

## COORDINATION COMPOUNDS

Read the passage given below and answer the following questions:

In spite of the predictions of stable noble gas compounds since at least 1902, unsuccessful attempts at their synthesis gave rise to the widely held opinion that noble gases are not only noble but also inert. It was not until 1962 that this dogma was shattered when Bartlett in Canada published the first stable noble gas compound  $\text{XePtF}_6$ . This discovery triggered a worldwide frenzy in this area, and within a short time span many new xenon, radon, and krypton compounds were prepared and characterized. The recent discoveries show the ability of xenon to act as a ligand. The discovery by Seppelt's group that more than one xenon atom can attach itself to a metal center which in the case of gold leads to surprisingly stable Au-Xe bonds. The bonding in  $[\text{AuXe}_4]^{2+}$  involves 4 Xe ligands attached by relatively strong bonds to a single Au(II) center in a square planar arrangement with a Xe-Au bond length of about 274 pm. This discovery provides not only the first example of multiple xenon ligands but also represents the first strong metal - xenon bond.

- In the complex ion  $[\text{AuXe}_4]^{2+}$ , Xe acts as :  
**a. central atom b. ligand c. chelating agent d. electrophile**
- Hybridisation shown by Au in  $[\text{AuXe}_4]^{2+}$  is :  
**a.  $sp^3$  b.  $sp^3d$  c.  $sp^3d^2$  d.  $sp^2$**
- Compounds of noble gases except \_\_\_\_\_ are known.  
**a. Krypton b. Radon c. Helium d. Xenon**
- Xe is a \_\_\_\_\_ ligand  
**a. ambidentate b. bidentate c. unidentate d. hexadentate**

ANSWERS :

1a

2 b

3 c

4 c

2. Out of the following transition elements, the maximum number of oxidation states are shown by:

(a) Cr (Z = 24) (b) Sc (Z = 21) (c) Fe (Z = 26) (d) Mn (Z = 25)

ANSWER: Mn(Z=25)

3. Using valence bond theory, the complex  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  can be described as :

(a)  $d^2sp^3$ , inner orbital complex, paramagnetic

(b)  $d^2sp^3$ , outer orbital complex, diamagnetic

(c)  $sp^3d^2$ , outer orbital complex, paramagnetic

(d)  $dsp^2$ , inner orbital complex, diamagnetic

ANSWER: (a)

4. (i) Give the electronic configuration of the d-orbitals of Ti in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion and explain why this complex is coloured? [At. No. of Ti = 22]

(ii) Write IUPAC name of  $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ .

ANSWER:

(i) 1. In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , the central metal ion is  $\text{Ti}^{3+}$  which has  $d^1$  configuration. This single electron occupies one of the  $t_{2g}$  orbitals in the octahedral aqua ligand field.

2. When white light falls on this complex, the d electron absorbs light and promotes itself to  $e_g$  level.

3. The spectral data show the absorption maximum is at  $20000 \text{ mol}^{-1}$  corresponding to the crystal field splitting energy ( $\Delta_0$ )  $239.7 \text{ kJ mol}^{-1}$ . The transmitted colour associated with this absorption is purple and hence the complex appears in purple in colour.

(ii) hexaaquatitanium(III)

5. Determine the structure and magnetic behaviour of  $[\text{CoCl}_4]^{2-}$  using valence bond theory

ANSWER:  $sp^3$  hybridisation, tetrahedral geometry and paramagnetic

6. Write the IUPAC name of the following complex :  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$

ANSWER: tertaammineaquachloridecobalt(III)chloride

7. What is the difference between an Ambidentate ligand and a Bidentate ligand?

The key difference between bidentate and ambidentate ligands is that bidentate ligands can bind to a central atom via two bonds at the same time whereas ambidentate ligands can form two bonds with a central atom, but form only one bond at a time.

8. Out of  $[\text{Fe}(\text{NH}_3)_6]^{3+}$  and  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ , which complex is more stable and why?

ANSWER:  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  is more stable because it forms chelate rings.

9. In which of the following ions, number of unpaired electron is zero?

(a)  $\text{Fe}^{2+}$  (Z=26) (b)  $\text{Cr}^{2+}$  (Z=24) (c)  $\text{Zn}^{2+}$  (Z=24) (d)  $\text{Cu}^{2+}$  (Z=29)

ANSWER:  $\text{Zn}^{2+}$

10. Why is  $[\text{Ni}(\text{CN})_4]^{2-}$  diamagnetic while  $[\text{NiCl}_4]^{2-}$  is paramagnetic in nature:

(a) In  $[\text{Ni}(\text{CN})_4]^{2-}$ , no unpaired electrons are present while in  $[\text{NiCl}_4]^{2-}$  two unpaired electrons are present.

