = 36$ [Kr]
$Ni(CO)_4$	0	28	4	$(28-0) + (4 \times 2) = 36$ [Kr]
$K_2[Ni(CN)_4]$	+2	28	4	$(28-2) + (4 \times 2) = 34$
$K_2[PtCl_6]$	+4	78	6	$(78-2) + (6 \times 2) = 86$ [Rn]
$K_3[Cr(C_2O_4)_3]$	+3	24	6	$(24-3) + (6 \times 2) = 33$
$K_3[Fe(C_2O_4)_3]$	+3	26	6	$(26-3) + (6 \times 2) = 35$
$K_2[HgI_4]$	+2	80	4	$(80-2) + (4 \times 2) = 86$ [Rn]
$[Ag(NH_3)_2]Cl$	+1	47	2	$(47-1) + (2 \times 2) = 50$
$K_2[PdCl_4]$	+2	46	4	$(46-2) + (4 \times 2) = 52$

## DO YOUR SELF – 3

- Which one of the following complex species does not obey the EAN rule?  
(A)  $[\text{Cu}(\text{CN})_4]^{3-}$  (B)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  (C)  $[\text{Fe}(\text{CN})_6]^{4-}$  (D)  $[\text{Ni}(\text{CO})_4]$
- EAN of a metal carbonyl  $\text{M}(\text{CO})_x$  is 36. If atomic number of metal M is 26, what is the value of x?  
(A) 4 (B) 8 (C) 5 (D) 6
- Following Sidgwick's rule of EAN,  $\text{Co}(\text{CO})_x$  will be :  
(A)  $\text{Co}_2(\text{CO})_4$  (B)  $\text{Co}_2(\text{CO})_3$  (C)  $\text{Co}_2(\text{CO})_8$  (D)  $\text{Co}_2(\text{CO})_{10}$
- Coordination number of platinum in  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$  ion is :  
(A) 4 (B) 2 (C) 8 (D) 6
- In dodecacarbonyl dicobalt, the oxidation state of Cobalt is :  
(A) 1 (B) 2 (C) 3 (D) Zero

## (C) VALENCE BOND THEORY :

The main features of this theory are -

- Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond.
- During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.
- The number of vacant orbitals provided is equal to the coordination number of metal ion.

**Example :** In the formation of  $[\text{Fe}(\text{NH}_3)_6]^{3+}$ ,  $\text{Fe}^{+3}$  ion provides six vacant orbitals.

In  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $\text{Cu}^{+2}$  ion provides four vacant orbitals.

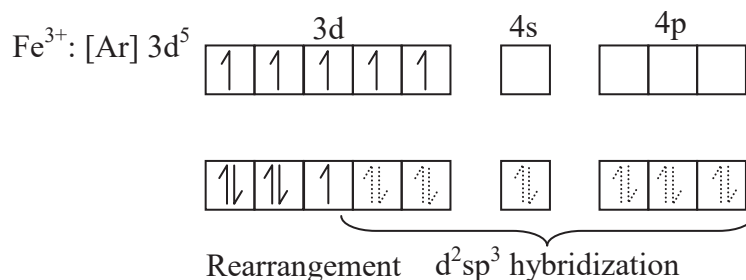
- The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.
- The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.
- The number of such overlappings is equal to the coordination number of metal ion.
- The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and accordingly complexes are called as Inner orbital complexes and outer orbital complexes respectively.
- In certain complexes pairing of electrons takes place in ligand field, resulting in decrease in spin only magnetic moment, such complexes are known as Low spin complexes
- Paramagnetism is represented in the term of spin only magnetic moment.

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

n = Number of unpaired electrons

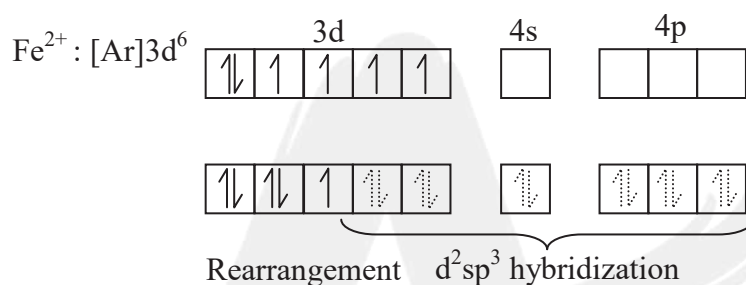
**Example :**  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic while  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic.

**Solution :**  $[\text{Fe}(\text{CN})_6]^{3-}$  involves  $d^2sp^3$  hybridization



One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[\text{Fe}(\text{CN})_6]^{4-}$  also involves  $d^2sp^3$  hybridization but it has  $\text{Fe}^{2+}$  ion as central ion.



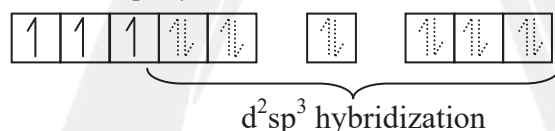
All electrons are paired, hence it is diamagnetic in nature.

•  **$[\text{Cr}(\text{NH}_3)_6]^{3+}$**

(a)  $\text{Cr} : [\text{Ar}] 4s^1 3d^5$



(c)  $\text{Cr}^{3+}$  in  $d^2sp^3$  hybridized state



(d) This  $d^2sp^3$  hybridisation leads to octahedral geometry. The complex  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  will be octahedral in shape

(e) Complex ion has 3 unpaired electrons so it must be paramagnetic.

(f) Other complexes of chromium with similar inner structure are  $[\text{Cr}(\text{CN})_6]^{3-}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

• **Outer orbital complexes**

(a) In these complexes s, p as well as d orbitals involved in hybridization, belong to the highest quantum number (n)

(b) Complexes formed by the use of outer nd orbitals will be paramagnetic.

(c) These complexes are called high-spin or spin free complexes

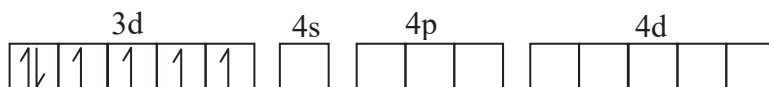
(d) The outer orbital complexes have greater number of unpaired electrons.

- $[\text{CoF}_6]^{3-}$

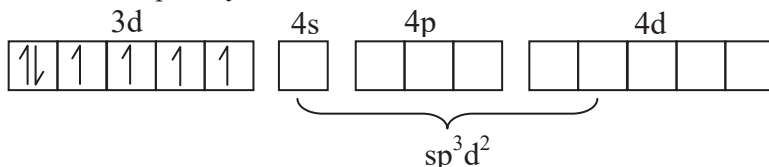
(a)  $_{27}\text{Co}$



(b)  $\text{Co}^{3+}$  ion



(c)  $\text{Co}^{3+}$  ion in  $sp^3d^2$  hybridised state



(d) Due to octahedral orientation of six  $sp^3d^2$  hybridised orbitals shape  $[\text{CoF}_6]^{3-}$  complex ion is octahedral

(e) Due to presence of four unpaired electrons in 3d orbital  $[\text{CoF}_6]^{3-}$  ion has paramagnetic character

(f) Other examples are  $[\text{FeF}_6]^{3-}$ ,  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Cu}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

- $[\text{Zn}(\text{NH}_3)_4]^{2+}$

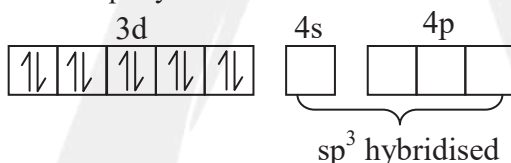
(a) Configuration of  $\text{Zn}_{30}$  :  $[\text{Ar}]4s^23d^{10}$



(b) Electronic configuration of  $\text{Zn}^{3+}$  :  $[\text{Ar}]4s^03d^{10}$



(c)  $\text{Zn}^{2+}$  in  $sp^3$  hybridised state

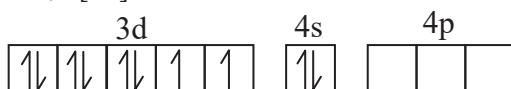


(d) Since the complex is formed by  $sp^3$  hybridisation, it is tetrahedral

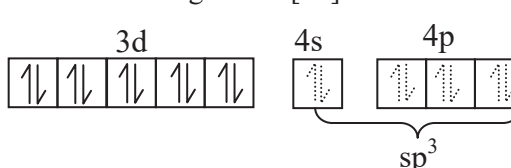
(e) Since all electrons are paired it is diamagnetic

- $[\text{Ni}(\text{CO})_4]$

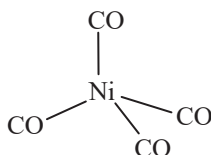
(a)  $\text{Ni}_{28}$  :  $[\text{Ar}]4s^23d^8$



(b) Ni after rearrangement:  $[\text{Ar}]4s^03d^{10}$



- (c) The empty one 4s and three 4p orbitals mix to form four  $sp$ - hybridised orbitals
- (d) each orbital accepts one electron pair from carbon monoxide molecule forming  $[\text{Ni}(\text{CO})_4]$
- (e) The shape of nickel tetra carbonyl is tetrahedral as shown below
- (f) is diamagnetic in nature



• **Square planar complex.**

These are formed due to  $dsp^2$  hybridisation.

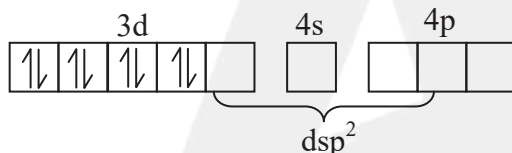
These complexes tend to be formed when the central ion has only one d orbital available in the inner shell



- (a) Electronic configuration of Ni :  $[\text{Ar}]4s^23d^8$



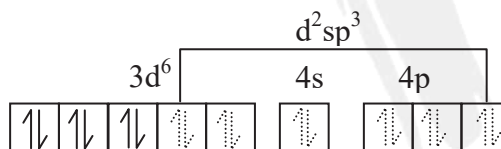
- (b) Electronic configuration of  $\text{Ni}^{2+}$  :  $[\text{Ar}]4s^03d^8$



- (c) The rearrangement is due to presence of strong ligand  $\text{CN}^-$ . The four orbitals make  $dsp^2$  hybridisation
- (d) The shape of resulting complex is square planar
- (e) Due to paired electrons it is diamagnetic.

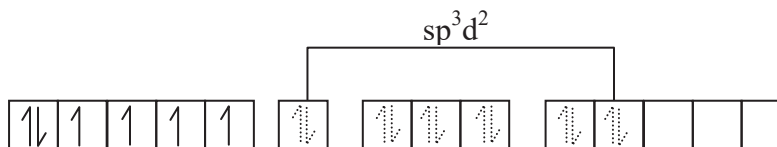
**Illustration :**  $[\text{Fe}(\text{CN})_6]^{4-}$  is diamagnetic while  $[\text{FeF}_6]^{4-}$  is strongly paramagnetic. Why?

**Solution :**  $\text{CN}^-$  is strong field ligand and so it pairs up the electrons leading to the formation of low spin complex which is diamagnetic.



Octahedral, diamagnetic complex

$\text{F}^-$  is weak field ligand so it forms high spin paramagnetic complex.

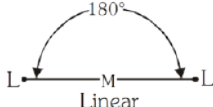
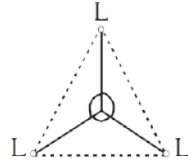
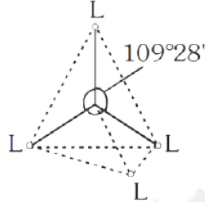
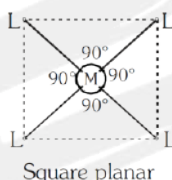
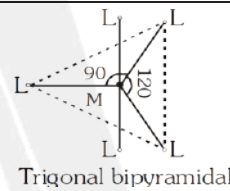
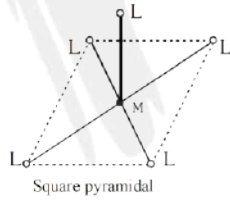
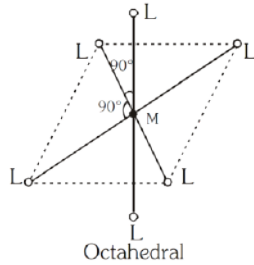


Octahedral, paramagnetic complex





Some Example:

Coordination Number	Hybridised orbitals	Geometrical shape of the complex	Examples of Complex
2	sp		$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{Ag}(\text{CN})_2]^-$
3	$\text{sp}^2$		$[\text{HgI}_3]^-$
4	$\text{sp}^3$		$[\text{CuCl}_4]^{2-}$ $[\text{ZnCl}_4]^{2-}$ $[\text{FeCl}_4]^-$ $[\text{Ni}(\text{CO})_4]$ $[\text{Zn}(\text{NH}_3)_4]^{+2}$
4	$\text{dsp}^2$ $d = d_{x^2-y^2}$		$[\text{PdCl}_4]^{2-}$ $[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Pt}(\text{NH}_3)_4]^{+2}$ $[\text{Cu}(\text{NH}_3)_4]^{+2}$ $[\text{PtCl}_4]^{2-}$
5	$\text{sp}^3d$ ( $d = d_{z^2}$ ) or $\text{dsp}^3$ ( $d = d_{z^2}$ )		$[\text{Fe}(\text{CO})_5]$ $[\text{CuCl}_5]^{3-}$
5	$\text{sp}^3d$ ( $d = d_{x^2-y^2}$ ) or $\text{dsp}^3$ ( $d = d_{x^2-y^2}$ )		$[\text{Ni}(\text{CN})_5]^{-3}$
6	$d^2\text{sp}^3$ (inner orbital complex) or $\text{sp}^3d^2$ (outer orbital complex) in both case d-orbitals are $d_{z^2}$ & $d_{x^2-y^2}$ .		$[\text{Cr}(\text{NH}_3)_6]^{+3}$ $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ $[\text{Fe}(\text{CN})_6]^{-3}$ $[\text{Co}(\text{NH}_3)_6]^{+3}$ $[\text{PtCl}_6]^{-2}, [\text{CoF}_6]^{-3}$

● **Drawback of valence bond theory :**

- (a) It describes bonding in co-ordination compounds only qualitatively but not account for the relative stabilities for different co-ordination complexes.
- (b) It does not offer any explanation for optical absorption spectra (coloration) of complexes
- (c) It does not describe the detailed magnetic properties of co-ordination compounds.

**DO YOUR SELF – 4**

1. What will be spin only magnetic moment of  $[\text{Fe}(\text{CN})_2(\text{H}_2\text{O})_4]\text{NO}_3$ ?  
 (A)  $\sqrt{8}$  B.M.      (B)  $\sqrt{15}$  B.M.      (C)  $\sqrt{24}$  B.M.      (D)  $\sqrt{35}$  B.M.
2. The complex  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  has ..... structure:  
 (A) square planar      (B) tetrahedral      (C) pyramidal      (D) pentagonal
3. Which has maximum paramagnetic nature?  
 (A)  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$       (B)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$       (C)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$       (D)  $[\text{Fe}(\text{CN})_6]^{4-}$
4. Which is correct in the case of  $[\text{NiCl}_4]^{2-}$  complex?  
 (A)  $\text{sp}^3$  hybridisation      (B) Paramagnetic and tetrahedral  
 (C) Two unpaired electrons      (D) All are correct
5. The shape of  $[\text{Cu}(\text{NH}_3)_4\text{Cl}_2]$  is :  
 (A) Tetrahedral      (B) Octahedral      (C) Square planar      (D) Pyramidal

- (D) **CRYSTAL FIELD THEORY:** The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the Crystal Field Theory. The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of polar molecules like  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

## (a) Crystal field splitting in octahedral coordination entities:

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in d orbitals of metal and the electrons (or negative charges) of the ligands. Such repulsion is more when the d orbitals of metal are directed towards the ligand than when it is away from the ligand.

Thus, the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals (axial orbitals) which point towards the axis along the direction of the ligand will experience more repulsion and will be raised in energy ; and the  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals (non-axial) orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy,  $t_{2g}$  set and two orbitals of higher energy,  $e_g$  set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by  $\Delta_o$  (the subscript o is for octahedral). Thus, the energy of the two  $e_g$  orbitals will increase by  $(3/5)\Delta_o$  and that of the three  $t_{2g}$  will decrease by  $(2/5)\Delta_o$ .

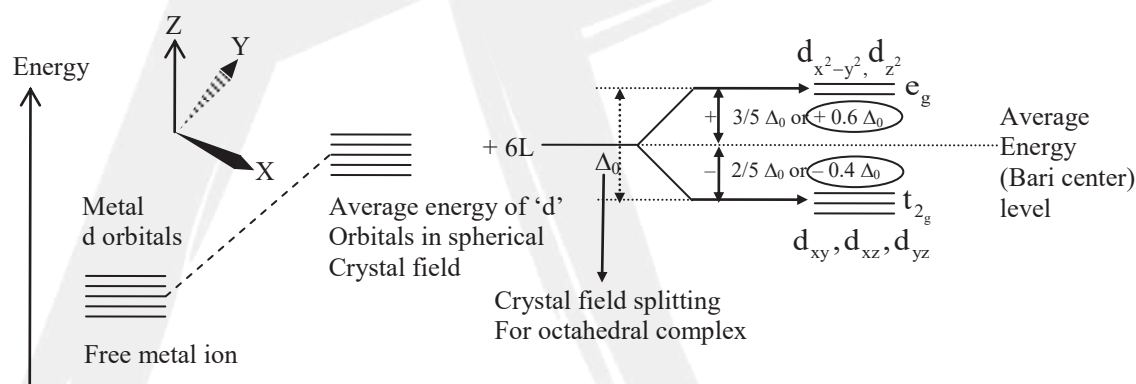
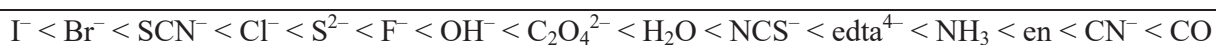


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting,  $\Delta_o$ , depends upon the fields produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below :



**Note :** In  $\text{SCN}^-$ , S is donating atom and in  $\text{NCS}^-$ , N is donating atom.

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. For  $d^4$  configuration, the fourth electron will singly occupy  $e_g$  orbital (according to Hund's rule) or will undergo pairing in  $t_{2g}$  orbital, which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting,  $\Delta_0$  and the pairing energy,  $P$  ( $P$  represents the energy required for electron pairing in a single orbital). The two possibilities are :

- (i) If  $\Delta_0 < P$ , the fourth electron enters in one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ .

Ligands for which  $\Delta_0 < P$  are known as weak field ligands and form high spin complexes.

- (ii) If  $\Delta_0 > P$ , it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ . Ligands which produce this effect are known as strong field ligands and form low spin complexes.

#### Crystal Field stabilising energy in Octahedral field :

**Formula :**  $\text{CFSE} = [-0.4 n_{t_{2g}} + 0.6 n_{e_g}] \Delta_0 + xP$ .

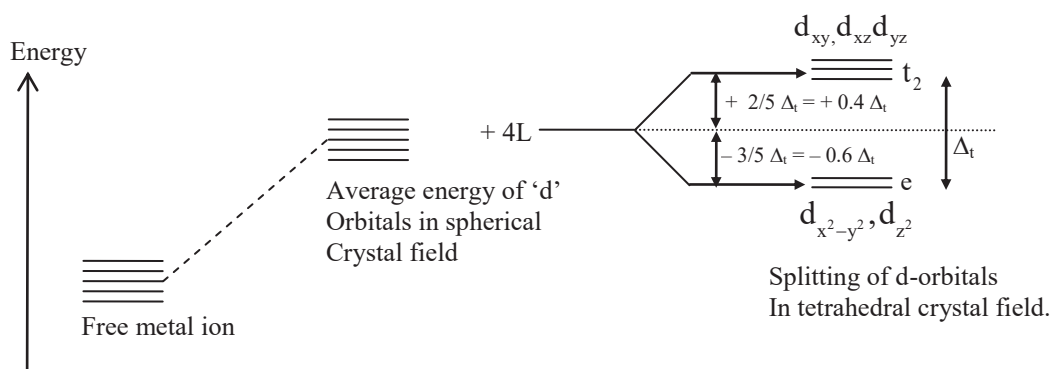
Where  $n_{t_{2g}}$  &  $n_{e_g}$  are number of electron(s) in  $t_{2g}$  &  $e_g$  orbitals respectively and  $\Delta_0$  crystal field splitting energy for octahedral complex. "x" represents the number of electron pairs and  $P$  is mean pairing energy.

#### (b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that  $\Delta_t = (4/9)\Delta_0$ . This may attributes to the following two reasons.

- (i) There are only four ligands instead of six, so the ligand field is only two thirds the size ; as the ligand field splitting is also the two thirds the size.
- (ii) The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly further two third. So  $\Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9} \Delta_0$ .

Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.



**Figure showing crystal field splitting in tetrahedral complex.**

Since  $\Delta_t < \Delta_o$  crystal field splitting favours the formation of octahedral complexes.

### Crystal Field stabilising energy in Tetrahedral field :

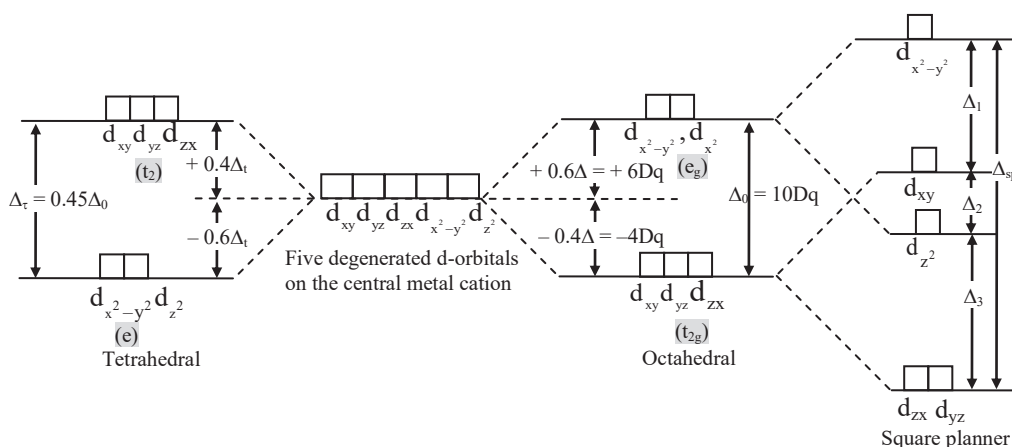
**Formula :**  $CFSE = [-0.6 n_e + 0.4 n_{t_2}] \Delta_t + xP$ .

where  $n_{t_2}$  &  $n_e$  are number of electron(s) in  $t_2$  &  $e$  orbitals respectively and  $\Delta_t$  crystal field splitting energy for tetrahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

### (c) Crystal field splitting in square planar co-ordination entities:

The square planar arrangement of ligands may be considered to be one derived from the octahedral field by removing two trans-ligands located along the Z-axis. In the process, the  $e_g$  and  $t_{2g}$  sets of orbitals is lifted i.e., these orbitals will no longer be degenerate.

The four ligands in square planar arrangement around the central metal ion are shown in Fig. As the ligands approach through the x and y axis, they would have greatest influence on  $d_{x^2-y^2}$  orbital, so the energy of this orbital, will be raised most. The  $d_{xy}$  orbital, lying in the same plane, but between the ligands will also have a greater energy though the effect will be less than that on the  $d_{x^2-y^2}$  orbitals. On the other hand, due to absence of ligands along Z-axis, the  $d_{z^2}$  orbital becomes stable and has energy lower than that of  $d_{xy}$  orbital. Similarly  $d_{yz}$  and  $d_{xz}$  become more stable. The energy level diagram may be represented as shown in figure along with tetrahedral and octahedral fields.



The value of  $\Delta_{sp}$  has been found larger than  $\Delta_o$  because of the reason that  $d_{xz}$  and  $d_{yz}$  orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands.  $\Delta_{sp}$  has been found equal to  $1.3\Delta_o$ . Thus,

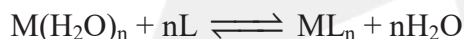
$$\Delta_{sp} = (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_o \text{ and } \Delta_{sp} = 1.3 \Delta_o.$$

### (E) STABILITY OF COORDINATION COMPOUNDS :

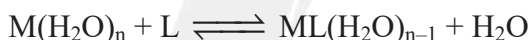
The stability of a coordination compound  $[ML_n]$  is measured in terms of the stability constant (equilibrium constant) given by the expression,

$$\beta_n = [ML_n] / [M(H_2O)_n][L]^n$$

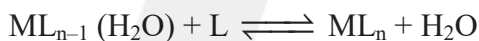
for the overall reaction :



By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant,  $K_1$ ,  $K_2$ ,  $K_3$ , .....  $K_n$  for each step as represented below :



$$K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$$



$$K_n = [ML_n] / \{[ML_{n-1}(H_2O)][L]\}$$



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

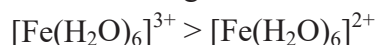
$\beta_n$ , the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing, water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above.

$K_1, K_2, K_3 \dots K_n$  representing the stepwise stability (or formation) constants.

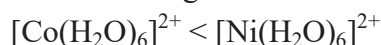
The above is thermodynamic stability criteria, there can be another kind of stability called kinetic stability, which measures the rate of ligand replacement.

**(F) FACTORS INFLUENCING THE MAGNITUDE OF C.F.S.E. :**

**(a) Different charges on the cation of the same metal :** The cation with a higher oxidation state has a larger value of CFSE than that with lower oxidation state e.g.,



**(b) Same charges on the cation but the number of d-electrons are different:** The metal cation the magnitude of CFSE with the increase of the number of d-electrons, e.g.,



**(c) Quantum number (n) of the d-orbitals of the central metal ion :** As 'n' increase CFSE increases.

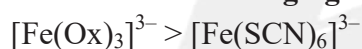


**(d) Types of Hybridisation :**  $\Delta_t = \frac{4}{9} \Delta_o$

The order of CFSE :-

$$\Delta_{\text{sq}} > \Delta_o > \Delta_t$$

**(e) Presence of chelating ligand increases CFSE :**



**DO YOUR SELF – 5**

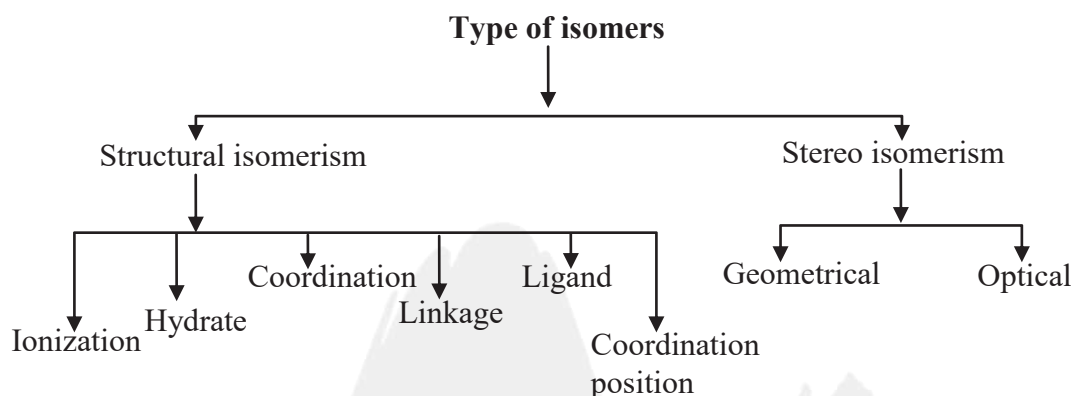
- Among the following ions, which one has the highest paramagnetism?  
(A)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (B)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (C)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
- Which of the following complex involves  $d^2sp^3$  hybridisation?  
(A)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (B)  $[\text{CoF}_6]^{3-}$  (C)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
- In Ziese's salt C = C bond length is :  
Note :  $\begin{cases} \text{C}-\text{C} \text{ both length in ethane is } 1.54 \text{ \AA} \\ \text{C}=\text{C} \text{ both length in ethene is } 1.34 \text{ \AA} \\ \text{C}\equiv\text{C} \text{ both length in ethyne is } 1.20 \text{ \AA} \end{cases}$   
(A) 1.37 Å (B) 1.19 Å (C) 1.87 Å (D) 1.34 Å
- The ligand that shows synergic effect is :  
(A)  $\text{H}_2\text{O}$  (B)  $\text{NH}_3$  (C) CO (D)  $\text{C}_5\text{H}_5\text{N}$
- All the metal ions contains  $t_{2g}^6 e_g^0$  configurations. Which of the following complex will be paramagnetic?  
(A)  $[\text{FeCl}(\text{CN})_4(\text{O}_2)]^{4-}$  (B)  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
(C)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (D)  $[\text{Fe}(\text{CN})_5(\text{O}_2)]^{-5}$



## ☞ ISOMERISM IN COMPLEXES

- (a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as Isomers.
- (b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

## • CLASSIFICATION OF ISOMERISM



## (A) Structural isomerism

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

## (a) Ionisation isomerism

The type of isomerism which is due to the exchange of groups or ions between the coordination sphere and the ionisation sphere.

