

## CHAPTER

# 8

# COORDINATION COMPOUNDS

## Syllabus

- Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative inclusion, extraction of metals and biological system).

## Chapter Analysis

List of Topics	2016		2017		2018
	D	OD	D	OD	D/OD
Structural formula, IUPAC name	1Q (2 marks)	1Q (2 marks)	1Q (3 marks)*		
Isomerism			1Q (3 marks)*	1Q (3 marks)#	1Q (3 marks)^
Coordination Number and Oxidation state					1Q (1 mark)
Hybridization, Magnetic Character, Spin, Number of Unpaired Electrons and Isomers of Complex	1Q (3 marks)	1Q (3 marks)			1Q (3 marks)^
Write the formula for IUPAC name				1Q (2 marks)	1Q (3 marks)^
Properties			1Q (3 marks)*	1Q (3 marks)#	

- \* One question of 3 marks on Isomerism, Properties of compounds and IUPAC name was asked.
- # One question of 3 marks on Isomerism and Properties of compounds was asked.
- ^ One question of 3 marks on Writing the formula, Isomerism, Hybridization and Number of Unpaired Electrons was asked.

On the basis of above analysis, it can be said that from exam point of view, IUPAC, Structural formula, Isomerism, Hybridization, Magnetic Character, Spin, Number of Unpaired Electrons and Isomers of Complex and Properties of Complex are the most important topics of the chapter. Also, writing the formula for IUPAC name is frequently asked.



## TOPIC-1

### Coordination Compounds and their Properties, IUPAC Nomenclature of Mono Nuclear Coordination Compounds

## Revision Notes

- **Coordination Compound** : A coordination compound contains a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules. There is a coordinate bond between metal atom and these ions or molecules, e.g.,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ .
- **Double Salt** : When two or more salts are added to form a stable solid together and break into constituent ions when dissolved in water or any solvent e.g.,  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (Mohr's salt).

### TOPIC - 1

Coordination Compounds and their Properties, IUPAC Nomenclature of Mono Nuclear Coordination Compounds .... P. 161

### TOPIC - 2

Werner's Theory Bonding in Coordination Compound, VBT, CFT and Importance of Coordination Compounds .... P. 172

➤ **Properties of double salts :**

- (i) They give simple ions in aqueous solution because they are ionic compounds.
- (ii) They do not contain coordinate bonds.
- (iii) They exist only in solid state as double salt.
- (iv) They are soluble in water.

➤ **Coordinate bonds :** A type of covalent bond in which one of the atoms supplies both the electrons. It can be considered as a combination of transfer and sharing of electrons. Coordinate bonds are also called semipolar bonds.

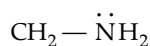
➤ **Central metal atom or ion :** The metal atom or ion surrounded by fixed number of ions or molecules is called central metal atom or ion, *e.g.*, in  $K_4[Fe(CN)_6]$ ,  $Fe^{2+}$  is central metal ion.

➤ **Ligand :** The neutral molecules or ions (usually anions) which are attached with the central metal atom or ion in complex compound. *e.g.*,  $Cl^-$ ,  $OH^-$ ,  $CN^-$ ,  $CO$ ,  $NH_3$ ,  $H_2O$  etc. A ligand may be neutral or charged species. It always act as a Lewis base.

● **Types of ligands :**

(a) **On the basis of number of donor sites :**

(i) **Unidentate ligands :** Contain one donor atom. *e.g.*,  $\ddot{N}H_3$ ,  $H_2\ddot{O}$ :



(ii) **Bidentate ligands :** Contain two donor atom. *e.g.*,  $(COO^-)_2$ ,  $\begin{array}{c} CH_2 - \ddot{N}H_2 \\ | \\ CH_2 - \ddot{N}H_2 \end{array}$

(iii) **Polydentate ligands :** Contain several donor atoms. *e.g.*, EDTA.

(b) **On the basis of charge :**

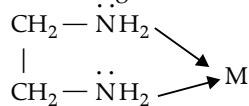
(i) **Cationic ligands :** Carry positive charge. *e.g.*,  $NO_2^+$ ,  $N_2H_5^+$ .

(ii) **Anionic ligands :** Carry negative charge. *e.g.*,  $X^-$  (halo),  $CN^-$  (cyano).

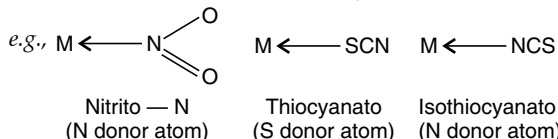
(iii) **Neutral ligands :** Do not carry any charge. *e.g.*,  $\ddot{N}H_3$  (amine),  $H_2\ddot{O}$  (aqua).

(c) **On the basis of charge :**

(i) **Chelate ligands :** A bidentate or polydentate uses its two or more donor atoms to bind a single metal ion, then a ring like structure is obtained. It is called chelate and the ligand is known as chelate ligand. *e.g.*,



(ii) **Ambidentate ligand :** A ligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal/ion is called ambidentate ligand.



➤ **Coordination number :** Number of monodentate ligands attached to central metal ion in a complex is called coordination number. It may also be defined as total number of chemical bonds formed between central metal ion and donor atom of ligand *e.g.*, in  $[Ni(NH_3)_6]^{2+}$ , the coordination number of  $Ni^{2+}$  is 6.

➤ **Coordination polyhedron :** The spatial arrangement of the ligand atoms which are directly attached to the central atoms or ions define a coordination polyhedron about the central atom *e.g.*,  $[PtCl_4]^{2-}$  is square planar.

➤ **Charge on the complex ion :** The charge on the complex ion is equal to the algebraic sum of the charges on all the ligands coordinated to the central metal ion.

➤ **Donor atom :** An atom in the Lewis base that forms the bond with the central atom/ion is called donor atom because it donates the pair of electrons.

➤ **Denticity :** The number of ligating groups or coordinating atoms in a ligand is called denticity *e.g.*, unidentate, didentate etc.

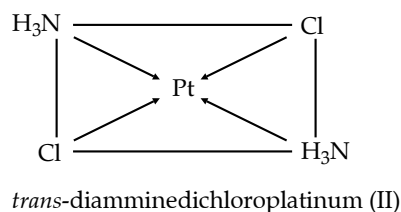
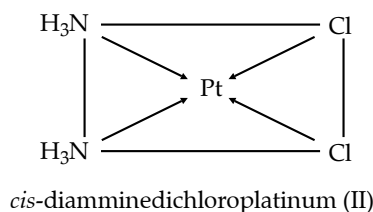
➤ **Applications of chelates :**

- (i) In the softening of hard water.
- (ii) In the separation of lanthanoids and actinoids.
- (iii) In the detection as well as estimation of some metal ions such as nickel (II) ion.

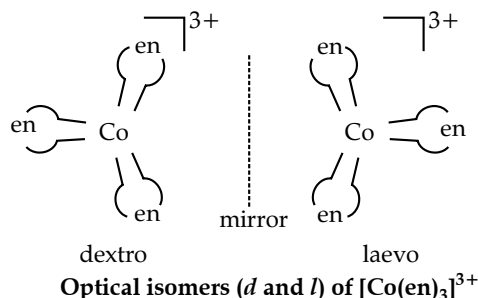
➤ **Coordination sphere :** The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as coordination sphere *e.g.*, in the complex  $K_4[Fe(CN)_6]$ , the coordination sphere is  $[Fe(CN)_6]^{4-}$ .

➤ **Flexidentate character of ligands :** Certain polydentate ligands have flexible character and are called flexidentates. *e.g.*, EDTA is hexadentate in nature but in some cases, it may act as pentadentate or tetradentate ligand.

- **Oxidation number of central atom :** It is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. It is represented by Roman numerical.
- **Homoleptic and Heteroleptic complexes :** Complexes in which the metal atom or ion is linked to only one type of ligands are called homoleptic complexes *e.g.*,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  etc. The complexes in which the metal atom or ion is linked to more than one kind of ligands are called heteroleptic complexes. *e.g.*,  $[\text{Co}(\text{NH}_4)\text{Cl}_2]^+$  and  $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$  etc.
- **Homonuclear and Polynuclear complexes :** Complexes in which only one metal atom is present are known as homonuclear complexes. *e.g.*  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ . Complexes in which more than one metal atom is present are known as polynuclear complexes.
- **Counter ions :** The ions which are not included in the primary coordination sphere are known as counter ions. *e.g.*, in  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{K}^+$  ions are counter ions.
- **Coordination ions :** The coordination entity with charge is called as coordination ion.
- **Nomenclature of coordination compounds :**
  - (i) The cation whether simple or complex is named first followed by anion.
  - (ii) Ligands are named in alphabetical order.
  - (iii) For indicating the number of each kind of ligand within the coordination entity, two kinds of numerical prefixes are used (di, tri, tetra etc.) For ligands containing any of these prefixes in their names, their numbers are indicated by prefixes bis, tris, tetrakis etc. Anionic ligands end in -o. Neutral retain their names while cationic end in -ium.
  - (iv) The coordination sphere is written in square bracket.
  - (v) In naming, ligands are named first in alphabetical order followed by metal atom and then the oxidation state of metal by a Roman numeral in parenthesis.
  - (vi) Name of coordination compounds starts with a small letter and the complex part is written as one word.
  - (vii) Oxidation number of central atom is indicated in Roman numerals. No space is left between the number and the rest of the name.
- **Isomers :** Two or more coordination compounds which have the same molecular formula but have their ligands attached to the isomers metal atom or ion in different ways are known as isomers. The phenomenon of different isomers is known as isomerism.
- **Types of isomerism :** Two types of isomerism observed in coordination compounds are :
  - **Structural isomerism is of following types :**
    - (i) **Ionisation isomerism :** In this type of isomerism, isomers have same molecular formula but gives different ions in solution. *e.g.*,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$ .
    - (ii) **Coordination isomerism :** This type of isomerism is shown by those complexes in which both the cation and the anion are complex ions and they differ in the coordination of ligands. *e.g.*,  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$ .
    - (iii) **Solvate isomerism :** Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. *e.g.*,  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
    - (iv) **Linkage isomerism :** Isomers having the same molecular formula but different linking atom, this is due to the presence of ambident ligands. *e.g.*,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ .
  - **Stereo isomerism is of following types :**
    - (i) **Geometrical isomerism or cis-trans isomerism :** In tetra coordinated square planar complexes, the cis-isomer has the same groups on the same side whereas trans-isomer has same groups on opposite sides *e.g.*,



- (ii) **Optical isomerism :** Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called *dextro* (*d*) and *laevo* (*l*) depending upon the direction in which they rotate the plane of polarised light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving didentate ligands.