(b)  $[\text{NiCl}_4]^{2-}$  shows  $sp^2$  hybridisation, hence it is paramagnetic.

(c)  $[\text{Ni}(\text{CN})_4]^{2-}$  shows  $sp^3$  hybridisation, hence it is diamagnetic.

(d) In  $[\text{NiCl}_4]^{2-}$ , no unpaired electrons are present while in  $[\text{Ni}(\text{CN})_4]^{2-}$  two unpaired electrons are present.

In both  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$ , Ni is in +2 oxidation state with configuration  $3d^8$  and it contains two unpaired electrons. In  $[\text{NiCl}_4]^{2-}$  due to presence of weak ligand  $\text{Cl}^-$  no pairing takes place and hence it is paramagnetic

whereas in  $[\text{Ni}(\text{Cl})_4]^{2-}$ ,  $\text{CN}^-$  is a strong field ligand and pairing occurs and hence it becomes diamagnetic.

11. Write the IUPAC name and geometrical isomer of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

**ANSWER:** The given compound shows Geometrical isomerism. Hence it would have cis and trans forms as the isomers.

Name of the isomers:

Cis-Diamminedichloridoplatinum (II) and trans-Diamminedichloridoplatinum (II)

12. Determine the structure and magnetic behaviour of  $[\text{Fe}(\text{CN})_6]^{4-}$  ion on the basis of valence bond theory.

**ANSWER:** In the above coordination complex, iron exists in the +2 oxidation state.

$\text{Fe}^{2+}$ : Electronic configuration is  $3d^6$ .

Orbitals of  $\text{Fe}^{2+}$  ion:

As  $\text{CN}^-$  is a strong ligand, it causes the pairing of the unpaired 3d electrons.

since there are six ligands around the central metal ion, the most feasible hybridization is  $d^2sp^3$ .

$d^2sp^3$  hybridized orbitals of  $\text{Fe}^{2+}$  are 6 electron pairs are from  $\text{CN}^-$  ion occupy the six hybrid  $d^2sp^3$  orbitals.

Hence, the geometry of the complex is octahedral and the complex is diamagnetic (as there are no unpaired electrons).

13. The magnitude of CFSE (crystal field splitting energy,  $T_0$ ) can be related to the configuration of d-orbital in a coordination entity as:

(a) if  $T_0 < P$ , the configuration is  $t_2g^3 e_g^3$  = weak field ligand and high spin complex

(b) if  $T_0 > P$ , the configuration is  $t_2g^4 e_g^0$  = strong field ligand and high spin complex

(c) if  $T_0 > P$ , the configuration is  $t_2g^5 e_g^1$  = strong field ligand and low spin complex

(d) if  $T_0 = P$ , the configuration is  $t_2g^4 e_g^2$  = strong field ligand and high spin complex

14. Give an example of linkage isomerism

**ANSWER:** Linkage isomerism : When more than one atom in an ambidentate ligand is linked with central metal ion to form two types of complexes, then

the formed isomers are called linkage isomers and the phenomenon is called linkage isomerism.

$[\text{Cr}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$  Pentaaquathiocyanate chromium (III) ion

$[\text{Cr}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$

Pentaaquaisothiocyanate chromium (III) ion

15. Give an example of coordination isomerism

ANSWER: Example :  $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$  and

$[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$

16. Give an example of ionization isomerism

ANSWER: Example :  $[\text{Pt}(\text{NH}_3)_5(\text{Br})_3] \text{SO}_4$  and

$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)] \text{Br}$

17. Give IUPAC name of ionization isomer of  $[\text{Ni}(\text{NH}_3)_3\text{NO}_3]\text{Cl}$ .

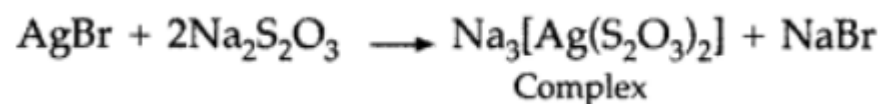
ANSWER: Triammine nitrato nickel (III) chloride

18. 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)

ANSWER: It shows ionisation isomerism and linkage isomerism.

19. Which complex ion is formed when undecomposed AgBr is washed with hypo solution in photography?

ANSWER: Sodium dithiosulphato argentate (I) complex is formed



20. Give IUPAC name of the ionization isomer of  $[\text{Ni}(\text{NH}_3)_3\text{NO}_3]\text{Cl}$ .

ANSWER: Triammine chlorido nickel (II) nitrate  $[\text{Ni}(\text{NH}_3)_3\text{NO}_3]\text{Cl}$

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

ANSWER: (i) EDTA (Ethylene diamine tetra-acetic acid)

(ii) Dimethyl glyoxime (DMG)

22. Which of the following is more stable complex and why?

$[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{en})_3]^{3+}$

ANSWER:  $[\text{Co}(\text{en})_3]^{3+}$  is more stable complex than  $[\text{Co}(\text{NH}_3)_6]^{3+}$  because of chelate effect.

