

## 5. CO-ORDINATION CHEMISTRY

### Choose the correct answer:

- The sum of primary valance and secondary valance of the metal M in the complex  $[M(en)_2(Ox)]Cl$  is  
a) 3                      b) 6                      c) -3                      d) 9
- An excess of silver nitrate is added to 100ml of a 0.01M solution of pentaquachloridochromium(III)chloride. The number of moles of AgCl precipitated would be  
a) 0.02                      b) 0.002                      c) 0.01                      d) 0.2
- A complex has a molecular formula  $MSO_4 \cdot Cl \cdot 6H_2O$ . The aqueous solution of it gives white precipitate with Barium chloride solution and no precipitate is obtained when it is treated with silver nitrate solution. If the secondary valence of the metal is six, which one of the following correctly represents the complex?  
a)  $[M(H_2O)_4Cl]SO_4 \cdot 2H_2O$                       b)  $[M(H_2O)_6]SO_4$   
c)  $[M(H_2O)_5Cl]SO_4 \cdot 2H_2O$                       d)  $[M(H_2O)_3Cl]SO_4 \cdot 3H_2O$
- Oxidation state of Iron and the charge on the ligand NO in  $[Fe(H_2O)_5NO]SO_4$  are  
a) +2 and 0 respectively                      b) +3 and 0 respectively  
c) +3 and -1 respectively                      d) +1 and +1 respectively
- As per IUPAC guidelines, the name of the complex  $[Co(en)_2(ONO)Cl]Cl$  is  
a) chlorobisethylenediaminenitritocobalt(III) chloride  
b) chloridobis(ethane-1,2-diamine)nitro- $\kappa$ -Ocobaltate(III) chloride  
c) chloridobis(ethane-1,2-diammine)nitrito- $\kappa$ -Ocobalt(II) chloride  
d) chloridobis(ethane-1,2-diamine)nitro- $\kappa$ -Ocobalt(III) chloride
- IUPAC name of the complex  $K_3[Al(C_2O_4)_3]$  is  
a) potassiumtrioxalatoaluminium(III)                      b) potassiumtrioxalatoaluminate(II)  
c) potassiumtrisoxalatoaluminate(III)                      d) potassiumtrioxalatoaluminate(III)
- A magnetic moment of 1.73BM will be shown by one among the following (NEET)  
a)  $TiCl_4$                       b)  $[CoCl_6]^{4-}$                       c)  $[Cu(NH_3)_4]^{2+}$                       d)  $[Ni(CN)_4]^{2-}$
- Crystal field stabilization energy for high spin  $d^5$  octahedral complex is  
a)  $-0.6\Delta_0$                       b) 0                      c)  $2(P-\Delta_0)$                       d)  $2(P+\Delta_0)$
- In which of the following coordination entities the magnitude of  $\Delta_0$  will be maximum?  
a)  $[Co(CN)_6]^{3-}$                       b)  $[Co(C_2O_4)_3]^{3-}$                       c)  $[Co(H_2O)_6]^{3+}$                       d)  $[Co(NH_3)_6]^{3+}$
- Which one of the following will give a pair of enantiomorphs?  
a)  $[Cr(NH_3)_6][Co(CN)_6]$                       b)  $[Co(en)_2Cl_2]Cl$   
c)  $[Pt(NH_3)_4][PtCl_4]$                       d)  $[Co(NH_3)_4Cl_2]NO_2$
- Which type of isomerism is exhibited by  $[Pt(NH_3)_2Cl_2]$ ?  
a) Coordination isomerism                      b) Linkage isomerism  
c) Optical isomerism                      d) Geometrical isomerism
- How many geometrical isomers are possible for  $[Co(en)_3]^{3+}$ ?  
a) 3                      b) 4                      c) 0                      d) 15
- Which one of the following pairs represents linkage isomers?  
a)  $[Cu(NH_3)_4][PtCl_4]$  and  $[Pt(NH_3)_4][CuCl_4]$   
b)  $[Co(NH_3)_5(NO_3)]SO_4$  and  $[Co(NH_3)_5(ONO)]Cl$   
c)  $[Co(NH_3)_4(NCS)_2]Cl$  and  $[Co(NH_3)_4(SCN)_2]Cl$   
d) both (b) and (c)
- Which kind of isomerism is possible for a complex  $[Co(en)_3]^{3+}$ ?  
a) geometrical and ionization                      b) geometrical and optical  
c) optical and ionization                      d) geometrical only
- Which one of the following complexes is not expected to exhibit isomerism?  
a)  $[Ni(NH_3)_4(H_2O)_2]^{2+}$                       b)  $[Fe(en)_3]^{3+}$   
c)  $[Co(NH_3)_5SO_4]Cl$                       d)  $[Fe(en)_3]^{3+}$
- A complex in which the oxidation number of the metal is zero is  
a)  $K_4Fe(CN)_6$                       b)  $[Fe(CN)_3(NH_3)_3]$                       c)  $[Fe(CO)_5]$                       d) both (b) and (c)