## Example:

- (i)  $\text{Co}(\text{NH}_3)_4 \text{Br}_2 \text{SO}_4$  can be represented as  $[\text{Co}(\text{NH}_3)_4 \text{Br}_2] \text{SO}_4$  (red violet) and  $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] \text{Br}_2$  (red)  
These complexes give sulphate ion and bromide ion respectively
- (ii)  $[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2] \text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4 \text{Br}_2] \text{Cl}_2$
- (iii)  $[\text{Co}(\text{NH}_3)_4 (\text{NO}_3)_2] \text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] (\text{NO}_3)_2$

## (b) Hydrate isomerism:

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

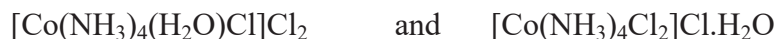
## Example:

$\text{Cr}(\text{H}_2\text{O})_6 \text{Cl}_3$  has four possible structures

- (i)  $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$  violet                      (ii)  $[\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$  green
- (iii)  $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$  dark green.      (iv)  $[\text{Cr}(\text{H}_2\text{O})_3 \text{Cl}_3] \cdot 3\text{H}_2\text{O}$  dark green.



These complexes differ from one another with respect to the number of water molecules acting as ligands. Other hydrate isomers are



**(c) Linkage isomerism**

- (i) This type of isomerism arises due to presence of ambidentate ligands like  $\text{NO}_2^-$ ,  $\text{CN}^-$  and  $\text{SCN}^-$
- (ii) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.
- (iii) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

**Example :**

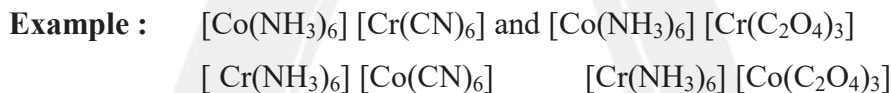


In  $\text{NO}_2^-$  ligand, The coordinating sites are nitrogen i.e.,  $\text{NO}_2^-$  (Nitro) or through oxygen i.e.  $\text{ONO}^-$  (Nitrito)

The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

**(d) Coordination isomerism**

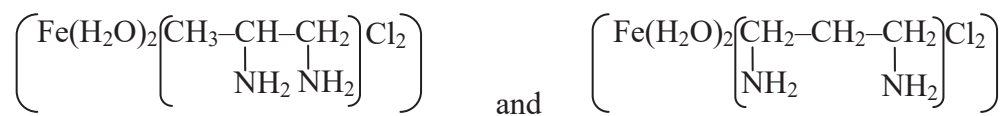
- (i) This type of isomerism is exhibited when the complex has two complex ions in it -'cationic and anionic'.
- (ii) This type of isomerism is caused by the interchange of ligands between the two complex ions of the same complex.



**(e) Ligand isomerism**

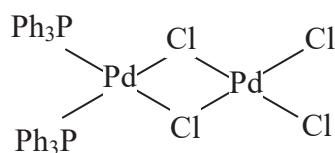
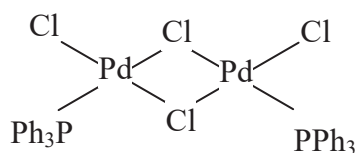
- (i) Ligands with  $\text{C}_3\text{H}_6(\text{NH}_2)_2$  have two different structures i.e. 1, 3-diamino propane and 1, 2-diaminopropane(propylene diamine).
- (ii) Those complexes which have same molecular formula, but differ with respect to their ligands are called as Ligand isomers.

**Example :**  $[\text{Fe}(\text{H}_2\text{O})_2 \text{C}_3\text{H}_6(\text{NH}_2)_2\text{Cl}_2]$  has two different structures



**(f) Co-ordination position isomerisation:**

It is shown by polynuclear complexes, due interchange of ligands between the different metal nuclei.

**(g) Polymerization Isomerism:**

This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights.

**Example.**  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

$[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$

**Illustration :** Select correct code about complex  $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$

(I) IUPAC name of the compound is Pentaamminenitrito-N-chromium(III) tetrachloridozincate (II)

(II) It shows geometrical isomerism

(III) It shows linkage isomerism

(IV) It shows co-ordination isomerism

(A) III, IV

(B) I, III & IV

(C) II, III & IV

(D) I, II, III & IV

**Ans. (B)**

**Sol. (I)**  $[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$

IUPAC name of this compound is Pentaamminenitrito-N-chromium(III) tetrachloridozincate(II)

**(III)** It shows linkage isomerism due to presence of ambidentate ligands

$[\text{Cr}(\text{NO}_2)(\text{NH}_3)_5][\text{ZnCl}_4]$

$[\text{Cr}(\text{ONO})(\text{NH}_3)_5][\text{ZnCl}_4]$

**(IV)** Because both complex ions have different ligands

**(B) Stereo isomerism**

They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion. The two stereo isomers which are possible Geometrical and Optical.

**(a) Geometrical isomerism**

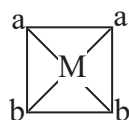
**(i)** The ligands occupy different positions around the central metal ion.

**(ii)** When two identical ligands are co-ordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).

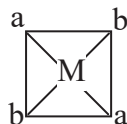
**(iii)** If the two identical ligands are co-ordinated to the metal ion from opposite side then it is **trans isomer** (in Latin, trans means across).

**Geometrical isomers with co-ordination number = 4 (Square planar complexes)**

- (i) Complexes with general formula,  $\text{Ma}_2\text{b}_2$  (where both a and b are monodentate) can have cis-and trans isomers.

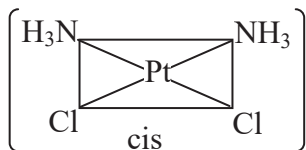


Cis-isomer

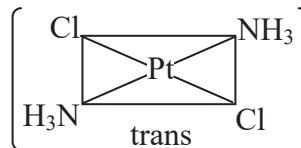


trans-isomer

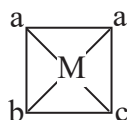
**Example :**  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$



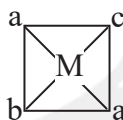
(cis-platin) anti cancer



- (ii) Complexes with general formula  $\text{Ma}_2\text{b}_2\text{c}$  can have cis – and trans-isomers.

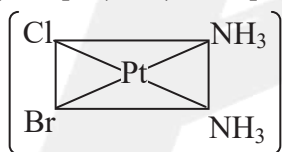


cis

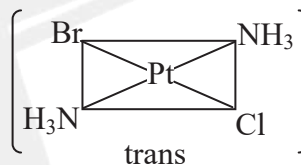


trans

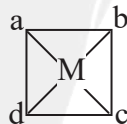
**Example :**  $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]$



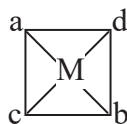
(cis-platin) anti cancer agent



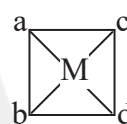
- (iii) Complexes with general formula  $\text{Mabcd}$  can have cis – and trans-isomers.



(i)



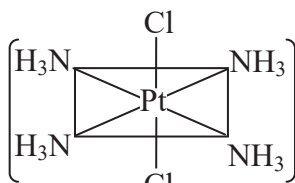
(ii)



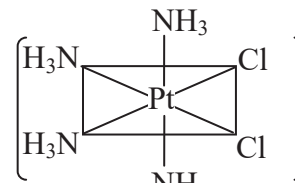
(iii)

**Geometrical isomers with co-ordination number = 6**

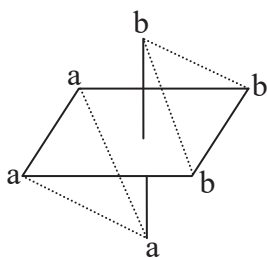
**Example:**  $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]$



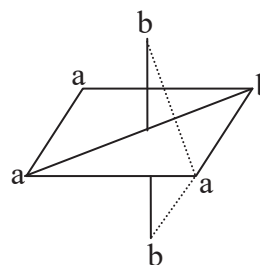
trans



cis

(vi) Facial and Meridional isomerism ( $\text{Ma}_3\text{b}_3$ )

Facial (fac)

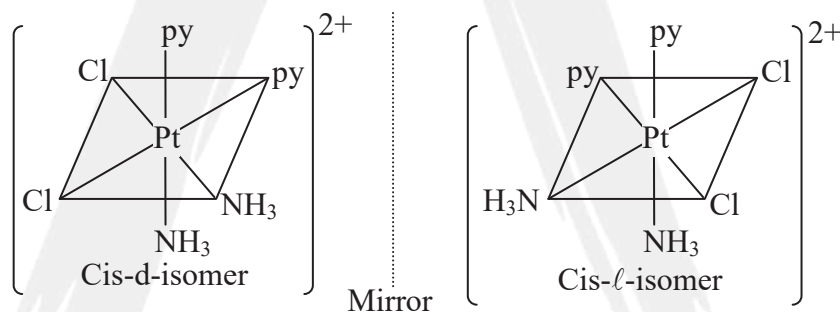
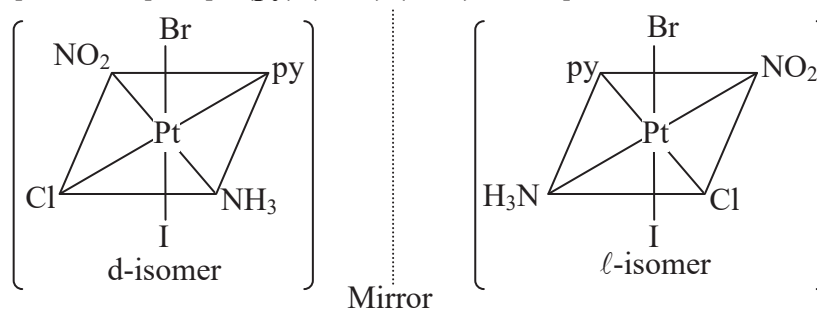


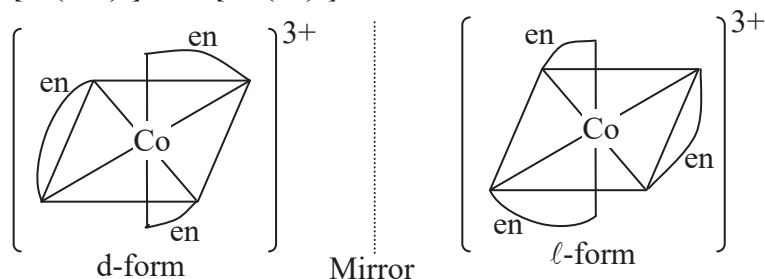
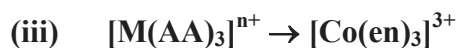
Meridional (Mer)

## (b) Optical isomers

- (i) Optically active complexes are those which are nonsuperimposable over the mirror image structure.
- (ii) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.
- (iii) The complex which rotates plane polarised light to left hand side is **laevo rotatory** i.e. ' $\ell$ ' or ' $-$ ' and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory** ' $d$ ' or ' $+$ '.
- (iv) Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.
- (v) The ' $d$ ' and ' $\ell$ ' isomers of a compound are called as **Enantiomers or Enantiomorphs**.
- (vi) Optical isomerism is expected in tetrahedral complexes of the type  $\text{Mabcd}$ .

## • Optical isomers with Co-ordination number = 6

(i)  $[\text{Ma}_2\text{b}_2\text{c}_2]^{n+} \rightarrow [\text{Pt}(\text{py})_2(\text{NH}_3)_2\text{Cl}_2]^{2+}$ (ii)  $[\text{Mabcedf}] \rightarrow [\text{Pt}(\text{py})(\text{NH}_3)(\text{NO}_2)\text{ClBrI}]$ 



**NUMBER OF POSSIBLE ISOMERS FOR SPECIFIC COMPLEXES**  
(For coordination number = 6)

Formula	Geometrical Isomers	Cis	Trans	Pairs of Enantiomers	Number of stereoisomers
Ma <sub>6</sub>	—	—	—	—	1
Ma <sub>5</sub> b	—	—	—	—	1
Ma <sub>4</sub> b <sub>2</sub>	2	1	1	—	2
Ma <sub>3</sub> b <sub>3</sub>	2	Fac	Mer	—	2
Ma <sub>4</sub> bc	2	1	1	—	2
Ma <sub>3</sub> b <sub>2</sub> c	3	1	2	—	3
Ma <sub>3</sub> bcd	4	1	3	1	5
Ma <sub>2</sub> b <sub>2</sub> c <sub>2</sub>	5	1	4	1	6
Ma <sub>2</sub> b <sub>2</sub> cd	6	2	4	2	8
Ma <sub>2</sub> bcde	9	6	3	6	15
Mabcdef	15	—	—	15	30
M(AA) <sub>3</sub>	—	—	—	1	2
M(AA) <sub>2</sub> b <sub>2</sub>	2	1	1	1	3
M(AA) <sub>2</sub> bc	2	1	1	1	3
M(AA)b <sub>4</sub>	—	—	—	—	1
M(AA)b <sub>3</sub> c	2	1	1	—	2
M(AA)b <sub>2</sub> c <sub>2</sub>	3	1	2	1	4
M(AA)b <sub>2</sub> cd	4	2	2	2	6
M(AA)bcde	6	—	—	6	12
M(AB) <sub>3</sub>	2	1	1	2	4

$M(AB)_2c_2$	5	1	4	3	8
$M(AB)_2cd$	6	2	4	5	11
$M(AB)c_4$	—	—	—	—	1
$M(AB)c_3d$	3	1	2	1	4
$M(AB)c_2d_2$	4	2	2	2	6
$M(AB)c_2de$	7	4	3	5	12
$M(AB)cdef$	12	—	—	12	24
$M(AA)(BC)de$	5	—	—	5	10
$M(AB)(CD)ef$	10	—	—	10	20

**NUMBER OF POSSIBLE ISOMERS FOR SPECIFIC SQUARE PLANAR COMPLEXES**  
(For coordination number = 4)

Formula	Geometrical Isomers	Cis	Trans	Number of stereoisomers
$Ma_4$	—	—	—	1
$Ma_3b$	—	—	—	1
$Ma_2b_2$	2	1	1	2
$Ma_2bc$	2	1	1	2
$Mabcd$	3	—	—	3
$M(AA)_2$	—	—	—	1
$M(AA)b_2$	—	—	—	1
$M(AA)bc$	—	—	—	1
$M(AB)_2$	2	1	1	2
$M(AB)c_2$	—	—	—	1
$M(AB)cd$	2	—	—	2

**Note :** Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.

(AA) → Symmetrical bidentate ligand

(AB)/(BC)/(CD) → unsymmetrical bidentate ligand

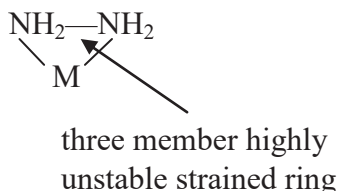
## DO YOUR SELF – 6

1. Which of the following complexes shows ionization isomerism?  
(A)  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$     (B)  $[\text{Cr}(\text{en})_2]\text{Cl}_2$     (C)  $[\text{Cr}(\text{en})_3]\text{Cl}_3$     (D)  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
2. The complex  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  are called  
(A) ionisation isomer    (B) linkage isomers  
(C) coordination isomer    (D) geometrical isomer
3. The two compounds pentaamminesulphatocobalt (III) bromide and pentaamminesulphatocobalt (III) chloride represent:  
(A) Linkage isomerism    (B) Ionization isomerism  
(C) Coordination isomerism    (D) No isomerism
4. Geometrical isomerism is found in coordination compounds having coordination number:  
(A) 2    (B) 3    (C) 4 (tetrahedral)    (D) 6
5. Geometrical isomerism can be shown by:  
(A)  $[\text{Ag}(\text{NH}_3)(\text{CN})]$     (B)  $\text{Na}_2[\text{Cd}(\text{NO}_2)_4]$   
(C)  $[\text{PtCl}_4\text{I}_2]$     (D)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Au}(\text{CN})_4]$

## SOLVED EXAMPLES

1.  $\text{NH}_2\text{NH}_2$ , although possesses two electron pair for donation but not acts as chelating agent. Why?

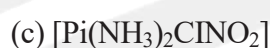
**Sol.** The co-ordinating by  $\text{NH}_2\text{NH}_2$ , leads to a three member highly unstable strained ring and thus it does not acts as chelating agent.



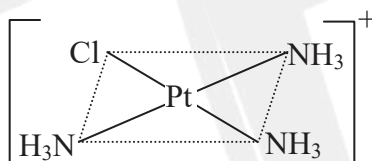
2. Square planar complexes with co-ordination number four exhibit geometrical isomerism whereas tetrahedral complexes do not. Why ?

**Sol.** In tetrahedral complexes, the relative position of atoms with respect to each other is same thus these do not show geometrical isomerism. Square planar complexes show cis, trans isomerism.

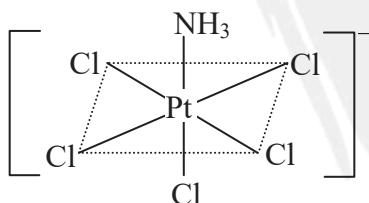
3. Platinum (II) forms square planar complexes and plant inum (IV) gives octahedral complexes. How many geometrical isomers are possible for each of the following complexes ? Describe their structures -



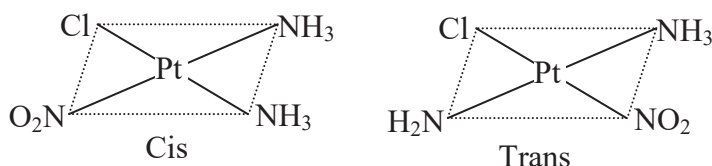
**Sol.** (a) Square planar complex of the type  $\text{Ma}_3\text{b}$  shows no isomerism.



(b) an octahedral complex of the type  $\text{Ma}_5\text{b}$  shows no isomerism.

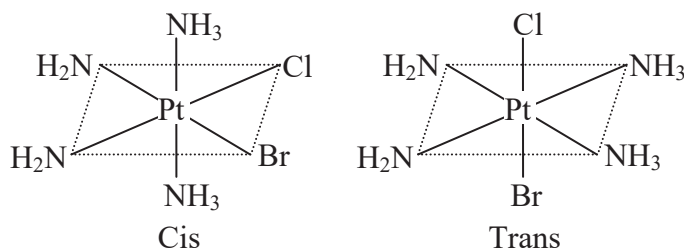


(c) A square planar complex of the type  $\text{Ma}_2\text{b}_2$  exists as cis the trans isomers



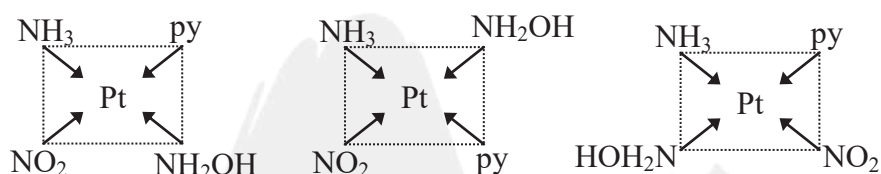


(d) An octahedral complex of the type  $Ma_4bc$  shows cis and trans isomerism.



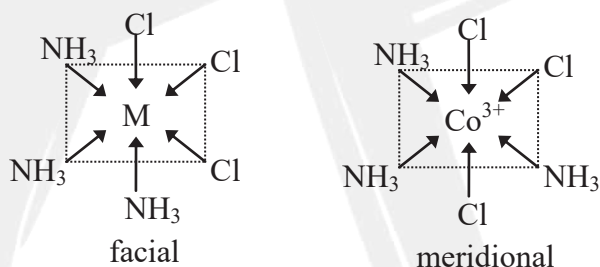
4. How many geometrical isomers with formula  $[MABCD]$  e.g.,  $[Pt(NH_3)py(NH_2OH)NO_2]^+$  are possible?

Sol. Three isomers



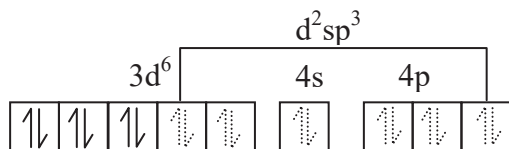
5. What are facial and meridional isomers? Explain with examples.

Sol. For the complexes of the type  $[Ma_3b_3]$  e.g.,  $[Co(NH_3)_3Cl_3]$  and  $[Rh(py)_3Cl_3]$ ; the isomer is called facial (fee) when all similar ligands occupy same face of an octahedron as shown below. When all similar ligands are not on the same face then isomer is called meridional (mer).



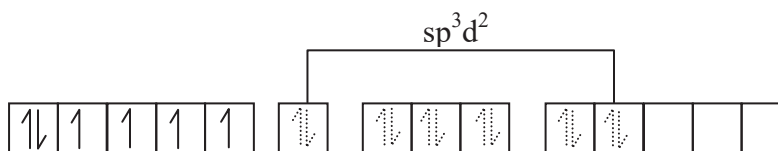
6.  $[Fe(CN)_6]^{4-}$  is diamagnetic while  $[FeF_6]^{4-}$  is strongly paramagnetic. Why?

Sol.  $CN^-$  is strong field ligand and so it pairs up the electrons leading to the formation of low spin complex which is diamagnetic.



Octahedral, diamagnetic complex

$F^-$  is weak field ligand so it forms high spin paramagnetic complex.

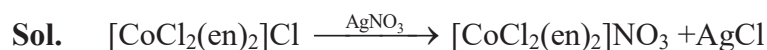


Octahedral, paramagnetic complex

7. If excess of  $\text{AgNO}_3$  solution is added to 100 mL of a 0.024 M solution of dichlorobis (ethylene diamine) cobalt (III) chloride, how many mol of  $\text{AgCl}$  be precipitated:

(A) 0.0012                      (B) 0.0016                      (C) 0.0024                      (D) 0.0048

**Ans.** (C)



Mole of  $[\text{CoCl}_2(\text{en})_2]\text{Cl} = \text{molarity} \times v(\text{Lt.})$

0.0024 mole of  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  gives

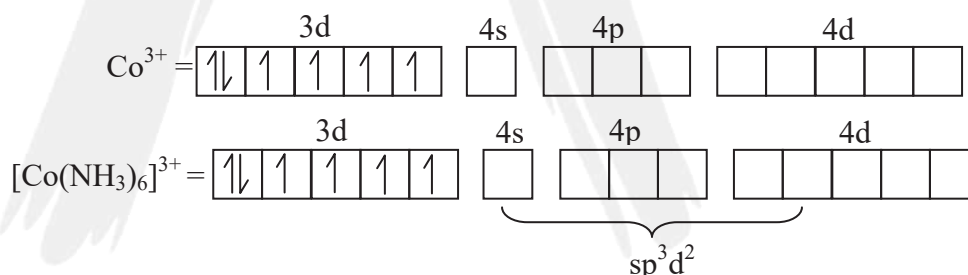
$$\frac{100}{1000} \times 0.024 = 0.0024 \text{ mole of } \text{Cl}^-$$

Which precipitate 0.0024 mole of  $\text{AgNO}_3$  because 1 mole  $\text{Ag}^+$  required 1 mole  $\text{Cl}^-$  to precipitate

8. Find out the hybridization, geometry and magnetic moment of the complexes:

(i)  $[\text{Co}(\text{NH}_3)_6]^{3+}$                       (ii)  $[\text{Cr}(\text{CN})_6]^{3-}$

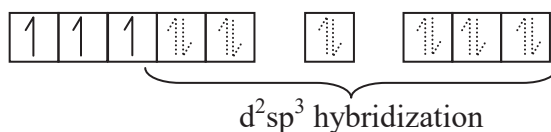
**Sol.** (i) The oxidation state of cobalt in the complex is +3. The electronic configuration of  $\text{Co}^{3+}$  ions is



(ii) The oxidation state of chromium in the complex is +3. The electronic configuration of  $\text{Cr}^{3+}$  ion is



$\text{Cr}^{3+}$  in  $d^2sp^3$  hybridized state



$$\text{Octahedral, magnetic moment} = \sqrt{3 \times (3 + 2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

9. The magnetic moment of  $[\text{MnCl}_4]^{2-}$  is 5.92 B.M. On the basis of its magnetic moment, write configuration of  $\text{Mn}^{2+}$  in this complex.

**Sol.** For an atom/ion

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

(n = No. of unpaired electrons)

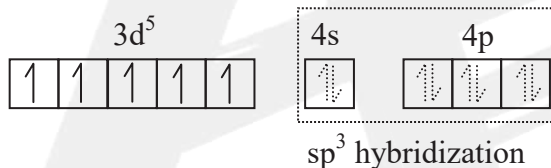
Given that  $\mu = 5.92 \text{ B.M.}$

$$\therefore 5.92 = \sqrt{n(n+2)}$$

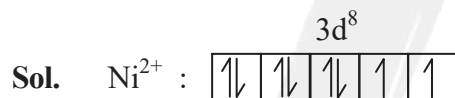
or  $n = 5$

Thus in this complex Mn contains five unpaired electrons and so its possible configuration may be  $\text{Mn}^{2+}$  in  $[\text{MnCl}_4]^{2-} = [\text{Ar}]3d^5 4s^0$

so hybridisation of  $\text{Mn}^{2+}$  in the given complex must be  $sp^3$ .



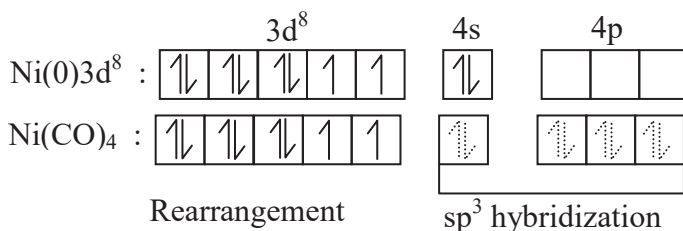
10. All the octahedral complexes of  $\text{Ni}^{2+}$  are outer orbital complexes, why?



Thus only one vacant 3d-orbital is available after pairing up of electrons due to strong field ligand. Therefore,  $d^2sp^3$  hybridisation is not possible. Only  $sp^3d^2$  is possible which represents outer complex.

11.  $\text{Ni}(\text{CO})_4$  possesses tetrahedral geometry while  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar, why?

**Sol.** In the formation of  $\text{Ni}(\text{CO})_4$ , nickel undergoes  $sp^3$  hybridization, hence it is tetrahedral in shape.