23. What is the IUPAC name of the complex  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ ?

ANSWER: Hexaamminenickel (II) chloride

24. What is meant by chelate effect?

ANSWER: Chelate effect : When a bidentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six membered ring is formed. This effect is called Chelate effect. As a result, the stability of the complex increases.

Example: the complex of  $\text{Ni}^{2+}$  with 'en' is more stable than  $\text{NH}_3$ .

25. Why are low spin tetrahedral complexes not formed?

ANSWER: Low spin tetrahedral complexes are rarely observed because orbital splitting energies for tetrahedral complexes are sufficiently large for forcing pairing.

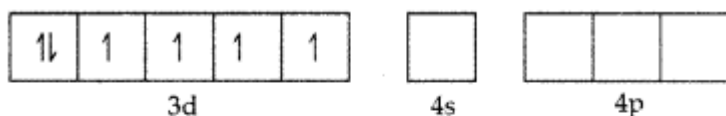
26. Describe the shape and magnetic behaviour of following complexes :

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

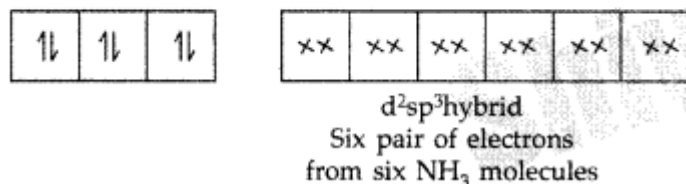
(ii)  $[\text{Ni}(\text{CN})_4]^{2-}$  (At. No. Co = 27, Ni = 28)

ANSWER:  $[\text{Co}(\text{NH}_3)_6]^{3+}$  :

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

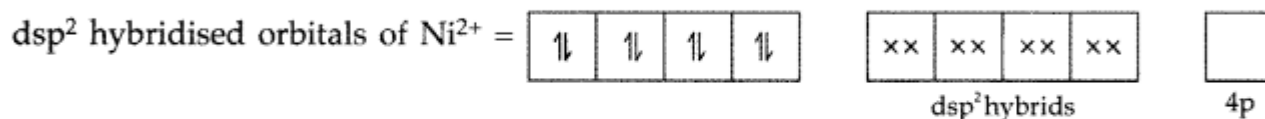
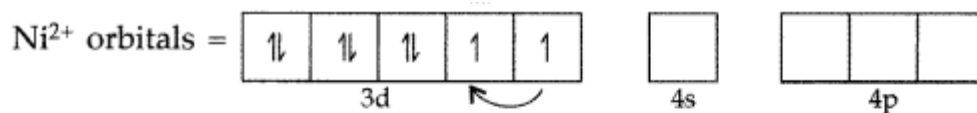


\*  $d^2sp^3$  hybridised orbitals of  $\text{Co}^{3+}$  :



Hybridization :  $d^2sp^3$  Shape : Octahedral Magnetic behaviour : Diamagnetic (absence of unpaired electrons)

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



Containing 4 pairs of electrons from 4 CN molecules

**Shape** : Square planar

**Hybridisation** :  $dsp^2$

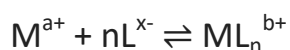
**Magnetic behaviour** : Diamagnetic (no unpaired electrons)

27. How is the stability of a co-ordination compound in solution decided ?

How is the dissociation constant of a complex defined?

ANSWER: Stability of a complex in solution means the measure of resistance to the replacement of a ligand by some other ligand. This stability can be expressed in terms of equilibrium constant.

Let the reaction between metal and ligand be represented as



Stability or Dissociation constant (K)

$$= \frac{[ML_n^{b+}]}{[M^{a+}][L^{x-}]^n}$$

The reciprocal of the stability constant K is known as instability constant or dissociation constant

$$K_i = \frac{1}{K} = \frac{[M^{a+}][L^{x-}]^n}{[ML_n^{b+}]}$$

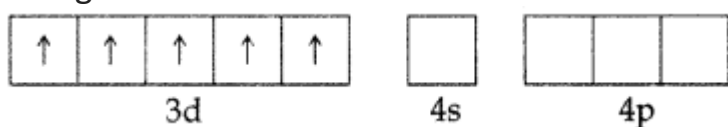
Factors affecting the stability of a complex ion

(i) Nature of metal ion : Greater the charge and smaller the size of the ion, more is its charge density and greater will be stability of the complex.