17. Formula of tris(ethane-1,2-diamine)iron(II)phosphate

- a)  $[\text{Fe}(\text{CH}_3-\text{CH}(\text{NH}_2)_2)_3](\text{PO}_4)_3$  b)  $[\text{Fe}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2)_3](\text{PO}_4)_3$   
 c)  $[\text{Fe}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2)_3](\text{PO}_4)_2$  d)  $[\text{Fe}(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2)_3](\text{PO}_4)_2$

18. Which of the following is paramagnetic in nature?

- a)  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  c)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  d)  $[\text{Ni}(\text{CN})_4]^{2-}$

19. Fac-mer isomerism is shown by

- a)  $[\text{Co}(\text{en})_3]^{3+}$  b)  $[\text{Co}(\text{NH}_3)_4(\text{Cl})_2]^+$  c)  $[\text{Co}(\text{NH}_3)_3(\text{Cl})_3]$  d)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

20. Choose the correct statement.

- a) Square planar complexes are more stable than octahedral complexes  
 b) The spin only magnetic moment of  $[\text{Cu}(\text{Cl})_4]^{2-}$  is 1.732 BM and it has square planar structure.  
 c) Crystal field splitting energy ( $\Delta_0$ ) of  $[\text{FeF}_6]^{4-}$  is higher than the ( $\Delta_0$ ) of  $[\text{Fe}(\text{CN})_6]^{4-}$   
 d) crystal field stabilization energy of  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$  is higher than the crystal field stabilization of  $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$

### ANSWER

1	2	3	4	5	6	7	8	9	10
<i>d</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>c</i>	<i>b</i>	<i>a</i>	<i>b</i>
11	12	13	14	15	16	17	18	19	20
<i>d</i>	<i>a</i>	<i>c</i>	<i>a</i>	<i>d</i>	<i>c</i>	<i>d</i>	<i>c</i>	<i>c</i>	<i>d</i>

## TEXTBOOK QUESTIONS AND ANSWERS

1. Write the IUPAC names for the following complexes.

- i)  $\text{Na}_2[\text{Ni}(\text{EDTA})]$  - Sodium 2,2',2'',2'''-(ethane-1,2-diyl)dinitrilo)tetraacetatoNickelate(II)  
 ii)  $[\text{Ag}(\text{CN})_2]^-$  - dicyanidoargentate(I) ion  
 iii)  $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$  - tris(ethane-1,2-diamine)cobalt(III)sulphate  
 iv)  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$  - pentaamminenitrito-k-O-cobalt(III)ion  
 v)  $\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)$  - diamminechloridonitrito- k-N-platinum(II)

2. Write the formula for the following coordination compounds.

- a) potassiumhexacyanidoferrate(II) -  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 b) pentacarbonyliron(0) -  $[\text{Fe}(\text{CO})_5]$   
 c) pentaamminenitrito- K -N-cobalt(III)ion -  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$   
 d) hexaamminecobalt(III)sulphate -  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$   
 e) sodiumtetrafluorodihydroxidochromate(III) -  $\text{Na}_3[\text{CrF}_4(\text{OH})_2]$

3. Arrange the following in order of increasing molar conductivity

i)  $\text{Mg}[\text{Cr}(\text{NH}_3)(\text{Cl})_5]$  ii)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]_3[\text{CoF}_6]_2$  iii)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$

On ionisation,

- i)  $\text{Mg}[\text{Cr}(\text{NH}_3)(\text{Cl})_5] \longrightarrow \text{Mg}^{2+} + [\text{Cr}(\text{NH}_3)(\text{Cl})_5]^{2-}$   
 ii)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]_3[\text{CoF}_6]_2 \longrightarrow 3[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+} + 2[\text{CoF}_6]^{3-}$   
 iii)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3] \longrightarrow$  does not ionize

As the number of ions in solution increases, their molar conductivity also increases.

Therefore  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3] < \text{Mg}[\text{Cr}(\text{NH}_3)(\text{Cl})_5] < [\text{Cr}(\text{NH}_3)_5\text{Cl}]_3[\text{CoF}_6]_2$

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

Coordination compound used in medicine:

Ca- EDTA chelate radioactive poisoning removing lead and radioactive metal ions from body.

Cis- Platin antitumour drug cancer treatment

Biologically important coordination compounds:

Coordination Complex	Central metalion	Uses
RBC composed of heme group	$\text{Fe}^{2+}$	Carrying oxygen from lungs to tissue, CO <sub>2</sub> from tissue to lungs
Chlorophyll	$\text{Mg}^{2+}$	Photosynthesis

**5. Based on VB theory explain why  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is paramagnetic, while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Complex**

$[\text{Cr}(\text{NH}_3)_6]^{3+}$   
Central metal atom/ ion and its electronic configuration  
Cr(III)  $3d^3 4s^0$   
Outer orbitals of metal atom/ion  
 $3d^3 4s^1 4p$

**Nature of ligand:**

$\text{NH}_3$  is a weak ligand pairing of 3d electrons in the metal does not take place

**Magnetic property:**

The number of unpaired electron  $n=3$

Therefore the magnetic moment is

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

$$\mu_s = \sqrt{3(3+2)}$$

$$= 3.87 \text{ BM}$$

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

Ni(II)  $3d^8 4s^0$

$3d^8 4s^2 4p$

$\text{CN}^-$  is a strong field ligand causes the pairing of 3d electrons in the metal

The number of unpaired electron  $n=0$

Therefore the magnetic moment is

$$\mu_s = 0 \text{ BM}$$

**6. Draw all possible geometrical isomers of the complex  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  and identify the optically active isomer.**

Trans isomer  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  does not show optical isomerism because of plane of symmetry.