## Know the Terms

- **Coordination chemistry** : The study of the coordination compounds is known as coordination chemistry.
- **Labile complex** : A complex in which ligand substitution is fast.
- **Inert complex** : A complex in which ligand substitution is slow.
- **Synergic bonding** : A ligand donates a pair of electrons to the metal atom or ion and then accepts a pair of electrons back in its vacant orbital also from *d*-orbitals of the metal or ion. This is called synergic bonding and the ligands involved are known as  $\pi$ -donor ligands.
- **Effective Atomic Number (EAN)** : It can be calculated for the metal atom or ion in the coordination complex by using following relation :  

$$\text{EAN} = \text{Atomic no. (Z) of metal atom} - \text{Oxidation number} + 2\text{C.N. where, C.N. is coordination number.}$$
- **Facial or fac isomer** : When three ligands with donor atoms are on the same triangular face of the octahedron, the geometrical isomer is known as **facial or fac isomer**.
- **Meridional or mer isomer** : When three ligands with donor atoms are on the same equatorial plane of the octahedron or around the meridian of the octahedron, the isomer is called meridional or mer isomer.
- **Perfect or penetrating complexes** : These are the complexes in which complex ion is fairly stable and either completely or feebly dissociates in solution.
- **Imperfect or abnormal complexes** : These are the complexes in which the complex ion is less stable and is dissociated reversibly to give enough simple ions.



## Very Short Answer-Objective Type Questions (1 mark each)

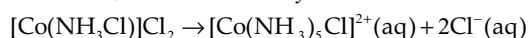
### A. Multiple choice Questions:

- Q. 1.** When 0.1 mol  $\text{CoCl}_3(\text{NH}_3)_5$  is treated with excess of  $\text{AgNO}_3$ , 0.2 mol of  $\text{AgCl}$  are obtained. The conductivity of solution will correspond to
- (a) 1 : 3 electrolyte.      (b) 1 : 2 electrolyte.  
 (c) 1 : 1 electrolyte.      (d) 3 : 1 electrolyte.

[U] [NCERT Exmp. Q. 3, Page 120]

**Ans. Correct option :** (b)

**Explanation :** One mole of  $\text{AgNO}_3$  precipitates one mole of chloride ion. In the above reaction, when 0.1 mole  $\text{CoCl}_3(\text{NH}_3)_5$  is treated with excess of  $\text{AgNO}_3$ , 0.2 mole of  $\text{AgCl}$  is obtained and thus, there must be two free chloride ions in the solution of electrolyte. So, molecular formula of complex will be  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and electrolyte solution must contain  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  and two  $\text{Cl}^-$  as constituent ions. Thus, it is 1 : 2 electrolyte.



- Q. 2.** The correct IUPAC name of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is

- (a) Diamminedichloridoplatinum (II).  
 (b) Diamminedichloridoplatinum (IV).  
 (c) Diamminedichloridoplatinum (I).  
 (d) Dichloridodiammineplatinum (IV).

[A] [NCERT Exmp. Q. 5, Page 121]

**Ans. Correct option :** (a)

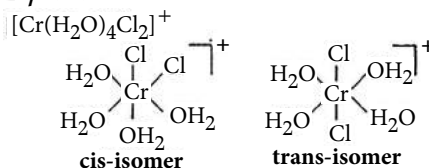
- Q. 3.** Indicate the complex ion which shows geometrical isomerism.

- (a)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$       (b)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]$   
 (c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       (d)  $[\text{Co}(\text{CN})_5(\text{NC})]^{3+}$

[A] [NCERT Exmp. Q. 7, Page 121]

**Ans. Correct option :** (a)

**Explanation :**



- Q. 4.** Which of the following species is not expected to be a ligand?

- (a) NO      (b)  $\text{NH}_4^+$   
 (c)  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$       (d) CO

[U] [NCERT Exmp. Q. 12, Page 122]

**Ans. Correct option :** (b)

**Explanation :** Ligand must donate a pair of electrons or loosely held electron pair to metal and form a M–L bond.

In the above case  $\text{NH}_4^+$  does not have any pair of electrons. Hence,  $\text{NH}_4^+$  is not a ligand.

Q. 5. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?

- (a) Thiosulphato (b) Oxalate  
(c) Glycinato (d) Ethane-1,2-diamine

[U] [NCERT Exemp. Q. 11, Page 122]

Ans. Correct option : (a)

**Explanation :** Thiosulphato or  $S_2O_3^{2-}$  is not a chelating agent since it is a monodentate ligand.

B. Match the following :

Q. 1. Match the species given in Column I with those mentioned in Column II.

Column I (Complex species)		Column II (Isomerism)	
A.	$[Co(NH_3)_4Cl_2]^+$	(1)	Optical
B.	$cis-[Co(en)_2Cl_2]^+$	(2)	Ionisation
C.	$[Co(NH_3)_5(NO_2)]Cl_2$	(3)	Coordination
D.	$[Co(NH_3)_6][Cr(CN)_6]$	(4)	Geometrical
		(5)	Linkage

Code :

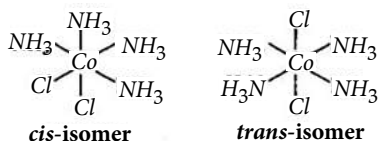
- (a) A(1), B (2), C(4), D(5)  
(b) A(4), B (3), C(2), D(1)  
(c) A(4), B (1), C(5), D(3)  
(d) A(4), B (1), C(2), D(3)

[NCERT Exemp. Q. 39, Page 126]

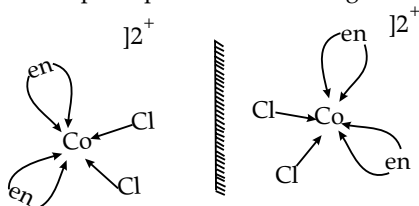
Ans. Correct Code : (d)

**Explanation :** Isomerism in coordination compound is decided by type of ligands and geometry of coordination and arrangements of ligands.

- (a)  $[Co(NH_3)_4Cl_2]^+$  shows geometrical isomerism due to presence of two type of ligands whose  $[Co(NH_3)_4Cl_2]^+$  arrangement around central metal ion.



- (b)  $cis-[Co(en)_2Cl_2]^+$  shows optical isomer due to its non-superimposable mirror-image relationship.



- (c)  $[Co(NH_3)_5(NO_2)]Cl_2$  shows ionisation isomer due to its inter-changing ligand from outside the ionisation sphere.  
(d)  $[Co(NH_3)_6][Cr(CN)_6]$  shows coordination isomer due to inter-changing of ligand in between two metal ions from one coordination sphere to another coordination sphere.

C. Answer the following:

Q. 1. Write IUPAC name of the complex:  $[CoCl_2(en)_2]^+$ .

[A] [CBSE Comptt. OD Set-1, 3 2017]

Ans. Dichloridobis (ethane-1, 2-diamine) cobalt (III) ion.  
[CBSE Marking Scheme 2017] 1

#### Commonly Made Error

- There is confusion in oxidation state of central metal ion.

#### Answering Tip

- Practice and understand writing nomenclature and oxidation state of ligands.

Q. 2. Write IUPAC name of the complex  $[Co(NH_3)_4Cl(NO_2)]^+$ .

[A] [CBSE Comptt. OD Set-2 2017]

Ans. Tetraamminechloronitrocobalt (III) ion. 1  
[CBSE Marking Scheme 2017]

Q. 3. Write the IUPAC name of the following coordination compound  $[NiCl_4]^{2-}$ .

[A] [CBSE Comptt. Delhi 2016]

Ans. Tetrachloridonickelate (II) ion. 1  
[CBSE Marking Scheme 2016]

Q. 4. What is the IUPAC name of the complex  $[Ni(NH_3)_6]Cl_2$ ?

[A] [CBSE Comptt. Delhi 2015]

Ans. Hexaamminenickel (II) chloride. 1  
[CBSE Marking Scheme 2015]

Q. 5. Give two examples of ligands which form coordination compounds useful in analytical chemistry.

[R] [CBSE Comptt. OD 2013]

Ans. EDTA (Ethylene-diammine-tetraacetate) and DMG (Dimethylglyoxime). 1

[AI] Q. 6. Give IUPAC name of ionization isomer of  $[Ni(NH_3)_3NO_3]Cl$ .

[A] [CBSE Comptt. OD 2012]

Ans. Ionization isomer is  $[Ni(NH_3)_3Cl]NO_3$ . IUPAC name is Triamminechloridonickel (II) nitrate. 1

Q. 7. Write the coordination isomer of  $[Cu(NH_3)_4][PtCl_4]$ .

[A] [CBSE Comptt. Delhi/OD 2018]

Ans.  $[Pt(NH_3)_4][CuCl_4]$  1  
[CBSE Marking Scheme 2018]

Q. 8. Write the coordination number and oxidation state of Platinum in the complex  $[Pt(en)_2Cl_2]$

[A] [CBSE Delhi/OD 2018]

Ans. Coordination Number = 6, Oxidation State = +2  
 $1/2 + 1/2$   
[CBSE Marking Scheme 2018]

Q. 9. What is meant by chelate effect?

[R] [CBSE Comptt. OD 2015]

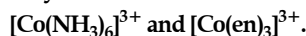
Ans. Formation of stable complex with a polydentate ligand due to stronger bonding is known as chelate effect. 1

[CBSE Marking Scheme 2015]

OR

Formation of stable complex with a polydentate ligand due to stronger bonding than the non chelate complexes is known as chelate effect.

**Q. 10.** Which of the following is more stable complex and why ?



[U] [CBSE Comptt. OD 2015]

**Ans.**  $[\text{Co}(\text{en})_3]^{3+}$  : Because (en) is a chelating ligand/bidentate ligand.  $\frac{1}{2} + \frac{1}{2}$

[CBSE Marking Scheme 2015]

**Q. 11.** What is the denticity of coordination compound used for the treatment of lead poisoning ?

[U] [CBSE SQP 2012]

**Ans.** In Lead poisoning, EDTA (Ethylene diamine tetraacetate) is used as ligand which is hexadentate i.e., the denticity of EDTA is 6. EDTA binds with metal in octahedral manner by two N-atoms and four acetate oxygen atoms. 1

**Q. 12.** How many ions are produced from the complex,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$  in solution ? [A] [CBSE SQP 2016]

**Ans.** Three ions.  $[\text{Co}(\text{NH}_3)_6]^{2+}$ ,  $2\text{Cl}^-$ . 1

**Q. 13.** Why are low spin tetrahedral complexes not formed? [A&E] [CBSE Comptt. Delhi Set-1, 2, 3 2017]

**Ans.** Orbital splitting energies are not sufficiently large for forcing pairing. 1

[CBSE Marking Scheme 2017]

**Q. 14.** Low spin configuration are rarely observed in tetrahedral coordination entity formation. Explain. [A&E] [CBSE SQP 2018-2019]

**Ans.** The orbital splitting energies,  $\Delta_t$  are not sufficiently large for forcing pairing of electrons in the tetrahedral coordination entity formation. 1

[CBSE Marking Scheme 2018]

**Q. 15.** A coordination compound with molecular formula  $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$  precipitates one mole of  $\text{AgCl}$  with  $\text{AgNO}_3$  solution. Its molar conductivity is found to be equivalent to two ions. What is the structural formula and name of the compound?