(ii) Nature of ligand : More the basicity of ligand, more is its tendency to donate electron pair and therefore, more is the stability of the complex.

28.  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is strongly paramagnetic whereas  $[\text{Fe}(\text{CN})_6]^{3-}$  is weakly paramagnetic. Explain. (At. no. Fe = 26)

ANSWER: In both the cases, Fe is in oxidation state +3. Outer electronic configuration of Fe+3 is :



In the presence of  $\text{CN}^-$ , the 3d electrons pair up leaving only one unpaired electron. The hybridisation involved is  $d^2sp^3$  forming inner orbital complex which is weakly paramagnetic. In the presence of  $\text{H}_2\text{O}$  (a weak ligand), 3d electrons do not pair up. The hybridisation involved is  $sp^3d^2$  forming an outer orbital complex. As it contains five unpaired electrons so it is strongly paramagnetic.

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

ANSWER: In  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , the d-electrons of  $\text{Co}^{3+}$  ( $[\text{Ar}]3d^6$   $45^\circ$ ) get paired leaving behind two empty d-orbital and undergo  $d^2sp^3$  hybridization and hence inner orbital complex, while in  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  the d-electrons of  $\text{Ni}^{2+}$  ( $[\text{Ar}]3d^8$   $45^\circ$ ) do not pair up and use outer 4d subshell hence outer orbital complex.

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

ANSWER: IUPAC name : Tetraamine dichlorido chromium (III) ion.

It exhibits geometrical isomerism.

31. (i) Write down the IUPAC name of the following complex :

$[\text{Cr}(\text{NH}_3)_2\text{Cl}_3(\text{en})]\text{Cl}$  (en = ethylenediamine)

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

ANSWER: (i)  $[\text{Cr}(\text{NH}_3)_2\text{Cl}_3(\text{en})]\text{Cl}$

IUPAC name : Diammine dichlorido ethylenediamine chromium (III) chloride.

(ii)  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$

32. (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)

ANSWER: (i)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

IUPAC name : Pentaammine chlorido cobalt (III) ion

(ii) Formula of the complex potassium tetrachloridonickelate (II)  $\text{K}_2[\text{NiCl}_4]$

33. When a co-ordination compound  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  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.

ANSWER: (i) The complex formed on mixing a coordination compound

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  with  $\text{AgNO}_3$  is as follows

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O} + \text{AgNO}_3 \rightarrow [\text{Cr}(\text{H}_2\text{O}_5)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$

(ii) Pentaquachloridochromium (III) chloride monohydrate

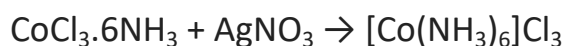
34. When a coordination compound  $\text{CoCl}_3 \cdot 6\text{NH}_3$  is mixed with  $\text{AgNO}_3$ , 3 moles of  $\text{AgCl}$  are precipitated per mole of the compound. Write



(i) Structural formula of the complex

(ii) IUPAC name of the complex

ANSWER: (i) Complex so formed is:



(ii) IUPAC name of complex is: Hexaamminecobalt (III) chloride

35. Using IUPAC norms write the formulae for the following:

(i) Sodium dicyanidoaurate (I)

(it) Tetraamminechloridonitrito-N-platinum (IV) sulphate

ANSWER: (i)  $\text{Na}[\text{Au}(\text{CN})_2]$

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

36. Using IUPAC norms write the formulae for the following:

(a) Tris(ethane-1,2-diamine) chromium (III) chloride

(b) Potassium tetrahydroxozincate(II)

ANSWER: (a)  $[\text{Cr}(\text{en})_3] \text{Cl}_3$

(b)  $\text{K}_2[\text{Zn}(\text{OH})_4]$

37. Using IUPAC norms write the formulae for the following:

(a) Potassium trioxalatoaluminate (III)

(b) Dichloridobis(ethane-1, 2-diamine) cobalt (III)

ANSWER: (a)  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$

(b)  $[\text{Co}(\text{Cl})_2(\text{en})_2]^+$

38. For the complex  $[\text{Fe}(\text{en})_2\text{Cl}_2]$ , Cl, (en = ethylene diamine), identify

(i) the oxidation number of iron,

(ii) the hybrid orbitals and the shape of the complex,

(iii) the magnetic behaviour of the complex,

(iv) the number of geometrical isomers,

(v) whether there is an optical isomer also, and

(vi) name of the complex. (At. no. of Fe = 26)

ANSWER: (i)  $[\text{Fe}(\text{en})_2\text{Cl}_2] \text{Cl}$  or  $x + 0 + 2(-1) + (-1) = 0$

$x + (-3) = 0$  or  $x = +3$

∴ Oxidation number of iron,  $x = +3$

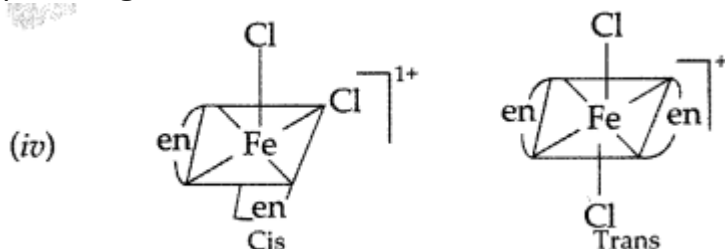
(ii) The complex has two bidentate ligands and two monodentate ligands.