Cis isomer shows optical isomerism because it is unsymmetry.

**7.  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured, while  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless- explain.**

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$   
Central metal ion :  $\text{Ti}^{3+}$   
Electronic Configuration :  $3d^1$   
Number of unpaired electron : 1  
 $\text{Ti}^{3+}$  has one unpaired electron for d-d transition, hence it is coloured

$[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$   
 $\text{Sc}^{3+}$   
 $3d^0$   
0  
No unpaired electron, so d-d transition is not possible hence it is not coloured

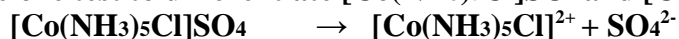
**8. Give an example for complex of the type.  $[\text{Ma}_2\text{b}_2\text{c}_2]$  where a, b, c are monodentate ligands and give the possible isomers.**

$[\text{PdI}_2(\text{ONO})_2(\text{H}_2\text{O})_2]$  Diaquadiiododinitrito-K -O Palladium (IV)

$[\text{PdI}_2(\text{NO}_2)(\text{H}_2\text{O})_2]$  Diaquadiiododinitrito-K -N palladium (IV)

They will exhibit linkage isomerism

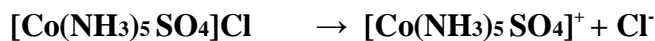
**9. Give one test to differentiate  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ .**



This complex produces sulphate ion in aqueous solution.

On addition of  $\text{BaCl}_2$ , white precipitate of  $\text{BaSO}_4$  is produced.

No reaction with  $\text{AgNO}_3$



This complex produces chloride ion in aqueous solution.

On addition of  $\text{AgNO}_3$ , curdy white precipitate of  $\text{AgCl}$  is produced.

No reaction with  $\text{BaCl}_2$

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

The energy of the orbitals  $d_{x^2-y^2}$  and  $d_{z^2}$  (represented as  $e_g$  orbitals) will increase by  $35\Delta_o$  while that of the other three orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  (represented as  $t_{2g}$  orbitals) decrease by  $25\Delta_o$ . Here,  $\Delta_o$  represents the crystal field splitting energy in the octahedral field.

### 11. What is linkage isomerism? Explain with an example.

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms. ( $-\text{NO}_2/-\text{ONO}-$ )

Example :  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  &  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$

### 12. Classify the following ligand based on the number of donor atoms.

a)  $\text{NH}_3$       b) en      c)  $\text{ox}^{2-}$       d) triaminotriethylamine      e) pyridine

Ligand	Number of donoratom	Type of ligand
$\text{NH}_3$	1 (N-donor)	Monodentate
en	2 (2N-donor)	Bidentate
$\text{ox}^{2-}$ (oxalato)	2 (2 -O- donor)	Bidentate
Triaminotriethylamine	3 (3N-donor)	Tridentate
Pyridine	1 (N-donor)	Monodentate

### 13. Give the difference between double salts and coordination compounds.

S.NO	Double salt	Coordination compound
1	Double salts lose their identity in aqueous solution by completely dissociating in to ions in the solvent	They don't lose their identity in aqueous solution as they do not ionize completely (the complex ion further doesnot get ionized)
2	They give test for all the constituent ions Example : $\text{K}_2\text{SO}_4.\text{Al}_2(\text{SO}_4)_3.24\text{H}_2\text{O}$	Example : $\text{K}_4[\text{Fe}(\text{CN})_6]$

### 14. Write the postulates of Werner's theory.

- Most of the elements exhibit, two types of valence. Primary valence, Secondary valence
- Primary valence is referred as the oxidation state of the metal atom and the Secondary valence as the coordination number.
- The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions.
- The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these.
- According to Werner, there are two spheres of attraction around a metal atom/ion in a complex.  
The inner sphere is known as coordination sphere.  
The outer sphere is called ionisation sphere.
- The primary valences - non-directional, the secondary valences - directional.
- The geometry of the complex is determined by the spacial arrangement of the groups which satisfy the secondary valence.  
Six - octahedral geometry.  
Four -either tetrahedral or square planar geometry.

**15. Why tetrahedral complexes do not exhibit geometrical isomerism.**

All the four ligands are adjacent or equidistant to one another in tetrahedral complex.

As the relative positions of donor atoms of ligands attached to the central atom are same with respect to each other.

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

Coordination compounds which possess chirality exhibit optical isomerism.

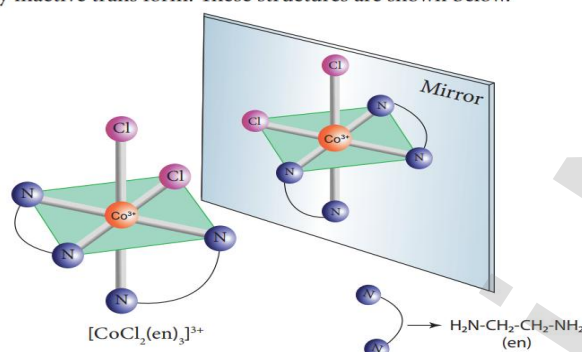
The pair of two optically active isomers which are mirror images of each other are called enantiomers.