[A] [CBSE SQP 2017]

**Ans.**  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$   
Tetraaquadichloridochromium (III) chloride. 1

[CBSE Marking Scheme 2017]



## Short Answer Type Questions

(2 marks each)

**Q. 1.** Using IUPAC norms write the formulae for the following:

- Sodium dicyanidoaurate (I)
- Tetraamminechloridonitrito-N-platinum (IV) sulphate

[A] [CBSE OD Set-1 2017]

**Ans. (i)**  $\text{Na}[\text{Au}(\text{CN})_2]$  1

**(ii)**  $[\text{Pt}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{SO}_4$  1

[CBSE Marking Scheme 2017]

**Q. 2.** Using IUPAC norms write the formulae for the following:

- Tris(ethane-1,2-diamine)chromium(III) chloride
- Potassium tetrahydroxozincate(II)

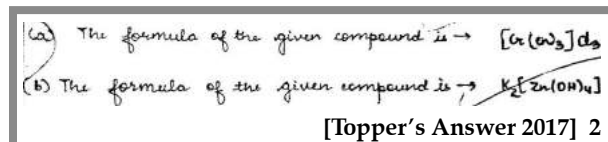
[A] [CBSE OD Set-2 2017]

**Ans. (i)**  $[\text{Cr}(\text{en})_3]\text{Cl}_3$  1

**(ii)**  $\text{K}_2[\text{Zn}(\text{OH})_4]$  1

[CBSE Marking Scheme 2017]

OR



[Topper's Answer 2017] 2

**Q. 3.** Using IUPAC norms write the formulae for the following:

- Potassium trioxalatoaluminate (III)
- Dichloridobis(ethane-1,2-diamine)cobalt(III)

[A] [CBSE OD Set-3 2017]

**Ans. (i)**  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$  1

**(ii)**  $[\text{CoCl}_2(\text{en})_2]^+$  1

[CBSE Marking Scheme 2017]

**Q. 4. (i)** Write the IUPAC name of the isomer of the following complex:



- Write the formula for the following:  
Tetraammineaquachloridocobalt (III) nitrate

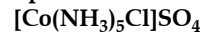
[A] [CBSE Foreign Set-1 2017]

**Ans. (i)** cis/trans-diamminedichloridoplatinum (II) 1

**(ii)**  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}](\text{NO}_3)_2$  1

[CBSE Marking Scheme 2017]

**Q. 5. (i)** Write the IUPAC name of the isomer of the following complex:



- Write the formula for the following:  
Diamminechloridonitrito-N-platinum(II)

[A] [CBSE Foreign Set-2 2017]

**Ans. (i)** Pentaamminechlorocobalt (III) sulphate 1

**(ii)**  $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$  1

[CBSE Marking Scheme 2017]

**Q. 6. (i)** Write the IUPAC name of the following complex:  
 $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$

- Write the formula for the following:  
Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride

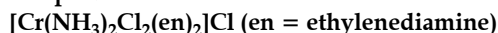
[A] [CBSE Foreign Set-3 2017]

**Ans. (i)** Tetraamminechloridonitrito-N-cobalt (III) chloride. 1

**(ii)**  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  1

[CBSE Marking Scheme 2017]

**Q. 7. (i)** Write down the IUPAC name of the following complex :



- (ii) Write the formula for the following complex :  
Pentaamminenitrito-o-Cobalt (III).

[A] [CBSE Delhi 2015]

Ans. (i) Diamminedichloridobisethylenediaminechromium (III) chloride

(ii)  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$   
[CBSE Marking Scheme 2015] 1+1

- Q. 8. (i) Write down the IUPAC name of the following complex :  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

- (ii) Write the formula for the following complex :  
Potassium tetrachloridonickelate (II)

[A] [CBSE Delhi 2015]

Ans. (i) Pentaamminechloridocobalt (III) ion 1

(ii)  $\text{K}_2[\text{NiCl}_4]$  1

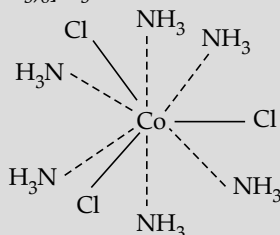
- Q. 9. When a co-ordination compound  $\text{CoCl}_3 \cdot 6\text{NH}_3$  is mixed with  $\text{AgNO}_3$ , 3 moles of  $\text{AgCl}$  are precipitated per mole of the compound. Write

- (i) Structural formula of the complex,

- (ii) IUPAC name of the complex.

[A] [CBSE OD 2016]

Ans. (i)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$



(ii) IUPAC name : Hexamminecobalt (III) chloride. 1

[CBSE Marking Scheme 2016]

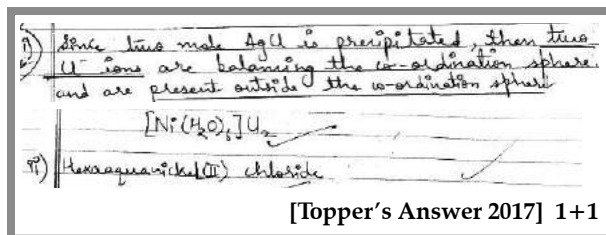
#### Commonly Made Error

- Students often make errors in naming the central atom and ligand in the coordinate compounds.

#### Answering Tip

- Understand and practice the naming of coordinate compounds.

OR



[Topper's Answer 2017] 1+1

- Q. 10. When a co-ordination compound  $\text{CrCl}_3 \cdot 6\text{NH}_3$  is mixed with  $\text{AgNO}_3$ , 2 moles of  $\text{AgCl}$  are precipitated per mole of the compound. Write

- (i) Structural formula of the complex.

- (ii) IUPAC name of the complex.

[A] [CBSE Delhi 2016]

Ans. (i)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  1

(ii) Pentaquachloridochromium (III) chloride monohydrate. 1

[CBSE Marking Scheme 2016]

- Q.11. Write the IUPAC name of the complex  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ . What type of isomerism does it exhibit ?

[A] [CBSE Delhi 2014]

Ans. (i) Tetraamminedichlorido chromium (III) ion. 1

(ii) Geometrical isomerism / cis-trans. 1

[CBSE Marking Scheme 2014]

- [AI] Q.12. Indicate the types of isomerisms exhibited by the complex  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ .

(At. No. Co = 27). [A] [CBSE Comptt. OD 2012]

Ans. Linkage and ionisation isomerism.

It can show linkage isomerism:

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})](\text{NO}_3)_2$  1

It can show ionization isomerism:

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)(\text{NO}_2)$  1

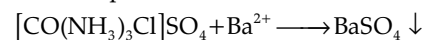
#### Commonly Made Error

- Many students give incorrect types of isomerism.

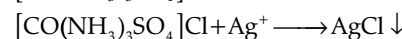
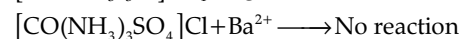
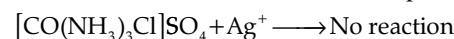
- Q. 13. Give evidence that  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$  are ionisation isomers.

[C] [NCERT]

Ans. When ionisation isomers are dissolved in water, they ionise to give different ions. These ions then react differently with different reagents to give different products.



White precipitate



White precipitate

2

## ? Long Answer Type Questions-I

(3 marks each)

- Q. 1. Write the IUPAC name of the following :

(i)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

(ii)  $[\text{NiCl}_4]^{2-}$

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

[A] [CBSE Comptt. OD 2015]

Ans. (i) Hexaamminecobalt (III) chloride. 1

(ii) Tetrachloridonickelate (II) ion. 1

(iii) Potassiumhexacyanoferrate (III) 1

[CBSE Marking Scheme 2015]

**Q. 2.** Write IUPAC name for each of the following complexes:

- (i)  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$   
 (ii)  $\text{K}_3[\text{Fe}(\text{CN})_6]$   
 (iii)  $[\text{Co}(\text{en})_3]^{3+}$  [A] [CBSE Comptt. Delhi/OD 2018]

Ans. (i) Hexaamminenickel(II) chloride 1  
 (ii) Potassium hexacyanidoferrate(III) 1  
 (iii) Tris(ethane-1,2-diamine)cobalt(III) ion 1  
 [CBSE Marking Scheme 2018]

**Q. 3.** Indicate the types of isomerism exhibited by the following complexes :

- (i)  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$   
 (ii)  $[\text{Co}(\text{en})_3]\text{Cl}_3$  (en = ethylenediamine)  
 (iii)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  [A] [CBSE Comptt. Delhi 2015]

Ans. (i) Linkage isomerism. 1  
 (ii) Optical isomerism. 1  
 (iii) Cis - trans / Geometrical isomerism. 1  
 [CBSE Marking Scheme 2015]

#### Commonly Made Error

- (i) Some students write 'ligand isomerism' instead of 'linkage isomerism'.

**Q. 4.** (i) What type of isomerism is shown by the complex  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ ?

- (ii) Why a solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green while a solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless? (At. No. of Ni = 28) [KVS]  
 (iii) Write the IUPAC name of the following complex:  $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)\text{Cl}]$ . [A] [CBSE Delhi Set-1, 2 2017]

Ans. (i) Coordination isomerism 1  
 (ii) Unpaired electrons in  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ /d-d transition 1  
 (iii) Pentaamminecarbonatocobalt(III) Chloride 1  
 [CBSE Marking Scheme 2017]

**Detailed Answer:**

- (ii)  $[\text{Ni}(\text{CN})_4]^{2-}$  has no unpaired electron in its d-subshell therefore d-d transition is not possible whereas  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  has unpaired electron in its d-subshell resulting in d-d transition imparting colour. 1

**Q. 5.** (i) What type of isomerism is shown by the complex  $[\text{Co}(\text{en})_3]\text{Cl}_3$ ?

- (ii) Write the hybridization and magnetic character of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{2-}$ . (At. no. of Co = 27)

(iii) Write IUPAC name of the following Complex  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$  [A] [CBSE Delhi Set-3 2017]

Ans. (i) Optical isomerism 1  
 (ii)  $d^2sp^3$ , diamagnetic  $\frac{1}{2} + \frac{1}{2}$   
 (iii) Triamminetrichloridochromium (III) 1  
 [CBSE Marking Scheme 2017]

#### Commonly Made Error

- (ii) Many students write  $sp^3d^2$  and paramagnetic whereas the correct answer is  $d^2sp^3$  and diamagnetic.

**Q. 6.** (i) What type of isomerism is shown by the complex  $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$ ?

- (ii) Why is  $[\text{NiCl}_4]^{2-}$  paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic? (Atomic number of Ni = 28)

(iii) Why are low spin tetrahedral complexes rarely observed? [A&E] [CBSE OD Set-1, 2, 3 2017]

Ans. (i) Linkage isomerism 1  
 (ii) In  $[\text{NiCl}_4]^{2-}$ , due to the presence of  $\text{Cl}^-$ , a weak field ligand no pairing occurs whereas in  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $\text{CN}^-$  is a strong field ligand and pairing takes place/diagrammatic representation 1  
 (iii) Because of very low CFSE which is not able to pair up the electrons. 1

[CBSE Marking Scheme 2017]

OR

(21) (a) Linkage isomerism is shown by the complex  $[\text{Co}(\text{NH}_3)_5(\text{SCN})]$  due to presence of ambidentate ligand.