12. Consider the following complexes-

- (i)  $K_2PtCl_6$                       (ii)  $PtCl_4 \cdot 2NH_3$                       (iii)  $PtCl_4 \cdot 3NH_3$                       (iv)  $PtCl_4 \cdot 5NH_3$

Their electrical conductance's in aq. solutions are -

- (A) 256.0.97.404                      (B) 404. 0.97, 256                      (C) 256.97.0,404                      (D) 404. 97. 256.0

**Sol.** (A) Coordination number of Pt is 6 hence

I         $K_2[PtCl_6]$         – Three ions

II        $[Pt(NH_3)_2Cl_4]$  – Zero ions

III       $[Pt(NH_3)_3Cl_3]Cl$  – Two ions

IV       $[Pt(NH_3)_5Cl]Cl_3$  – Four ions

Conductivity  $\propto$  no. of ions

13. Determine the oxidation state of metal in the complex ion,  $[PtCl_6]^{2-}$

**Sol.** Charge on the complex ion = Oxidation state of metal + charge on ligands

$$-2 = x + 6 \times (-1) \text{ or } x = +4$$

The oxidation of Pt in the complex ion is +4.

14. The pair in which both species have same magnetic moment (spin only value) is-

- (A)  $[Cr(H_2O)_6]^{2+}$ ,  $[CoCl_4]^{2-}$                       (B)  $[Cr(H_2O)_6]^{2+}$ ,  $[Fe(H_2O)_6]^{2+}$   
(C)  $[Mn(H_2O)_6]^{2+}$ ,  $[Cr(H_2O)_6]^{2+}$                       (D)  $[CoCl_4]^{2-}$ ,  $[Fe(H_2O)_6]^{2+}$

**Ans.** (B)

**Sol.** Same magnetic moment – same number of unpaired electrons =  $\sqrt{n(n+2)}$

where n = number of unpaired electrons

$$Co^{2+} = 3d^7, 3 \text{ unpaired electrons}$$

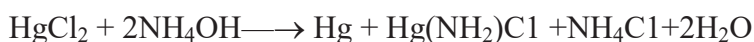
$$Cr^{2+} = 3d^4, 4 \text{ unpaired electrons}$$

$$Mn^{2+} = 3d^5, 5 \text{ unpaired electrons}$$

$$Fe^{2+} = 3d^6, 4 \text{ unpaired electrons}$$

15. The colour of  $Hg_2Cl_2$  changes from white to black when treated with  $NH_3$ . Why ?

**Sol.**  $Hg_2Cl_2$  reacts with  $NH_4OH$ , to give black complex.



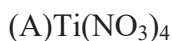
(Black)

16. Write the formula of the following complexes.

- (i) Pentamminechlorocobalt (III) ion                      (ii) Lithium tetrahydridoaluminate (III)

**Sol.** (i)  $[Co(NH_3)_5Cl]^{2+}$ ;                      (ii)  $Li[AlH_4]$

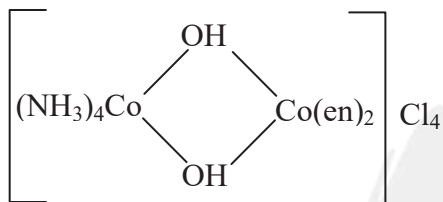
17. Identify the complexes which are expected to be coloured and explain.



Ans. (C) and (D)

Sol. Are coloured because  $\text{Cr}^{3+}$  in  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $\text{V}^{3+}$  in  $[\text{VF}_6]^{3-}$  have  $3d^3$  and  $3d^2$  configuration respectively and thus show 'd-d' transition.

18. Write the IUPAC name of the given compound.



Sol. Tetraamine cobalt (III) di- $\mu$ -hydroxo bis ethylenediamine cobalt (III) chloride.

19. Explain the following with appropriate reasons:

$[\text{Fe}(\text{CN})_6]^{3-}$  ion has magnetic moment 1.73 BM, while  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has a magnetic moment 5.92 B.M.

Sol.  $1.73 = \sqrt{n(n+2)}$

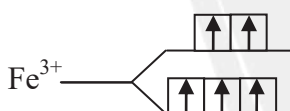
$n = 1$



Due to strong field ligands ( $\text{CN}^-$ )

$5.92 = \sqrt{n(n+2)}$

$n = 5$



(Due to weak ligands ( $\text{H}_2\text{O}$ ))

## EXERCISE-1

General Problems on Coordination Chemistry

- For the complex  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$ , the oxidation number of Cr is .....and the coordination number of Cr is .....  
 (A) +3, 6                      (B) +3, 4                      (C) +2, 6                      (D) +2, 4
- Consider the complex ion  $[\text{Cr}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2]^-$ . What is the  
 (i) oxidation number of the metal atom.  
 (ii) coordination number of the metal atom.  
 (iii) charge on the complex if all ligands were chloride ions ?  

	(i)	(ii)	(iii)
(A)	-1	6	-3
(B)	+3	6	-3
(C)	+3	6	-1
(D)	-1	5	-3
- Some salts although containing two different metallic elements give test for one of them in solution. Such salts are  
 (A) complex salt              (B) double salt              (C) normal salt              (D) none of these
- Which of the following forms with an excess of  $\text{CN}^-$ , a complex having coordination number two ?  
 (A)  $\text{Cu}^{2+}$                       (B)  $\text{Ag}^+$                       (C)  $\text{Ni}^{2+}$                       (D)  $\text{Fe}^{2+}$
- Aqueous solution of  $\text{FeSO}_4$  gives tests for both  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$  but after addition of excess of KCN, solution ceases to give test for  $\text{Fe}^{2+}$ . This is due to the formation of  
 (A) the double salt  $\text{FeSO}_4 \cdot 2\text{KCN} \cdot 6\text{H}_2\text{O}$   
 (B)  $\text{Fe}(\text{CN})_3$   
 (C) the complex ion  $[\text{Fe}(\text{CN})_6]^{4-}$   
 (D) the complex ion  $[\text{Fe}(\text{CN})_6]^{3-}$
- Which one of the following species does not represent cationic species of vanadium formed in aqueous solution  
 (A)  $\text{VO}_2^+$                       (B)  $\text{VO}^{2+}$                       (C)  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$                       (D)  $\text{VO}_2^{2+}$

**Ligands**

7. The correct name of,  $[\text{Ni}(\text{DMG})_2]$  a rosy red precipitate is  
 (A) bis (dimethyl glyoximato) nickel (II) (B) bis (dimethyl glyoximato) nickelate (II)  
 (C) bis (dimethyl glyoxime) nickel (II) (D) bis (dimethyl glyoxime) nickelate (II)
8. How many  $\text{EDTA}^{4-}$  molecules are required to make an octahedral complex with a  $\text{Ca}^{2+}$  ion ?  
 (A) Six (B) Three (C) One (D) Two
9. Diethylene triamine is:  
 (A) Chelating agent (B) Polydentate ligand  
 (C) Tridentate ligand (D) All of these
10. Which of the following has five donor (coordinating) sites?  
 (A) Triethylene tetramine (B) Ethylenediamine tetracetate ion  
 (C) Ethylenediamine triacetate ion (D) Diethylene triamine
11. Which of the following species is not expected to be a ligand  
 (A)  $\text{NO}^+$  (B)  $\text{NH}_4^+$  (C)  $\text{NH}_2^- + \text{NH}_3^+$  (D) CO
12. The number of donor sites in dimethyl glyoxime, glycinate, diethylene triamine and EDTA are respectively:  
 (A) 2, 2, 3 and 4 (B) 2, 2, 3 and 6 (C) 2, 2, 2 and 6 (D) 2, 3, 3 and 6
13. The disodium salt of ethylene diamine tetracetic acid can be used to estimate the following ion(s) in the aqueous solution  
 (A)  $\text{Mg}^{2+}$  ion (B)  $\text{Ca}^{2+}$  ion (C)  $\text{Na}^+$  ion (D) both  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$

**Synergic Bonding**

14. Which of the following ligands is called  $\pi$ -acceptors ?  
 CO CN<sup>-</sup> NO<sup>+</sup>  
 (I) (II) (III)  
 (A) I, II, III only correct. (B) I, II only correct  
 (C) II, III only correct (D) III only correct
15. In  $\text{Fe}(\text{CO})_5$ , the Fe-C bond possesses :  
 (A)  $\pi$  character only (B)  $\sigma$  character only  
 (C) ionic character only (D) both  $\pi$  and  $\sigma$  characters



16.  $\pi$ -bonding is not involved in:  
 (A) ferrocene (B) dibenzene chromium  
 (C) Zeise's salt (D) Grignard reagent
17. Which of the following is not considered as an organometallic compound ?  
 (A) Ferrocene (B) Cis-platin (C) Ziese's salt (D) Grignard reagent
18. Formula of ferrocene is:  
 (A)  $[\text{Fe}(\text{CN})_6]^{4-}$  (B)  $[\text{Fe}(\text{CN})_6]^{3+}$  (C)  $[\text{Fe}(\text{CO})_5]$  (D)  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$
19. Which of the following is  $\pi$  complex:  
 (A) Trimethyl aluminium (B) Ferrocene  
 (C) Diethyl zinc (D) Nickel carbonyl
20. In the isoelectronic series of metal carbonyl, the C–O bond strength is expected to increase in the order.  
 (A)  $[\text{Mn}(\text{CO})_6]^+ < [\text{Cr}(\text{CO})_6] < [\text{V}(\text{CO})_6]^-$  (B)  $[\text{V}(\text{CO})_6]^- < [\text{Cr}(\text{CO})_6] < [\text{Mn}(\text{CO})_6]^+$   
 (C)  $[\text{V}(\text{CO})_6]^- < [\text{Mn}(\text{CO})_6]^+ < [\text{Cr}(\text{CO})_6]$  (D)  $[\text{Cr}(\text{CO})_6] < [\text{Mn}(\text{CO})_6]^+ < [\text{V}(\text{CO})_6]^-$

### Effective Atomic Number (EAN)

21. Each of the following obey Sidgwick effective atomic number rule except  
 (A)  $[\text{Cr}(\text{CO})_6]$  (B)  $[\text{Co}(\text{NH}_3)_6]^{3+}$   
 (C)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  (D)  $[\text{PtCl}_6]^{2-}$
22. Effective atomic number of  $\text{Co}(\text{CO})_4$  is 35, hence it is less stable. It attains stability by  
 (A) Oxidation of Co (B) Reduction of Co  
 (C) Dimerization (D) Both (B) & (C)
23. In the complex  $\text{Fe}(\text{CO})_x$ , the value of x is:  
 (A) 3 (B) 4 (C) 5 (D) 6
24. The EAN of platinum in potassium hexachloroplatinate (IV) is:  
 (A) 46 (B) 86 (C) 36 (D) 84
25. The EAN of metal atoms in  $\text{Fe}(\text{CO})_2(\text{NO})_2$  and  $\text{Co}_2(\text{CO})_8$  respectively are  
 (A) 34, 35 (B) 34, 36 (C) 36, 36 (D) 36, 35

Werner's Theory

26. Consider the following statements:

According to the Werner's theory.

- (a) Ligands are connected to the metal ions by covalent bonds.
- (b) Secondary valencies have directional properties
- (c) Secondary valencies are non-ionisable

Of these statements:

- (A) a, b and c are correct
- (B) b and c are correct
- (C) a and c are correct
- (D) a and b are correct

27. A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is:

- (A)  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_4$
- (B)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$
- (C)  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$
- (D)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$

28. Which one is the most likely structure of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  if  $1/3$  of total chlorine of the compound is precipitated by adding  $\text{AgNO}_3$  to its aqueous solution:

- (A)  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
- (B)  $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot (\text{H}_2\text{O})_3$
- (C)  $[\text{CrCl}_2(\text{H}_2\text{O})_4] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$
- (D)  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$

29. The molar ionic conductances of the octahedral complexes.

- (I)  $\text{PtCl}_4 \cdot 5\text{NH}_3$       (II)  $\text{PtCl}_4 \cdot 4\text{NH}_3$       (III)  $\text{PtCl}_4 \cdot 3\text{NH}_3$       (IV)  $\text{PtCl}_4 \cdot 2\text{NH}_3$
- (A)  $\text{I} < \text{II} < \text{III} < \text{IV}$
- (B)  $\text{IV} < \text{III} < \text{II} < \text{I}$
- (C)  $\text{III} < \text{IV} < \text{II} < \text{I}$
- (D)  $\text{IV} < \text{III} < \text{I} < \text{II}$

30. Which of the following complex will NOT conduct electricity ?

- (A)  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- (B)  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$
- (C)  $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$
- (D)  $[\text{Co}(\text{NH}_3)_4]\text{Cl}_2$

31. The formula of a complex with composition  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  giving the following observations:

Number of ions = 3 ; Number of  $\text{Cl}^-$  ions = 2 ; Number of non-ionic Cl = 1 is

- (A)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
- (B)  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- (C)  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$
- (D)  $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$

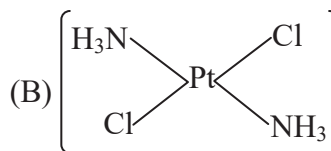
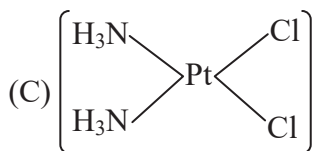
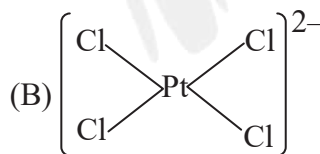
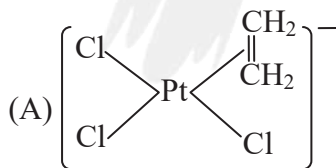
IUPAC

32. The complex ion in the compound  $\text{Cs}[\text{MnF}_4(\text{H}_2\text{O})_2]$  is octahedral and high spin. The name of the compound and the d-orbital splitting diagram is
- (A) Cesium diaquatetrafluoridomanganese (III)  $\begin{array}{c} \uparrow \\ \text{---} \\ \uparrow \uparrow \uparrow \end{array}$
- (B) Cesium diaquatetrafluoridomanganate (III)  $\begin{array}{c} \uparrow \\ \text{---} \\ \uparrow \uparrow \uparrow \end{array}$
- (C) Cesium diaquatetrafluoridomanganate (III)  $\begin{array}{c} \text{---} \text{---} \\ \uparrow \downarrow \uparrow \uparrow \end{array}$
- (D) Cesium diaquatetrafluoridomanganate (IV)  $\begin{array}{c} \text{---} \text{---} \\ \uparrow \downarrow \uparrow \uparrow \end{array}$
33. The IUPAC name of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is:
- (A) Potassium hexacyanido ferrate (II) (B) Potassium hexacyanido ferrate (4-)  
(C) Tetrapotassium hexacyanido ferrate (D) All are correct
34. Trioxalato aluminate (III) and tetrafluoro-borate (III) ions are respectively
- (A)  $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ ,  $[\text{BF}_4]^{3-}$  (B)  $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3+}$ ,  $[\text{BF}_4]^{3+}$   
(C)  $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ ,  $[\text{BF}_4]^-$  (D)  $[\text{Al}(\text{C}_2\text{O}_4)_3]^{2-}$ ,  $[\text{BF}_4]^{2-}$
35. The IUPAC name of the red coloured complex  $[\text{Fe}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2]$  obtained from the reaction of  $\text{Fe}^{2+}$  and dimethyl glyoxime
- (A) bis (dimethyl glyoxime) ferrate (II)  
(B) bis (dimethyl glyoximato) iron (II)  
(C) bis (2, 3-butanediol dioximato) iron (II)  
(D) bis (2, 3-butanedione dioximato) iron (II)
36. The IUPAC name for the coordination compound  $\text{Ba}[\text{BrF}_4]_2$  is
- (A) Barium tetrafluorobromate (V) (B) Barium tetrafluorobromate (III)  
(C) Barium bis (tetrafluorobromate) (III) (D) none of these
37. The formula of the complex hydridotrimethoxidoborate (III) ion is:
- (A)  $[\text{BH}(\text{OCH}_3)_3]^{2-}$  (B)  $[\text{BH}_2(\text{OCH}_3)_3]^{2-}$   
(C)  $[\text{BH}(\text{OCH}_3)_3]^-$  (D)  $[\text{BH}(\text{OCH}_3)_3]^+$

38. The IUPAC name of the Wilkinson's catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  is  
 (A) Chloridotris(triphenylphosphine)rhodium(I)  
 (B) Chloridotris(triphenylphosphine)rhodium(IV)  
 (C) Chloridotris(triphenylphosphine)rhodium(0)  
 (D) Chloridotris(triphenylphosphine)rhodium(VI)
39. The formula for the compound tris (ethane-1, 2-diamine)cobalt (III) sulphate is  
 (A)  $[\text{Co}(\text{en})_3]\text{SO}_4$  (B)  $[\text{Co}(\text{SO}_4)_4(\text{en})_3]$  (C)  $[\text{Co}(\text{en})_3](\text{SO}_4)_2$  (D)  $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$

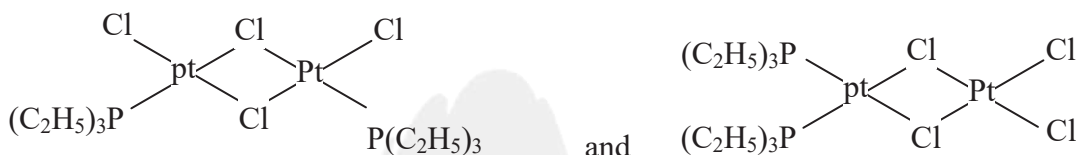
**Isomerism**

40. Coordination compounds  $[\text{Pt}(\text{NH}_3)_3(\text{NCS})]$  and  $[\text{Pt}(\text{NH}_3)_3(\text{SCN})]$  are examples of.....isomerism  
 (A) coordination (B) linkage  
 (C) ionization (D) optical
41. In which of the following pairs both the complexes show optical isomerism ?  
 (A)  $\text{cis}[\text{Cr}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{3-}$ ,  $\text{trans}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$   
 (B)  $[\text{Co}(\text{en})_3]\text{Cl}_3$ ,  $\text{cis}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$   
 (C)  $[\text{PtCl}(\text{dien})]\text{Cl}$ ,  $[\text{NiCl}_2\text{Br}_2]^{2-}$   
 (D)  $[\text{Co}(\text{NO}_3)_3(\text{NH}_3)_3]$ ,  $\text{cis}[\text{Pt}(\text{en})_2\text{Cl}_2]$
42. The type of isomerism present in pentaamminenitrochromium (III) chloride is :  
 (A) optical (B) linkage (C) hydrate (D) polymerisation
43. Which of the following does not have optical isomer ?  
 (A)  $[\text{Co}(\text{en})_3]\text{Cl}_3$  (B)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (C)  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  (D)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$
44. Which of the following is considered to be an anticancer species ?



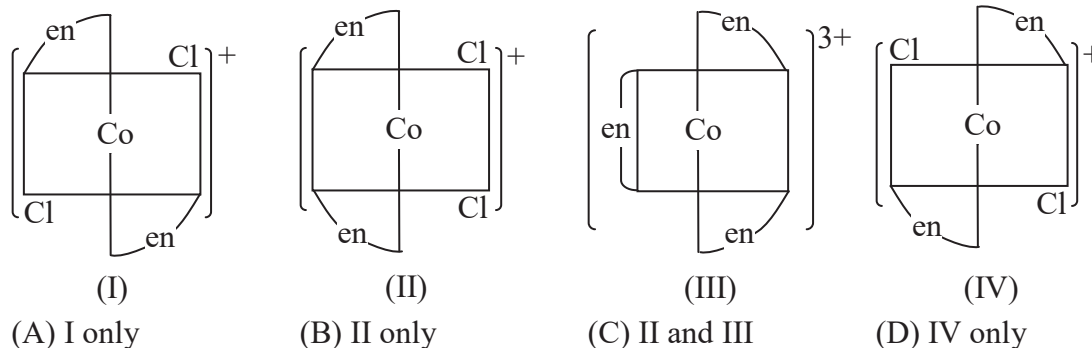
45. Which of the following can exhibit geometrical isomerism ?  
 (A)  $[\text{MnBr}_4]^{2-}$  (B)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$   
 (C)  $[\text{PtCl}_2 \cdot [\text{P}(\text{C}_2\text{H}_5)_3]_2]_2$  (D)  $[\text{Fe}(\text{H}_2\text{O})_5\text{NOS}]^{2+}$
46. Type of isomerism exhibited by  $[\text{Cr}(\text{NCS})(\text{NH}_3)_5][\text{ZnCl}_4]$   
 (A) Coordination isomerism (B) Linkage isomerism  
 (C) Ionization isomerism (D) Both coordination and linkage isomerism

47. The complexes given below show:

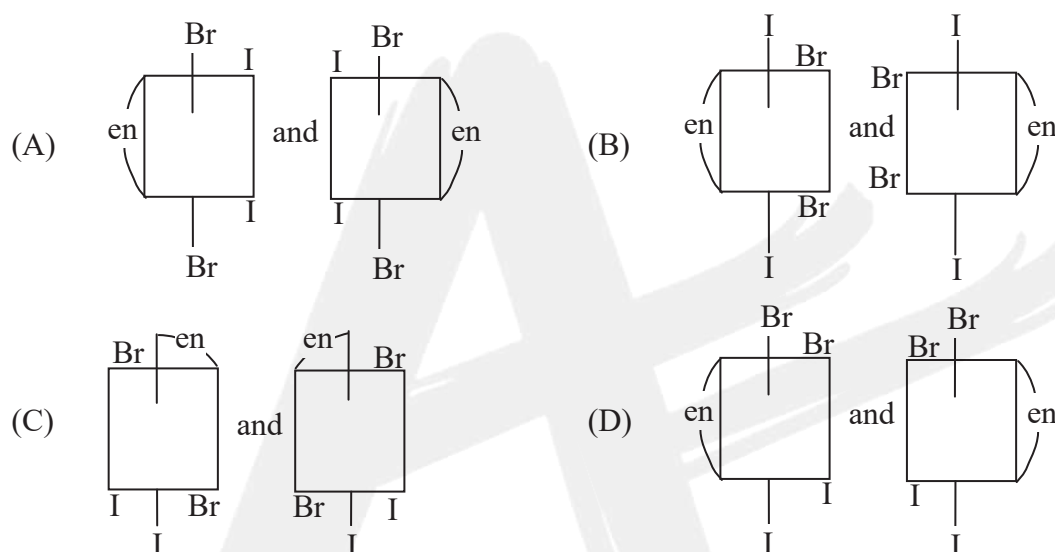


- (A) Optical isomerism (B) Co-ordination isomerism  
 (C) Geometrical isomerism (D) Co-ordination position isomerism
48. The total number of possible isomers of the compound  $[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Pt}^{\text{II}}\text{Cl}_4]$  are:  
 (A) 3 (B) 5 (C) 4 (D) 6
49. Which complex is likely to show optical activity:  
 (A)  $\text{Trans}-[\text{CoCl}_2(\text{NH}_3)_4]^+$  (B)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$   
 (C)  $\text{Cis}-[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$  (D)  $\text{Trans}-[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$
50. The two compounds  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$  and  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$  represent:  
 (A) Linkage isomerism (B) Ionisation isomerism  
 (C) Co-ordination isomerism (D) No isomerism
51. Which of the following statements is correct?  
 (A) Geometrical isomerism is not observed in complexes of C.N.4 having tetrahedral geometry  
 (B) Square planar complexes generally do not show geometrical isomerism  
 (C) The square planar complex of general formulae  $\text{Ma}_3\text{b}$  or  $\text{Mab}_3$  exhibits cis-trans isomerism  
 (D) The platinum glycinate complex,  $[\text{Pt}(\text{Gly})_2]$  does not show geometrical isomerism
52. Geometrical isomerism can be shown by  
 (A)  $[\text{Ag}(\text{CN})(\text{NH}_3)]$  (B)  $\text{Na}_2[\text{Cd}(\text{NO}_2)_4]$  (C)  $[\text{PtCl}_4\text{I}_2]$  (D)  $\text{PtCl}(\text{NH}_3)_3[\text{Au}(\text{CN})_4]$

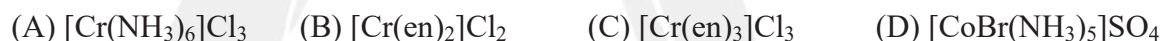
53. Which of the following ions are optically active?



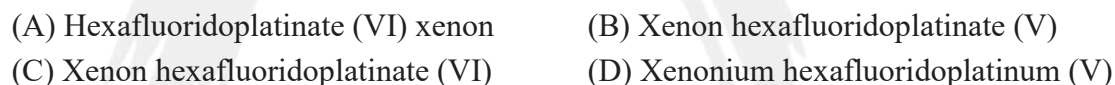
54. The complex ion has two optical isomers. Their correct configurations are :



55. Which of the following complex shows ionization isomerism



56. The IUPAC name of Xe  $[\text{Pt F}_6]$  is



### VBT

57. The complex ion which has no d electrons in the central metal atom is (At No. Cr = 24, Mn = 25, Fe = 26, Co = 27) :



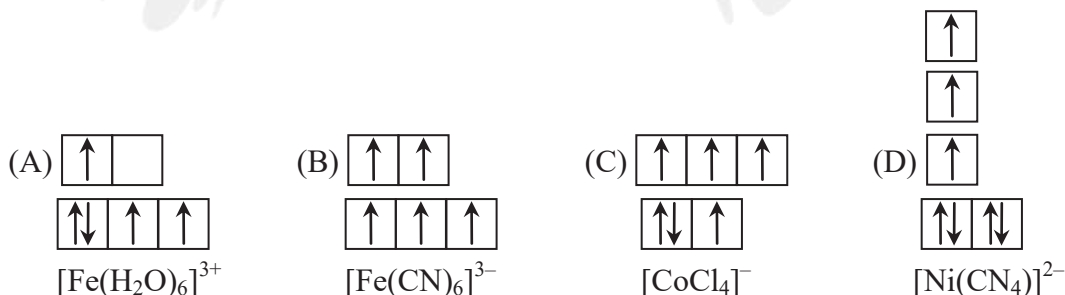
58. The structure of iron pentacarbonyl is:



59.  $\text{Ni}(\text{CO})_4$  and  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  do not differ in  
 (A) magnetic moment (B) oxidation number of Ni  
 (C) geometry (D) EAN
60. For the correct assignment of electronic configuration of a complex, the valence bond theory often requires the measurement of  
 (A) molar conductance (B) optical activity  
 (C) magnetic moment (D) dipole moment
61. A complex of certain metal has the magnetic moment of 4.91 BM whereas another complex of the same metal with same oxidation state has zero magnetic moment. The metal ion could be  
 (A)  $\text{Co}^{2+}$  (B)  $\text{Mn}^{2+}$  (C)  $\text{Fe}^{2+}$  (D)  $\text{Fe}^{3+}$

**CFT**

62. The magnitude of crystal field stabilisation energy in octahedral field depends on  
 I : the nature of the ligand  
 II : the charge on the metal ion  
 III : whether the metal is in the first, second or third row of the transition elements.  
 (A) I, II, III are correct. (B) I, II are correct  
 (C) II, III are correct (D) III is only correct
63. Which of the following statements is correct ?  
 (A)  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  both are paramagnetic complexes.  
 (B)  $[\text{CoF}_6]^{3-}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  both are high spin complexes.  
 (C)  $[\text{CoF}_6]^{3-}$  is octahedral while  $[\text{Co}(\text{NH}_3)_6]^{3+}$  has a pentagonal pyramid shape.  
 (D)  $[\text{CoF}_6]^{3-}$  is outerorbital complex while  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is inner orbital complex.
64. The correct crystal field splitting and electron distribution is





65.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (atomic number of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3d electrons in the chromium present in the complex is:
- (A)  $3d_{xy}^1, 3d_{yz}^1, 3d_{zx}^1$  (B)  $3d_{xy}^1, 3d_{yz}^1, 3d_{z^2}^1$   
 (C)  $3d_{(x^2-y^2)}^1, 3d_{z^2}^1, 3d_{xz}^1$  (D)  $3d_{xy}^1, 3d_{(x^2-y^2)}^1, 3d_{yz}^1$
66. The correct order of magnetic moments is:
- (A)  $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$  (B)  $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$   
 (C)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$  (D)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$
67. Which one of the following complexes is an outer orbital complex?
- (A)  $[\text{Fe}(\text{CN})_6]^{4-}$  (B)  $[\text{Mn}(\text{CN})_6]^{4-}$   
 (C)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (D)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$
68. Assign the hybridization, shape and magnetic moment of  $\text{K}_3[\text{Cu}(\text{CN})_4]$ :
- (A)  $sp^3$ , tetrahedral, 1.73 B.M. (B)  $dsp^2$ , square planar, 1.73 B.M.  
 (C)  $sp^3$ , tetrahedral, diamagnetic (D)  $dsp^2$ , square planar, 2.44 B.M.
69. In which of the following coordination entities, the magnitude of  $\Delta_0$  [CFSE in octahedral field] will be maximum? :
- (A)  $[\text{Co}(\text{CN})_6]^{3-}$  (B)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  (C)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (D)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
70. The number of unpaired electrons calculated in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{CoF}_6]^{3-}$  are :
- (A) 4 and 4 (B) 0 and 2 (C) 2 and 4 (D) 0 and 4
71. The magnetic moment of a salt containing  $\text{Zn}^{2+}$  ion is :
- (A) 0 (B) 1.87 (C) 5.92 (D) 2
72. Geometry, hybridisation and magnetic moment of the ions  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{MnBr}_4]^{2-}$  and  $[\text{FeF}_6]^{4-}$  respectively are :
- (A) tetrahedral, square planar, octahedral :  $sp^3, dsp^2, sp^3d^2$  : 5.9, 0, 4.9  
 (B) tetrahedral, square planar, octahedral :  $dsp^2, sp^3, sp^3d^2$  : 0, 5.9, 4.9  
 (C) square planar, tetrahedral, octahedral :  $dsp^2, sp^3, d^2sp^3$  : 5.9, 4.9, 0  
 (D) square planar, tetrahedral, octahedral :  $dsp^2, sp^3, sp^3d^2$  : 0, 5.9, 4.9

73. Which of the following is not correctly matched?

	Complex ion	CFSE
(A)	$[\text{Co}(\text{NH}_3)_6]^{3+}$	24 Dq
(B)	$[\text{Cr}(\text{NH}_3)_6]^{3+}$	12 Dq
(C)	$[\text{FeF}_6]^{3-}$	4 Dq
(D)	$[\text{Fe}(\text{CN})_6]^{3-}$	20 Dq

74. Which of the following is correctly matched?

(A)	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	Diamagnetic
(B)	$[\text{Ni}(\text{CN})_4]^{2-}$	Para magnetic
(C)	$[\text{MnCl}_4]^{2-}$	Diamagnetic
(D)	$[\text{Fe}(\text{CN})_6]^{4-}$	Diamagnetic

75. Which ion has tetrahedral geometry:

(A) $[\text{Fe}(\text{CO})_5]$	(B) $[\text{Co}(\text{NH}_3)_6]^{2+}$	(C) $[\text{NiCl}_4]^{2-}$	(D) $[\text{Ni}(\text{CN})_4]^{2-}$
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76. An ion  $\text{M}^{2+}$ , forms the complexes  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{M}(\text{en})_3]^{2+}$  and  $[\text{MBr}_6]^{4-}$ , match the complex with the appropriate colour.