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

The octahedral complexes of type  $[M(xx)_3]^{n\pm}$ ,  $[M(xx)_2AB]^{n\pm}$  and  $[M(xx)_2B_2]^{n\pm}$  exhibit optical isomerism.

**Example:**

The coordination complex  $[CoCl_2(en)_2]^+$  has three isomers, two optically active cis forms and one optically inactive trans form. These structures are shown below.

**17. What are hydrate isomers? Explain with an example.**

The exchange water molecules in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called hydrate isomers.

**Example :**

$CrCl_3 \cdot 6H_2O$  has three hydrate isomers as shown below.

$[Cr(H_2O)_6]Cl_3$	violet colour	Gives three chloride ions in solution
$[Cr(H_2O)_5Cl]Cl_2 \cdot 2H_2O$	pale green colour	Gives two chloride ions in solution
$[Cr(H_2O)_4Cl_2]Cl \cdot H_2O$	dark green colour	Gives one chloride ion in solution.

**18. What is crystal field splitting energy?**

The splitting of five d-orbitals of the metal ion in the presence of ligand field into two sets having different energies is called crystal field splitting or energy level splitting. The difference in the energy of the two sets is called crystal field splitting energy.

**19. What is crystal field stabilization energy (CFSE) ?**

The crystal field stabilization energy is defined as the energy difference of electronic configurations in the ligand field ( $E_{LF}$ ) and the isotropic field/barycentre ( $E_{iso}$ ).

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

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

$nt_{2g}$  = the number of electrons in  $t_{2g}$  orbitals

$n_{eg}$  = number of electrons in  $e_g$  orbitals

$n_p$  = number of electron pairs in the ligand field

$n'_p$  = number of electron pairs in the isotropic field (barycentre).

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

Central metal ion

:  $Ni^{2+}$

$Ni^{2+}$

Electronic Configuration

:  $3d^8$

$3d^8$

Number of unpaired electron : 2

0

$Ti^{3+}$  has one unpaired electron for d-d transition, hence it is coloured

No unpaired electron, so d-d transition is not possible hence it is not coloured



**21. Discuss briefly the nature of bonding in metal carbonyls.**

In metal carbonyls, the bond between metal atom and the carbonyl ligand consists of two components.

An electron pair donation from the carbon atom of carbonyl ligand into a vacant d-orbital of central metal atom.

This electron pair donation forms  $M \leftarrow CO$  sigma bond ( $\sigma$ ).

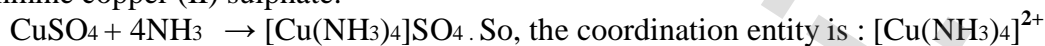
This sigma bond formation increases the electron density in metal d orbitals and makes the metal electron rich.

In order to compensate for this increased electron density, a filled metal d-orbital interacts with the empty  $\pi^*$  orbital on the carbonyl ligand and transfers the added electron density back to the ligand. This second component is called  $\pi$ -back bonding.

Thus in metal carbonyls, electron density moves from ligand to metal through sigma bonding and from metal to ligand through pi bonding, this synergic effect accounts for strong  $M \leftarrow CO$  bond in metal carbonyls.

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

When excess of liquid ammonia is added to an aqueous solution of copper sulphate it gives tetraammine copper (II) sulphate.

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

Central metal /atom	: Co(III)
Electronic configuration	: Co: $3d^7 4s^2 4p$
Geometry	: Octahedral
Hybridization	: $d^2sp^3$
Number of unpaired electron	: $n = 0$ ; diamagnetic
	$C_2O_4^{2-}$ is a strong field ligand.
	$3d^6 4s^0 4p$
	Inner orbital (low spin) complex

**24. What are the limitations of VB theory?**

1. It does not explain the colour of the complex
2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal. For example,  $[Fe(CN)_6]^{4-}$  is diamagnetic (low spin) whereas  $[FeF_6]^{4-}$  is paramagnetic (high spin).

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

Oxidation state :  $4(+1) + x + 6(-1) = 0$ ;  $x = +2$

Coordination number : 6

Nature of ligand :  $CN^-$  Monodentate ligand

Magnetic property : Paramagnetic(one unpaired electron)

Electronic configuration in octahedral crystal field,  $CN^-$  is strong field ligand.  $t_{2g}^5 e_g^0$