(b)  $[\text{NiCl}_4]^{2-}$  is paramagnetic, but  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic, because  $\text{Cl}^-$  is a weak field ligand, so the electrons in d subshell do not get paired up, but  $\text{CN}^-$  is a strong field ligand, so the electrons get paired up.

Atomic no. of Ni = 28 ; Oxidation state of Ni = +2 in both.

electronic configuration of  $\text{Ni}^{2+} = [\text{Ar}]^{18} 3d^8 4s^0$

$\text{Cl}^-$  is a weak ligand.

So,  $[\text{NiCl}_4]^{2-}$  has  $sp^3$  hybridization.

The diagram shows the electronic configuration of  $\text{Ni}^{2+}$  as  $[\text{Ar}]^{18} 3d^8 4s^0$ . It then shows the  $3d$ ,  $4s$ , and  $4p$  orbitals. For  $[\text{NiCl}_4]^{2-}$ , it shows the  $3d$  orbitals with 8 electrons (two unpaired) and the  $sp^3$  hybrid orbitals. For  $[\text{Ni}(\text{CN})_4]^{2-}$ , it shows the  $3d$  orbitals with 8 electrons (all paired) and the  $sp^3$  hybrid orbitals.



Handwritten notes on lined paper:

•  $\text{en}^-$  is a strong ligand.

Diagram showing orbital splitting for a tetrahedral complex. The d-orbitals are split into two higher energy orbitals (each with one electron) and three lower energy orbitals (each with one electron). The hybridization is labeled as  $dsp^2$  hybrid.

(c) Low spin tetrahedral complexes are rarely observed, because for the same metal and same ligand, it is observed that

$$\Delta_t = \frac{4}{9} \Delta_o$$

where,  $\Delta_t$  = Crystal field Splitting energy in Tetrahedral complex  
 $\Delta_o$  = Crystal field splitting energy in Octahedral complex.

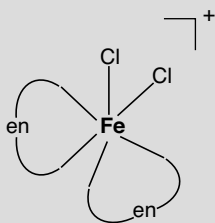
Hence, the  $\Delta_t$  rarely exceeds the pairing energy, so, mainly low high spin tetrahedral complexes are formed.

3  
[Topper's Answer 2017]

Q. 7. For the complex ion  $[\text{Fe}(\text{en})_2\text{Cl}_2]^+$  write the hybridization type and magnetic behaviour. Draw one of the geometrical isomer of the complex ion which is optically active. [Atomic No.: Fe = 26]

[R + A] [CBSE Comptt. OD Set-1 2017]

Ans. Hybridisation:  $d^2sp^3$  1  
 Magnetic character: Paramagnetic 1

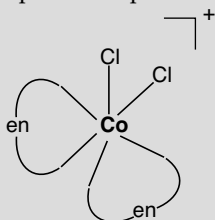


1  
[CBSE Marking Scheme 2017]

Q. 8. For the complex ion  $[\text{CoCl}_2(\text{en})_2]^+$  write hybridization type and spin behaviour. Draw one of the geometrical isomer of the complex ion which is optically active. [Atomic number: Co = 27]

[R + A] [CBSE Comptt. OD Set-2 2017]

Ans. Hybridisation:  $d^2sp^3$  1  
 Spin: Low spin 1



1  
[CBSE Marking Scheme 2017]

Q. 9. For the complex ion  $[\text{CoF}_6]^{3-}$  write the hybridization type, magnetic character and spin nature. [Atomic number: Co = 27]

[A] [CBSE Comptt. Delhi Set-1, 2 2017]

Ans. Hybridisation :  $sp^3d^2$  1  
 Magnetic character : Paramagnetic 1  
 Spin nature : High spin 1

[CBSE Marking Scheme 2017]

Q. 10. For the complex ion  $[\text{Ni}(\text{CN})_4]^{2-}$  write the hybridization type, magnetic character and spin nature. [Atomic number: Ni = 28]

[A] [CBSE Comptt. Delhi Set-3 2017]

Ans. Hybridisation :  $dsp^2$  1  
 Magnetic character : Diamagnetic 1  
 Spin nature : Low spin 1

[CBSE Marking Scheme 2017]

Q. 11. (a) Write the formula of the following coordination compound :

Iron(III) hexacyanoferrate(II)

(b) What type of isomerism is exhibited by the complex  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  ?

(c) Write the hybridisation and number of unpaired electrons in the complex  $[\text{CoF}_6]^{3-}$ . (Atomic No. of Co = 27) [A] [CBSE Delhi/OD 2018]

Ans. (i)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  1  
 (ii) Ionisation isomerism 1  
 (iii)  $sp^3d^2$  octahedral complex with 4 unpaired electrons 1

[CBSE Marking Scheme 2018]

**Q. 12.** When a coordination compound  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  is mixed with  $\text{AgNO}_3$  solution, 3 moles of  $\text{AgCl}$  are precipitated per mole of the compound. Write:

- Structural formula of the complex
- IUPAC name of the complex
- Magnetic and spin behavior of the complex

[A] [CBSE Comptt. OD Set-3 2017]

Ans. (i) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	1
(ii) Hexaaquachromium(III) chloride	1
(iii) Paramagnetic and high spin	$\frac{1}{2} + \frac{1}{2}$
[CBSE Marking Scheme 2017]	

**Q.13. (i)** For the complex  $[\text{Fe}(\text{CN})_6]^{3-}$ , write the hybridization, magnetic character and spin nature of the complex. (At. number : Fe = 26).

- Draw one of the geometrical isomers of the complex  $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$  which is optically active.

[A] [CBSE Delhi 2016]

**Q.15. (a)** For the complex  $[\text{Fe}(\text{CN})_6]^{4-}$ , write the hybridization, magnetic character and spin type of the complex. (At. number : Fe = 26)

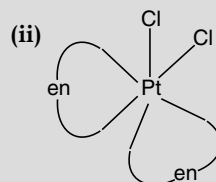
- Draw one of the geometrical isomers of the complex  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  which is optically active.

[A] [CBSE OD Set-2 2016]

Ans. (i) Hybridization :  $d^2sp^3$

Magnetic character : Paramagnetic

Spin nature of the complex : Low spin.  $1 + \frac{1}{2} + \frac{1}{2}$



1

[CBSE Marking Scheme 2016]

#### Commonly Made Error

- Incorrect electronic configuration of ions.

**Q.14.** Write the hybridization, shape and magnetic character of  $[\text{Fe}(\text{CN})_6]^{4-}$ .

[A] [CBSE Comptt. Delhi 2016]

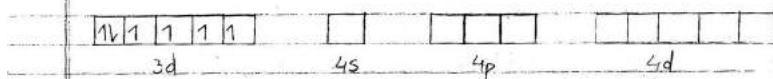
Ans. Hybridization :  $d^2sp^3$

Shape : Octahedral

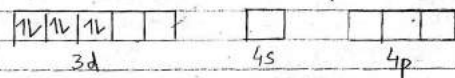
Magnetic character : Diamagnetic.  $1+1+1$

Ans. 12(a) Oxidation number of Fe is +2 in  $[\text{Fe}(\text{CN})_6]^{4-}$

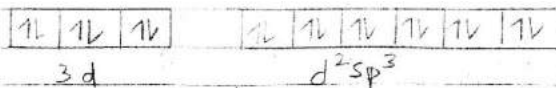
$\text{Fe}^{2+} - 3d^6$



CN is a strong ligand. It pairs up the electron in the 3d orbital of  $\text{Fe}^{2+}$



The six  $\text{CN}^-$  ions give their 6 pairs of electron to the empty orbitals. The orbitals utilised for hybridisation are  $d^2sp^3$  i.e. two 3d orbitals, one 4s orbital and three 4p orbitals



hybrid orbitals

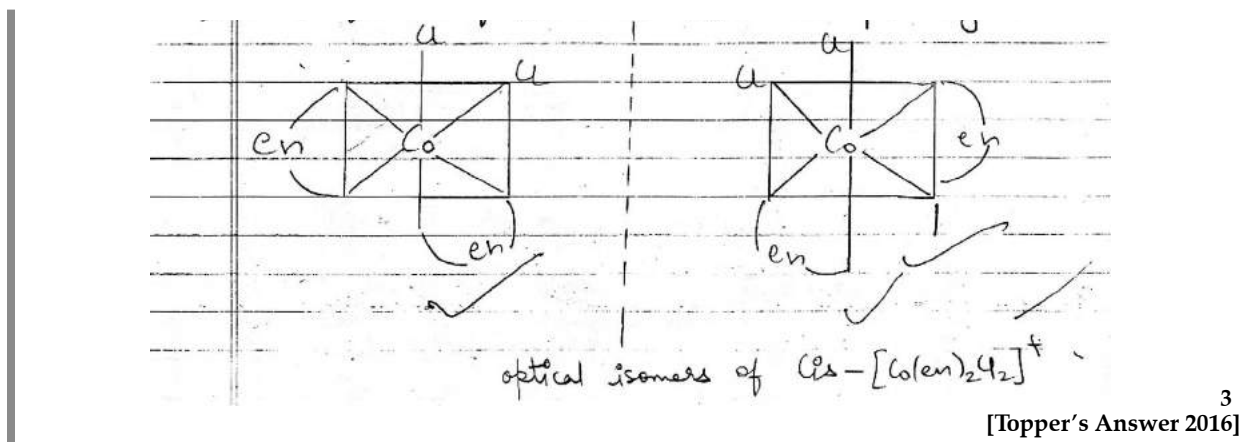
Hybridisation -  $d^2sp^3$

Magnetic character - diamagnetic

Magnetic moment = 0

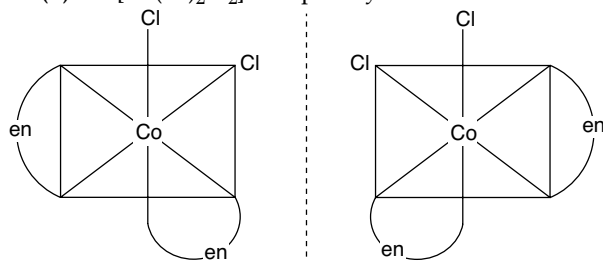
Spin type - low spin complex

b) cis-form of  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is optically active



**Detailed Answer:**

- (a) Hybridization :  $d^2sp^3$   
Magnetic character : Diamagnetic.  
Spin type: Low spin complex
- (b)  $\text{Cis} - [\text{Co}(\text{en})_2\text{Cl}_2]^+$  is optically active.