(A) Green, blue and red	(B) Blue, red and green
(C) Green, red and blue	(D) Red, blue and green

77. Among  $\text{TiF}_6^{2-}$ ,  $\text{CoF}_6^{3-}$ ,  $\text{Cu}_2\text{Cl}_2$  and  $[\text{NiCl}_4]^{2-}$  the colourless species are:

(A) $\text{CoF}_6^{3-}$ and $[\text{NiCl}_4]^{2-}$	(B) $\text{TiF}_6^{2-}$ and $\text{CoF}_6^{3-}$
(C) $[\text{NiCl}_4]^{2-}$ and $\text{Cu}_2\text{Cl}_2$	(D) $\text{TiF}_6^{2-}$ and $\text{Cu}_2\text{Cl}_2$

78. Oxidation number of Fe in violet coloured complex  $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$  is:

(A) 0	(B) 2	(C) 3	(D) 4
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79. Which of the following statements is not correct?

- (A)  $[\text{Ti}(\text{NO}_3)_4]$  is a colourless compound
- (B)  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  is a coloured compound
- (C)  $\text{K}_3[\text{VF}_6]$  is a colourless compound
- (D)  $[\text{Cu}(\text{NCCCH}_3)_4]\text{BF}_4$  is a colourless compound

80. Of the following which is diamagnetic in nature?  
 (A)  $[\text{CoF}_6]^{3-}$  (B)  $[\text{NiCl}_4]^{2-}$  (C)  $[\text{CuCl}_4]^{2-}$  (D)  $[\text{Ni}(\text{CN})_4]^{2-}$
81. The number of geometrical isomers for octahedral  $[\text{CoCl}_4(\text{NH}_3)_2]^-$ , square planar  $[\text{AuBr}_2\text{Cl}_2]^-$  and  $[\text{PtCl}_2(\text{en})]$  are  
 (A) 2, 2, 2 (B) 2, 2, no isomerism (C) 3, 2, 2 (D) 2, 3, no isomerism
82. Which of the following is correctly matched ?
- | Column I                         | Column II    | Column III                                |
|----------------------------------|--------------|---|
| (A) $[\text{Cr}(\text{CO})_6]$   | Paramagnetic | Octahedral, $\text{sp}^3\text{d}^2$       |
| (B) $[\text{Fe}(\text{CO})_5]$   | Paramagnetic | Trigonal bipyramid, $\text{sp}^3\text{d}$ |
| (C) $[\text{Co}(\text{CO})_4]^-$ | diamagnetic  | tetrahedral, $\text{sp}^3$                |
| (D) $[\text{Ni}(\text{CO})_4]$   | diamagnetic  | square planar, $\text{dsp}^2$             |
83. Other than the X-ray diffractions, how could be the following pairs of isomers be distinguished from one another by  
 $[\text{Cr}(\text{NH}_3)_6]$   $[\text{Cr}(\text{NO}_2)_6]$  and  $[\text{Cr}(\text{NO}_2)_2(\text{NH}_3)_4]$   $[\text{Cr}(\text{NO}_2)_4(\text{NH}_3)_2]$   
 (A) measuring osmotic pressure of solution at same concentration  
 (B) measurement of molar conductance  
 (C) measuring magnetic moments  
 (D) None of these
84. Octahedral complex of Ni(II) must be  
 (A) inner orbital  
 (B) outer orbital  
 (C) inner or outer orbital depending upon the strong or weak field ligand  
 (D) none of these
85. The tetrahedral  $[\text{CoI}_4]^{2-}$  and square planar  $[\text{PdBr}_4]^{2-}$  complex ions are respectively  
 (A) low spin, high spin (B) high spin, low spin  
 (C) both low spin (D) both high spin
86. Among the following ions which one has the highest paramagnetism  
 (A)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (B)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  (C)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (D)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

87. Among the following, the compound that is both paramagnetic and coloured is  
(A)  $K_2Cr_2O_7$  (B)  $(NH_4)_2[TiCl_6]$  (C)  $VO SO_4$  (D)  $K_3[Cu(CN)_4]$
88. The magnetic moment of  $[NiX_4]^{2-}$  ion is found to be zero. Then the metal of the complex ion is (X = monodentate anionic ligand).  
(A)  $sp^3$  hybridised (B)  $sp^2$  hybridised  
(C)  $dsp^2$  hybridised (D)  $d^2sp$  hybridised
89. In the complex  $FeK_2[Fe(CN)_6]$ ,  
(A) Both Fe atoms are in the same oxidation state.  
(B) Both Fe atoms are in different oxidation state.  
(C) The coordination number of ion is 4.  
(D) The complex is a high spin complex.
90. In the formula of brown ring complex  $[Fe(H_2O)_5(NO)]SO_4$ , the magnetic moment is 3.87 B.M. The oxidation state of Fe and number of unpaired electrons present respectively are:  
(A) 1+, 3 (B) 2+, 3 (C) 3+, 3 (D) 3+, 5
91. Each of the following complex shows colour except  
(A)  $K_3[VF_6]$  (B)  $[Cr(NH_3)_6]Cl_3$  (C)  $[Sc(H_2O)_6]^{3+}$  (D)  $Na_2[NiCl_4]$
92. For which of the following types of dn configuration, the number of unpaired electrons in octahedral complexes remains same irrespective of the ligand field strength.  
(A)  $d^3$  (B)  $d^4$  (C)  $d^5$  (D)  $d^6$
93. The complex ion which has no 'd' electrons in the central metal atom is  
(A)  $[MnO_4]^-$  (B)  $[Co(NH_3)_6]^{3+}$  (C)  $[Fe(CN)_6]^{3-}$  (D)  $[Cr(H_2O)_6]^{3+}$
94. The spin only magnetic moment of cobalt in the compound  $K_2[Co(SCN)_4]$  is  
(A)  $\sqrt{3}$  BM (B)  $\sqrt{8}$  BM (C)  $\sqrt{15}$  BM (D)  $\sqrt{24}$  BM
95. Which of the following electronic arrangement gives the highest value of the magnetic moment?  
(A)  $d^6$ , strong field (B)  $d^7$ , high spin  
(C)  $d^4$ , weak field (D)  $d^2$ , strong field

96. Select the correct statement among the following :
- (A)  $\text{Cu}^{+2}$  with coordination number 6 forms perfect octahedral geometry.
- (B)  $\text{Cu}^{+2}$  in an octahedral complex have symmetrical electron distribution in eg orbitals.
- (C)  $\text{Cu}^{+2}$  in an octahedral complex have symmetrical electron distribution in  $t_{2g}$  orbitals.
- (D) All are correct.

### Miscellaneous

97. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect ?
- (A) Chlorophyll is a green pigment in plants and contains calcium
- (B) Haemoglobin is the red pigment of blood and contains iron
- (C) Cyanocobalamin is  $\text{B}_{12}$  and contains cobalt
- (D) Carboxypeptidase A is an enzyme and contains zinc
98. From the stability constant (hypothetical values), given below, predict which is the strongest ligand:
- (A)  $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $K = 4.5 \times 10^{11}$
- (B)  $\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_4]^{2-}$ ,  $K = 2.0 \times 10^{27}$
- (C)  $\text{Cu}^{2+} + 2\text{en} \rightleftharpoons [\text{Cu}(\text{en})_2]^{2+}$ ,  $K = 3.0 \times 10^{15}$
- (D)  $\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ,  $K = 9.5 \times 10^8$
99. The oxidation state of Mo in its oxo-complex species  $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O})_2]^{2-}$  is:
- (A) +2 (B) +3 (C) +4 (D) +5
100. On treatment of  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  with concentrated HCl, two compounds I and II having the same formula,  $[\text{NiCl}_2(\text{NH}_3)_2]$  are obtained, I can be converted into II by boiling with dilute HCl. A solution of I reacts with oxalic acid to form  $[\text{Ni}(\text{C}_2\text{O}_4)(\text{NH}_3)_2]$  whereas II does not react. Point out the correct statement of the following
- (A) I cis, II trans; both tetrahedral (B) I cis, II trans; both square planar
- (C) I trans, II cis; both tetrahedral (D) I trans, II cis; both square planar
101. Which one of the following statement is incorrect ?
- (A) Greater the formation constant ( $K_f$ ) of a complex ion, greater is its stability.
- (B) Greater the positive charge on the central metal ion, greater is the stability of the complex
- (C) Greater is the basic character of the ligand, lesser is the stability of the complex.
- (D) Chelate complexes have high stability constants.

102. The number of ions formed, when bis (ethane-1,2-diamine) copper (II) sulphate is dissolved in water will be  
(A) 1 (B) 2 (C) 3 (D) 4
103. A white precipitate of AgCl dissolves in  $\text{NH}_4\text{OH}$  due to the formation of  
(A)  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  (B)  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$   
(C)  $[\text{Ag}(\text{NH}_4)_2]^{2+}$  (D)  $[\text{Ag}(\text{NH}_3)_3]\text{Br}$
104. The oxidation state of iron in  $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$  is  
(A) 1+ (B) 2+ (C) 3+ (D) zero
105.  $\text{Zn}(\text{II})$  ion first gives a white precipitate with  $\text{NaOH}$  which dissolves in excess of  $\text{NaOH}$ . This is due to the formation of a complex. The oxidation state of zinc in this complex will be.  
(A) Zero (B) + II (C) +IV (D) +VI

## EXERCISE – II

More than one may be correct

- Which of the following exhibit geometrical isomerism (M stands for a metal, and a and b are achiral ligands)?  
(A)  $\text{Ma}_2\text{b}_2$  (Sq. Pl.) (B)  $\text{Ma}_4\text{b}_2$  (C)  $\text{Ma}_5\text{b}$  (D)  $\text{Ma}_6$
- Which of the following statement(s) is (are) correct ?  
(A) The oxidation state of iron in sodium nitroprusside  $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$  is +2.  
(B)  $[\text{Ag}(\text{NH}_3)_2]^+$  is linear in shape.  
(C) In  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , Fe is  $d^2sp^3$  hybridized.  
(D) In  $\text{Ni}(\text{CO})_4$ , the oxidation state of Ni is zero.
- Which of the following compound(s) show(s) optical isomerism.  
(A)  $[\text{Pt}(\text{bn})_2]^{2+}$  (B)  $[\text{CrCl}_2(\text{en})_2]^+$  (C)  $[\text{Co}(\text{en})_3][\text{CoF}_6]$  (D)  $[\text{Zn}(\text{gly})_2]$
- Choose incorrect statement(s) regarding following complex ion.  
 $[\text{Fe}(\text{ox})_3]^{3-}$  and  $[\text{Fe}(\text{NO}_2)_6]^{3-}$   
(A)  $[\text{Fe}(\text{ox})_3]^{3-}$  complex ion is more stable than  $[\text{Fe}(\text{NO}_2)_6]^{3-}$ .  
(B) Both complex ions are optically inactive.  
(C) Both follow Sidgwick's rule of E.A.N.  
(D) Both are paramagnetic.
- For which of the following  $d^n$  configuration of octahedral complex(es), cannot exist in both high spin and low spin forms.  
(A)  $d^3$  (B)  $d^5$  (C)  $d^6$  (D)  $d^8$
- Select **incorrect** statement(s) for  $[\text{Cu}(\text{CN})_4]^{3-}$ ,  $[\text{Cd}(\text{CN})_4]^{2-}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex ion.  
(A) Both  $[\text{Cd}(\text{CN})_4]^{2-}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  have square planar geometry  
(B)  $[\text{Cu}(\text{CN})_4]^{3-}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  have equal no. of unpaired electron  
(C)  $[\text{Cu}(\text{CN})_4]^{3-}$  and  $[\text{Cd}(\text{CN})_4]^{2-}$  can be separated from the mixture on passing  $\text{H}_2\text{S}$  gas.  
(D) All the three complexes have magnetic moment equal to zero.
- Which of the following statement(s) is/are **incorrect**?  
(A) The state of hybridisation of central atom of anionic part of solid  $\text{PBr}_5$  is  $sp^3d^2$ .  
(B)  $[\text{Co}(\text{NH}_3)_6]^{2+}$  ion is easily oxidisable while  $[\text{Co}(\text{NO}_2)_6]^{4-}$  is not.  
(C) Bis(glycinato)zinc(II) is optically active.  
(D)  $d_{z^2}$  orbital of central metal atom / ion is used in  $dsp^2$  hybridisation.



8. Which of the following will have two stereoisomeric forms?  
 (A)  $[\text{Cr}(\text{NO}_3)_3(\text{NH}_3)_3]$  (B)  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$   
 (C)  $[\text{CoCl}_2(\text{en})_2]^+$  (D)  $[\text{CoBrCl}(\text{Ox})_2]^{3-}$
9. Which is / are not correctly matched.
- | Complex compounds   | IUPAC name                              |
|---|---|
| (A) $\text{K}[\text{CrF}_4\text{O}]$  | Potassium tetrafluoridooxidochromate(V) |
| (B) $\text{Na}[\text{BH}(\text{OCH}_3)_3]$                                    | Sodium hydridotrimethoxyborate(III)     |
| (C) $[\text{Be}(\text{CH}_3\text{--CO--CH}_2\text{--CO--C}_6\text{H}_5)_2]^0$ | Bis(benzoylacetonato)beryllium(III)     |
| (D) $\text{H}[\text{AuCl}_4]$   | Hydrogen tetrachloroaurate(III)         |
10. Which of the following statement(s) is/are incorrect  
 (A) In  $[\text{CoBrCl}(\text{en})_2]^+$  geometrical isomerism exists, while optical isomerism does not exist  
 (B) Potassium aquadicyanidosuperoxidoperoxidochromate(III) is IUPAC name for  $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)(\text{H}_2\text{O})]$   
 (C) There are 3 geometrical isomers and 15 stereoisomers possible for  $[\text{Pt}(\text{NO}_2)(\text{NH}_3)(\text{NH}_2\text{OH})(\text{py})]^+$  and  $[\text{PtBr Cl}(\text{NO}_2)(\text{NH}_3)(\text{py})]$  respectively  
 (D) cis and trans forms are not diastereomers to each other
11. Which of the following statement is **true** about the complex  $[\text{CrCl}_3(\text{OH})_2(\text{NH}_3)]^{2-}$  ion.  
 (A) It has three geometrical isomers.  
 (B) Only one space isomer is optically active and remaining are inactive.  
 (C) There are total four space isomers.  
 (D) The magnetic moment of complex ion is 3.89 B.M.
12. A d-block element forms octahedral complex but its magnetic moment remains same either in strong field or in weak field ligand. Which of the following is/are **correct**?  
 (A) Element always forms colourless compound.  
 (B) Number of electrons in  $t_{2g}$  orbitals are higher than in eg orbitals.  
 (C) It can have either  $d^3$  or  $d^8$  configuration.  
 (D) It can have either  $d^7$  or  $d^8$  configuration.
13. Which of the following is correct about?  
 Tetraamminedithiocyanato-scobalt(III) tris(oxalato)cobaltate(III)  
 (A) formula of the complex is  $[\text{Co}(\text{SCN})_2(\text{NH}_3)_4][\text{Co}(\text{ox})_3]$   
 (B) It is a chelating complex and show linkage isomerism.  
 (C) It shows optical isomerism.  
 (D) It shows geometrical isomerism.
14. Which is correct statement(s)?  
 (A)  $[\text{Ag}(\text{NH}_3)_2]^+$  is linear with  $sp$  hybridised  $\text{Ag}^+$  ion  
 (B)  $\text{NiCl}_4^{2-}$ ,  $\text{VO}_4^{3-}$  and  $\text{MnO}_4^-$  have tetrahedral geometry  
 (C)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  &  $[\text{Ni}(\text{CN})_4]^{2-}$  have  $dsp^2$  hybridisation of the metal ion  
 (D)  $\text{Fe}(\text{CO})_5$  has trigonal bipyramidal structure with  $d_{z^2}$   $sp^3$  hybridised iron.



## EXERCISE-III

Match the column

1. Match the complexes in column I with their stereoproperties in column II

**Column I**

- (A)  $[\text{CoCl}_3(\text{NH}_3)_3]$   
 (B)  $[\text{Cr}(\text{OX})_3]^{3-}$   
 (C)  $[\text{CrCl}_2(\text{OX})_2]$   
 (D)  $[\text{RhCl}_3(\text{Py})_3]$

**Column II**

- (P) Show facial isomer  
 (Q) Cis form is optically active  
 (R) Trans form is optically inactive  
 (S) Show meridional form  
 (T) Two optically active isomer

2. Match the complexes in column-I with the EAN of central atom in column-II:

**Column-I**

- (A)  $[\text{Fe}(\text{CO})_4]^{2-}$   
 (B)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 (C)  $\text{K}_2[\text{Ni}(\text{CN})_4]$   
 (D)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$

**Column-II**

- (P) 34  
 (Q) 35  
 (R) 36  
 (S) 37

3. Match the column :

**Column-I**

- (A)  $[\text{Fe}(\text{NH}_3)_6]^{2+}$   
 (B)  $[\text{NiF}_6]^{2-}$   
 (C)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
 (D)  $[\text{Pt}(\text{Cl})_2(\text{NH}_3)_4]\text{Cl}_2$

**Column-II**

- (P)  $d^2sp^3$   
 (Q)  $sp^3d^2$   
 (R) diamagnetic  
 (S) paramagnetic  
 (T) outer orbital complex

4. **Column-I**

- (A)  $[\text{Ma}_2\text{bcde}]^{n\pm}$   
 (B)  $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$   
 (C)  $[\text{Ma}_3\text{bcd}]^{n\pm}$   
 (D)  $[\text{M}(\text{AB})\text{c}_2\text{d}]^{n\pm}$

**Column II**

- (P) 3 optically inactive isomers  
 (Q) 4 geometrical isomers  
 (R) 6 stereo(space)isomers  
 (S) 2 optically active isomers

(where  $\text{AB} \rightarrow$  Unsym. bidentate ligand having no chiral center, a,b,c,d & e  $\rightarrow$  monodentate ligands)

- |   |   |
|---|---|
| <p>5. <b>Column I</b></p> <p>(A) <math>[\text{Ni}(\text{gly})_3]^-</math></p> <p>(B) <math>[\text{FeBr}_2\text{Cl}_2(\text{NO}_3)(\text{OH})]^{4-}</math></p> <p>(C) <math>[\text{IrCl}_2(\text{gly})_2]^-</math></p> <p>(D) <math>[\text{Co}(\text{CN})_2(\text{NO}_2)_2(\text{NH}_3)(\text{py})]^-</math></p> | <p><b>Column II</b></p> <p>(P) Four optically active isomers</p> <p>(Q) Eight stereo isomers</p> <p>(R) Paramagnetic complex</p> <p>(S) Diamagnetic complex</p>             |
| <p>6. <b>Column - I</b></p> <p>(A) <math>\text{Na}_2 [\text{Fe}(\text{CN})_5 \text{NO}]</math></p> <p>(B) <math>[\text{Fe}(\text{H}_2\text{O})_5 \text{NO}] \text{SO}_4</math></p> <p>(C) <math>[\text{Ag}(\text{CN})_2]^-</math></p> <p>(D) <math>\text{K}_4[\text{Fe}(\text{CN})_6]</math></p>                | <p><b>Column -II</b></p> <p>(P) <math>\mu = 0</math> B.M.</p> <p>(Q) octahedral</p> <p>(R) <math>\mu = \sqrt{15}</math> B.M.</p> <p>(S) <math>\text{NO}^+</math> ligand</p> |

**Assertion Reason :**

7. **Statement-1:** Cis-isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  shows optical activity.  
**Statement-2:** Cis-isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  is a symmetric molecule.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
8. **Statement-1:** Complexes containing three bidentate groups such as  $[\text{Cr}(\text{ox})_3]^{3-}$  and  $[\text{Co}(\text{en})_3]^{3+}$  do not show optical activity.  
**Statement-2:** Octahedral complex,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  shows geometrical isomerism.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
9. **Statement-1:**  $\text{K}_3[\text{Fe}(\text{CN})_6]$  is a low spin complex.  
**Statement-2:**  $\text{Fe}^{2+}$  ion in this complex undergoes  $\text{sp}^3\text{d}^2$  hybridization.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

10. **Statement-1:** Coordination isomerism occurs when both cation and anion are complex.  
**Statement-2:** The complexes with coordination number 6 form octahedral complexes involving either  $sp^3d^2$  or  $d^2sp^3$  hybridization.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
11. **Statement-1:** After splitting of d-orbitals during complex formation, the orbitals form two sets of orbitals  $t_{2g}$  and  $e_g$  octahedral field.  
**Statement-2:** Splitting of d-orbitals occurs only in the case of strong field ligands such as  $CN^-$ .  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
12. **Statement-1:** Organometallic compounds are those which have one or more metal-carbon bonds.  
**Statement-2:** Metallic carbonyls are organometallic compounds having both  $\sigma$  and  $\pi$  - bonds.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
13. **Statement-1:**  $[Ti(H_2O)_6]^{3+}$  is coloured while  $[Sc(H_2O)_6]^{3+}$  is colourless.  
**Statement-2:** d-d transition is not possible in  $[Sc(H_2O)_6]^{3+}$  because no d-electron is present while possible for  $Ti^{3+}$  having  $d^1$  system.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.

**Comprehension (Q.14 to Q.16)**

Ligands are neutral or ionic species capable of donating at least one electron pair to central metal. Hence ligands can be of different denticities.

14. For a given metal  $M^{3+}$  coordination number is six, then for which set of ligands, complex will be more stable-  
 (A)  $6H_2O$  (B)  $6F^-$  (C)  $EDTA^{-4}$  (D)  $2H_2O$  and  $2C_2O_4^{2-}$
15.  $[Mn(CO)_5]$  can attain more stability by :  
 (A) Oxidation of itself (B) Reduction of itself  
 (C) Dimerization (D) Both (B) and (C)
16. The metal cation that has least tendency to accept electron pair from  $NH_3$  is  
 (A)  $Fe^{3+}$  (B)  $Rh^{3+}$  (C)  $Zn^{2+}$  (D)  $Ba^{++}$

**Comprehension (Q.17 to Q.19)**

Complex compounds are molecular compounds which retain their identities even when dissolved in water. They do not give all the simple ions in solution but instead furnish complex ions with complicated structures. The complex compounds are often called coordination compounds because certain groups called ligands are attached to the central metal ion by coordinate or dative bonds. Coordination compounds exhibit isomerism, both structural and stereoisomerism. The structure, magnetic property, colour and electrical properties of complexes are explained by various theories.

17. Arrange the following compounds in order of their Molar conductance:  
 (I)  $K[Co(NO_2)_4(NH_3)_2]$  (II)  $[Cr(ONO)_3(NH_3)_3]$   
 (III)  $[Cr(NO_2)(NH_3)_5]_3[Co(NO_2)_6]_2$  (IV)  $Mg[Cr(NO_2)_5(NH_3)]$   
 (A)  $II < I < IV < III$  (B)  $I < II < III < IV$   
 (C)  $II < I < III < IV$  (D)  $IV < III < II < I$
18. The oxidation number and coordination number of chromium in the following complex is  $[Cr(C_2O_4)_2(NH_3)_2]^{1-}$   
 (A) O.N. = +4, C.N. = 4 (B) O.N. = +3, C.N. = 4  
 (C) O.N. = -1, C.N. = 4 (D) O.N. = +3, C.N. = 6
19. In which of the following pairs, both the complexes have the same geometry but different hybridisation  
 (A)  $[NiCl_4]^{2-}$ ,  $[Ni(CN)_4]^{2-}$  (B)  $[CoF_6]^{3-}$ ,  $[Co(NH_3)_6]^{3+}$   
 (C)  $[Ni(CO)_4]$ ,  $[Ni(CN)_4]^{2-}$  (D)  $[Cu(NH_3)_4]^{2+}$ ,  $[Ni(NH_3)_6]^{2+}$

**Comprehension (Q.20 to Q.22)**

The crystal field theory (C.F.T.) is now much more widely accepted than the valence bond theory. It assumes that the attraction between the central metal and the ligands in a complex is purely electrostatic. According to C.F.T. ligands are treated as point charges and crystal field splitting energy (CFSE) increases the thermodynamic stability of the complexes. Value of CFSE depends upon nature of ligand and a spectrochemical series has been made experimentally. For tetrahedral complexes,  $\Delta$  is about  $4/9$  times  $\Delta_0$  (CFSE for octahedral complexes). This energy lies in the visible region and i.e. why electronic transitions are responsible for colour.