**ONE MARK FROM INSIDE THE LESSON**

- Heteroleptic complex from the following  
a)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  c) Both a and b d) None
- IUPAC Name of  $\text{P}(\text{Ph})_3$  is  
a) pyridine b) Phosphine c) triphenylphosphane d) Phenyl
- Primary and secondary valencies of Cu in  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  is  
a) 4,4 b) 2,4 c) 4,1 d) 4,2
- According to CFT, five d-orbitals of an octahedral complex split to give  
a) One orbital with lower energy and four orbitals with higher energy.  
b) Two orbital with lower energy and three orbitals with higher energy.  
c) Three orbital with lower energy and two orbitals with higher energy  
d) Four orbital with lower energy and one orbitals with higher energy.
- Which among the following square planar complexes will exhibits geometrical isomerism?  
a)  $[\text{Ma}_2\text{B}_2]^{n\pm}$  b)  $[\text{MA}_2\text{BC}]^{n\pm}$  c)  $[\text{M}(\text{xy})]^{n\pm}$  d) **All the above**
- The type of isomerism found in the complexes  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{SO}_4$  and  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{NO}_2$   
a) Hydrate isomerism b) Coordination isomerism c) Linkage isomerism d) **Ionization**
- Which of the following is wrong about double salts?  
a) Retain their properties only in solid state  
b) Contains two or more salt in stoichiometric proportions  
c) They don't dissociate into its constituent ions  
d) None of the above
- \_\_\_\_\_ is used as an antitumor drug in cancer treatment  
a) Ca-EDTA b) Cis-platin c) Sodium thio sulphate d) Nickel chloride
- Crystal field stabilization energy for high  $d^4$  octahedral complex is \_\_\_\_\_.  
a)  $-0.6\Delta_0$  b)  $-1.6\Delta_0$  c)  $-1.4\Delta_0$  d)  $+0.6\Delta_0$
- The geometry and hybridization of  $[\text{Fe}(\text{CO})_5]$   
a) Trigonal planar,  $\text{dsp}^3$  b) Octahedral,  $\text{dsp}^2$   
c) Trigonal bipyramidal,  $\text{dsp}^3$  d) Octahedral,  $\text{d}^2\text{sp}^3$
- Outer orbital complex from the following  
a)  $[\text{FeF}_6]^{4-}$  b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  c)  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  d) All of these
- complexes can undergo rapid ligand substitution; such complexes are called  
a) labile complexes b) Inert complex c) Inner complex d) outer complex
- Polymerization of ethene catalysed by  
a) Wilkinson's catalyst b) Ziegler-Natta catalyst c) DMG d) EDTA
- Which one is used in printing ink and in the packaging industry?  
a) Mader dye b) Phthalo blue c) Malachite green d) None
- $\alpha$  is a  
a) Dissociation equilibrium constant b) Instability constant  
c) Both a and b d) None

**ANSWER**

1	2	3	4	5	6	7	8	9	10
a	c	b	c	d	d	c	b	a	c
11	12	13	14	15					
a	a	b	b	c					

### ADDITIONAL QUESTIONS AND ANSWERS

**1. When a co-ordination compound  $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$  is mixed with silver nitrate solution, one mole of silver chloride is precipitated per mole of the compound. There are no free solvent molecules in that compound. Assign the secondary valence to the metal and write the structural formula of the compound.**

One mole of silver chloride is formed therefore there is one ionizable chloride ion  $\text{Cl}^-$  (counter ion) There are no free solvent molecules therefore all the water molecules are coordinated Hence, the coordination compound is  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$  Secondary valency is 6

**2. In the complex,  $[\text{Pt}(\text{NO}_2)(\text{H}_2\text{O})(\text{NH}_3)_2]\text{Br}$ . identify the following**

- (i) Central metal atom/ion :  $\text{Pt}^{2+}$
- (ii) Ligands and their types :  $\text{NO}_2$  is negative ligand,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  neutral monodentate ligand
- (iii) Coordination entity :  $[\text{Pt}(\text{NO}_2)(\text{H}_2\text{O})(\text{NH}_3)_2]^{+1}$
- (iv) Oxidation number of central metal atom : 2+
- (v) Coordination number : 4

**3. Write the IUPAC name for the following compounds.**

- (i)  $\text{K}_2[\text{Fe}(\text{CN})_3(\text{Cl})_2(\text{NH}_3)]$  - Potassium amminedichloridotricyanidoFerrate(III)
- (ii)  $[\text{Cr}(\text{CN})_2(\text{H}_2\text{O})_4][\text{Co}(\text{ox})_2(\text{en})]$  - Tetraaquadicyanidochromium(III)(ethane-1,2-diamine)di(oxalato) cobaltate(III)
- (iii)  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]$  - diamminedichloridocopper(II)
- (iv)  $[\text{Cr}(\text{NH}_3)_3(\text{NC})_2(\text{H}_2\text{O})]^+$  - triammineaquadicyandio-K -N-chromium(III) ion
- (v)  $[\text{Fe}(\text{CN})_6]^{4-}$  - Hexacyanidoferrate(II) ion

**4. Give the structure for the following compounds.**

- (i) diamminesilver(I) dicyanidoargentate(I) -  $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$
- (ii) pentamminenitrito-K -Ncobalt(III) ion -  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{+2}$
- (iii) hexafluoridocobaltate(III) ion -  $[\text{CoF}_6]^{3-}$
- (iv) dichloridobis(ethylenediamine)Cobalt(III) sulphate -  $[\text{Co}(\text{en})_2\text{Cl}_2]_2\text{SO}_4$
- (v) Tetracarbonylnickel(0) -  $[\text{Ni}(\text{CO})_4]$

**5. A solution of  $[\text{Co}(\text{NH}_3)_4\text{I}_2]\text{Cl}$  when treated with  $\text{AgNO}_3$  gives a white precipitate. What should be the formula of isomer of the dissolved complex that gives yellow precipitate with  $\text{AgNO}_3$ . What are the above isomers called?**

Silver nitrate reacts with chloride ions to give silver chloride white precipitate, therefore in one isomer the  $\text{Cl}^-$  is the counter ion. Whereas silver nitrate reacts with Iodide ion to form yellow precipitate therefore the counter ion is  $\text{I}^-$ . Therefore the isomers are called ionization isomer.