Therefore, the coordination number is 6 and hybridization will be  $d^2sp^3$  and shape will be octahedral.

(iii) In the complex  ${}_{26}\text{Fe}^{3+} = 3d^5 4s^0 4p^0$



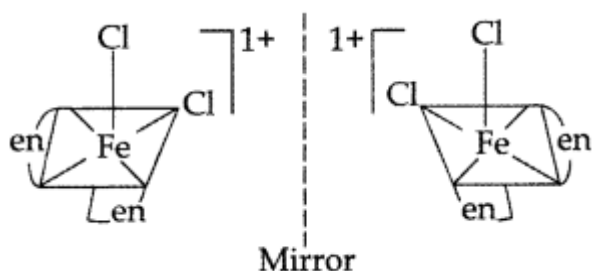
Due to presence of one unpaired electrons in d orbitals the complex is paramagnetic.



The number of geometrical

isomers are two.

(v) In coordination complex of  $[\text{Fe}(\text{en})_2\text{Cl}_2]^+$ , only cis-isomer shows optical isomerism.



(vi) Name of complex: Dichloridobis (ethane-1, 2- diamine) Iron (III) chloride.

39. Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved :

(i)  $[\text{CoF}_4]^{2-}$

(ii)  $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$

(iii)  $[\text{Ni}(\text{CO})_4]$  (Atomic number : Co = 27, Cr = 24, Ni = 28)

ANSWER: (i)  $[\text{CoF}_4]^{2-}$  : Tetrafluorido cobalt (III) ion

Coordination number = 4 Shape = Tetrahedral Hybridisation =  $sp^3$

$$\therefore \text{Magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ BM} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

(ii)  $[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^-$  : Diaquadioxalato chromium (III) ion

Coordination number = 6 Shape = Octahedral Hybridisation =  $d^2sp^3$

$$\therefore \text{Magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ BM} = \sqrt{15} = 3.87 \text{ BM}$$

(iii)  $[\text{Ni}(\text{CO})_4]$  : Tetracarbonyl nickel (0)

Coordination no. = 4 Shape = Tetrahedral Hybridisation =  $sp^3$

$$\therefore \text{Magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ BM} = \sqrt{0(0+2)} = 0$$

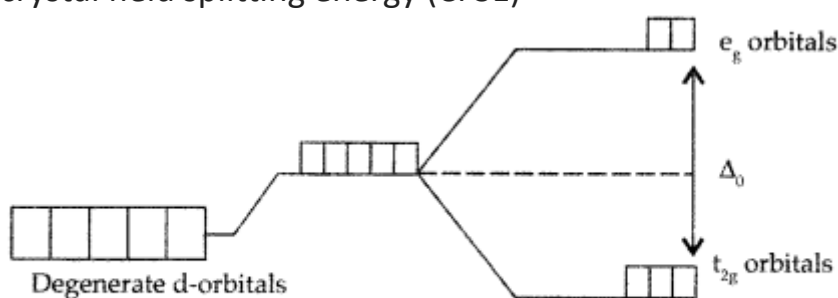
40. Giving a suitable example for each, explain the following :

(i) Crystal field splitting

(ii) Linkage isomerism

(iii) Ambidentate ligand

ANSWER: (i) Crystal field splitting: It is the splitting of the degenerate energy levels due to the presence of ligands. When ligand approaches a transition metal ion, the degenerate d-orbitals split into two sets, one with lower energy and the other with higher energy. This is known as crystal field splitting and the difference between the lower energy set and higher energy set is known as crystal field splitting energy (CFSE)



*Splitting of d-orbitals in an octahedral complex*

Example :  $3d^5$  of  $Mn^{2+}$

(ii) Linkage isomerism: When more than one atom in an ambidentate ligand is linked with central metal ion to form two types of complexes, then the formed isomers are called linkage isomers and the phenomenon is called linkage isomerism.