20. Which of the following statements is not correct about C.F.T. -
- (A) Diamagnetic metal ions cannot have an odd number of electrons.
  - (B) In an octahedral crystal field, the d electrons of a metal ion occupy the  $e_g$  set of orbitals before they occupy the  $t_{2g}$  set of orbitals.
  - (C) Low spin complex may be paramagnetic.
  - (D) In high spin octahedral complex,  $\Delta_0$  is less than the electron pairing energy and is relatively very small.
21. Crystal field stabilization energy for  $[\text{CoF}_6]^{3-}$  is
- (A)  $0.6 + P$                       (B)  $-0.4 + P$                       (C)  $1.2 + 2P$                       (D)  $2.4 + 4P$
- [P is pairing energy]
22.  $\text{Ti}^{3+}(\text{aq})$  is violet while  $\text{Ti}^{4+}(\text{aq})$  is colourless because -
- (A) There is no crystal field effect in  $\text{Ti}^{4+}$
  - (B) The energy difference between  $t_{2g}$  and  $e_g$  of  $\text{Ti}^{4+}$  is quite high and does not fall in the visible region.
  - (C)  $\text{Ti}^{4+}$  has  $d^0$  configuration.
  - (D)  $\text{Ti}^{4+}$  is very small in comparison to  $\text{Ti}^{3+}$  and hence does not absorb any radiation.

## EXERCISE : JEE-MAIN

- In  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ , the isomerism shown is - [AIEEE-2002]  
 (1) Ligand (2) Optical (3) Geometrical (4) Ionization
- In the complexes  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{SCN})_6]^{3-}$ ,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  and  $[\text{FeCl}_6]^{3-}$ , more stability is shown by - [AIEEE-2002]  
 (1)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  (2)  $[\text{Fe}(\text{SCN})_6]^{3-}$  (3)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  (4)  $[\text{FeCl}_6]^{3-}$
- One mole of the complex compound  $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ , gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of  $\text{AgNO}_3$  solution to yield two moles of  $\text{AgCl}(\text{s})$ . The structure of the complex is - [AIEEE-2003]  
 (1)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$  (2)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{NH}_3$   
 (3)  $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2 \cdot \text{NH}_3$  (4)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- In the coordination compound  $\text{K}_4[\text{Ni}(\text{CN})_4]$ , the oxidation state of nickel is - [AIEEE-2003]  
 (1) 0 (2) +1 (3) +2 (4) -1
- The number of 3d-electrons remained in  $\text{Fe}^{2+}$  (At.no. of Fe = 26) ion is - [AIEEE-2003]  
 (1) 4 (2) 5 (3) 6 (4) 3
- Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in alkaline solutions but not in acidic solution. What is the reason for it :- [AIEEE-2003]  
 (1) In acidic solutions hydration protects copper ions  
 (2) In acidic solutions protons coordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available  
 (3) In alkaline solutions insoluble  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of any alkali  
 (4) Copper hydroxide is an amphoteric substance
- Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by  $\text{CN}^-$  ion towards metal species is :- [AIEEE-2004]  
 (1) c, a (2) b, c (3) a, b (4) a, b, c
- The coordination number of a central metal atom in a complex is determined by: [AIEEE-2004]  
 (1) The number of ligands around a metal ion bonded by sigma and pi-bonds both  
 (2) The number of ligands around a metal ion bonded by pi-bonds  
 (3) The number of ligands around a metal ion bonded by sigma bonds  
 (4) The number of only anionic ligands bonded to the metal ion

9. Which one of the following complexes is an outer orbital complex :- [AIEEE-2004]  
 (1)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (2)  $[\text{Mn}(\text{CN})_6]^{4-}$   
 (3)  $[\text{Fe}(\text{CN})_6]^{4-}$  (4)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$   
 (Atomic number: Mn=25 ; Fe=26 ; Co=27 ; Ni = 28)
10. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect ? [AIEEE-2004]  
 (1) Cyanocobalamin is vitamin B<sub>12</sub> and contains cobalt  
 (2) Haemoglobin is the red pigment of blood and contains iron  
 (3) Chlorophylls are green pigments in plants and contain calcium  
 (4) Carboxypeptidase - A is an enzyme and contains zinc
11. The correct order of magnetic moments (spin only values in B.M.) among is :- [AIEEE-2004]  
 (1)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$  (2)  $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$   
 (3)  $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$  (4)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$   
 (Atomic nos. : Mn = 25, Fe = 26, Co = 27)
12. For octahedral complex, the value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is [AIEEE-2005]  
 (1)  $d^4$  (in strong ligand field) (2)  $d^4$  (in weak ligand field)  
 (3)  $d^3$  (in weak as well as in strong field) (4)  $d^5$  (in strong ligand field)
13. The IUPAC name for the complex  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$  is - [AIEEE-2006]  
 (1) pentaammine nitrito-N- cobalt (II) chloride  
 (2) pentaammine nitrito-N- cobalt (III) chloride  
 (3) nitrito-N- pentaamminecobalt (III) chloride  
 (4) nitrito-N- pentaamminecobalt (II) chloride
14. Nickel (Z=28) combines with a uninegative monodentate ligand  $\text{X}^-$  to form a paramagnetic complex  $[\text{NiX}_4]^{2-}$ . The number of unpaired electron in the nickel and geometry of this complex ion are, respectively. [AIEEE-2006]  
 (1) one, square planar (2) two, square planar  
 (3) one, tetrahedral (4) two, tetrahedral



15. In  $\text{Fe}(\text{CO})_5$ , the Fe–C bond possesses [AIEEE–2006]  
 (1) ionic character (2)  $\sigma$  – character only  
 (3)  $\pi$  –character only (4) both  $\sigma$  and  $\pi$  character
16. How many EDTA (ethylenediaminetetraacetate) molecules are required to make an octahedral complex with a  $\text{Ca}^{2+}$  ion ? [AIEEE–2006]  
 (1) One (2) Two (3) Six (4) Three
17. The "spin-only" magnetic moment [in units of Bohr magneton, ( $\mu_B$ )] of  $\text{Ni}^{2+}$  in aqueous solution would be (At. No. Ni= 28)- [AIEEE–2006]  
 (1) 0 (2) 1.73 (3) 2.84 (4) 4.90
18. Which one of the following has a square planar geometry :- [AIEEE–2007]  
 (Co = 27, Ni = 28, Fe=26, Pt = 78)  
 (1)  $[\text{CoCl}_4]^{2-}$  (2)  $[\text{FeCl}_4]^{2-}$  (3)  $[\text{NiCl}_4]^{2-}$  (4)  $[\text{PtCl}_4]^{2-}$
19. The coordination number and the oxidation state of the element 'E' in the complex  $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4^{2-})]\text{NO}_2^-$  (where en) is ethylene diamine) are, respectively - [AIEEE–2008]  
 (1) 6 and 2 (2) 4 and 2 (3) 4 and 3 (4) 6 and 3
20. In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of  $\Delta_0$  be the highest ? [AIEEE–2008]  
 (1)  $[\text{Co}(\text{CN})_6]^{3-}$  (2)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  (3)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  (4)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
21. Which of the following pairs represents linkage isomers ? [AIEEE–2009]  
 (1)  $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$   
 (2)  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$   
 (3)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$   
 (4)  $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$  and  $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$
22. Which of the following has an optical isomer? [AIEEE–2009]  
 (1)  $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$  (2)  $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$   
 (3)  $[\text{Co}(\text{NH}_3)_3\text{Cl}]^+$  (4)  $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$
23. Which one of the following has an optical isomer ? [AIEEE–2010]  
 (1)  $[\text{Zn}(\text{en})_2]^{2+}$  (2)  $[\text{Zn}(\text{en})(\text{NH}_3)_2]^{2+}$  (3)  $[\text{Co}(\text{en})_3]^{3+}$  (4)  $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$   
 (en = ethylenediamine)



24. Which of the following facts about the complex  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  is wrong ? [AIEEE-2011]  
 (1) The complex is an outer orbital complex  
 (2) The complex gives white precipitate with silver nitrate solution  
 (3) The complex involves  $d^2sp^3$  hybridisation and is octahedral in shape  
 (4) The complex is paramagnetic
25. The magnetic moment (spin only) of  $[\text{NiCl}_4]^{2-}$  is :- [AIEEE-2011]  
 (1) 2.82 BM (2) 1.41 BM (3) 1.82 BM (4) 5.46 BM
26. Among the ligands  $\text{NH}_3$ , en,  $\text{CN}^-$  and CO the correct order of their increasing field strength, is [AIEEE-2011]  
 (1)  $\text{CO} < \text{NH}_3 < \text{en} < \text{CN}^-$  (2)  $\text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$   
 (3)  $\text{CN}^- < \text{NH}_3 < \text{CO} < \text{en}$  (4)  $\text{en} < \text{CN}^- < \text{NH}_3 < \text{CO}$
27. Which one of the following complex ions has geometrical isomers ? [AIEEE-2011]  
 (1)  $[\text{Co}(\text{en})_3]^{3+}$  (2)  $[\text{Ni}(\text{NH}_3)_5\text{Br}]^+$   
 (3)  $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$  (4)  $[\text{Cr}(\text{NH}_3)_4(\text{en})]^{3+}$
28. Which among the following will be named as dibromidobis-(ethylenediamine)chromium(III) bromide ? [AIEEE-2012]  
 (1)  $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$  (2)  $[\text{Cr}(\text{en})_3]\text{Br}_3$  (3)  $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$  (4)  $[\text{Cr}(\text{en})\text{Br}_4]^-$
29. The complex ion [Pt(NO<sub>2</sub>)(Py)(NH<sub>3</sub>)(NH<sub>2</sub>OH)]<sup>+</sup> will give :- [J-MAIN-2012, Online]  
 (1) 4 isomers (Geometrical) (2) 2 isomers (Geometrical)  
 (3) 3 isomers (Geometrical) (4) 6 isomers (Geometrical)
30. Which of the following complex ions will exhibit optical isomerism? [J-MAIN-2012, Online]  
 (en = 1, 2-diamine ethane)  
 (1)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  (2)  $[\text{Zn}(\text{en})_2]^{2+}$   
 (3)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  (4)  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2]^+$
31. Which of the following complex species is not expected to exhibit optical isomerism ? [J-MAIN-2013]  
 (1)  $[\text{Co}(\text{en})_3]^{3+}$  (2)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$   
 (3)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (4)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$

32. Type of isomerism which exists between  $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$  and  $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NCS})_2]$  is : [J-MAIN-2013, Online]  
 (1) Solvate isomerism (2) Ionisation isomerism  
 (3) Linkage isomerism (4) Coordination isomerism
33. Which of the following is diamagnetic ? [J-MAIN-2013, Online]  
 (1)  $[\text{CoF}_6]^{3-}$  (2)  $[\text{FeF}_6]^{3-}$  (3)  $[\text{Fe}(\text{CN})_6]^{3-}$  (4)  $[\text{Co}(\text{Ox})_3]^{3-}$
34. The magnetic moment of the complex anion  $[\text{Cr}^{\text{I}}(\text{NO})(\text{NH}_3)(\text{CN})_4]^{2-}$  is : [J-MAIN-2013, Online]  
 (1) 2.82 BM (2) 5.91 BM (3) 1.73 BM (4) 3.87 BM
35. The octahedral complex of a metal ion  $\text{M}^{3+}$  with four monodentate ligands  $\text{L}_1$ ,  $\text{L}_2$ ,  $\text{L}_3$  and  $\text{L}_4$  absorb wavelength in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is : [J-MAIN-2014]  
 (1)  $\text{L}_3 < \text{L}_2 < \text{L}_4 < \text{L}_1$  (2)  $\text{L}_1 < \text{L}_2 < \text{L}_4 < \text{L}_3$   
 (3)  $\text{L}_4 < \text{L}_3 < \text{L}_2 < \text{L}_1$  (4)  $\text{L}_1 < \text{L}_3 < \text{L}_2 < \text{L}_4$
36. The equation which is balanced and represents the correct product (s) is : [J-MAIN-2014]  
 (1)  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} + (\text{EDTA})^{4-} \xrightarrow{\text{excess NaOH}} [\text{Mg}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$   
 (2)  $\text{CuSO}_4 + 4\text{KCN} \rightarrow \text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$   
 (3)  $\text{Li}_2\text{O} + 2\text{KCl} \rightarrow 2\text{LiCl} + \text{K}_2\text{O}$   
 (4)  $[\text{CoCl}(\text{NH}_3)_5]^+ + 5\text{H}^+ \rightarrow \text{Co}^{2+} + 5\text{NH}_4^+ + \text{Cl}^-$
37. The correct statement about the magnetic properties of  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{FeF}_6]^{3-}$  is : ( $Z = 26$ ). [J-MAIN-2014, Online]  
 (1)  $[\text{Fe}(\text{CN})_6]^{3-}$  is paramagnetic,  $[\text{FeF}_6]^{3-}$  is diamagnetic.  
 (2) both are diamagnetic.  
 (3)  $[\text{Fe}(\text{CN})_6]^{3-}$  is diamagnetic,  $[\text{FeF}_6]^{3-}$  is paramagnetic.  
 (4) both are paramagnetic
38. An octahedral complex of  $\text{Co}^{3+}$  is diamagnetic. The hybridisation involved in the formation of the complex is : [J-MAIN-2014]  
 (1)  $d^2sp^3$  (2)  $dsp^3d$   
 (3)  $dsp^2$  (4)  $sp^3d^2$

39. Which of the following name formula combinations is not correct? [J-MAIN-2014, Online]

Formula	Name
(1) $K[Cr(NH_3)_2Cl_4]$	Potassium diamminetetrachlorochromate(III)
(2) $[Co(NH_3)_4(H_2O)I]SO_4$	Tetraammineaquaiodocobalt(III) sulphate
(3) $[Mn(CN)_5]^{2-}$	Pentacyanomagnate(II) ion
(4) $K_2[Pt(CN)_4]$	Potassium tetracyanoplatinate(II)

40. Consider the coordination compound,  $[Co(NH_3)_6]Cl_3$ . In the formation of this complex, the species which acts as the Lewis acid is : [J-MAIN-2014, Online]

- (1)  $[Co(NH_3)_6]^{3+}$       (2)  $NH_3$       (3)  $Co^{3+}$       (4)  $Cl^-$

41. Among the following species the one which causes the highest CFSE,  $\Delta_0$  as a ligand is :-

[J-MAIN-2014, Online]

- (1)  $CN^-$       (2)  $NH_3$       (3)  $CO$       (4)  $F^-$

42. Which one of the following complexes will most likely absorb visible light ?

[J-MAIN-2014, Online]

(At nos. Sc = 21, Ti = 22, V = 23, Zn = 30) :-

- (1)  $[Ti(NH_3)_6]^{4+}$       (2)  $[V(NH_3)_6]^{3+}$       (3)  $[Zn(NH_3)_6]^{2+}$       (4)  $[Sc(H_2O)_6]^{3+}$

43. Nickel ( $Z = 28$ ) combines with a uninegative monodentate ligand to form a diamagnetic complex  $[NiL_4]^{2-}$ . The hybridisation involved and the number of unpaired electrons present in the complex are respectively : [J-MAIN-2014, Online]

- (1)  $sp^3$ , zero      (2)  $sp^3$ , two      (3)  $dsp^2$ , one      (4)  $dsp^2$ , zero

44. The number of geometrical isomers that can exist for square planar  $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$  is (py = pyridine) : [J-MAIN-2015]

- (1) 4      (2) 6      (3) 2      (4) 3

45. The color of  $KMnO_4$  is due to :

[J-MAIN-2015]

- (1)  $L \rightarrow M$  charge transfer transition      (2)  $\sigma - \sigma^*$  transition  
(3)  $M \rightarrow L$  charge transfer transition      (4)  $d - d$  transition

46. Which of the following complex ions has electrons that are symmetrically filled in both  $t_{2g}$  and  $e_g$  orbitals ? [J-MAIN-2015, Online]

- (1)  $[CoF_6]^{3-}$       (2)  $[Mn(CN)_6]^{4-}$       (3)  $[FeF_6]^{3-}$       (4)  $[Co(NH_3)_6]^{2+}$

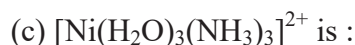
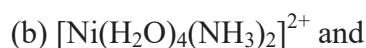
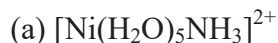
47. When concentrated HCl is added to an aqueous solution of  $\text{CoCl}_2$ , its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction ?:-

[J-MAIN-2015, Online]

- (1)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$       (2)  $[\text{CoCl}_6]^{3-}$       (3)  $[\text{CoCl}_4]^{2-}$       (4)  $[\text{CoCl}_6]^{4-}$

48. The correct statement on the isomerism associated with the following complex ions,

[J-MAIN-2015, Online]



(1) (a) and (b) show geometrical and optical isomerism

(2) (b) and (c) show geometrical and optical isomerism

(3) (a) and (b) show only geometrical Isomerism

(4) (b) and (c) show only geometrical Isomerism

49. Which one of the following complexes shows optical isomerism :-

[J-MAIN-2016]

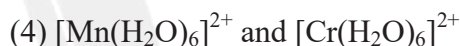
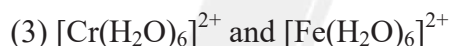
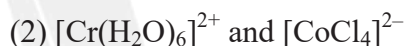


(en = ethylenediamine)

50. The pair having the same magnetic moment is:-

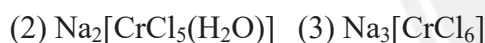
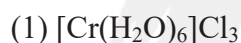
[J-MAIN-2016]

[At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]



51. Which one of the following complexes will consume more equivalents of aqueous solution of  $\text{Ag}(\text{NO}_3)$  ?

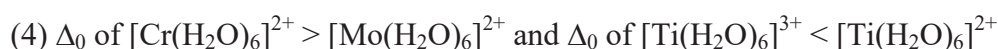
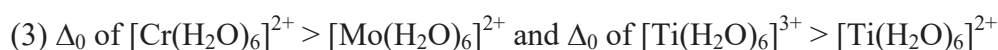
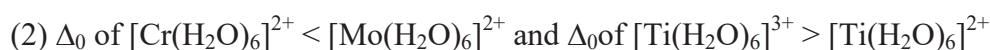
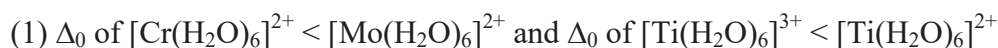
[J-MAIN-2016, Online]



52. Identify the correct trend given below :

[J-MAIN-2016, Online]

(Atomic No. = Ti : 22, Cr : 24 and Mo : 42)



53. Consider the following reaction and statements : [JEE MAIN 2018]  

$$[\text{Co}(\text{NH}_3)_4\text{Br}_2]^+ + \text{Br}^- \rightarrow [\text{Co}(\text{NH}_3)_3\text{Br}_3] + \text{NH}_3$$
 (I) Two isomers are produced if the reactant complex ion is a cis-isomer  
 (II) Two isomers are produced if the reactant complex ion is a trans-isomer  
 (III) Only one isomer is produced if the reactant complex ion is a trans-isomer.  
 (IV) Only one isomer is produced if the reactant complex ion is a cis-isomer.  
 (1) (II) and (IV) (2) (I) and (II)  
 (3) (I) and (III) (4) (III) and (IV)
54. The oxidation states of Cr in  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ,  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ , and  $\text{K}_2[\text{Cr}(\text{CN})_2(\text{O})_2(\text{O}_2)(\text{NH}_3)]$  respectively are [JEE MAIN 2018]  
 (1) +3, 0, and +4 (2) +3, +4, and +6  
 (3) +3, +2, and +4 (4) +3, 0, and +6
55. Two complexes  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (A) and  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  (B) are violet and yellow coloured, respectively. The incorrect statement regarding them is : [JEE MAIN 2019]  
 (1)  $\Delta_0$  value of (A) is less than that of (B).  
 (2)  $\Delta_0$  value of (A) and (B) are calculated from the energies of violet and yellow light, respectively  
 (3) Both absorb energies corresponding to their complementary colors.  
 (4) Both are paramagnetic with three unpaired electrons.
56. Homoleptic octahedral complexes of a metal ion ' $\text{M}^{3+}$ ' with three monodentate ligands  $\text{L}_1$ ,  $\text{L}_2$  and  $\text{L}_3$  absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligands strength is: [JEE MAIN 2019]  
 (1)  $\text{L}_1 < \text{L}_2 < \text{L}_3$  (2)  $\text{L}_3 < \text{L}_1 < \text{L}_2$  (3)  $\text{L}_3 < \text{L}_2 < \text{L}_1$  (4)  $\text{L}_2 < \text{L}_1 < \text{L}_3$
57. The highest value of the calculated spin only magnetic moment (in BM) among all the transition metal complex is : [JEE MAIN 2019]  
 (1) 5.92 (2) 3.87 (3) 6.93 (4) 4.90
58. The complex that has highest crystal field splitting energy ( $\Delta$ ) is : [JEE MAIN 2019]  
 (1)  $\text{K}_2[\text{CoCl}_4]$  (2)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 (3)  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$  (4)  $\text{K}_3[\text{Co}(\text{CN})_6]$

59. Wilkinson catalyst is : [JEE MAIN 2019]  
 (1)  $[(Et_3P)_3RhCl]$  (2)  $[(Ph_3P)_3RhCl]$  (Et =  $C_2H_5$ )  
 (3)  $[(Ph_3P)_3IrCl]$  (4)  $[(Et_3P)_3IrCl]$
60. The total number of isomers for a square planar complex  $[M(F)(Cl)(SCN)(NO_2)]$  is :  
 (1) 4 (2) 8 (3) 12 (4) 16 [JEE MAIN 2019]
61. A reaction of cobalt (III) chloride and ethylenediamine in a 1 : 2 mole ratio generates two isomeric products A (violet coloured) and B (green coloured). A can show optical activity, B is optically inactive. What type of isomers does A and B represent? [JEE MAIN 2019]  
 (1) Coordination isomers (2) Ionisation isomers  
 (3) Linkage isomers (4) Geometrical isomers
62. The difference in the number of unpaired electrons of a metal ion in its high-spin and low-spin octahedral complexes is two. The metal ion is: [JEE MAIN 2019]  
 (1)  $Ni^{2+}$  (2)  $Mn^{2+}$  (3)  $Fe^{2+}$  (4)  $Co^{2+}$
63. Match the metals (column I) with the coordination compound(s)/enzyme(s) (column II): [JEE MAIN 2019]
- | (Column-I) | (Column-II)                         |
|------------|-------------------------------------|
| Metals     | Coordination compounds(s)/enzyme(s) |
| (A) Co     | (i) Wilkinson catalyst              |
| (B) Zn     | (ii) Chlorophyll                    |
| (C) Rh     | (iii) Vitamin B <sub>12</sub>       |
| (D) Mg     | (iv) Carbonic anhydrase             |
- (1) (A)→(i); (B)→(ii); (C)→(iii); (D)→(iv)  
 (2) (A)→(iii); (B)→(iv); (C)→(i); (D)→(ii)  
 (3) (A)→(ii); (B)→(i); (C)→(iv); (D)→(iii)  
 (4) (A)→(iv); (B)→(iii); (C)→(i); (D)→(ii)
64. The coordination number of Th in  $K_4[Th(C_2O_4)_4(OH_2)_2]$  is :- [JEE MAIN 2019]  
 ( $C_2O_4^{2-}$  = Oxalato)  
 (1) 6 (2) 14 (3) 8 (4) 10
65. The number of bridging CO ligand(s) and Co-Co bond(s) in  $Co_2(CO)_8$ , respectively are :-  
 (1) 0 and 2 (2) 4 and 0 (3) 2 and 1 (4) 2 and 0 [JEE MAIN 2019]

66. The metal d-orbitals that are directly facing the ligands in  $K_3[Co(CN)_6]$  are :  
[JEE MAIN 2019]
- (A)  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$   
(B)  $d_{x^2-y^2}$  and  $d_{z^2}$   
(C)  $d_{xy}$  and  $d_{x^2-y^2}$   
(D)  $d_{xz}$ ,  $d_{yz}$  and  $d_{z^2}$
67.  $Mn_2(CO)_{10}$  is an organometallic compound due to the presence of :  
[JEE MAIN 2019]
- (A) Mn – O bond  
(B) Mn – C bond  
(C) Mn – Mn bond  
(D) C – O bond
68. The pair of metal ions that can give a spin only magnetic moment of 3.9 BM for the complex  $[M(H_2O)_6]Cl_2$ , is :  
[JEE MAIN 2019]
- (A)  $V^{2+}$  and  $Co^{2+}$   
(B)  $Co^{2+}$  and  $Fe^{2+}$   
(C)  $V^{2+}$  and  $Fe^{2+}$   
(D)  $Cr^{2+}$  and  $Mn^{2+}$
69. The magnetic moment of an octahedral homoleptic Mn (II) complex is 5.9 BM. The suitable ligand for this complex is :  
[JEE MAIN 2019]
- (A) CO  
(B)  $NCS^-$   
(C) ethylenediamine  
(D)  $CN^-$
70. Correct IUPAC name of  $[Pt(NH_3)_2Cl(CH_3NH_2)]Cl$  is: [JEE-MAIN 2020]
- (A) Bis(amine)chlorido(methylamine)platinum(II) chloride

- (B) Diamminechlorido(methylamine)platinum(II) chloride  
(C) Diamminechlorido(aminomethyl)platinum(II) chloride  
(D) Chloridobis(ammine)methylamineplatinum(II) chloride
71. For the complex  $[Ma_2b_2]$  if M is  $sp^3$  or  $dsp^2$  hybridised respectively then total number of optical isomers are respectively : [JEE-MAIN 2020]  
(A) 1,1  
(B) 2,1  
(C) 0,0  
(D) 1,2
72. For octahedral Mn(II) and tetrahedral Ni(II) complexes, consider the following statements: [JEE-MAIN 2020]  
(I) both the complexes can be high spin.  
(II) Ni (II) complex can very rarely be low spin.  
(III) with strong field ligands, Mn(II) complexes can be low spin.  
(IV) aqueous solution of Mn (II) ions is yellow in colour.  
The correct statements are :  
(A) (I), (III) and (IV) only  
(B) (I) and (II) only  
(C) (II), (III) and (IV) only  
(D) (I), (II) and (III) only
73. The d-electron configuration of  $[Ru(en)_3]Cl_2$  and  $[Fe(H_2O)_6]Cl_2$ , respectively are [JEE-MAIN 2020]  
(A)  $t_{2g}^6e_g^0$  and  $t_{2g}^6e_g^0$   
(B)  $t_{2g}^6e_g^0$  and  $t_{2g}^4e_g^2$   
(C)  $t_{2g}^4e_g^2$  and  $t_{2g}^4e_g^2$   
(D)  $t_{2g}^4e_g^2$  and  $t_{2g}^6e_g^0$



74. Given below are two statements : [JEE-MAIN 2021]

Statement I : The identification of  $\text{Ni}^{2+}$  is carried out by dimethyl glyoxime in the presence of  $\text{NH}_4\text{OH}$  Statement II : The dimethyl glyoxime is a bidentate neutral ligand.