Example:

$[\text{Co}(\text{NH}_3)_4\text{I}_2]\text{Cl}$  - white precipitate ,  $[\text{Co}(\text{NH}_3)_4\text{Cl I}]\text{I}$  - Yellow precipitate

**6. Three compounds A,B and C have the molecular formula  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  they are kept in a container with a dehydrating agent and they lost water and attaining constant weight as shown below.**

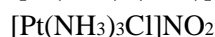
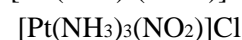
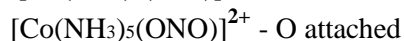
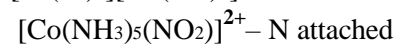
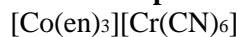
Compound	Initial weight of compound (in g)	Constant weight after dehydration (in g)
A	4	3.46
B	0.5	0.466
C	3	3

Compound A:  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$   
 Compound B:  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$   
 Compound C:  $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$



### 7. Indicate the possible type of isomerism for the following complexes and draw their isomers

#### Given Compound



#### Isomer Type

Coordination Isomerism

Linkage Isomerism

Ionization Isomerism

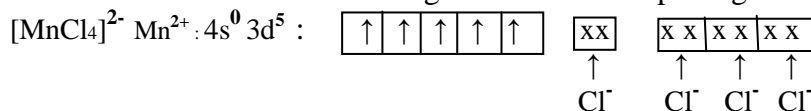
### 8. The spin only magnetic moment of tetrachloridomanganate(II) ion is 5.9 BM. On the basis of VBT predict the type of hybridization and geometry of the compound

Given complex  $[\text{MnCl}_4]^{2-}$

When magnetic moment is 5.9 BM it means it has 5 unpaired electron i.e.,  $n=5$



Chlorido is a weak ligand therefore no pairing takes place.



Hybridization :  $sp^3$

Shape : Tetrahedral

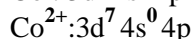
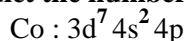
Number of unpaired electron,  $n=5$

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

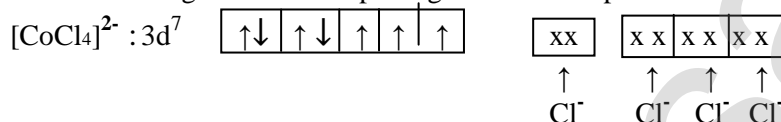
$$\mu_s = \sqrt{5(5+2)}$$

$$= 5.9 \text{ BM}$$

### 9. Predict the number of unpaired electrons in $[\text{CoCl}_4]^{2-}$ ion on the basis of VBT.



$\text{Cl}^-$  is a weak ligand therefore pairing does not take place



Number of unpaired electron,  $n=3$

### 10. A metal complex having composition $\text{Co}(\text{en})_2\text{Cl}_2\text{Br}$ has been isolated in two forms A and B. (B) reacted with silver nitrate to give a white precipitate readily soluble in ammonium hydroxide. Whereas A gives a pale yellow precipitate. Write the formula of A and B. State the hybridization of Co in each and calculate their spin only magnetic moment.

Compound A - pale yellow precipitate counter ion  $\text{Br}^-$

Compound B - white precipitate - counter ion  $\text{Cl}^-$



### 11. The mean pairing energy and octahedral field splitting energy $[\text{Mn}(\text{CN})_6]^{4-}$ are $28,800 \text{ cm}^{-1}$ and $38500 \text{ cm}^{-1}$ respectively. Whether this complex is stable in low spin or high spin?

Given mean pairing energy  $28000 \text{ cm}^{-1}$  and Octahedral splitting energy is  $38500 \text{ cm}^{-1}$

For  $[\text{Mn}(\text{CN})_6]^{4-}$  the electronic configuration  $\text{Mn}^{3+}$  is  $3d^4$  :  $\uparrow \uparrow \uparrow \uparrow$

Case I: High Spin complex  $t_{2g}^3 e_g^1$

$$\begin{aligned} \text{CFSE} &= \{ [n_{t_{2g}}(-0.4) + n_{e_g}(0.6)] \Delta_o + n_p P \} - \{ n_p P \} \\ &= \{ 3(-0.4) + 1(0.6) \} \Delta_o + 0xP - 0 \\ &= \{ -1.2 + 0.6 \} \Delta_o \\ &= -0.6 \Delta_o \\ &= -0.6 \times 38500 \\ &= -23100 \text{ cm}^{-1} \end{aligned}$$