$[Cr(H_2O)_5(NCS)]^{2+}$  Pentaaquathiocyanate chromium (III) ion

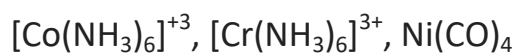
$[Cr(H_2O)_5(NCS)]^{2+}$

Pentaaquaisothiocyanate chromium (III) ion

(iii) Ambidentate ligand: The monodentate ligands with more than one coordinating atoms is known as ambidentate ligand. Monodentate ligands have only one atom capable of binding to a central metal atom or ion. For example, the nitrate ion  $NO_2^-$  can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms.

Example : — SCN thiocyanate, — NCS isothiocyanate

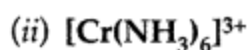
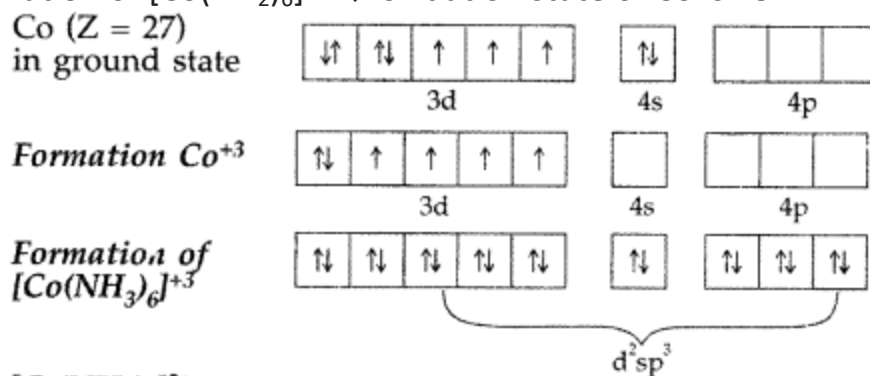
41. Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units :



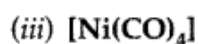
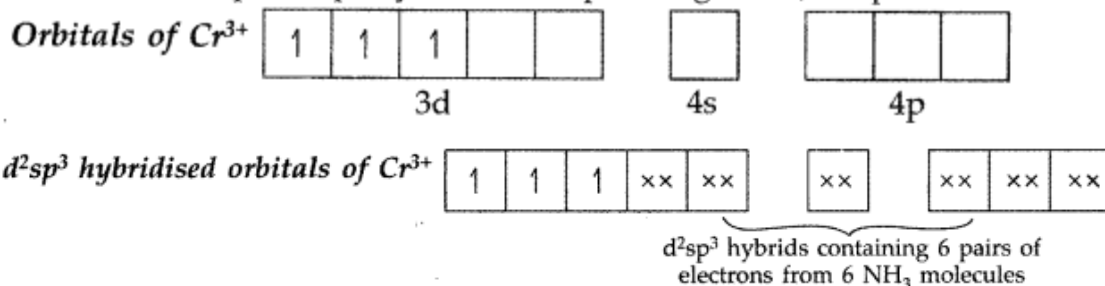
(At. nos. : Co = 27, Cr = 24, Ni = 28)

ANSWER: (i)  $[\text{Co}(\text{NH}_3)_6]^{+3} \rightarrow$  Octahedral shape,  $d^2sp^3$  hybridisation, diamagnetic

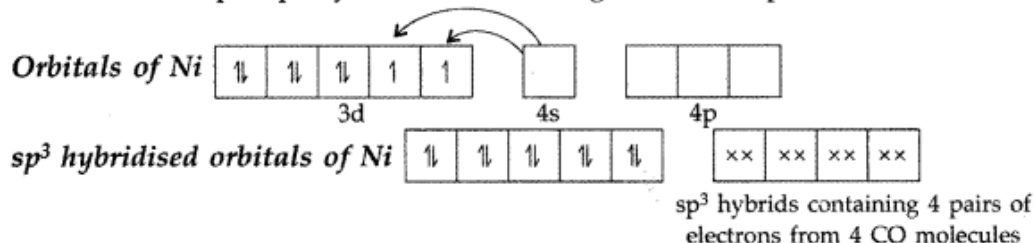
Formation of  $[\text{Co}(\text{NH}_3)_6]^{+3} \rightarrow$  oxidation state of Co is +3.



Octahedral shape,  $d^2sp^3$  hybridisation paramagnetic (3 unpaired electrons)



Tetrahedral shape,  $sp^3$  hybridisation, diamagnetic (no unpaired electrons)



42. Explain the following :

(i) Low spin octahedral complexes of nickel are not known.

(ii) The  $\pi$ -complexes are known for transition elements only.

(iii) CO is a stronger ligand than NTL, for many metals.

ANSWER: (i) The electronic configuration of Ni is  $[\text{Ar}] 3d^8 4s^2$  which shows that it can only form two types of complexes i.e. square planar ( $dsp^2$ ) in presence of strong ligand and tetrahedral ( $sp^3$ ) in presence of weak ligand. There are four empty orbitals in Ni while octahedral complexes require six empty orbitals.