**Q. 16. (i) How is a double salt different from a complex ?**

(ii) Write IUPAC names of the following :

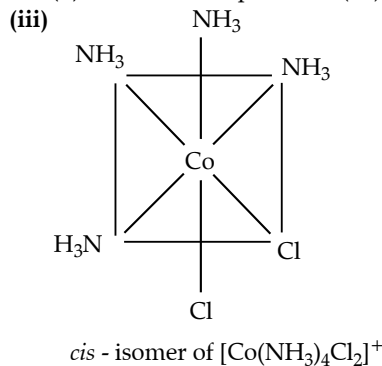
- (a)  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$   
(b)  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$

(iii) Draw the structure of cis-isomer of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ . [U + A] [CBSE Comptt. Delhi 2013]

Ans. (i)

Double Salt	Complex Compound
They dissociate into simple ions completely when dissolved in water. e.g., $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .	They do not dissociate into simple ions when dissolved in water. e.g., $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

- (ii) (a) Potassium trioxalatoferrate (III) 1/2  
(b) Hexaammineplatinum (IV) chloride. 1/2



**Q. 17.  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic whereas  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic. Explain.**

[A&E] [NCERT]

Ans. In both  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ , Fe exists in the +3 oxidation state, that is, in  $d^5$  configuration.



Since  $\text{CN}^-$  is a strong-field ligand, it causes the pairing of electrons. Therefore, there is only one unpaired electron left in the  $d$ -orbital.



Therefore,

$$\begin{aligned} \therefore \mu &= \sqrt{n(n+2)} \\ &= \sqrt{1(1+2)} \\ &= \sqrt{3} \\ &= 1.732 \text{ BM} \end{aligned} \quad 1\frac{1}{2}$$

On the other hand,  $\text{H}_2\text{O}$  is a weak-field ligand. Therefore, it cannot cause the pairing of electrons. This means that the number of unpaired electrons is 5.

$$\begin{aligned} \therefore \mu &= \sqrt{n(n+2)} \\ &= \sqrt{5(5+2)} \\ &= \sqrt{35} \\ &= 5.916 \text{ BM} \end{aligned}$$

Thus, it is evident that  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic, while  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic. 1/2

**Q. 18. A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms A and B. The form A reacts with  $\text{AgNO}_3$  to give a white precipitate readily soluble in dilute aqueous ammonia whereas B gives a pale yellow precipitate soluble in concentrated ammonia.**

- (i) Write the formulae of isomers A and B.  
(ii) State the hybridisation of chromium in each of them.  
(iii) Calculate the magnetic moment (spin only value) of the isomer A. [A] [CBSE SQP 2018-2019]

1

- Ans. (i)** Isomer A:  $[\text{Cr}(\text{NH}_3)_4\text{BrCl}]\text{Cl}$   $\frac{1}{2}$   
**Isomer B:**  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Br}$   $\frac{1}{2}$   
**(ii)** Hybridisation of Cr in isomer A and B is  $d^2sp^3$ . 1  
**(iii)** Number of unpaired electrons in  $\text{Cr}^{3+}(3d^3)$  is 3

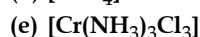
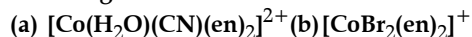
$$\begin{aligned}\text{Magnetic moment} &= \sqrt{n(n+2)} \\ &= \sqrt{3(3+2)} \\ &= 3.87 \text{ BM} \quad 1 \\ &(\text{deduct half mark for wrong unit/unit not written}) \\ &\text{[CBSE Marking Scheme 2018]}\end{aligned}$$



## Long Answer Type Questions-II

(5 marks)

**Q. 1.** Specify the oxidation numbers of the metals in the following coordination entities :



[A] [NCERT]

**Ans. (a)**  $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$

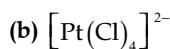
Let the oxidation number of Co be  $x$ . The charge on the complex is +2.

$$\begin{array}{ccccccc} \text{Co} & & (\text{H}_2\text{O}) & & (\text{CN}) & & (\text{en})_2 \\ \downarrow & & \downarrow & & \downarrow & & \downarrow \\ x & + & 0 & + & (-1) & + & 2(0) = +2 \end{array}$$

$$x - 1 = +2$$

$$x = +3$$

1



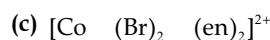
Let the oxidation number of Pt be  $x$ . The charge on the complex is -2.

$$\begin{array}{ccc} \text{Pt} & & (\text{Cl})_4 \\ \downarrow & & \downarrow \\ x & + & 4(-1) = -2 \end{array}$$

$$x - 4 = -2$$

$$x = +2$$

1

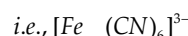
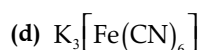


$$\begin{array}{ccccccc} \downarrow & & \downarrow & & \downarrow & & \\ x & + & 2(-1) & + & 2(0) & = & +1 \end{array}$$

$$x - 2 = +1$$

$$x = +3$$

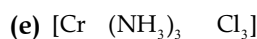
1



$$\begin{array}{ccc} \downarrow & & \downarrow \\ x & + & 6(-1) = -3 \end{array}$$

$$x = +3$$

1



$$\begin{array}{ccc} \downarrow & & \downarrow \\ x & + & 3(0) + 3(-1) = 0 \end{array}$$

$$x - 3 = 0$$

$$x = +3$$

1



## TOPIC-2

### Werner's Theory Bonding in Coordination Compound, VBT, CFT and Importance of Coordination Compounds

## Revision Notes

### ➤ Werner's Theory of Co-ordination compounds :

Different postulates of werner's co-ordination theory are given below :

- (i) Metal ions possess two types of valency (a) primary or ionisable valency and (b) Secondary or non ionisable valency.
- (ii) Every metal ion has a fixed number of secondary valency and this is known as coordination number.
- (iii) **Primary valencies** are satisfied by anions while secondary valencies are satisfied by negative group or neutral molecules with lone pair of electrons.
- (ii) **Secondary valencies** are directed in space towards internal positions.

### ➤ Limitation of Werner's theory : This theory does not explain the following queries—

- (i) Why is the complex forming tendency limited to a few elements only ?
- (ii) Why bonds in the coordination complexes are of directional nature ?
- (iii) Why are certain complexes of magnetic nature and show geometrical and optical isomerism ?

### ➤ Valence Bond theory : It was developed by Pauling. The brief points are :

- (i) A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bond with the ligands.

- (ii) Central metal ion can use appropriate number of  $s$ ,  $p$  or  $d$ -orbitals for hybridisation depending upon total number of ligands.
- (iii) The hybridised orbitals are allowed to overlap with those ligand orbitals that can donate an electron pair for bonding.
- (iv) The outer orbitals (high spin) or inner orbitals (low spin) complexes are formed depending upon whether outer  $d$ -orbitals or inner  $d$ -orbitals are used.

➤ **Limitation of valence bond theory :**

- (i) It cannot explain the detailed magnetic properties of complex compounds.
- (ii) It cannot explain the optical absorption spectra of coordination compounds.
- (iii) It cannot predict property whether a particular 4 coordinate complex is square planar or tetrahedral in nature.
- (iv) It fails to make distinction between strong and weak ligands.
- (v) It does not explain thermodynamic or kinetic stabilities of coordination compounds.

➤ **Crystal field theory (CFT) :**

- (i) The ligands are considered as point charge or point dipole.
- (ii) Interaction between metal ion and ligand is considered as electrostatic in nature.
- (iii) Metal ion is supposed to be present at the origin of the axis. Ligands approach to metal ion along the axis of octahedral complex between the axis of tetrahedral complex and in the case of square planar complex four ligand approach to metal ion along  $x, y$  Plane.
- (iv) Due to the approach of the ligand hence due to the electrostatic interaction between ligands electrons and metal  $d$ -orbital electron degeneracy of  $d$ -orbital is lost and splitting of  $d$ -orbitals occurred.
- (v) 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 and called as spectrochemical series :

$\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{EDTA}^{4-} < \text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$

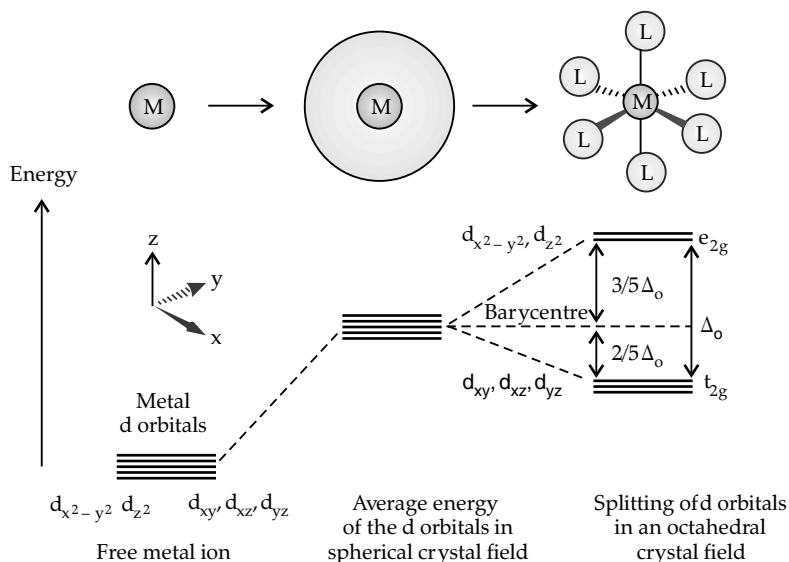


Fig. 1:  $d$  orbital splitting in an octahedral crystal field

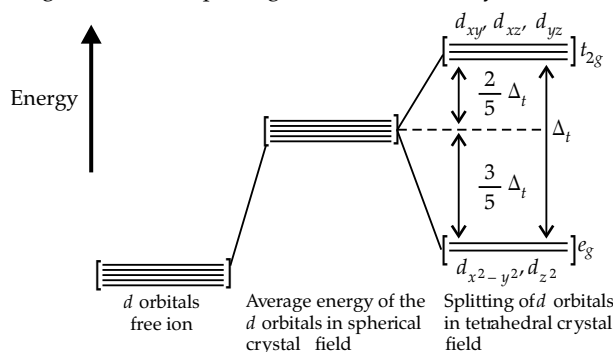


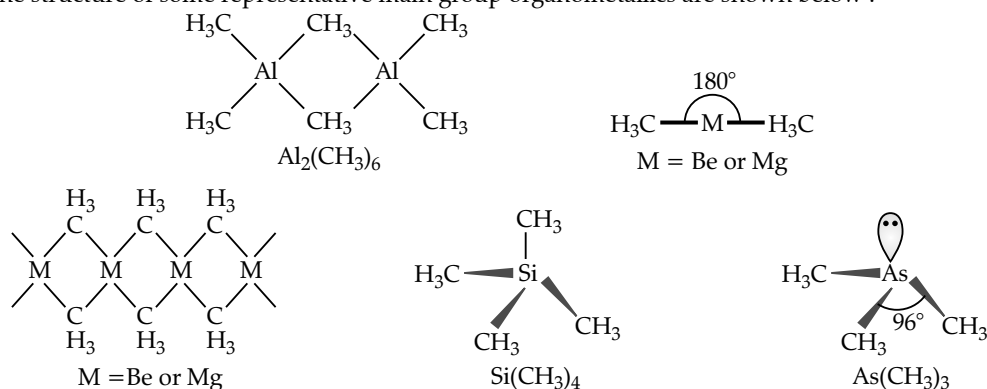
Fig. 2:  $d$  orbital splitting in a tetrahedral crystal field

- (vi) Explanation of colour and magnetic behaviour in complexes is possible by crystal field theory.