Case II: low Spin complex  $t_{2g}^4 e_g^0$

$$\begin{aligned} \text{CFSE} &= \{ [n_{t_{2g}}(-0.4) + n_{e_g}(0.6)] \Delta_o + n_p P \} - \{ n_p P \} \\ &= \{ 4(-0.4) + 0(0.6) \} \Delta_o + 1xP - 0 \\ &= \{ -1.6 \} \Delta_o + P \\ &= -1.6(38500) + 28800 \\ &= -61600 + 28800 \\ &= -32800 \text{ cm}^{-1} \end{aligned}$$

Large negative CFSE indicate in case II that the complex is stable in low spin

**12. Draw energy level diagram and indicate the number of electron in each level for the complex  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . Whether the complex is paramagnetic or diamagnetic?**

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion is a stretched octahedron. The electronic configuration of copper(II) ion is  $[\text{Ar}] 3d^9$ . When the complex ion formed by  $\text{Cu}^{2+}$  has an octahedral structure, the d orbitals will split in to two different orbitals  $t_{2g}$  and  $e_g$ . The electronic configuration is  $(t_{2g})^6 (e_g)^3$ , the 3 electrons in  $e_g$  level can be arranged in two different ways  $t_{2g}^6 e_g^3 (d_{z^2})^2 (d_{x^2-y^2})^1$  or  $t_{2g}^6 e_g^3 (d_{z^2})^1 (d_{x^2-y^2})^2$ . To break the degeneracy there is a distortion of the octahedral splitting. The presence of one unpaired electron in the  $e_g$  level makes  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  as paramagnetic

**13. For the  $[\text{CoF}_6]^{3-}$  ion in the mean pairing is found to be  $21000 \text{ cm}^{-1}$ . The magnitude of  $\Delta_o$  is  $13000 \text{ cm}^{-1}$ . Calculate the crystal field stabilization energy for this complex ion corresponding to low spin and high spin states.**

Given mean pairing energy  $21000 \text{ cm}^{-1}$  and Octahedral splitting energy is  $13000 \text{ cm}^{-1}$

For the  $[\text{CoF}_6]^{3-}$  electronic configuration  $\text{Co}^{3+}$  is  $3d^6$ 

$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
----------------------	------------	------------	------------	------------

Case I: High Spin complex  $t_{2g}^4 e_g^2$

CFSE:  $\{ [n t_{2g}(-0.4) + n e_g(0.6)] \Delta_o + n_p P \} - \{ n_p P \}$

$$= \{ 4(-0.4) + 2(0.6) \} \Delta_o + 1 \times P - 1P$$

$$= \{ -1.6 + 1.2 \} \Delta_o$$

$$= -0.4 \Delta_o$$

$$= -0.4 \times 13000$$

$$= -5200 \text{ cm}^{-1}$$

Case II: low Spin complex  $t_{2g}^6 e_g^0$

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

$$= \{ 6(-0.4) + 0(0.6) \} \Delta_o + 3 \times P - 1P$$

$$= \{ -2.4 \} \Delta_o + 2P$$

$$= -2.4(13000) + 2 \times 21000$$

$$= 10,800 \text{ cm}^{-1}$$

High positive CFSE indicate in case II that low spin complex is not favorable one

**14. Write the postulates of Valence bond theory.**

1. The ligand  $\rightarrow$  metal bond in a coordination complex is covalent in nature. It is formed by sharing of electrons (provided by the ligands) between the central metal atom and the ligand.
2. Each ligand should have at least one filled orbital containing a lone pair of electrons.
3. In order to accommodate the electron pairs donated by the ligands, the central metal ion present in a complex provides required number (coordination number) of vacant orbitals.
4. These vacant orbitals of central metal atom undergo hybridisation, the process of mixing of atomic orbitals of comparable energy to form equal number of new orbitals called hybridised orbitals with same energy.
5. The vacant hybridised orbitals of the central metal ion, linearly overlap with filled orbitals of the ligands to form coordinate covalent sigma bonds between the metal and the ligand.
6. The hybridised orbitals are directional and their orientation in space gives a definite geometry to the complex ion.

Coordination number	Hybridisation	Geometry	Complexes
2	Sp	Linear	$[\text{CuCl}_2]^-$ , $[\text{Ag}(\text{CN})_2]$

7. The complexes containing a central metal atom with unpaired electron(s) are paramagnetic.

If all the electrons are paired, then the complexes will be diamagnetic.

8. Ligands such as  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{en}$ , and  $\text{NH}_3$  present in the complexes cause pairing of electrons present in the central metal atom. Such ligands are called strong field ligands.

9. Greater the overlapping between the ligand orbitals and the hybridised metal orbital greater is the bond strength.

**15. What is Stability constant?**

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

$$\beta = \left( \frac{1}{\alpha} \right)$$

## 16. Explain Crystal Field Theory of complexes.

1. Crystal Field Theory (CFT) assumes that the bond between the ligand and the central metal atom is purely ionic. i.e. the bond is formed due to the electrostatic attraction between the electron rich ligand and the electron deficient metal.
2. In the coordination compounds, the central metal atom/ion and the ligands are considered as point charges (in case of charged metal ions or ligands) or electric dipoles (in case of neutral metal atoms or ligands).
3. According to crystal field theory, the complex formation is considered as the following series of hypothetical steps.