(ii) Due to presence of empty d-orbitals in transition metals, they can accept electron pairs from ligands containing  $\pi$  electrons and hence can form ic-

bonding complexes.

Example : ligands like  $C_5H_5$ ,  $C_6H_6$  etc.

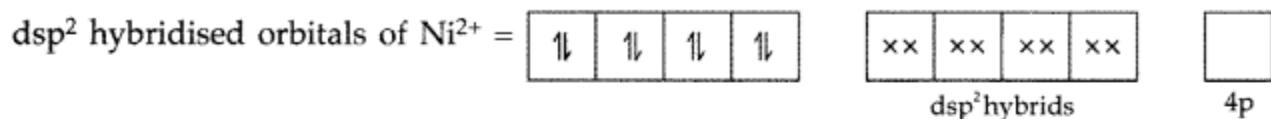
(iii) Due to greater magnitude of  $\Delta_0$ , CO produces strong fields which cause more splitting of d-orbitals and moreover it is also able to form  $\pi$  bond due to back bonding.

43. Compare the following complexes' with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units :

(i)  $[Ni(CN)_4]^{2-}$  (ii)  $[NiCl_4]^{2-}$  (iii)  $[CoF_6]^{3-}$

[At. Nos. : Ni = 28; Co = 27]

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



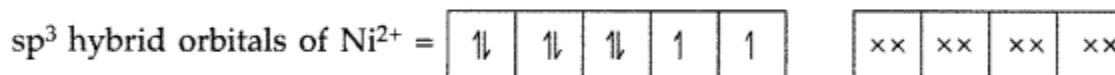
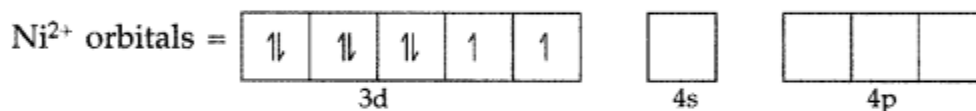
Containing 4 pairs of electrons from 4 CN molecules