➤ **Classification of organometallic compounds :** The broad divisions of organometallic compounds are :

- (i) **Main group organometallics :** The *s*- and *p*-block organometallics are called main group organometallics, *e.g.*,  
 $(\text{CH}_3)_4\text{Sn}$ , Tetramethyl stannane  
 $\text{Si}(\text{CH}_3)_4$  Tetramethylsilane  
 $\text{B}(\text{CH}_3)_3$  Trimethylborane  
 $\text{As}(\text{CH}_3)_3$  Trimethylarsene

The structure of some representative main group organometallics are shown below :

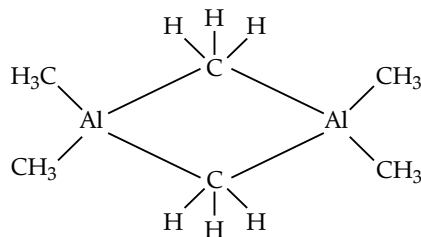


#### Structure of some representative main group organometallic compounds

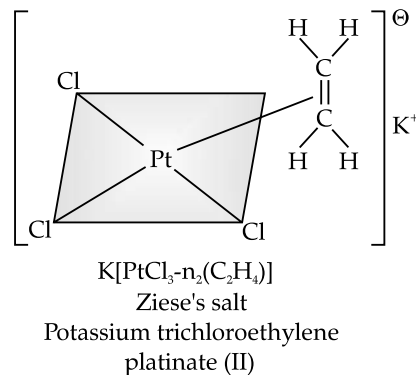
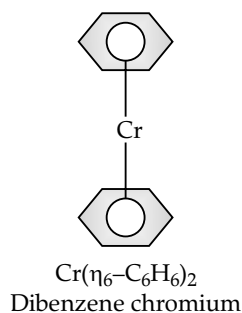
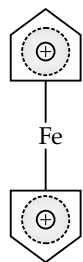
- (ii) ***d*- and *f*-block organometallics :** The organometallics formed by *d* and *f*-block elements are called *d*- and *f*-block organometallics, *e.g.*,  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ ,  $[\text{Ni}(\text{CO})_4]$ ,  $(\text{C}_5\text{H}_5)_2\text{Fe}$ . The first *f*-block organometallic compound,  $[\text{ThH}(\text{OR})(\text{C}_5\text{Me}_5)_2]$  was prepared in late 1970s. Pentamethyl cyclopentadienyl ligand ( $\text{C}_5\text{Me}_5$ ) forms stable *f*-block compounds.
- **Metal carbonyls :** Homoleptic carbonyls are formed by *d*-block elements and contain carbonyl ligands only. *e.g.*,  $\text{V}(\text{CO})_6$ ,  $\text{Cr}(\text{CO})_6$ ,  $[\text{Mo}(\text{CO})_6]$ ,  $[\text{W}(\text{CO})_6]$ ,  $[\text{Mn}_2(\text{CO})_{10}]$ ,  $[\text{Fe}(\text{CO})_5]$ ,  $[\text{Fe}_2(\text{CO})_9]$ ,  $[\text{Co}_2(\text{CO})_8]$ ,  $[\text{Co}_4(\text{CO})_{12}]$ ,  $[\text{Ni}(\text{CO})_4]$ , etc. Metal carbonyls of outside the central part of *d*-block are unstable.

#### Properties of metal carbonyls :

- Metal carbonyls are mostly solids at room temperature and pressure. Exceptions being iron and nickel carbonyls which are liquids.
- The mononuclear carbonyls are volatile and toxic.
- Most of metal carbonyls are soluble in hydrocarbon solvents except  $[\text{Fe}_2(\text{CO})_9]$ .
- Mononuclear carbonyls are either colourless or light coloured.
- They are highly reactive due to metal centre and the CO ligands.
- Metal carbonyls are used as industrial catalyst and as precursor in organic synthesis.



Dimer of trimethylaluminium



- **Bonding in  $\pi$ -bonded complex** : It also involves both  $\sigma$ - and  $\pi$ -bond.  $\sigma$ -bond is formed by overlapping of  $\pi$ -electrons of alkene with vacant  $d$ -orbitals of transition metal.  $\pi$ -bond is formed by back donation of pair of electrons from  $d$ -orbital of transition metal to vacant antibonding orbital of carbon of alkene.
- **Bonding in metal carbonyls** : It also involves both  $\sigma$ - and  $\pi$ -bond.  $\sigma$ -bond is formed by overlapping of lone pair on CO to the vacant  $d$ -orbitals of metal whereas  $\pi$ -bond is formed by back donation of pair of  $d$ -electrons to vacant antibonding orbital of carbonyl.
- **Factors affecting the stability of complexes** :
  - (i) **Nature of the central ion** : Greater the charge density on the central metal ion, greater is the stability of the complex.
  - (ii) **Nature of the ligand** : More basic ligands have a tendency to donate the electron pairs to central metal ion more easily resulting in a stable complex.
  - (iii) **Chelate effect** : Entropy increases when chelation occurs and so the formation of the complex becomes more favourable.
- **Application of complex compounds** :
  - (i) They are used in photography, i.e., AgBr forms soluble complex with sodium thiosulphate in photography.
  - (ii)  $K[Ag(CN)_2]$  is used for electroplating of silver,  $K[Au(CN)_2]$  is used for gold plating.
  - (iii) Some of ligands oxidise  $Co^{2+}$  to  $Co^{3+}$  ion.
  - (iv) EDTA is used for estimation of  $Ca^{2+}$  and  $Mg^{2+}$  in hard water.
  - (v) Silver and gold are extracted by treating Zn with their cyanide complexes.
  - (vi)  $Ni^{2+}$  is tested and estimated by DMG (dimethyl glyoxime).
  - (vii) Cis-platin  $[Pt(NH_3)_2Cl_2]$  is used as antitumor agent in the treatment of cancer.
  - (viii) EDTA is used to remove Pb by forming Pb-EDTA complex which is eliminated in urine.
  - (ix) Haemoglobin contains Fe, chlorophyll contains (Mg) and vitamin  $B_{12}$  contain  $Co^{2+}$ .
  - (x) Bauxite is purified by forming complex with NaOH.
  - (xi) Coordination compounds are used as catalysts for many industrial processes.

## Know the Terms

- **Homogeneous Catalysis** : Organometallic compounds or intermediates derived from soluble transition metal complexes catalyse a variety of reaction in solutions. This is known as **homogeneous catalysis**.
- **Macrocyclic effect** : Multidentate ligands happen to be cyclic in nature without causing any steric hindrance, the stability of the complexes is further increased. This is known as **macrocyclic effect**.
- **Stability constants (K)** : The relative stabilities of coordination complexes can be compared in terms of stability constant (K) also denoted by  $\beta$  (Beta).
- **Metal carbonyl** : Organometallic compounds in which carbon monoxide acts as the ligand.



## Very Short Answer-Objective Type Questions (1 mark each)

### A. Multiple choice Questions:

- Q. 1. The CFSE for octahedral  $[CoCl_6]^{4-}$  is  $18,000\text{ cm}^{-1}$ . The CFSE for tetrahedral  $[CoCl_4]^{2-}$  will be
- (a)  $18,000\text{ cm}^{-1}$  (b)  $16,000\text{ cm}^{-1}$   
 (c)  $8,000\text{ cm}^{-1}$  (d)  $20,000\text{ cm}^{-1}$

[A] [NCERT Exemp. Q. 8, Page 121]

Ans. Correct option : (c)

**Explanation** : CFSE for tetrahedral complex is

$$\Delta_t = \frac{4}{9} \Delta_o$$

$$\Delta_t = \frac{4}{9} \times 18,000 = 8,000\text{ cm}^{-1}$$

### B. Match the following :

- Q. 1. Match the species given in Column I with those mentioned in Column II.

Column I (Complex ion)	Column II (Hybridisation, number of unpaired electrons)
A. $[Cr(H_2O)_6]^{3+}$	(1) $dsp^2$ , 1

B. $[Co(CN)_4]^{2-}$	(2)	$sp^3d^2$ , 5
C. $[Ni(NH_3)_6]^{2+}$	(3)	$d^2sp^3$ , 3
D. $[MnF_6]^{4-}$	(4)	$sp^3$ , 4
	(5)	$sp^3d^2$ , 2

Code :

- (a) A(3), B(1), C(5), D(2)  
 (b) A(4), B(3), C(2), D(1)  
 (c) A(3), B(2), C(4), D(1)  
 (d) A(4), B(1), C(2), D(3)

[NCERT Exemp. Q. 38, Page 125]

Ans. Correct Code : (a)

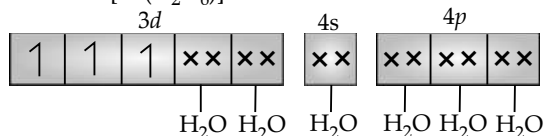
**Explanation** : Formation of inner-orbital complex and outer complex determines hybridisation of molecule which in turn depends upon field strength of ligand and number of vacant  $d$  orbitals.