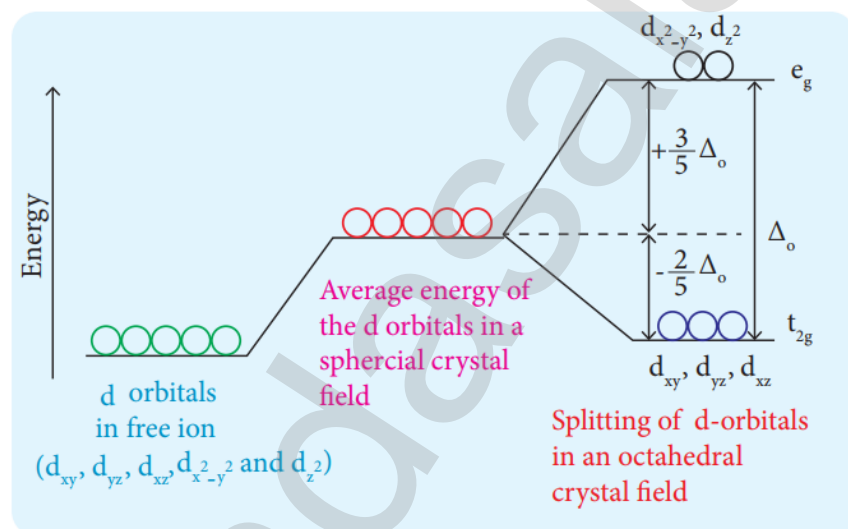
**Step 1:** In an isolated gaseous state, all the five d orbitals of the central metal ion are degenerate. Initially, the ligands form a spherical field of negative charge around the metal. In this field, the energies of all the five d orbitals will increase due to the repulsion between the electrons of the metal and the ligand.

**Step 2:** The ligands are approaching the metal atom in actual bond directions.

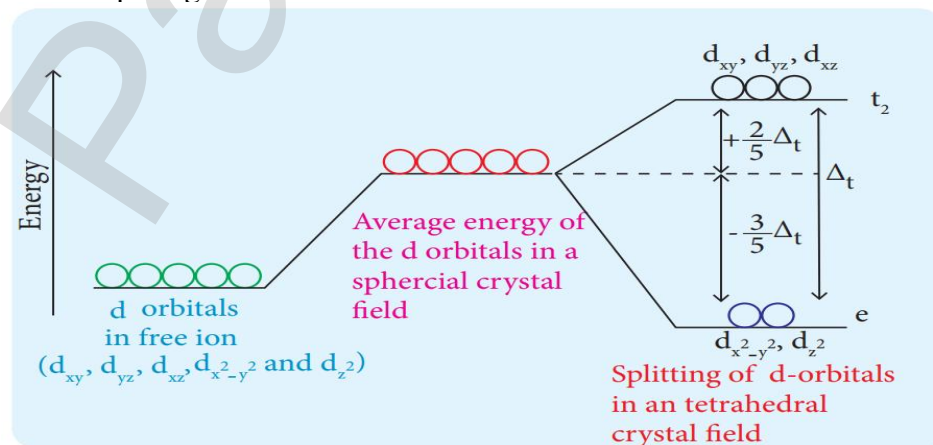
Thus the degenerate d orbitals now split into two sets and the process is called crystal field splitting.

**Step 3:** Up to this point the complex formation would not be favoured. However, when the ligands approach further, there will be an attraction between the negatively charged electron and the positively charged metal ion, that results in a net decrease in energy. This decrease in energy is the driving force for the complex formation.

### Crystal field splitting in octahedral complexes:



### 17. Draw the Crystal Field Splitting in Tetrahedral field.



**18. What are Labile and Inert complexes?**

Complexes can undergo rapid ligand substitution; such complexes are called labile complexes. However, some complexes undergo ligand substitution very slowly (or sometimes no substitution), such complexes are called inert complexes.

**19. How Stability constant related with Dissociation equilibrium constant?**

The reciprocal of dissociation equilibrium constant ( $\alpha$ ) is called as formation equilibrium constant or stability constant ( $\beta$ ).

$$\beta = \left( \frac{1}{\alpha} \right)$$

**20. Explain about the Metal complexes in biological systems .**

- (i) A red blood corpuscles (RBC) is composed of heme group, which is  $\text{Fe}^{2+}$ : Porphyrin complex. It plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.
- (ii) Chlorophyll, a green pigment present in green plants and algae, is a coordination complex containing  $\text{Mg}^{2+}$  as central metal ion surrounded by a modified Porphyrin ligand called corrin ring. It plays an important role in photosynthesis, by which plants converts  $\text{CO}_2$  and water into carbohydrates and oxygen.
- (iii) Vitamin  $\text{B}_{12}$ (cyanocobalamine) is the only vitamin consist of metal ion. it is a coordination complex in which the central metal ion is  $\text{Co}^{+}$  surrounded by Porphyrin like ligand.
- (iv) Many enzymes are known to be metal complexes, they regulate biological processes. For example, Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein.

**BY**

**S.JOSEPH SURESH, MSc, MEd., 9994342531**

**ACHYUTA ACADEMY MAT. HR. SEC. SCHOOL-DINDIGUL**