**Shape :** Square planar

**Hybridisation :**  $dsp^2$

**Magnetic behaviour :** Diamagnetic (no unpaired electrons)

(ii)  $[NiCl_4]^{2-}$



$sp^3$  hybrid orbitals containing 4 pairs of electrons from 4 Cl atoms

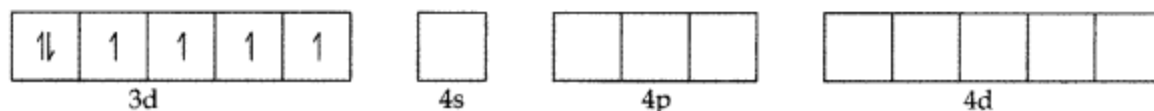
**Shape :** Tetrahedral

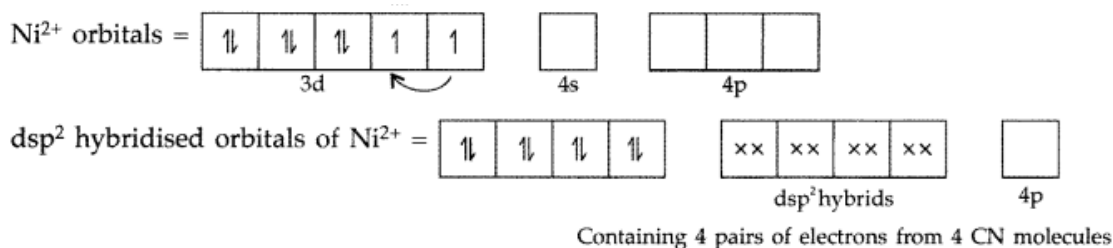
**Hybridisation :**  $sp^3$

**Magnetic behaviour :** Paramagnetic (2 unpaired electrons)

(iii)  $[CoF_6]^{3-}$

$Co^{3+}$  orbitals =



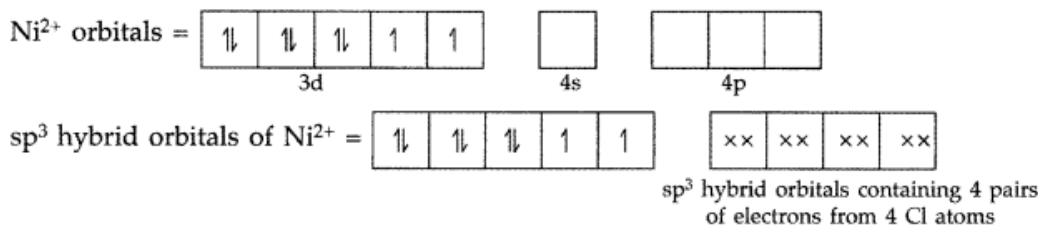


**Shape :** Square planar

**Hybridisation :**  $\text{dsp}^2$

**Magnetic behaviour :** Diamagnetic (no unpaired electrons)

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

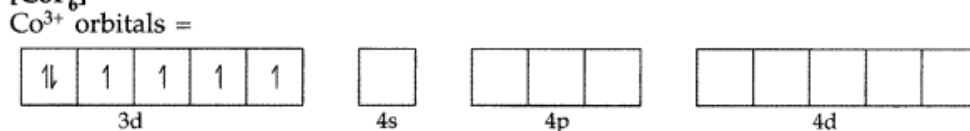


**Shape :** Tetrahedral

**Hybridisation :**  $\text{sp}^3$

**Magnetic behaviour :** Paramagnetic (2 unpaired electrons)

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



Shape : Octahedral outer orbital complex

Hybridisation :  $\text{sp}^3\text{d}^2$

Magnetic behaviour : Paramagnetic (4 unpaired electrons)

44. Explain the following cases giving appropriate reasons :

(i) Nickel does not form low spin octahedral complexes.

(ii) The  $\pi$ -complexes are known for the transition metals only.

ANSWER: i) Nickel does not form low spin octahedral complexes.

(ii) The  $\pi$ -complexes are known for the transition metals only. (All India 2010)

Answer:

(i) The electronic configuration of Ni is  $[\text{Ar}] 3\text{d}^8 4\text{s}^2$  which shows that it can only form two types of complexes i.e. square planar ( $\text{dsp}^2$ ) in presence of strong ligand and tetrahedral ( $\text{sp}^3$ ) in presence of weak ligand. There are four empty orbitals in Ni while octahedral complexes require six empty orbitals.

(ii) Due to presence of empty d-orbitals in transition metals, they can accept electron pairs from ligands containing  $\pi$  electrons and hence can form  $\pi$ -bonding complexes.

Example : ligands like  $\text{C}_5\text{H}_5$ ,  $\text{C}_6\text{H}_6$  etc.

(iii) Due to greater magnitude of  $\Delta_0$ , CO produces strong fields which cause more splitting of d-orbitals and moreover it is also able to form  $\pi$  bond due to back bonding.

45. Write the name, stereochemistry and magnetic behaviour of the following :

(At. nos. Mn = 25, Co = 27, Ni = 28)

(i)  $K_4[Mn(CN)_6]$

(ii)  $[Co(NH_3)_5 Cl]Cl_2$

(iii)  $K_2 [Ni(CN)_2]$

ANSWER: (i)  $K_4[Mn(CN)_6]$  : IUPAC name : Potassium Hexacyano manganate (II)

Geometry : Octahedral

Magnetic behaviour: Paramagnetic (one unpaired electron)

(ii)  $[Co(NH_3)_5 Cl]Cl_2$  :

Name : Pentaammine chlorido cobalt (III) chloride

Shape : Octahedral ( $\because$  Coordination number = 6)

Hybridization :  $d^2sp^3$  Magnetic behaviour : Diamagnetic (no unpaired electrons)

(iii)  $K_2 [Ni(CN)_4]$  :

Name : Potassium tetracyanonickelate (II)

Shape : Square planar Hybridization :  $dsp^2$  ( $\because$  Coordination number = 4)

Hybridization :  $dsp^2$  Magnetic behaviour : Diamagnetic

46. **Directions:** These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

**Assertion** :  $NF_3$  is a weaker ligand than  $N(CH_3)_3$ .

**Reason** :  $NF_3$  ionizes to give  $F^-$  ions in aqueous solution.

ANSWER: C

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

**Reason :**  $[\text{Fe}(\text{CN})_6]^{3-}$  has +3 oxidation state while  $[\text{Fe}(\text{CN})_6]^{4-}$  has +2 oxidation state.

ANSWER:B

48. **Assertion :**  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is coloured while  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless.

**Reason :** d-d transition is not possible in  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ .

ANSWER:A

49. The correct IUPAC name of  $(\text{Pt}(\text{NH}_3)_2\text{Cl}_2)$  is (a) diamminedichloridoplatnium (II) (b) diamminedichlorideoplatinum (IV) (c) diamminedichloridoplatnium (0) (d) dichloridodiammineplatinum (IV)

ANSWER:A

50. The stabilisation of coordination compounds due to chelation is called the chelate effect, which of the following is the most stable complex species ? (a)

$[\text{Fe}(\text{CO})_5]$  (b)  $[\text{Fe}(\text{CN})_6]^{3-}$  (c)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$  (d)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

ANSWER: C