In the light of the above statements, choose the correct answer from the options given below :

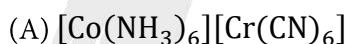
- (A) Both statement I and statement II are true  
 (B) Both statement I and statement II are false  
 (C) Statement I is false but statement II is true  
 (D) Statement I is true but statement II is false
75. If which of the following order the given complex ions are arranged correctly with respect to their decreasing spin only magnetic moment? [JEE-MAIN 2021]



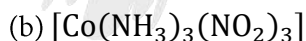
- (A) (ii) > (i) > (iii) > (iv) (B) (iii) > (iv) > (ii) > (i)  
 (C) (ii) > (iii) > (i) > (iv) (D) (i) > (iii) > (iv) > (ii)
76. Match List-I with List-II : [JEE-MAIN 2021]

List-I

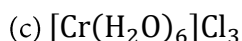
List-II



(i) Linkage isomerism



(ii) Solvate isomerism



(iii) Co-ordination isomerism



(iv) Optical isomerism

Choose the correct answer from the options given below :

- (A) (A) - (iii), (b) - (i), (c) - (ii), (d) - (iv)  
 (B) (A)-(iv), (b)-(ii), (c)-(iii), (d)-(i)

- (C) (A)-(ii), (b)-(i), (c)-(iii), (d)-(iv)  
(D) (A)-(i), (b)-(ii), (c)-(iii), (d)-(iv)
77. Spin only magnetic moment of an octahedral complex of  $\text{Fe}^{2+}$  in the presence of a strong field ligand in BM is : [JEE-MAIN 2021]  
(A) 4.89  
(B) 2.82  
(C) 0  
(D) 3.46
78. The Crystal Field Stabilization Energy (CFSE) and magnetic moment (spin-only) of an octahedral aqua complex of a metal ion ( $\text{M}^{2+}$ ) are  $-0.8\Delta_0$  and 3.87BM, respectively. Identify ( $\text{M}^{2+}$ ) : [JEE-MAIN 2021]  
(A)  $\text{V}^{3+}$   
(B)  $\text{Cr}^{3+}$   
(C)  $\text{Mn}^{4+}$   
(D)  $\text{Co}^{2+}$
79.  $[\text{Fe}(\text{CN})_6]^{3-}$  should be an inner orbital complex. Ignoring the pairing energy, the value of crystal field stabilization energy for this complex is  $(-)\Delta_0$ . (Nearest integer) [JEE-MAIN 2022]
80. The metal complex that is diamagnetic is (Atomic number: Fe, 26; Cu, 29) [JEE-MAIN 2022]  
(A)  $\text{K}_3[\text{Cu}(\text{CN})_4]$   
(B)  $\text{K}_2[\text{Cu}(\text{CN})_4]$   
(C)  $\text{K}_3[\text{Fe}(\text{CN})_4]$   
(D)  $\text{K}_4[\text{FeCl}_6]$
81. In the cobalt-carbonyl complex:  $[\text{Co}_2(\text{CO})_8]$ , number of Co – Co bonds is "X" and terminal CO ligands is "Y".  $X + Y = ?$  [JEE-MAIN 2022]

82. Given below are two statements: [JEE-MAIN 2022]

Statement I :  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar and diamagnetic complex. with  $\text{dsp}^2$  hybridization for Ni but  $[\text{Ni}(\text{CO})_4]$  is tetrahedral. paramagnetic and with  $\text{sp}^3$ - hybridization for Ni.

Statement II:  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$  both have same d-electron configuration have same geometry and are paramagnetic.

In light the above statements. choose the correct answer form the options given below:

- (A) Both Statement I and Statement II are true.  
 (B) Both Statement I and Statement II are false.  
 (C) Statement I is correct but statement II is false.  
 (D) Statement I is incorrect but statement II is true.
83. Which of the following cannot be explained by crystal field theory? [JEE-MAIN 2023]
- (A) The order of spectrochemical series  
 (B) Magnetic properties of transition metal complexes  
 (C) Colour of metal complexes  
 (D) Stability of metal complexes
84. Cobalt chloride when dissolved in water forms pink colored complex X which has octahedral geometry. This solution on treating with cone HCl forms deep blue complex, Y which has a Z geometry. X,Y and Z, respectively, are [JEE-MAIN 2023]
- (A)  $\text{X}=[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{Y}=[\text{CoCl}_4]^{2-}$ , Z= Tetrahedral  
 (B)  $\text{X}=[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{Y}=[\text{CoCl}_6]^{3-}$ , Z= Octahedral  
 (C)  $\text{X}=[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ,  $\text{Y}=[\text{CoCl}_6]^{3-}$ , Z= Octahedral  
 (D)  $\text{X}=[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ ,  $\text{Y}=[\text{CoCl}_4]^{2-}$ , Z= Tetrahedral
85. If the CFSE of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is  $-96.0 \text{ kJ/mol}$ , this complex will absorb maximum at wavelength nm. (nearest integer)  
 Assume Planck's constant ( $h$ )= $6.4 \times 10^{-34}$  Js Speed of light ( $c$ )= $3.0 \times 10^8 \text{ m/s}$  and Avogadro's constant ( $N_A$ )= $6 \times 10^{23}/\text{mol}$  [JEE-MAIN 2023]
86. The complex cation which has two isomers is [JEE-MAIN 2023]
- (A)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
 (B)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$   
 (C)  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$   
 (D)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]$

## EXERCISE : JEE-ADVANCED

- The complex ion which has no 'd' electrons in the central metal atom is : [JEE 2001]  
[Atomic number Cr = 24, Mn = 25, Fe = 26, Co = 27]  
(A)  $[\text{MnO}_4]^-$  (B)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (C)  $[\text{Fe}(\text{CH}_3)_6]^{3-}$  (D)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- The correct order of hybridisation of the central atom in the following species. [JEE 2001]  
 $\text{NH}_3$ ,  $[\text{PtCl}_4]^{2-}$ ,  $\text{PCl}_5$  and  $\text{BCl}_3$  is [At No. Pt = 78]  
(A)  $\text{dsp}^2, \text{sp}^3\text{d}, \text{sp}^2$  and  $\text{sp}^3$  (B)  $\text{sp}^3, \text{dsp}^2, \text{sp}^3\text{d}$ ,  $\text{sp}^2$   
(C)  $\text{dsp}^2, \text{sp}^2, \text{sp}^3$  and  $\text{sp}^3\text{d}$  (D)  $\text{dsp}^2, \text{sp}^3, \text{sp}^2$  and  $\text{sp}^3\text{d}$
- The species having tetrahedral shape is : [JEE 2004]  
(A)  $[\text{PdCl}_4]^{2-}$  (B)  $[\text{Ni}(\text{CN})_4]^{2-}$  (C)  $[\text{Pd}(\text{CN})_4]^{2-}$  (D)  $[\text{NiCl}_4]^{2-}$
- The pair of compounds having metals in their highest oxidation state is [JEE 2004]  
(A)  $\text{MnO}_2$ ,  $\text{FeCl}_3$  (B)  $[\text{MnO}_4]^-$ ,  $\text{CrO}_2\text{Cl}_2$   
(C)  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$  (D)  $[\text{NiCl}_4]^{2-}$ ,  $[\text{CoCl}_4]^-$
- Spin only magnetic moment of the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is [JEE 2004]  
(A)  $\sqrt{3}$  (B)  $\sqrt{15}$  (C)  $\sqrt{24}$  (D)  $\sqrt{8}$
- Which of the following pair is expected to exhibit same colour in solution? [JEE 2005]  
(A)  $\text{VOCl}_2$ ;  $\text{FeCl}_2$  (B)  $\text{CuCl}_2$ ;  $\text{VOCl}_2$  (C)  $\text{MnCl}_2$ ;  $\text{FeCl}_2$  (D)  $\text{FeCl}_2$ ;  $\text{CuCl}_2$
- Which type of isomerism is shown by  $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$ ? [JEE 2005]  
(A) Geometrical and Ionisation (B) Optical and Ionisation  
(C) Geometrical and Optical (D) Geometrical only

## Question No. 8 to 10 (3 questions)

[JEE 2006]

The coordination number of  $\text{Ni}^{2+}$  is 4. $\text{NiCl}_2 + \text{KCN (excess)} \rightarrow \text{A (cyano complex)}$  $\text{NiCl}_2 + \text{KCl (excess)} \rightarrow \text{B (chloro complex)}$ 

- The IUPAC name of A and B are  
(A) Potassium tetracyanonickelate (II), potassium tetrachloridonickelate (II)  
(B) Tetracyanidopotassiumnickelate (II), tetrachloridopotassiumnickelate (II)  
(C) Tetracyanidonickel (II), tetrachloridonickel (II)  
(D) Potassium tetracyanonickel (II), potassium tetrachloridonickel (II)

9. Predict the magnetic nature of A and B. [JEE 2006]  
 (A) Both are diamagnetic.  
 (B) A is diamagnetic and B is paramagnetic with one unpaired electron.  
 (C) A is diamagnetic and B is paramagnetic with two unpaired electrons.  
 (D) Both are paramagnetic.
10. The hybridization of A and B are [JEE 2006]  
 (A)  $dsp^2$ ,  $sp^3$  (B)  $sp^3$ ,  $sp^3$  (C)  $dsp^2$ ,  $dsp^2$  (D)  $sp^3d^2$ ,  $d^2sp^3$
11. If the bond length of CO bond in carbon monoxide is  $1.128\text{\AA}$ , then what is the value of CO bond length in  $\text{Fe}(\text{CO})_5$ ? [JEE 2006]  
 (A)  $1.15\text{\AA}$  (B)  $1.128\text{\AA}$  (C)  $1.72\text{\AA}$  (D)  $1.118\text{\AA}$
12. Among the following metal carbonyls, the C–O bond order is lowest in [JEE 2007]  
 (A)  $[\text{Mn}(\text{CO})_6]^+$  (B)  $[\text{Fe}(\text{CO})_5]$  (C)  $[\text{Cr}(\text{CO})_6]$  (D)  $[\text{V}(\text{CO})_6]^-$
13. Match the complexes in Column I with their properties listed in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. [JEE 2007]
- | Column I  | Column II                             |
|---|---------------------------------------|
| (A) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$ | (P) Geometrical isomers               |
| (B) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$                       | (Q) Paramagnetic                      |
| (C) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$         | (R) Diamagnetic                       |
| (D) $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$                | (S) Metal ion with 2+ oxidation state |
14. Among the following, the coloured compound is [JEE 2008]  
 (A)  $\text{CuCl}$  (B)  $\text{K}_3[\text{Cu}(\text{CN})_4]$  (C)  $\text{CuF}_2$  (D)  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$
15. The IUPAC name of  $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$  is [JEE 2008]  
 (A) Tetrachloronickel (II)-tetraamminenickel (II)  
 (B) Tetraamminenickel (II)-tetrachloronickel (II)  
 (C) Tetraamminenickel (II)-tetrachloronickelate (II)  
 (D) Tetrachloronickel (II)-tetraamminenickelate (0)

16. Both  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic. The hybridisations of nickel in these complexes, respectively, are [JEE 2008]  
 (A)  $\text{sp}^3$ ,  $\text{sp}^3$  (B)  $\text{sp}^3$ ,  $\text{dsp}^2$  (C)  $\text{dsp}^2$ ,  $\text{sp}^3$  (D)  $\text{dsp}^2$ ,  $\text{dsp}^2$
17. Statement-1 : The geometrical isomers of the complex  $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$  are optically inactive.  
 Statement-2 : Both geometrical isomers of the complex  $[\text{M}(\text{NH}_3)_4\text{Cl}_2]$  possess axis of symmetry.  
 (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True [JEE 2008]
18. Statement-1 :  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  is paramagnetic [JEE 2008]  
 Statement-2 : The Fe in  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  has three unpaired electrons.  
 (A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1  
 (B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True
19. The spin only magnetic moment value (in Bohr magneton units) of  $\text{Cr}(\text{CO})_6$  is [JEE 2009]  
 (A) 0 (B) 2.84 (C) 4.90 (D) 5.92
20. The compound(s) that exhibit(s) geometrical isomerism is (are) : [JEE 2009]  
 (A)  $[\text{Pt}(\text{en})\text{Cl}_2]$  (B)  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  (C)  $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$  (D)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
21. The number of water molecule(s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is. [JEE 2009]
22. The ionization isomer of  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$  is – [JEE 2010]  
 (A)  $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$  (B)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$   
 (C)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$  (D)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)] \cdot \text{H}_2\text{O}$

23. Total number of geometrical isomers for the complex  $[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$  is. [JEE 2010]
24. The correct structure of ethylenediaminetetraacetic acid (EDTA) is – [JEE 2010]
- (A)
- (B)
- (C)
- (D)
25. Geometrical shapes of the complexes formed by the reaction of  $\text{Ni}^{2+}$  with  $\text{Cl}^-$ ,  $\text{CN}^-$  and  $\text{H}_2\text{O}$  respectively, are - [JEE 2011]
- (A) octahedral, tetrahedral and square planar (B) tetrahedral, square planar and octahedral  
(C) square planar, tetrahedral and octahedral (D) octahedral, square planar and octahedral
26. Among the following complexes (K–P) [JEE 2011]  
 $\text{K}_3[\text{Fe}(\text{CN})_6]$  (K),  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (L),  $\text{Na}_3[\text{Co}(\text{oxalate})_3]$  (M),  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  (N),  
 $\text{K}_2[\text{Pt}(\text{CN})_4]$  (O) and  $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$  (P)  
 The diamagnetic complex are -  
 (A) K, L, M, N (B) K, M, O, P (C) L, M, O, P (D) L, M, N, O
27. The volume (in mL) of 0.1M  $\text{AgNO}_3$  required for complete precipitation of chloride ions present in 30 mL of 0.01M solution of  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ , as silver chloride is close to. [JEE 2011]
28. As per IUPAC nomenclature, the name of the complex  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$  is : [JEE 2012]
- (A) Tetraaquadiaminecobalt(III) chloride (B) Tetraaquadiamminecobalt(III) chloride  
(C) Diaminetetraaquacobalt(III) chloride (D) Diamminetetraaquacobalt(III) chloride

29. The colour of light absorbed by an aqueous solution of  $\text{CuSO}_4$  is - [JEE 2012]  
 (A) orange-red (B) blue-green (C) yellow (D) violet
30.  $\text{NiCl}_2\{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2$  exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of  $\text{Ni}^{2+}$  in the paramagnetic and diamagnetic states are respectively : [JEE 2012]  
 (A) tetrahedral and tetrahedral (B) square planar and square planar  
 (C) tetrahedral and square planar (D) square planar and tetrahedral
31. Consider the following complex ions P, Q and R ,  
 $\text{P} = [\text{FeF}_6]^{3-}$ ,  $\text{Q} = [\text{V}(\text{H}_2\text{O})_6]^{2+}$  and  $\text{R} = [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is - [JEE 2013]  
 (A)  $\text{R} < \text{Q} < \text{P}$  (B)  $\text{Q} < \text{R} < \text{P}$  (C)  $\text{R} < \text{P} < \text{Q}$  (D)  $\text{Q} < \text{P} < \text{R}$
32.  $\text{EDTA}^{4-}$  is ethylenediaminetetraacetate ion. The total number of N–Co–O bond angles in  $[\text{Co}(\text{EDTA})]^{-1}$  complex ion is [JEE 2013]
33. The pair(s) of coordination complex/ion exhibiting the same kind of isomerism is(are) – [JEE 2013]  
 (A)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  (B)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$   
 (C)  $[\text{CoBr}_2\text{Cl}_2]^{2-}$  and  $[\text{PtBr}_2\text{Cl}_2]^{2-}$  (D)  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$
34. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists. [JEE Adv. 2014]  
 {en =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  ' atomic numbers ; Ti = 22 ; Cr = 24 ; Co = 27 ; Pt = 78}

## List-I

- (P)  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (Q)  $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$   
 (R)  $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3$   
 (S)  $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$

Code :

## List-II

- (1) Paramagnetic and exhibits ionisation isomerism  
 (2) Diamagnetic and exhibits cis-trans isomerism  
 (3) Paramagnetic and exhibits cis-trans isomerism  
 (4) Diamagnetic and exhibits ionisation isomerism

	P	Q	R	S		P	Q	R	S
(A)	4	2	3	1	(B)	3	1	4	2
(C)	2	1	3	4	(D)	1	3	4	2



35. A list of species having the formula  $XZ_4$  is given below : [JEE Adv. 2014]  
 $XeF_4$ ,  $SF_4$ ,  $SiF_4$ ,  $BF_4^-$ ,  $BrF_4^-$ ,  $[Cu(NH_3)_4]^{2+}$ ,  $[FeCl_4]^{2-}$ ,  $[CoCl_4]^{2-}$  and  $[PtCl_4]^{2-}$ .  
Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

**Subjective**

36. Draw the structures of  $[Co(NH_3)_6]^{3+}$ ,  $[Ni(CN)_4]^{2-}$  and  $[Ni(CO)_4]$ . Write the hybridisation of atomic orbitals of the transition metal in each case. [JEE 2000]
37. A metal complex having composition  $Cr(NH_3)_4 Cl_2 Br$  has been isolated in two forms A and B. The form A reacts with  $AgNO_3$  to give a white precipitate readily soluble in dilute aqueous ammonia, whereas B gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of A and B and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). [JEE 2001]
38. Deduce the structures of  $[NiCl_4]^{2-}$  and  $[Ni(CN)_4]^{2-}$  considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. [JEE 2002]
39. Write the IUPAC name of the compound  $K_2[Cr(NO)(CN)_4(NH_3)]$ . Spin magnetic moment of the complex  $\mu = 1.73$  BM. Give the structure of anion. [JEE 2003]
40.  $NiCl_2$  in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of  $NH_4OH$ , giving a bright red colour. [JEE 2004]  
(a) Draw its structure and show H-bonding  
(b) Give oxidation state of Ni and its hybridisation  
(c) Predict whether it is paramagnetic or diamagnetic
41. For the octahedral complexes of  $Fe^{3+}$  in  $SCN^-$  (thiocyanato-S) and in  $CN^-$  ligand environments, the difference between the spin only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is : [Atomic number of Fe = 26] [JEE Ad. 2015]
42. In the complex acetylbromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe-C bond(s) is- [JEE Ad. 2015]

43. Among the complex ions,  $[\text{Co}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2\text{Cl}_2]^+$ ,  $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ ,  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$ ,  $[\text{Co}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ , the number of complex ion(s) that show(s) cis-trans isomerism is – **[JEE Ad. 2015]**
44. Among  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{NiCl}_4]^{2-}$ ,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ,  $\text{Na}_3[\text{CoF}_6]$ ,  $\text{Na}_2\text{O}_2$  and  $\text{CsO}_2$ , the total number of paramagnetic compounds is – **[JEE Ad. 2016]**  
 (A) 2 (B) 3 (C) 4 (D) 5
45. The number of geometric isomers possible for the complex  $[\text{CoL}_2\text{Cl}_2]^-$  ( $\text{L} = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$ ) is **[JEE Ad. 2016]**
46. The geometries of the ammonia complexes of  $\text{Ni}^{2+}$ ,  $\text{Pt}^{2+}$  and  $\text{Zn}^{2+}$ , respectively, are : **[JEE Ad. 2016]**  
 (A) octahedral, square planar and tetrahedral  
 (B) square planar, octahedral and tetrahedral  
 (C) tetrahedral, square planar and octahedral  
 (D) octahedral, tetrahedral and square planar
47. Addition of excess aqueous ammonia to a pink coloured aqueous solution of  $\text{MCl}_2 \cdot 6\text{H}_2\text{O}$  (X) and  $\text{NH}_4\text{Cl}$  gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess  $\text{HCl}$  at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. **[JEE Ad. 2017]**  
 Among the following options, which statement(s) is(are) correct ?  
 (A) The hybridization of the central metal ion in Y is  $d^2 sp^3$   
 (B) Z is a tetrahedral complex  
 (C) Addition of silver nitrate to Y gives only two equivalents of silver chloride  
 (D) When X and Z are in equilibrium at  $0^\circ\text{C}$ , the colour of the solution is pink
48. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers: Fe = 26, Ni = 28) **[JEE ADV. 2018]**  
 (A) Total number of valence shell electrons at metal centre in  $\text{Fe}(\text{CO})_5$  or  $\text{Ni}(\text{CO})_4$  is 16  
 (B) These are predominantly low spin in nature  
 (C) Metal–carbon bond strengthens when the oxidation state of the metal is lowered  
 (D) The carbonyl C–O bond weakens when the oxidation state of the metal is increased

49. The correct option(s) regarding the complex  $[\text{Co}(\text{en})(\text{NH}_3)_3(\text{H}_2\text{O})]^{3+}$  (en =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) is (are) [JEE ADV. 2018]
- (A) It has two geometrical isomers  
 (B) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands  
 (C) It is paramagnetic  
 (D) It absorbs light at longer wavelength as compared to  $[\text{Co}(\text{en})(\text{NH}_3)_4]^{3+}$

50. Match each set of hybrid orbitals from LIST-I with complex(es) given in LIST-II. [JEE ADV. 2018]

LIST-I		LIST-II	
P.	$\text{dsp}^2$	1.	$[\text{FeF}_6]^{4-}$
Q.	$\text{sp}^3$	2.	$[\text{Ti}(\text{H}_2\text{O})_3\text{Cl}_3]$
R.	$\text{sp}^3\text{d}^2$	3.	$[\text{Cr}(\text{NH}_3)_6]^{3+}$
S.	$\text{d}^2\text{sp}^3$	4.	$[\text{FeCl}_4]^{2-}$
		5.	$\text{Ni}(\text{CO})_4$
		6.	$[\text{Ni}(\text{CN})_4]^{2-}$

The correct option is

- (A)  $\text{P} \rightarrow 5$ ;  $\text{Q} \rightarrow 4,6$ ;  $\text{R} \rightarrow 2,3$ ;  $\text{S} \rightarrow 1$   
 (B)  $\text{P} \rightarrow 5,6$ ;  $\text{Q} \rightarrow 4$ ;  $\text{R} \rightarrow 3$ ;  $\text{S} \rightarrow 1,2$   
 (C)  $\text{P} \rightarrow 6$ ;  $\text{Q} \rightarrow 4,5$ ;  $\text{R} \rightarrow 1$ ;  $\text{S} \rightarrow 2,3$   
 (D)  $\text{P} \rightarrow 4,6$ ;  $\text{Q} \rightarrow 5,6$ ;  $\text{R} \rightarrow 1,2$ ;  $\text{S} \rightarrow 3$
51. Total number of cis N–Mn–Cl bond angles (that is, Mn–N and Mn–Cl bonds in cis positions) present in a molecule of cis- $[\text{Mn}(\text{en})_2\text{Cl}_2]$  complex is \_\_\_\_ (en =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) [JEE ADV. 2019]

52. Choose the correct statement(s) among the following: [JEE-ADVANCED-2020]

- (A)  $[\text{FeCl}_4]^-$  has tetrahedral geometry.  
 (B)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$  has 2 geometrical isomers.  
 (C)  $[\text{FeCl}_4]^-$  has higher spin-only magnetic moment than  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ .  
 (D) The cobalt ion in  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$  has  $\text{sp}^3\text{d}^2$  hybridization.

53. The calculated spin only magnetic moments of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  and  $[\text{CuF}_6]^{3-}$  in BM, respectively, are (Atomic numbers of Cr and Cu are 24 and 29, respectively).

[JEE-ADVANCED-2021]

- (A) 3.87 and 2.84 (B) 4.90 and 1.73  
 (C) 3.87 and 1.73 (D) 4.90 and 2.84

54. The total number of possible isomers for  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  is

[JEE-ADVANCED-2021]

55. The pair(s) of complexes wherein both exhibit tetrahedral geometry is(are)

(Note: py = pyridine, Given: Atomic numbers of Fe, Co, Ni and Cu are 26, 27, 28 and 29, respectively)

[JEE-ADVANCED-2021]

- (A)  $[\text{FeCl}_4]^-$  and  $[\text{Fe}(\text{CO})_4]^{2-}$  (B)  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{CoCl}]^{2-}$   
 (C)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  (D)  $[\text{Cu}(\text{py})]^+$  and  $[\text{Cu}(\text{CN})_4]^{3-}$

#### Statement for Questions 56 and 57

The reaction of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with freshly prepared  $\text{FeSO}_4$  solution produces a dark blue precipitate called Turnbull's blue. The reaction of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  with the  $\text{FeSO}_4$  solution in the complete absence of air produces a white precipitate X, which turns blue in the air. Mixing the  $\text{FeSO}_4$  solution with  $\text{NaNO}_3$ , followed by slow addition of concentrated  $\text{H}_2\text{SO}_4$  through the side of the test tube produces a brown ring.

56. Precipitate X is

- (A)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (B)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]$   
 (C)  $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$  (D)  $\text{KFe}[\text{Fe}(\text{CN})_6]$

57. Among the following, the brown ring is due to the formation of

- (A)  $[\text{Fe}(\text{NO})_2(\text{SO}_4)_2]^{2-}$  (B)  $[\text{Fe}(\text{NO})_2(\text{H}_2\text{O})_4]^{3+}$   
 (C)  $[\text{Fe}(\text{NO})_4(\text{SO}_4)_2]$  (D)  $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$

## ANSWER KEY

## Do yourself – 1

Question	1	2	3	4	5
Answer	D	A	B	D	B

## Do yourself – 2

Question	1	2	3	4	5
Answer	D	C	A	D	B

## Do yourself – 3

Question	1	2	3	4	5
Answer	B	C	C	D	D

## Do yourself – 4

Question	1	2	3	4	5
Answer	D	A	C	D	C

## Do yourself – 5

Question	1	2	3	4	5
Answer	B	A	A	C	A

## Do yourself – 6

Question	1	2	3	4	5
Answer	D	B	D	D	C

## EXERCISE – I

1.	A	2.	B	3.	A	4.	B	5.	C	6.	D	7.	A
8.	C	9.	D	10.	C	11.	B	12.	B	13.	D	14.	A
15.	D	16.	D	17.	B	18.	D	19.	B	20.	B	21.	C
22.	D	23.	C	24.	B	25.	C	26.	B	27.	C	28.	C
29.	B	30.	C	31.	B	32.	B	33.	D	34.	C	35.	B
36.	B	37.	C	38.	A	39.	D	40.	B	41.	B	42.	B
43.	B	44.	C	45.	C	46.	D	47.	D	48.	C	49.	C
50.	D	51.	A	52.	C	53.	C	54.	D	55.	D	56.	B
57.	A	58.	B	59.	A	60.	C	61.	C	62.	A	63.	D
64.	C	65.	A	66.	A	67.	D	68.	C	69.	A	70.	D
71.	A	72.	D	73.	C	74.	D	75.	C	76.	B	77.	D
78.	B	79.	C	80.	D	81.	B	82.	C	83.	B	84.	B
85.	B	86.	B	87.	C	88.	C	89.	A	90.	A	91.	C
92.	A	93.	A	94.	C	95.	C	96.	C	97.	A	98.	B
99.	B	100.	B	101.	C	102.	B	103.	A	104.	B	105.	B

## EXERCISE – II

1.	AB	2.	ABD	3.	ABCD	4.	ABC	5.	AD	6.	ABD	7.	ABD
8.	AB	9.	BCD	10.	ABCD	11.	AD	12.	BC	13.	BCD	14.	ABCD

## EXERCISE – III

1.	(A)- PS (B)- T(C)- QRT (D)- PS				2.	(A)- R (B)- R (C)- P (D)- Q							
3.	(A)- QST (B)- PR (C)- PR (D)- PR				4.	(A)- P ; (B)- RS (C)- PQS (D)- QR							
5.	(A)- PR ; (B)- PQR ; (C)- QS (D)- PQS				6.	(A)- PQS (B)- QRS (C)- P (D)- PQ							
7.	C	8.	D	9.	C	10.	B	11.	C	12.	B	13.	A
14.	C	15.	D	16.	D	17.	A	18.	D	19.	B	20.	B
21.	B	22.	C										

## EXERCISE – JEE MAIN

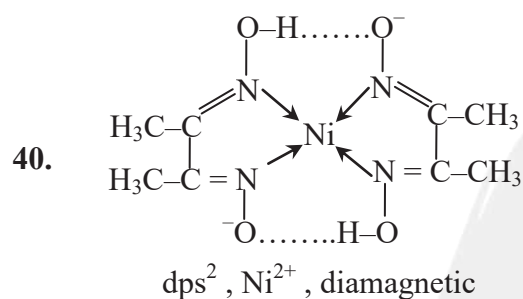
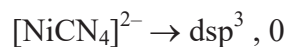
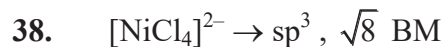
1.	2	2.	3	3.	4	4.	1	5.	3	6.	2	7.	1
8.	3	9.	4	10.	3	11.	3	12.	1	13.	2	14.	4
15.	4	16.	1	17.	3	18.	4	19.	4	20.	1	21.	4
22.	2	23.	3	24.	1	25.	1	26.	2	27.	3	28.	3
29.	3	30.	1	31.	3	32.	3	33.	4	34.	3	35.	4
36.	4	37.	4	38.	1	39.	3	40.	3	41.	3	42.	2
43.	4	44.	4	45.	1	46.	3	47.	3	48.	4	49.	3
50.	3	51.	1	52.	2	53.	3	54.	4	55.	2	56.	2
57.	1	58.	4	59.	2	60.	3	61.	4	62.	4	63.	2
64.	4	65.	3	66.	2	67.	2	68.	1	69.	2	70.	(B)
71.	(C)	72.	(D)	73.	(B)	74.	(D)	75.	(D)	76.	(A)	77.	(C)
78.	(D)	79.	2	80.	(A)	81.	7	82.	(B)	83.	(D)	84.	(A)
85.	(480)	86.	(C)										