- (i) Strong-field ligand forms inner orbital complex with hybridisation  $d^2sp^3$ .  
 (ii) Weak-field ligand forms outer-orbital complex with hybridisation  $d^2sp^3$ . According to VBT, hybridisation

and number of unpaired electrons of coordination compounds can be calculated as

(a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

MOEC (Molecular orbital electronic configuration) of  $\text{Cr}^{3+}$  in  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  is

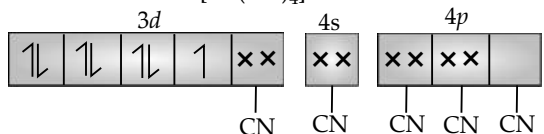


Hybridisation =  $d^2sp^3$

$n$  (number of unpaired electrons) = 3

(b)  $[\text{Co}(\text{CN})_4]^{2-}$  is

MOEC of  $\text{Co}^{2+}$  in  $[\text{Co}(\text{CN})_4]^{2-}$  is

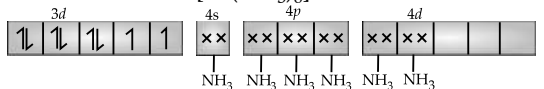


Hybridisation =  $dsp^2$

$n$  (number of unpaired electrons) = 1

(c)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$

MOEC of  $\text{Ni}^{2+}$  in  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is

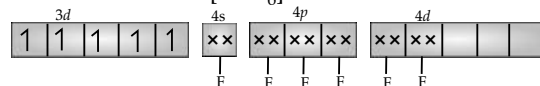


Hybridisation =  $sp^3d^2$

$n$  (number of unpaired electrons) = 2

(d)  $[\text{MnF}_6]^{4-}$

MOEC of  $\text{Mn}^{2+}$  in  $[\text{MnF}_6]^{4-}$  is



Hybridisation =  $sp^3d^2$

$n$  (number of unpaired electrons) = 5

**C. Answer the following :**

**Q. 1. Explain the following—**

$[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are of different colours in dilute solutions. [A&E] [CBSE Foreign 2012]

**Ans.**  $[\text{Fe}(\text{CN})_6]^{4-}$  does not have unpaired electrons (CN is a strong field ligand) whereas  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  has unpaired electrons and it absorbs light from visible region and radiates complementary colour. 1

**Q. 2. On the basis of crystal field theory, write the electronic configuration of  $d^6$  in terms of  $t_{2g}$  and  $e_g$  in an octahedral field when  $\Delta_0 < P$ .**

[A] [CBSE SQP 2018-2019]

**Ans.**  $t_{2g}^3 e_g^3$

1



## Short Answer Type Questions

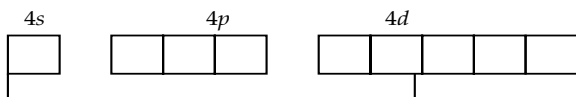
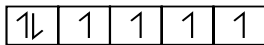
(2 marks each)

**Q. 1. Using the Valence Bond theory predict the geometry and magnetic behaviour of  $[\text{CoF}_6]^{3-}$ .**

[At. no. of Co = 27] [A] [CBSE Comptt. Delhi 2013]

**Ans.**  $[\text{CoF}_6]^{3-}$   $3d^6$

3d Orbitals of  $\text{Co}^{3+}$  ions :



$sp^3d^2$  hybridization

Fluorine ion is a weak ligand so pairing will not occur, so it possess octahedral geometry and paramagnetic in nature. 1

### Commonly Made Error

- There is confusion in electronic configuration of ions.

**Q. 2. Explain why  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is an inner complex whereas  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is an outer orbital complex. (At. no. Co = 27, Ni = 28)**

[A&E] [CBSE Comptt. OD 2013]

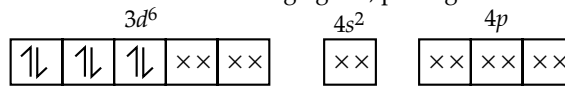
**Ans.** When the complex formed involves the inner  $(n-1)$   $d$ -orbitals for hybridization ( $d^2sp^3$ ), the complex is called inner orbital complex.  $[\text{Co}(\text{NH}_3)_6]^{3+}$  involves inner  $(n-1)$   $d$ -orbitals. Therefore, it is called inner orbitals complex. When the complex formed involves the use of outer  $n$   $d$ -orbitals for

hybridization ( $sp^3d^2$ ), the complex is called outer orbital complex.  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  involves  $nd$ -orbitals. Therefore, it is outer complex. 1

$[\text{Co}(\text{NH}_3)_6]^{3+}$  Co = 27 =  $4s^2 3d^7$

$\text{Co}^{3+} = 3d^6$

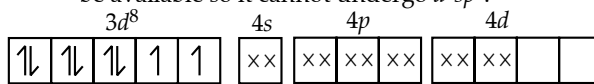
As ammonia is a strong ligand, pairing occurs.



$d^2sp^3$  hybridization

$[\text{Ni}(\text{NH}_3)_6]^{2+}$  Ni = 28 =  $4s^2 3d^8$

In  $\text{NH}_3$  if a pairing occurs, only one 3d orbital will be available so it cannot undergo  $d^2sp^3$ .



$sp^3d^2$  hybridization

1

**Q. 3. State reason for each of the following :**

(i) CO is stronger complexing reagent than  $\text{NH}_3$ .

(ii) The molecular shape of  $\text{Ni}(\text{CO})_4$  is not the same as that of  $[\text{Ni}(\text{CN})_4]^{2-}$ . [A&E] [CBSE Delhi 2012]

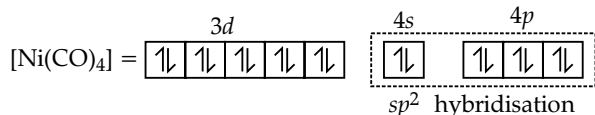
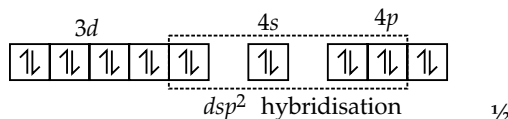
**Ans.** (i) CO can form  $\sigma$  as well as  $\pi$  bond, whereas  $\text{NH}_3$  has lone pair of electrons and can form  $\sigma$  bond only. Therefore, CO is a better complexing reagent than  $\text{NH}_3$ . 1



## (ii) Electronic configuration of :

Ni : [Ar]  $4s^2, 3d^8$ So Ni (0) : [Ar]  $4s^0, 3d^{10}$ 

CO ligand causes pairing of electrons and shifting of electrons from 4s to 3d.

[Ni(CO)<sub>4</sub>] has  $sp^3$  hybridisation and has tetrahedral shape.  $\frac{1}{2}$ [Ni(CN)<sub>4</sub>]<sup>2-</sup>Ni<sup>2+</sup> :  $4s^0, 3d^8$ 

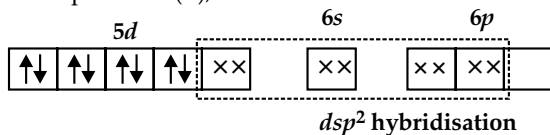
## Long Answer Type Questions-I

(3 marks each)

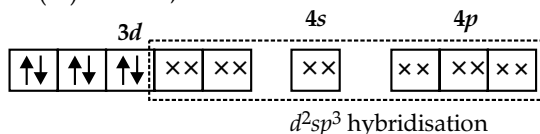
**Q. 1.** Write the name, the structure and the magnetic behaviour of each one of the following complexes :(i) [Pt(NH<sub>3</sub>)<sub>2</sub>Cl(NO<sub>2</sub>)](ii) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl(iii) Ni(CO)<sub>4</sub>

(At nos. Co = 27, Ni = 28, Pt = 78)

[A] [CBSE Delhi 2012]

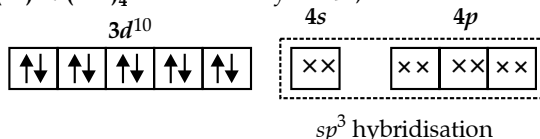
**Ans. (i)** [Pt(NH<sub>3</sub>)<sub>2</sub>Cl(NO<sub>2</sub>)] : Diamminechloridonitro-N-platinum (II); Pt<sup>2+</sup> =  $5d^8$ × × : Electron pair from the NH<sub>3</sub>, Cl<sup>-</sup> and NO<sub>2</sub>,

Structure : Square planar;

Magnetic behaviour : Diamagnetic. **1**(ii) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl : Tetraamminedichloro-cobalt (III) chloride; Co<sup>3+</sup> =  $3d^6$ 

Structure : Octahedral;

Magnetic behaviour : Diamagnetic

(iii) Ni(CO)<sub>4</sub> : Tetracarbonylnickel; Ni =  $3d^8, 4s^2$ 

× × : Electron pair from Ligand CO

Structure : Tetrahedral;

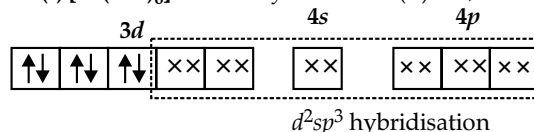
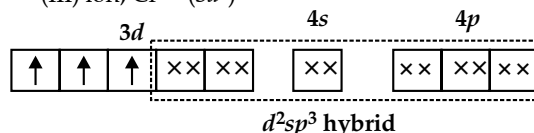
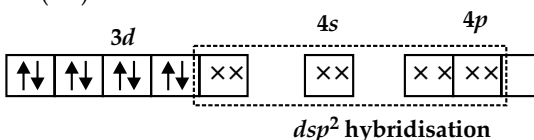
Magnetic behaviour : Diamagnetic. **1****Q. 2.** Name the following coordination entities and describe their structure :(i) [Fe(CN)<sub>6</sub>]<sup>4-</sup>(ii) [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>**Answering Tip**

- While describing the reason include cause and consequence of the condition.

**Q. 4.** Explain why [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> has magnetic moment value of 5.92 BM whereas [Fe(CN)<sub>6</sub>]<sup>3-</sup> has a value of only 1.74 BM. [A&E] [NCERT Exemp. Q. 31, Page 124]**Ans.** [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> and [Fe(CN)<sub>6</sub>]<sup>3-</sup> exist in the +3 oxidation state i.e., in  $d^5$  configuration.Due to presence of five unpaired electrons [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> has magnetic moment 5.92 BM whereas [Fe(CN)<sub>6</sub>]<sup>3-</sup> has 1.74 BM moment due to presence of one unpaired electron. **2**(iii) [Ni(CN)<sub>4</sub>]<sup>2-</sup>

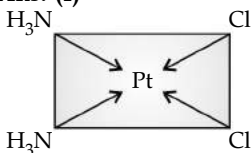
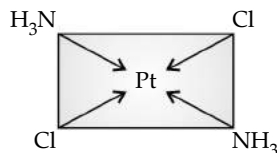
(Atomic numbers Fe = 26, Cr = 24, Ni = 28)

[A] [CBSE OD 2012]

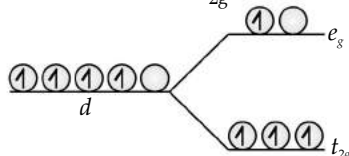
**Ans. (i)** [Fe(CN)<sub>6</sub>]<sup>4-</sup> : Hexacyanoferrate (II) ion; Fe<sup>2+</sup> ( $3d^6$ ) $d^2sp^3$ -hybridization in [Fe(CN)<sub>6</sub>]<sup>4-</sup> leads to octahedral structure. **1**(ii) [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> : Tetraamminedichloridochromium (III) ion, Cr<sup>3+</sup> ( $3d^3$ )× × : Electron pair from NH<sub>3</sub> molecule and Cl<sup>-</sup> ion  $d^2sp^3$  hybridization in [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> leads to octahedral structure. **1**(iii) [Ni(CN)<sub>4</sub>]<sup>2-</sup> : Tetracyanonickelate (II) ion ; Ni<sup>2+</sup> (II) ( $3d^8$ )× × : Electron pair from Cl<sup>-</sup> ion. $dsp^2$  hybridization in [Ni(CN)<sub>4</sub>]<sup>2-</sup> leads to square planar structure. **1****Q. 3. (i)** Draw the geometrical isomers of complex [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>].(ii) On the basis of crystal field theory, write the electronic configuration for  $d^4$  ion if  $\Delta_o < P$ .(iii) Write the hybridization and magnetic behaviour of the complex [Ni(CO)<sub>4</sub>]. (At. no. of Ni = 28)

[A] [CBSE Delhi 2015]

Ans. (i)

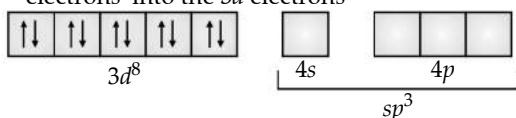
Cis-diamminedichloro  
platinum (II)Trans-diamminedichloro  
platinum (II)

- (ii) When  $\Delta_o < P$ , it is weak field and high spin situation. As a result, one electron entered in  $e_g$  orbital and 3 electrons in  $t_{2g}$ .