## EXERCISE – JEE ADVANCED

1.	A	2.	B	3.	D	4.	B	5.	B	6.	B	7.	A
8.	A	9.	C	10.	A	11.	A	12.	D				
13.	(A)-P, Q,S ; (B)-P,R,S ; (C)- Q,S ; (D)- Q,S							14.	C	15.	C	16.	B
17.	B	18.	A	19.	A	20.	CD						
21.													
22.	B	23.	3	24.	C	25.	B	26.	C	27.	6	28.	D
29.	A	30.	C	31.	B	32.	8	33.	BD	34.	B	35.	4
36.	$d^2sp^3$ , $dsp^2$ and $sp^3$												



In both Cr is  $d^2 sp^3$  hybridised and magnetic moment is  $\sqrt{15}$  BM



- |     |     |     |     |     |     |     |   |     |    |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|---|-----|----|-----|-----|-----|-----|
| 41. | 4   | 42. | 3   | 43. | 6   | 44. | B | 45. | 5  | 46. | A   | 47. | ABD |
| 48. | BC  | 49. | ABD | 50. | C   | 51. | 6 | 52. | AC | 53. | (A) | 54. | 6   |
| 55. | ABD | 56. | (C) | 57. | (D) |     |   |     |    |     |     |     |     |



## Hint's &amp; Solutions

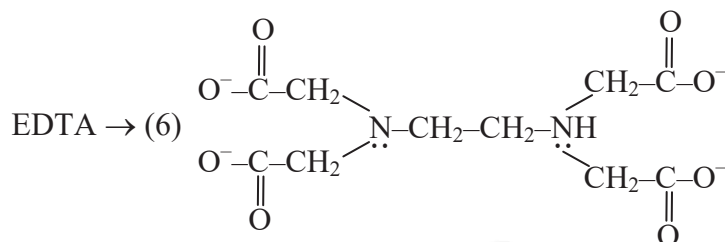
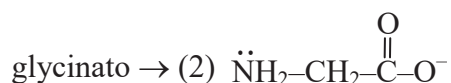
## EXERCISE-1

- For the complex  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$   
 Oxidation no. of Cr  $\rightarrow +3$   
 Co-ordination no. of Cr  $\rightarrow 6$
- $[\text{Cr}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2]^-$   
 Oxidation state  $\rightarrow -4 + x = -1$   
 $x = 3$   
 co-ordination number  $\rightarrow 2 + 4 = 6$   
 Charge on complex if all ligands were chloride ions  $= +3 + (-6)$   
 $= -3$
- $\text{Ag}^+ + \text{excess CN}^- \rightarrow [\text{Ag}(\text{CN})_2]^-$
- Geometrical isomerism can be shown by  
 It forms  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 $\Rightarrow$  it does not give test of  $\text{Fe}^{+2}$
- Vanadium does not show +6 oxidation state.
- Only one  $\text{EDTA}^{4-}$  molecules are required to form octahedral complex.
- Diethylenetriamine is tridentate ligand  

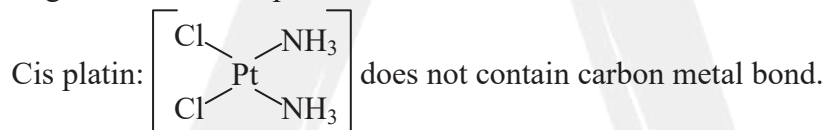
$$\begin{array}{c} \text{H}_2\text{N}-\text{H}_2\text{C}-\text{H}_2\text{C}-\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 \\ \swarrow \quad \downarrow \quad \searrow \\ \quad \quad \text{M} \end{array}$$
- Ethylenediamine triacetate ion  

$$\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{O}^- - \text{C} - \text{CH}_2 \quad \quad \text{CH}_2 - \text{C} - \text{O}^- \\ \quad \quad \quad \diagdown \quad \quad \diagup \\ \quad \quad \quad \text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH} \\ \quad \quad \quad \diagup \quad \quad \diagdown \\ \text{O}^- - \text{C} - \text{CH}_2 \quad \quad \text{CH}_2 - \text{C} - \text{O}^- \\ \parallel \quad \quad \parallel \\ \text{O} \quad \quad \quad \text{O} \end{array}$$
- $\text{NH}_4^+ \rightarrow$  not a ligand because it does not have lone pair
- glyoxime  $\rightarrow (2)$ 

$$\begin{array}{c} \text{O}^- - \ddot{\text{N}} = \text{C} - \text{CH}_3 \\ | \\ \text{OH} - \ddot{\text{N}} = \text{C} - \text{CH}_3 \end{array}$$



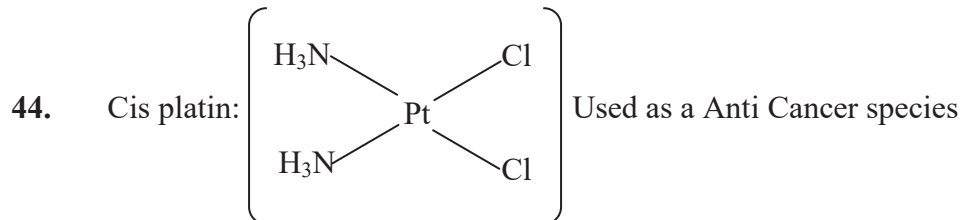
13. EDTA used to estimation of both  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$  ion.
14.  $\pi$  - acceptors ligands: These ligands accept electron into it's Vacant ABMO.  
 $\text{CO}$ ,  $\text{CN}^-$  &  $\text{NO}^+$  all are  $\pi$ -acceptor's ligand.
15. In  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe--C}$  possesses both  $\sigma$  &  $\pi$  character due to synergic bonding.
16.  $\text{R--MgX} \rightarrow$  These is no  $\pi$  bond in Grignard reagent
17. Organometallic compound contains at least on bond between carbon atoms & a metal.



19.  $[\text{Fe}(\text{C}_2\text{H}_5)_2] \rightarrow \pi$  complex contains  $\pi$  electron doner ligands  
ferrocene is an example of  $\pi$  complex
20.  $[\text{V}(\text{CO})_6]^- < [\text{Cr}(\text{CO})_6] < [\text{Mn}(\text{CO})_6]^+$   
Negative charge an metal increases the synergic bonding.  
Hence C--O bond strength decreases.
21.  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  does not follow Sedgwick effective atomic number rule.  
 $\text{EAN} = 28 - 2 + 6 \times 2$   
 $= 38$
23. Carbonyl compound follow the Sedgwick effective atomic number rule  
 $26 + 2 \times x = 36$   
 $x = 5$

- 97

43.  $[\text{Ma}_3\text{b}_3]$  type compound show facial and meridional isomerism

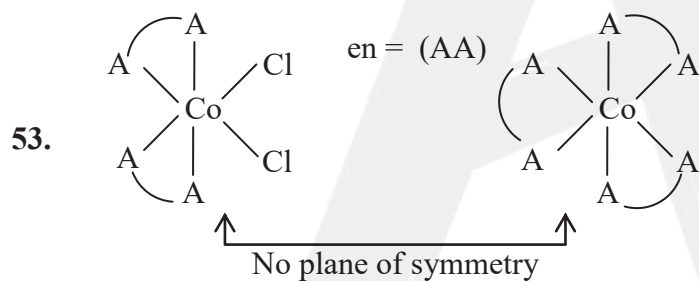


46.  $[\text{Cr}(\text{NCS})(\text{NH}_3)_5][\text{ZnCl}_4]$  show both co-ordination & Linkage Isomerism

48.  $[\text{Cu}(\text{NH}_3)_3\text{Cl}]$   $[\text{PtCl}_3(\text{NH}_3)]$   
 $[\text{CuNH}_3\text{Cl}_3]$   $[\text{PtCl}(\text{NH}_3)_3]$   
 $[\text{CuCl}_4]$   $[\text{Pt}(\text{NH}_3)_4]$   
 Total four isomers

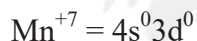
50.  $[\text{CoSO}_4(\text{NH}_3)_5]\text{Br}$  and  $[\text{CoSO}_4(\text{NH}_3)_5]\text{Cl}$  show no Isomerism because both have different compound.

52.  $[\text{PtCl}_4\text{I}_2]$  show cis-tran isomerism



55.  $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$  show ionization isomer  
 $\rightarrow$  it's isomer is  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$

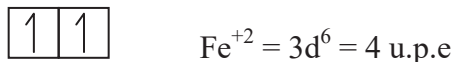
57. In  $[\text{MnO}_4]^-$ , oxidation state =  $x + (-8) = -1$   
 $x = +7$



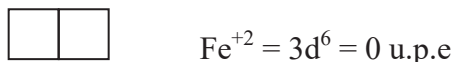
58. Iron Pentacarbonyl  $[\text{Fe}(\text{CO})_5]$   
 (CO) is strong field ligand  
 $\text{dsp}^2$  hybridisation  $\Rightarrow$  trigonal bipyramidal

59.  $\text{NiCO}_4$  &  $[\text{Ni}(\text{NH}_3)_4]^{2+}$  do not differ in  $\mu$  both have same magnetic moment

61. Case - 1 :  $3d^6$  in case of W.F.L.



- Case - 2 :  $3d^6$  in case of S.F.L.



63.  $[\text{CoF}_6]^{-3} \Rightarrow \text{Co}^{+3} = 3d^6 \Rightarrow \text{F}^-$  is a W.F.L.  $\rightarrow$  outer orbital complex  
 $[\text{Co}(\text{NH}_3)_6]^{+3} \Rightarrow \text{Co}^{+3} = 3d^6 \Rightarrow \text{NH}_3$  is a S.F.L.  $\rightarrow$  inner orbital complex

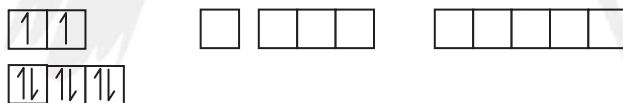
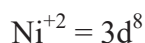
64.  $[\text{CoCl}_4]^-$   $\begin{array}{|c|c|c|c|} \hline 1 & 1 & 1 & \\ \hline \end{array}$   
 $\text{Co}^{+3} \Rightarrow 3d^6 \rightarrow \text{Cl}$  is W.F.L.  $\begin{array}{|c|c|c|} \hline 1\downarrow & 1 & \\ \hline \end{array}$

Tetrahedral compound

65.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 \Rightarrow \text{Cr}^{+3} = 3d^3$  ;  $\mu = 3.83 \text{ B.M}$   
 $3d_{xy}^1 3d_{yz}^1 3d_{zx}^1$


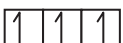
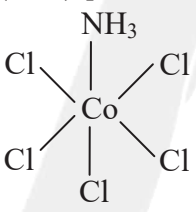
66.  $[\text{MnCl}_4]^{-2} \Rightarrow \text{Mn}^{+2} = 3d^5$   
 $\text{Cl}$  is W.F.L.  $\Rightarrow 5 \text{ u.p.e.}$   
 $[\text{CoCl}_4]^{-2} \Rightarrow \text{Cl}$  is W.F.L.  $\Rightarrow \text{Co}^{+2} = 3d^7 \Rightarrow 3 \text{ u.p.e.}$   
 $[\text{Fe}(\text{CN})_6]^{-2} = 3d^6 \Rightarrow \text{CN}^-$  is S.F.L.  $= 0 \text{ u.p.e}$

67. For S.F.L.  $\Delta_0 > P$



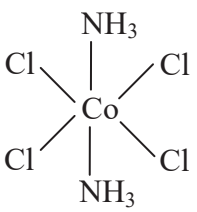
68.  $\Rightarrow \text{K}_3[\text{Cu}(\text{CN})_4]$  ,  $(\text{CN}^-)$  is a S.F.L  
 $\text{Cu}^+ \rightarrow 3d^{10}$  ,  $sp^3$ , tetrahedral, diamagnetic

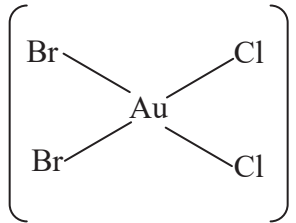
69. Strength of ligand increases  $\Rightarrow$  CSFE increases  
 $\text{CN}^-$  is strongest ligand among the above options

70.  $[\text{Co}(\text{NH}_3)_6]^{+3}$   $[\text{CoF}_6]^{-3}$   
 $\text{Co}^{+3} = 3d^6$   $\text{Co}^{+3} = 3d^6$   
 $\text{NH}_3$  is S.F.L.  $\text{F}^-$  is W.F.L.  
u.p.e = 0 u.p.e = 4
71.  $\text{Zn}^{+2} = 3d^{10} \Rightarrow \text{u.p.e} = 0 \Rightarrow \text{magnetic moment} = \text{zero}$
73.  $[\text{FeF}_6]^{-3} \Rightarrow \text{Fe}^{+3} = 3d^5 \Rightarrow \text{F is W.F.L.} \Rightarrow \Delta_0 < p$   
  
  
 $\text{CSFE} = 10\Delta_0 \times 3 \times (-0.4) + 10\Delta_0 \times 2(0.6)$   
 $= 0 \text{ Dq}$
75.  $\text{Ni}^{+2} = 3d^8 \Rightarrow \text{Cl}^-$  is W.F.L.  
 $\text{sp}^3$  hybridisation  $\Rightarrow$  tetrahedral
77.  $\text{Ti}^{+4}$  &  $\text{Cu}^+$  have no unpaired electron in  $\text{TiF}_6^{2-}$  and  $\text{Cu}_2\text{Cl}_2$   
Both compounds are colourless
78. Oxidation number of Fe in violet coloured Complex  $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NOS})]$   
 $x - 5 - 1 = -4$   
 $x = +2$
79. In  $\text{K}_3[\text{VF}_6]$ ,  $\text{V}^{+3} = 3d^2 = \text{two u.p.e.} \Rightarrow \text{it is coloured compound}$
81.  $[\text{CoCl}_4(\text{NH}_3)_2]^-$
- 

1

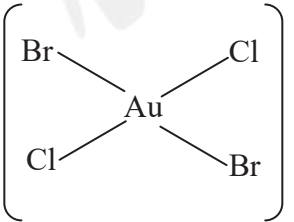
Cis

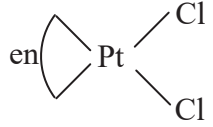


Trans
- 

2

Cis

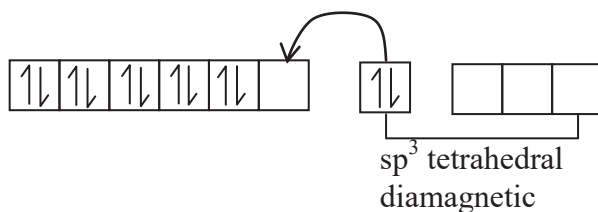


Trans
- 

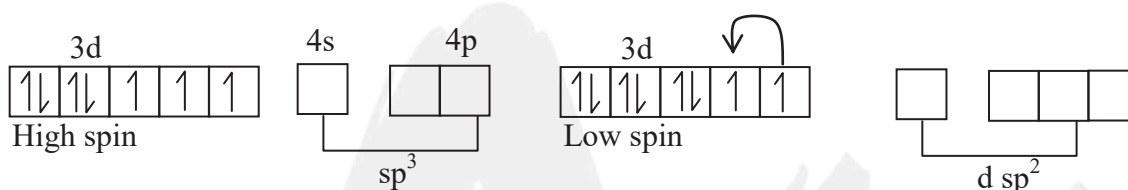
3

no isomerism

82.  $[\text{Co}(\text{CO})_4]^-$   
 $\text{Co}^- = 4s^2 3d^8 \Rightarrow \text{CO is S.F.L.} \Rightarrow \text{electron pair of } 4s \text{ orbital transfer into } 3d \text{ orbital}$



85.  $[\text{CoI}_4]^{-2} = \text{Co}^{+2}$   $[\text{PdBr}_4]^{-2}$   
 $\text{Co}^{+2} = 3d^7$   $\text{Pd}^{+2} = 4d^8$   
 CO is S.F.L.  $dsp^2 \Rightarrow \text{no u.p.e.} \Rightarrow \text{low spin complex}$   
 $sp^3 \Rightarrow 3 \text{ u.p.e.}$



86.  $\text{H}_2\text{O}$  being a W.F.L.  
 $\text{Cr}^{+3} = 3d^3 \Rightarrow 3 \text{ unpaired electron}$   
 $\text{Fe}^{+2} = 3d^6 \Rightarrow 4 \text{ unpaired electron}$   
 $\text{Cu}^{+2} = 3d^9 \Rightarrow 1 \text{ unpaired electron}$   
 $\text{Zn}^{+2} = 3d^{10} \Rightarrow 0 \text{ unpaired electron}$   
 No. of u.p.e increases  $\Rightarrow$  paramagnetism increases
87. In  $\text{VOSO}_4 \Rightarrow \text{V}^{+4} \Rightarrow 3d^1 \Rightarrow 1 \text{ u.p.e}^- \Rightarrow \text{paramagnetic \& coloured}$
88.  $\text{Ni}^{+2} = 3d^8 \Rightarrow \text{for C.N.} = 4 \Rightarrow \text{two hybridization is possible.}$   
 (i)  $dsp^2$ , square planer,  $\mu = 0$   
 (ii)  $sp^3$ , tetrahedral,  $\mu \neq 0$
89.  $\text{FeK}_2[\text{FeCN}_6]$   
**Case – 1** CMA is  $\text{Fe}^{+3}$   
 $\Rightarrow$  Charge on complex is  $= -3$   
 $\Rightarrow \text{FeK}_2 = +3$   
 $x + 2 = +3$   
 $x = +1$

**Case – 2** CMA is  $\text{Fe}^{+2}$   
 $\Rightarrow$  Charge on complex is  $= -4$   
 $\Rightarrow \text{FeK}_2 = +4$   
 $x + 2 = +4$   
 $x = +2$   
 so case 2 is valid

**90.** Brown ring complex  $= [\text{Fe}(\text{H}_2\text{O}_5)\text{NO}]\text{SO}_4$   
 M.M. = 3.87 B.M  
 number of unpaired  $e^- = 3$   
 Oxidation state of C.M.A  $\Rightarrow x + 0 + 1 = 2$   
 $x = +1$

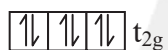
NO is present in form of  $\text{NO}^+$

**91.**  $[\text{Sc}(\text{H}_2\text{O}_6)]^{+3} \Rightarrow \text{Sc}^{+3} = 4s^0 3d^0$   
 $d^0$  configuration do not show colour.

**93.** In  $[\text{MnO}_4]^- \Rightarrow \text{Mn}^{+7} = 4s^0 3d^0 \Rightarrow$  no d electron

**95.** (A)  $d^6$ , S.F.L.  $\Rightarrow$  no. u.p. $e^-$   
 (B)  $d^7$ , high spin  $\Rightarrow 3$  u.p. $e^-$   
 (C)  $d^4$ , W.F.L.  $\Rightarrow 4$  u.p. $e^-$   
 (D)  $d^2$ , S.F.L.  $\Rightarrow 2$  u.p. $e^-$

**96.**



Symmetrical electron distribution in  $t_{2g}$  orbital

**97.** Chlorophyll contains  $\text{Mg}^{+2}$  not  $\text{Ca}^{+2}$  ion

**98.** Formation constant (K) $\uparrow \Rightarrow$  stability of complex  $\uparrow \Rightarrow$  strength of ligand  $\uparrow$

**99.**  $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O})]^{2-}$   
 $2x + (-8) = -2$   
 $x = +3$

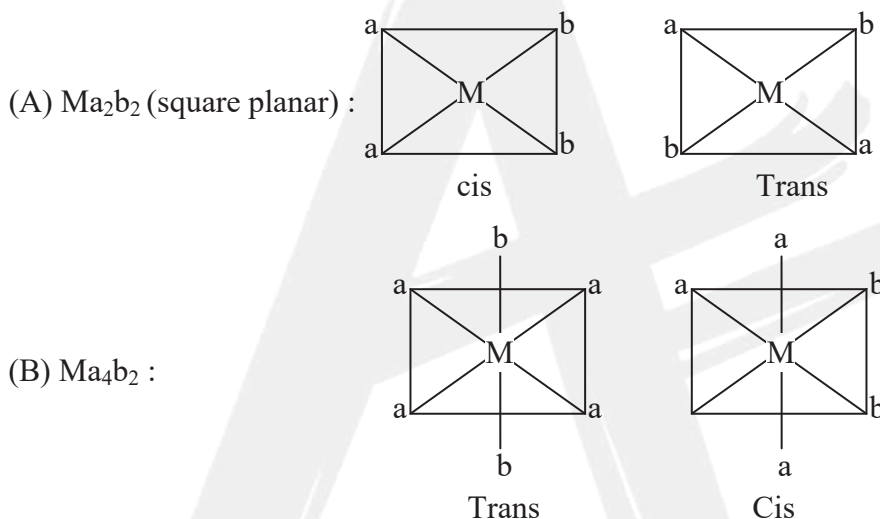
**100.** Only Cis form react with oxalic acid to form  $[\text{Ni}(\text{C}_2\text{O}_4)(\text{NH}_3)_2]$



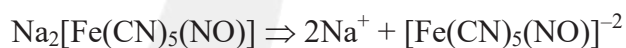
101. Basic character of ligand increases  $\Rightarrow$  stability of complex increases
102.  $[\text{Cu(en)}_2]\text{SO}_4$  Two ion are formed  $[\text{Cu(en)}_2]^{+2}$  and  $\text{SO}_4^{-2}$
103.  $\text{AgCl} + \text{NH}_4\text{OH} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$
104.  $[\text{Fe}(\text{CN})_5(\text{NOS})]^{-4}$   
 $x - 5 - 1 = -4$   
 $x = +2$
105. Oxidation state of Zinc will remain same during complex formation.

## EXERCISE II

1. molecule exhibit geometrical isomerism :



2. (A) The NO in sodium nitroprusside in +1 oxidation state so :



So oxidation state of Fe :

$$x + (-5) + 1 = -2$$

$$x - 4 = -2 \Rightarrow x = +2$$



Linear

$\text{sp}^2$ -hybridization

(D) CO is neutral ligand so oxidation of Ni in  $[\text{Ni}(\text{CO})_4]$  is zero.

5.  $d^n$  configuration of complex independent from high and low spin :

Ex.  $\rightarrow d^1, d^2, d^3$ -configuration.

$\rightarrow d^8$  to  $d^{10}$ -configuration.

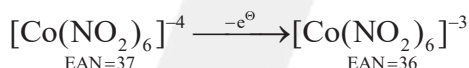
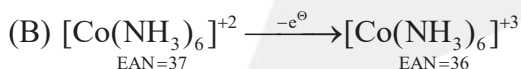
6.	$[\text{Cu}(\text{CN})_4]^{-3}$	$[\text{Cd}(\text{CN})_4]^{-2}$	$[\text{Cu}(\text{NH}_3)_4]^{+2}$
	Oxidation state of Cu $\Rightarrow +1$	Oxidation state of Cd $\Rightarrow +2$	Oxidation state fo Cu $\Rightarrow +2$
	$\text{Cu}^+ \Rightarrow 3d^{10}$	$\text{Cd}^{+2} \Rightarrow 4d^{10}$	$\text{Cu}^{+2} \Rightarrow 3d^9$
	geometry $\Rightarrow$ Tetrahedral	geometry $\Rightarrow$ Tetrahedral	geometry $\Rightarrow$ square planar
	hybridization $\Rightarrow sp^3$	hybridization $\Rightarrow sp^3$	hybridization $\Rightarrow dsp^2$ .
	Magnetic nature $\Rightarrow$	magnetic nature $\Rightarrow$	magnetic nature $\Rightarrow$
	diamagnetic	diamagnetic	paramagnetic
	$[\text{Cu}(\text{CN})_4]^{-3} + \text{H}_2\text{S} \longrightarrow \times$ (No reaction)		
	$[\text{Cd}(\text{CN})_4]^{-2} + \text{H}_2\text{S} \longrightarrow \text{CdS} \downarrow$ (yellow)		

“ $[\text{Cu}(\text{CN})_4]^{-2}$  act as perfect while  $[\text{Cd}(\text{CN})_4]^{-2}$  act as imperfect”

7. (A)  $\text{PBr}_5(\text{s}) \rightarrow \text{PBr}_4^+ + \text{Br}^\ominus$

$\text{PBr}_4^\oplus \Rightarrow$  geometry :- tetrahedral

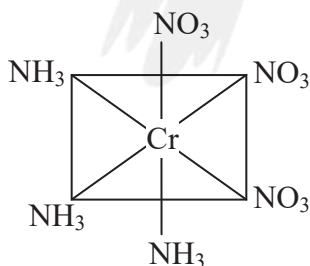
Hybridization :-  $sp^3$



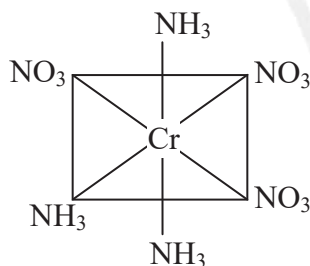
Both are oxidisable

- (D)  $d_{z^2}$  orbital never used in  $dsp^2$ - hybridization.

8. Compound having two stereo-isomeric form :

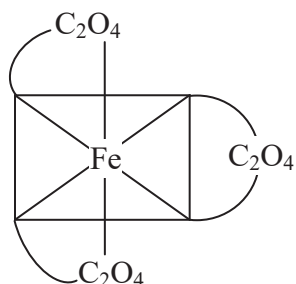


facial (POS present)

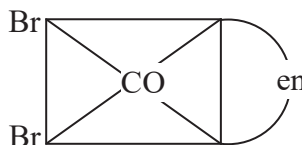


meridional (POS present)

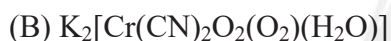
Stereo-isomers  $\Rightarrow 2$



POS absent  
(So total stereoisomerism = 2)



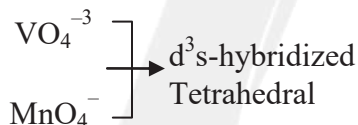
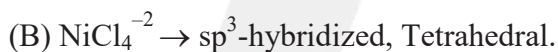
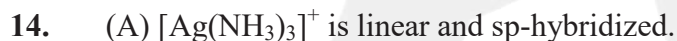
do not exhibit both  
geometrical and optical  
isomerism.



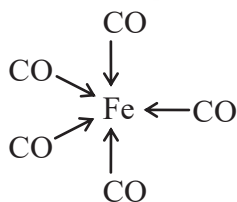
Potassium aquadicyanidosuperoxidoperoxidochromate (II)



(D) cis and Trans are diastereo-isomers.



(C) since  $NH_3$  is SFL and Pt belong to 4d series so both with WFL and SFL it form  $dsp^2$  with square planar geometry.



hybridization  $\Rightarrow d_{z^2} sp^3$   
geometry  $\Rightarrow$  Trigonal bipyramidal

13. Correct statement :



IUPACE name :

→ Tetra ammine di thiocyanato-N cobalt (III).

→ "It is chelating complex and contain. SCN (ambidentate ligand) so exhibit linkage also".

→ Anionic part of complex  $[\text{Co}(\text{Ox})_3]$  exhibit optical isomerism.

→ cation part of complex  $[\text{Co}(\text{SCN})_2(\text{NH}_3)_4]$  exhibit geometrical.

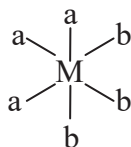
12. (A) element form coloured compound as it contain unpaired electron.

(B) Number of electron in  $t_{2g}$  orbital higher than eg.

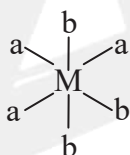
(C)  $d^1-d^3$    
  $d^8-d^{10}$  } configuration are independent from SFL or WFL.

### EXERCISE III

1. (A)  $[\text{CoCl}_3(\text{NH}_3)_3]$  is a case of  $\text{Ma}_3\text{b}_3$  it shows geometrical isomerism.

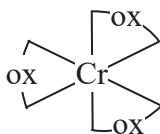


Facial



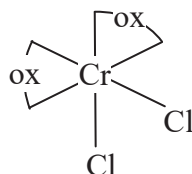
Meridional

(B)  $[\text{Cr}(\text{ox})_3]^{-3}$

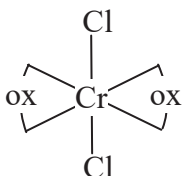


It does not show geometrical isomerism, but show optical isomerism

(C)  $[\text{CrCl}_2(\text{ox})_2]$  :



cis  
(optically active)

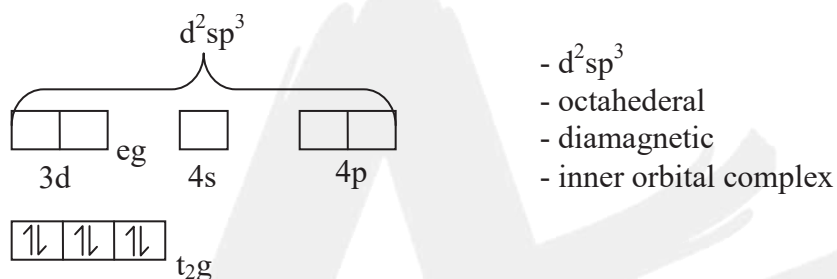


trans  
(optically inactive)

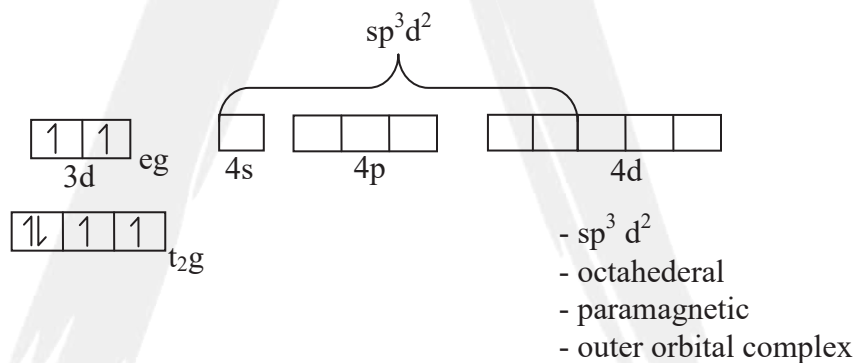
(D)  $[\text{RhCl}_3(\text{Py})_3]$  is same case as given above of  $\text{Ma}_3\text{b}_3$

2. (A)  $[\text{Fe}(\text{CO})_4]^{-2}$   
 $\text{EAN} = 26 + 2 + 2 \times 4 = 36$
- (B)  $[\text{CO}(\text{NH}_3)_5 \text{Cl}] \text{Cl}_2$   
 Refer to isomerism table given in sheet
- (C)  $\text{K}_2[\text{Ni}(\text{CO})_4]$   
 $\text{EAN} = 28 - 2 + 2 \times 4 = 34$
- (D)  $[\text{Cu}(\text{NH}_3)_4]^{+2}$   
 $\text{EAN} = 29 - 2 + 2 \times 4 = 35$

3. (A)  $[\text{Fe}(\text{NH}_3)_6]^{+2}$   
 $\text{Fe}^{+2} : [\text{Ar}] 4s^0 3d^6$ ,  $\text{NH}_3$  is S.F.L.



- (B)  $[\text{NiF}_6]^{-2}$   
 $\text{Ni}^{+4} : [\text{Ar}] 4s^0 3d^6$ ,  $\text{F}^-$  is WFL



- (C)  $[\text{Co}(\text{H}_2\text{O})_6]^{+3}$  -  $d^2sp^3$  (exception)  
 - octahedral  
 - diamagnetic  
 - inner orbital complex
- (D)  $[\text{Pt}(\text{Cl})_2(\text{NH}_3)_4]\text{Cl}_2$  -  $d^2sp^3$ , octahedral, diamagnetic, inner orbital complex

4. Refer to isomerism table given in sheet (page no.)

6. (A)  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$

$\text{Fe}^{2+} : [\text{Ar}] 4s^0 3d^6$ ,  $\text{CN}^-$  and  $\text{NO}^+$  both are S.F.L.

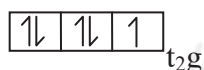
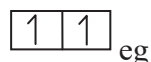
hence,  $d^2 sp^3$  hybridisation, diamagnetic ( $\mu = 0 \text{ BM}$ )

(B)  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  ;  $\text{Fe}^+$  ;  $[\text{Ar}] 4s^1 3d^6$

-  $\text{NO}$ , is present as  $\text{NO}^+$ .

-  $sp^3 d^2$ , octahedral

- paramagnetic  $\mu = \sqrt{15}$ , 3 unpaired  $e^-$  are present



(C)  $[\text{Ag}(\text{CN})_2]^-$   $sp$  hybridisation linear, diamagnetic ( $\mu = 0 \text{ BM}$ )

(D)  $\text{K}_4[\text{Fe}(\text{CN})_6]$

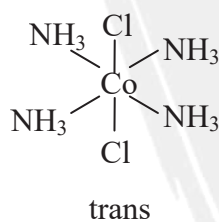
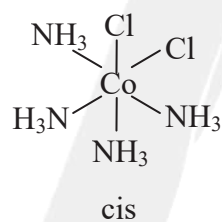
$\text{Fe}^{+2} : [\text{Ar}] 4s^0 3d^6$ ,  $\text{CN}^-$  is SFL

-  $d^2 sp^3$ , octahedral

- diamagnetic ( $\mu = 0 \text{ BM}$ )

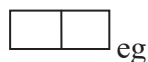
8.  $[\text{Cr}(\text{ox})_3]^{-3}$  &  $[\text{Co}(\text{en})_3]^{+3}$  show optical activity.

$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  shows G.I.



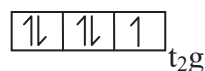
9.  $\text{K}_3[\text{Fe}(\text{CN})_6]$

$\text{Fe}^{+3} : [\text{Ar}] \Delta s^0 3d^5$ ,  $\text{CN}^-$  is SFL. thus pairing WFL occurs



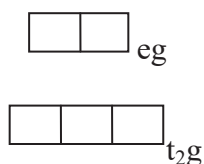
-  $d^2 sp^3$ , octahedral

- low spin complex



Fe is present in +3 oxidation state.

11. According to C.F.T. in octahedral complex splitting occurs as :

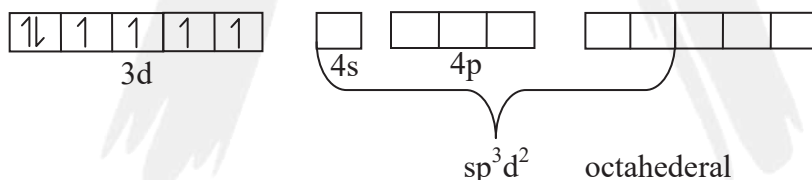


12. Organometallic compounds are those in which a polar metal – carbon bond is present. Metallic carboxyls are organometallic compounds.
13.  $\text{Ti}^{+3}$ :  $[\text{Ar}] 4s^0 3d^1$ , one unpaired electron is present hence d-d transition is possible & complex will be coloured.  
 $\text{Sc}^{+3}$ :  $[\text{Ar}] 4s^0 3d^0$ , zero unpaired electrons are present in 3d – subshell hence no d-d transition is possible.
14. Stability  $\propto$  strength of ligand
15.  $[\text{Mn}(\text{CO})_5]$  has EAN = 35 hence can attain stability by dimerisation or by accepting an  $e^-$ , so it can also behave as oxidising agent.
16. Ba is s-block metal, 5-block metals have least tendency to form complex compounds.
17. Molar conductance  $\propto$  no. of ions in aqueous solution.  
 Also Molar conductance  $\propto$  charge (present on ions)
18. Oxidation number of Cr in  $[\text{Cr}(\text{ox})_2(\text{NH}_3)_2]^{-1}$  is

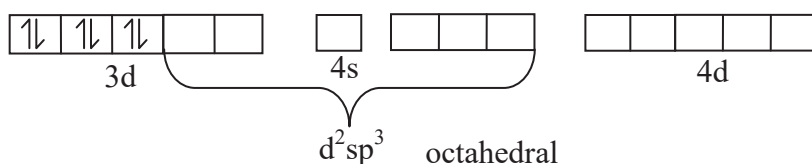
$$x + 2(-2) = -1 ; \quad x = +3$$

Coordination number = 6

19.  $[\text{CoF}_6]^{-3}$ ;  
 $\text{Co}^{+3}$ :  $[\text{Ar}] 4s^0 3d^6$ ,  $\text{F}^-$  is WFL



$\text{Co}^{+3}$   $[\text{Ar}] 4s^0 3d^6$ ,  $\text{NH}_3$  is SFL

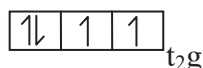
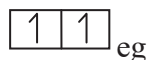


20. In octahedral geometry, after splitting the  $t_{2g}$  orbitals have lower energy as compared to  $e_g$  orbitals. So,  $t_{2g}$  will be filled first.

21.  $[\text{Co F}_6]^{-3}$



C.N. is 6 so geometry will be octahedral.



$$\text{CFSE} = (0.6 \eta_{e_g} - 0.4 \eta_{t_{2g}}) \Delta_0 + P_0$$

$$= (0.6 \times 2 - 0.4 \times 4) \Delta_0 + P_0$$

$$= (1.2 - 1.6) \Delta_0 + P_0$$

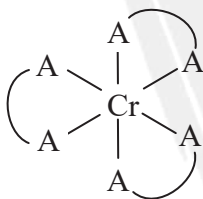
$$= -0.4 \Delta_0 + P_0$$

$P_0 \rightarrow$  pairing energy.

### JEE-MAINS SOLUTIONS

1.  $[\text{CrC}_2\text{O}_4]^{-3}$  show optical isomerism :

$\text{C}_2\text{O}_4^{-2}$  = symmetric ligand AA type



All the three pairs of AA are not in same plane

2.  $[\text{FeC}_2\text{O}_4]^{-3}$  is most stable because of chelation effect

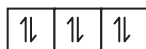
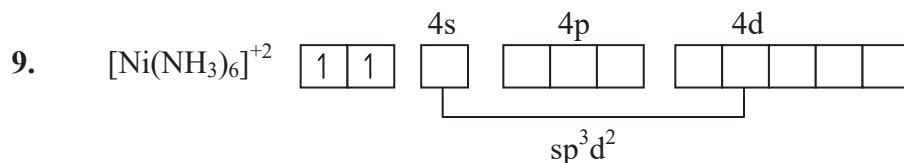
3. Structure of the complex is :  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

4.  $\text{K}_4[\text{Ni}(\text{CN})_4] = 4\text{K}^+ + [\text{Ni}(\text{CN})_4]^{-4}$

$\Rightarrow$  O.S. of nickel is = 0

6.  $\text{NH}_4^+$  can not as ligand as it has no L.P.



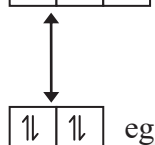
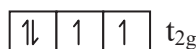


10. Chlorophyll contain magnesium.

11.  $\text{Mn}^{+2} > \text{Co}^{+2} > \text{Fe}^{+2}$

12.  $d^4$  in strong field ligand

14.  $[\text{NiX}_4]^{-2} \Rightarrow \text{Ni}^{+2}$



2 unpaired  $e^-$  and tetrahedral

15. Both  $\sigma$  and  $\pi$  character due to synergic bonding.

16. One  $\text{EDTA}^{-4}$  is hexadentate ligand.

20.  $[\text{Co}(\text{CN})_6]^{3-}$  because  $\text{CN}^-$  is a strong field ligand.

25.  $[\text{NiCl}_4]^{-2} \text{ Ni}^{+2} \Rightarrow 2$  unpaired electron

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

$$= \sqrt{8} = 2.83 \text{ BM}$$

27.  $\text{Ma}_2(\text{AA})_2$  type complex will show geometrical isomers i.e. cis and trans.

31.  $[\text{Ma}_3\text{b}_3]$  kind of complex do not show O.I.

32. Due to presence of ambidentate ligand it will show linkage isomerism.

37. In  $[\text{FeF}_6]^{3-}$ , 5 unpaired electron present

In  $[\text{FeCN}_6]^{3-}$ , 1 unpaired electron present.

38.  $\text{Co}^{+3}$  is diamagnetic & having  $d^2sp^3$  under S.F.L.

39. Correct Name of  $[\text{Mn}(\text{CN})_5]^{2-}$  is Pentacyanomagnate(III) ion.

40. Metal cation i.e.  $\text{Co}^{3+}$  act as a lewis acid which accept lone pair from ligands of  $\text{NH}_3$ .

41. CO is the strongest ligand therefore it has maximum CFSE value.

48. a does not show G.I.b and c show G.I.but all isomers are optically inactive.

56. The frequency order of given absorbed light is:

Blue > Green > Yellow > Red.

Respective  $L_4$   $L_2$   $L_3$   $L_1$

ligands

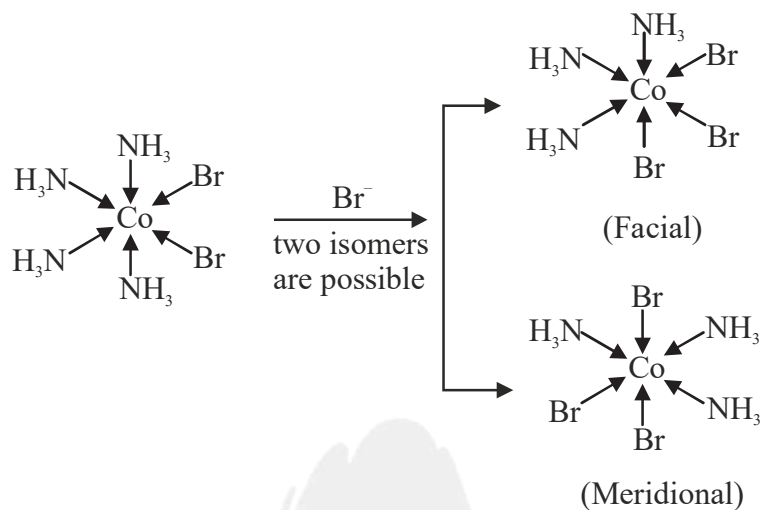
Hence the ligand strength order is  $L_4 > L_2 > L_3 > L_1$ .

Because strong field ligand causes higher splitting gap for octahedral-complex and absorbs high frequency light for d-d transition.

Hence the answer is 4.

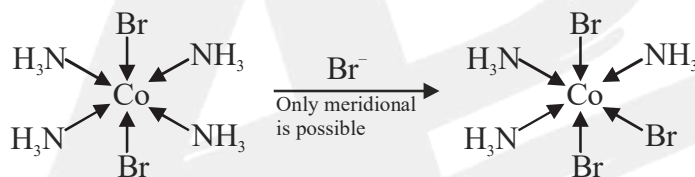
53. 3

Case : I If reactant is cis -

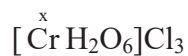


Case : II

If reactant is trans.



54. 4



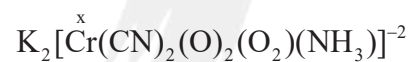
$$x + 0 = +3$$

$$x = 3 \quad \text{Cr} = +3$$



$$x + 0 = 0$$

$$x = 0 \quad \text{Cr} = 0$$



$$x + (-2) + (-4) + (-2) = -2$$

$$x - 8 = -2$$

$$x = 8 - 2$$

$$x = 6$$

Hence answer is 4

55. 2

Sol. According to the relation

$$\left( E = \frac{hc}{\lambda} \right) \quad \xrightarrow[\lambda \uparrow, E \downarrow]{\text{VIBGYOR}}$$

		transmitted	absorbed
$\Delta_{O1}$	$[\text{CrH}_2\text{O}_6\text{Cl}_3]$	Violet	yellow
$\Delta_{O2}$	$[\text{CrNH}_3\text{Cl}_3]$	yellow	violet

Relation between  $\Delta_{O1}$  and  $\Delta_{O2}$  :  $\Delta_{O2} > \Delta_{O1}$ 

56. 2

Sol. If strength of ligands increase then value of CFSE increases. Let CFSE value of complex corresponding to ligands  $L_1$ ,  $L_2$  and  $L_3$  is  $E_1$ ,  $E_2$  and  $E_3$  respectively.

Ligand  $L_1$  is absorbing wavelength in green region,  $L_2$  is absorbing blue and  $L_3$  is absorbing wavelength in Red region. Order of wavelength of green, blue and red is Blue < Green < Red

$$\left( \xrightarrow[\lambda]{\text{VIBGYOR}} \right)$$

$\therefore$  order of splitting energy caused by ligands  $L_1$ ,  $L_2$ ,  $L_3$  will be :

$$E_3 < E_1 < E_2$$

Hence strength of ligand :  $L_3 < L_1 < L_2$ 

57. 1

Sol. The highest number of unpaired electron contain by central atom is five for the octahedral complex.

58. 4

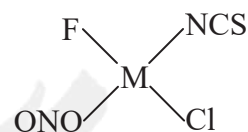
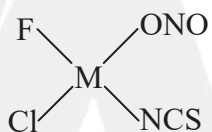
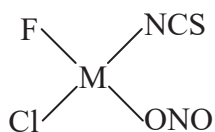
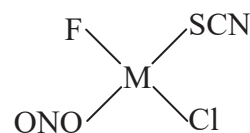
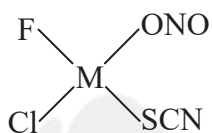
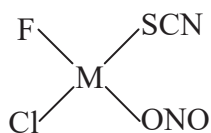
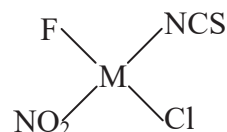
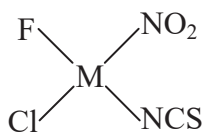
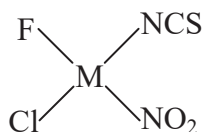
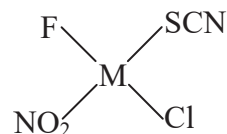
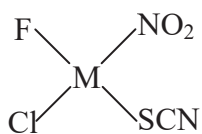
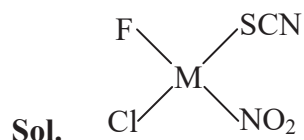
Sol.  $\Delta_t < \Delta_o$ 

greater the strength of ligand, greater will be the value of CFSE and hence greater will be the stability.

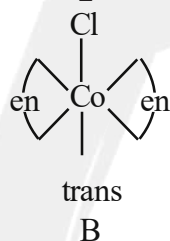
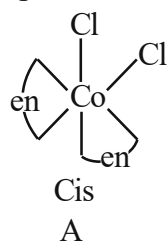
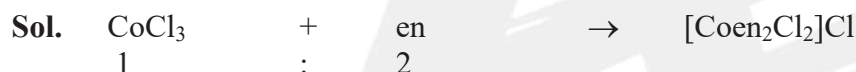
59. 2

Sol. wilkinson catalyst is  $[\text{RhPh}_3\text{P}_3\text{Cl}]$

60. 3



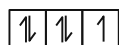
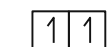
61. 4



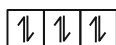
Both are geometrical isomers

62. 4

Sol. A metal ion with  $d^7$  configuration has the difference in the number of unpaired electrons in high spin & low spin octahedral complex is two.



High spin complex  
3 unpaired electrons



Low spin complex  
1 unpaired electron

$\therefore \text{Co}^{+2}: 4s^0 3d^7$  is the answer

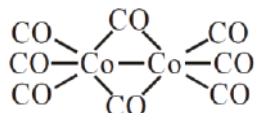
63. 2

Sol.  $\rightarrow$  Wilkins on catalyst :-  $[\text{RhCl}(\text{PPh}_3)_3]$   
 $\rightarrow$  Chlorophyll :-  $\text{C}_{55}\text{H}_{72}\text{MgN}_4\text{O}_8$   
 $\rightarrow$  Vitamin B<sub>12</sub> :-  $\text{C}_{63}\text{H}_{88}\text{CoN}_{14}\text{O}_{14}\text{P}$   
 $\rightarrow$  Carbonic anhydrase :- "contain Zn ion"

64. 4

Sol.  $\text{K}_4[\text{Th}(\text{C}_2\text{O}_4)_4(\text{OH}_2)_2]$   
 $\text{C}_2\text{O}_4^{2-}$  oxalate is a bidentate ligand  
 $\text{H}_2\text{O}$  water is a monodentate ligand

65. 3



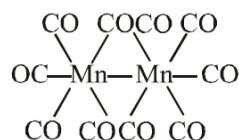
Sol.

Bridging CO are 2 and Co – Co bond is 1.

66. 2

Sol. Hybridization of  $\text{K}_3[\text{Co}(\text{CN})_6]$  is  $d^2sp^3$ ,  $e_g$  orbitals i.e.  $d_{x^2-y^2}$  &  $d_{z^2}$  are approaching metal along the axes.

67. 2



Sol.

Due to presence of Mn–C bond  $\text{Mn}_2\text{CO}_{10}$  is an organometallic compound

68. 1

Sol. For  $\mu = 3.9$  B.M., number of u.p.e<sup>-</sup> = 3

According to CFT,  $\text{H}_2\text{O}$  is a WFL.

$$\text{Fe}^{+2} = 3d^6 \Rightarrow 4 \text{ u.p.e}^-$$

$$\text{V}^{+2} = 3d^3 \Rightarrow 3 \text{ u.p.e}^-$$

$$\text{Co}^{+2} = 3d^7 \Rightarrow 3 \text{ u.p.e}^-$$

$$\text{Mn}^{+2} = 3d^5 \Rightarrow 5 \text{ u.p.e}^-$$

$$\text{Cr}^{+2} = 3d^4 \Rightarrow 4 \text{ u.p.e}^-$$

$\Rightarrow$  hence,  $\text{V}^{+2} = \text{Co}^{2+}$  have 3.9 B.M.

69. 2

Sol. Magnetic moment  $\mu = \sqrt{n(n+2)}$

$n$  = number of unpaired electrons

$$5.9 = \sqrt{n(n+2)} \Rightarrow n = 5$$

Mn II has 5 unpaired electron in given complex

$\Rightarrow$  Suitable legend for this complex is weak field legend which is NCS among given options.

## JEE-ADVANCE

1. (A)

In  $[\text{MnO}_4]^-$ , Mn is in +7 oxidation state.

Electronic configuration of Mn  $Z = 25$ :  $[\text{Ar}]3d^5 4s^2$

Electronic configuration of  $\text{Mn}^{7+}$ :  $[\text{Ar}]3d^0 4s^0$

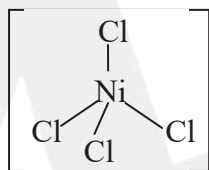
Central atom in other ions have definite number of d electrons

No. of electrons

$[\text{Co}(\text{NH}_3)_6]^{3+}$     $[\text{Fe}(\text{CN})_6]^{3-}$     $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$   
 In  $\text{Co}^{3+}$  = Six   In  $\text{Fe}^{3+}$  = Five   In  $\text{Cr}^{3+}$  = three

3. (B)

The configuration of  $\text{Ni}^{2+}$  is  $3d^8$ . For the elements of the first transition series,  $\text{Cl}^-$  behaves as a weak field/high spin ligand. hence Ni in  $[\text{NiCl}_4]^{2-}$  is  $sp^3$  hybridised leading to tetrahedral shape.



$sp^3$ , Tetrahedral

5. (C)

Tips/formulae :

$$\mu = \sqrt{n(n+2)}\text{BM} ; (\mu = \text{spin magnetic moment})$$

Here Co is present as  $\text{Co}^{2+}$  ion which has 3 unpaired electrons. So the spin magnetic moment

will be  $\sqrt{3(3+2)}$ , i.e.  $\sqrt{15}$  B.M.

6. (B)

Colour of transition metal ion salt is due to d-d transition of unpaired electrons of d-orbital. Metal ion salt having similar number of unpaired electrons is d-orbital. Metal ion salt having similar number of unpaired electrons in d-orbitals.

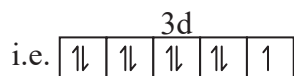
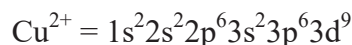
12. (D)

An anionic carbonyl complex can delocalise more electron density to antibonding pi-orbital of CO and hence, lowers the bond order.

14. (C)

Note : Colour is due to d-d transitions. coloured compounds contain partly filled d-orbital.

The oxidation state of copper in various compounds is +1 and +2. In  $\text{CuF}_2$  it is in +2 oxidation state. In +2 state its configuration is :



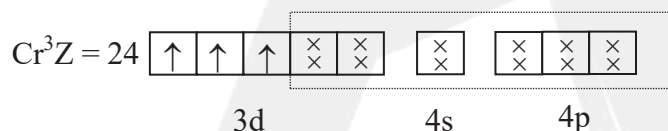
It has one unpaired electron due to this it is coloured. The colour is due to d-d transitions.

Note :  $\text{CuF}_2$  possesses blue colour in crystalline form

29. (A)

$\text{CuSO}_4$  will be absorbing orange-red colour and hence will be of blue colour.

37. Compound A on treatment with  $\text{AgNO}_3$  gives white precipitate of  $\text{AgCl}$ , which is readily soluble in dil.aq.  $\text{NH}_3$ . Therefore it has at least one  $\text{Cl}^-$  ion in the ionization sphere furthermore chromium has coordination number equal to 6. So its formula is  $[\text{CrNH}_3\text{BrCl}]\text{Cl}$ . Compound B on treatment with  $\text{AgNO}_3$  gives pale yellow precipitate of  $\text{AgBr}$  soluble in conc.  $\text{NH}_3$ . Therefore it has  $\text{Br}^-$  in the ionization sphere. So its formula is  $[\text{CrNH}_3\text{Cl}_2]\text{Br}$ .



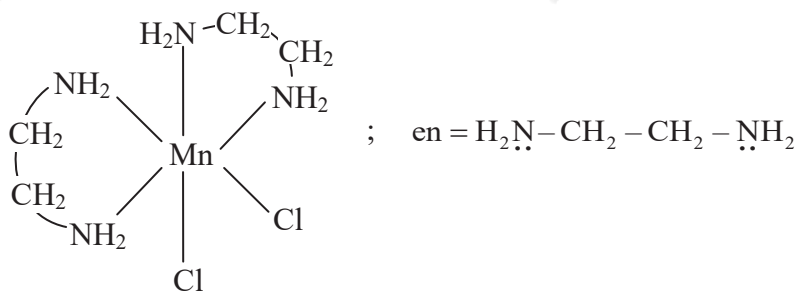
State of hybridization of chromium in both A and B is  $d^2sp^3$ .

Spin magnetic moment of A or B.

$$\mu_{\text{spin}} = \sqrt{n(n+2)} = \sqrt{3(3+3)} = \sqrt{15} = 3.87 \text{ BM}$$

51. (6)

cis isomer of  $[\text{Mn}(\text{en})_2\text{Cl}_2]$  complex :



Total 6 Mn-N and Mn-Cl angles are present at cis position.