Electronic configuration :  $t_{2g}^3 e_g^1$ 

- (iii)  $\text{Ni}(\text{CO})_4$  : The outermost electronic configuration will be  $3d^8 4s^2 4p^0$ .

CO is the strong ligand, causes pairing up of the 4s electrons into the 3d electrons



Thus, the hybridization will be  $sp^3$  (tetrahedral) 1  
 $\text{Ni}(\text{CO})_4$  will be diamagnetic in nature.

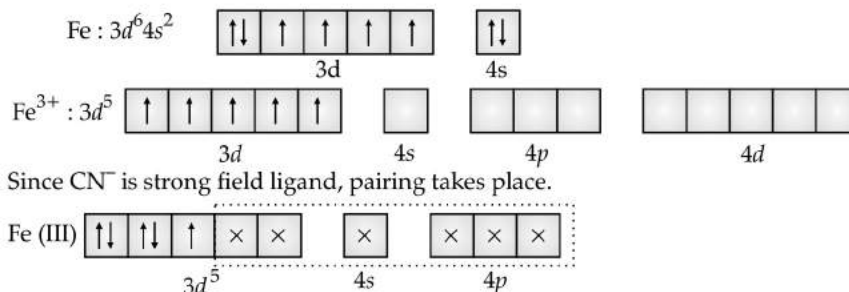
- Q. 4. (i) What type of isomerism is shown by the complex  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  ?

- (ii) On the basis of crystal field theory, write the electronic configuration for  $d^4$  ion if  $\Delta_o > P$ .

- Q. 6. (i) For the complex  $[\text{Fe}(\text{CN})_6]^{3-}$ , write the hybridization, magnetic character and spin nature of the complex. (At. number : Fe = 26).

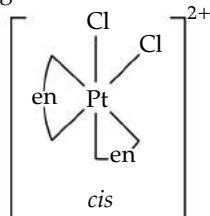
- (ii) Draw one of the geometrical isomers of the complex  $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$  which is optically active.

[A] [CBSE Delhi 2016]

Ans. (i)  $[\text{Fe}(\text{CN})_6]^{3-}$ 

Hybridization –  $d^2sp^3$  (octahedral), Magnetic character – Paramagnetic, Spin nature – Low spin complex 2

(ii)



1

**Commonly Made Error**

- (i) Incorrect electronic configuration of ions.

- (iii) Write the hybridization and shape of  $[\text{CoF}_6]^{3-}$ .

(Atomic number of Co = 27) [A] [CBSE OD 2015]

Ans. (i) Hydration isomerism 1

(ii) Electronic configuration is  $t_{2g}^4$  or by diagram. 1(iii) Hybridization is  $sp^3d^2$  and shape is octahedral. $\frac{1}{2} + \frac{1}{2}$ 

- Q. 5. (i) Write the IUPAC name of the complex  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ .

(ii) What type of isomerism is exhibited by the complex  $[\text{Co}(\text{en})_3]^{3+}$  ? (en = ethane-1, 2-diammine)(iii) Why is  $[\text{NiCl}_4]^{2-}$  paramagnetic but  $[\text{Ni}(\text{CO})_4]$  is diamagnetic ?

(At. nos. : Cr = 24, Co = 27, Ni = 28)

[A] [CBSE OD 2014]

Ans. (i) Tetraamminedichloridochromium (III) chloride.

(ii) Optical isomerism.

(iii) In  $[\text{NiCl}_4]^{2-}$ ;  $\text{Cl}^-$  act as weak ligand therefore does not cause forced pairing, thus electrons will remain unpaired hence paramagnetic.  $\frac{1}{2}$ In  $[\text{NiCO}_4]$ ; CO act as strong ligand therefore causes forced pairing, thus electrons will become paired hence diamagnetic.  $\frac{1}{2}$ 

[CBSE Marking Scheme 2014]

**Commonly Made Error**

- (iii) Students get confused between the terms associated with magnetic properties.

**Answering Tip**

- (iii) Read and understand the distinguishing characteristics between each magnetic property.



- (ii) In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , Ni is present in +2 state with the configuration  $3d^8$ . It has two unpaired electrons which do not pair up in the presence of the weak  $\text{H}_2\text{O}$  ligand. Therefore, it is green in colour. While undergoing d-d transition, red light is absorbed and complementary light emitted is green.

In case of  $[\text{Ni}(\text{CN})_4]^{2-}$ , Ni is in +2 state with the configuration  $3d^8$  but in presence of the strong CN<sup>-</sup> ligand, the two unpaired electrons in the 3d orbitals undergoes pairing. As there is no unpaired electron present, it is colourless. **1**

**Q.11. (i) Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for  $d^4$  ion if  $\Delta_o > P$ .**

- (ii)  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic whereas  $[\text{NiCl}_4]^{2-}$  is paramagnetic. Give reason. (At. no. of Ni = 28)

[R + A + A&E] [CBSE Foreign Set-2 2017]

**Ans. (i)** It is the magnitude of difference in energy between the two sets of d orbital i.e.  $t_{2g}$  and  $e_g$ . **1**  
 $t_{2g}^4 e_g^0$  **1**

- (ii) In  $[\text{Ni}(\text{CN})_4]^{2-}$ , CN<sup>-</sup> is a strong field ligand and pairing takes place whereas in  $[\text{NiCl}_4]^{2-}$ , due to the presence of Cl<sup>-</sup>, a weak field ligand no pairing occurs/diagrammatic representation. **1**

[CBSE Marking Scheme 2017]

**[AI] Q. 12. A metal ion  $M^{n+}$  having  $d^4$  valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming  $\Delta_o > P$ .**

- (i) Write the electronic configuration of  $d^4$  ion.  
 (ii) What type of hybridisation will  $M^{n+}$  ion has?  
 (iii) Name the type of isomerism exhibited by this complex. **[A] [CBSE SQP 2017]**

**Ans. (i)**  $t_{2g}^4 e_g^0$  **1**

(ii)  $sp^3d^2$  **1**

(iii) optical isomerism **1**

[CBSE Marking Scheme 2017]

## ? Long Answer Type Questions-II

(5 marks)

**Q. 1. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex :**

(a)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$

(b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

(c)  $[\text{CrCl}_3(\text{py})_3]$

(d)  $\text{Cs}[\text{FeCl}_4]$

(e)  $\text{K}_4[\text{Mn}(\text{CN})_6]$

[A] [NCERT]

**Ans. (a)**  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$  :

**IUPAC name :**

Potassiumdiaquadioxalatochromate(III)trihydrate.

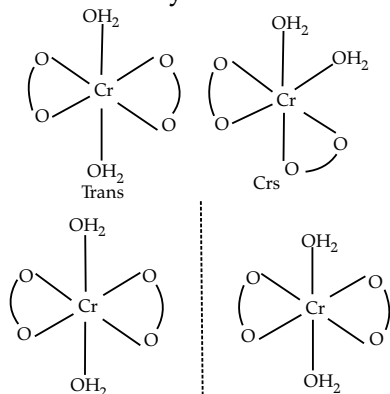
**Oxidation state of chromium :** 3

**Electronic configuration :**  $3d^3 : t_{2g}^3$

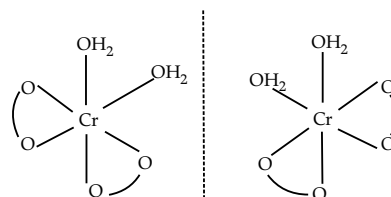
**Coordination number :** 6

**Shape :** Octahedral

**Stereochemistry :**



Trans is optically inactive



Crs is optically active

**Magnetic moment :**

$$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)}$$

$$= \sqrt{15} = 3.872 \approx 4 \text{ BM}$$

**1**

(b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  :

**IUPAC name :**

Pentaamminechloridocobalt(III)chloride

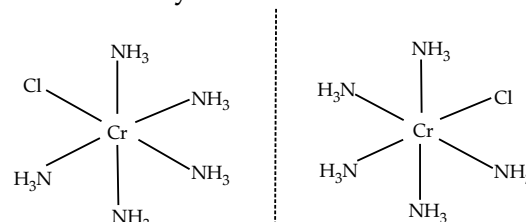
**Oxidation state of Co :** +3

**Coordination number :** 6

**Shape :** Octahedral

**Electronic configuration :**  $d^6 : t_{2g}^6$

**Stereochemistry :**



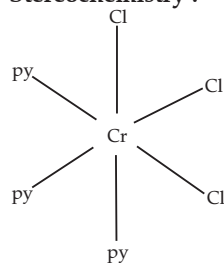
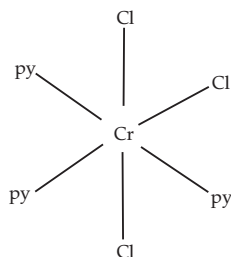
2 isomers

Magnetic moment = 0

**1**

(c)  $\text{CrCl}_3(\text{py})_3$  :**IUPAC name :**

Trichloridotripyridinechromium (III)

**Oxidation state of chromium :** +3**Electronic configuration for  $d^3$  :**  $t_{2g}^3$ **Coordination number :** 6**Shape :** Octahedral**Stereochemistry :****Facial isomer****Meridional isomer**

Both isomers are optically active. Therefore, a total of four isomers exist.

**Magnetic moment :**

$$m = \sqrt{n(n+2)} = \sqrt{3(3+2)}$$

$$= \sqrt{15} = 3.872 \approx 4 \text{ BM}$$

1

(d)  $\text{Cs}[\text{FeCl}_4]$  :**IUPAC name :** Caesiumtetrachloroferrate (III)**Oxidation state of Fe :** +3**Electronic configuration of  $d^6$  :**  $e_g^2 t_{2g}^3$ **Coordination number :** 4**Shape :** Tetrahedral**Stereochemistry :** Optically inactive**Magnetic moment :**

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

$$= \sqrt{35} = 5.916 \approx 6 \text{ BM}$$

1

(e)  $\text{K}_4[\text{Mn}(\text{CN})_6]$  :**IUPAC name :** Potassium hexacyanomanganate(II)**Oxidation state of manganese :** +2**Electronic configuration of  $d^{5+}$  :**  $t_{2g}^5$ **Coordination number :** 6**Shape :** Octahedral.**Stereochemistry :** Optically inactive**Magnetic moment :**

$$m = \sqrt{n(n+2)} = \sqrt{1(1+2)}$$

$$= \sqrt{3} = 1.732 \text{ BM}$$

1

