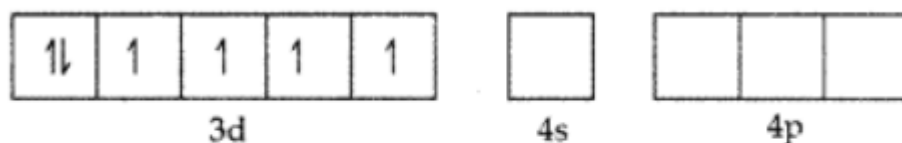


COORDINATION COMPOUNDS ANSWER KEY

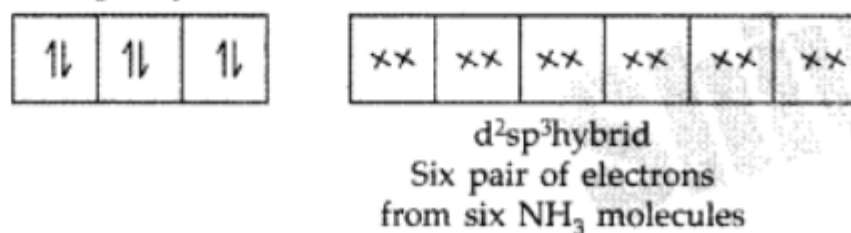
1. The stability of a complex in solution is the degree of association between the two species involved in the state of equilibrium. The instability constant is reciprocal of the formation constant. It is also called dissociation constant.
2. Hard water is titrated with EDTA complex for estimation of its hardness. During the process, the Ca^{2+} & Mg^{2+} ions form complex with EDTA replacing Na^+ . The method is based on the difference in the stability constant of calcium and magnesium complexes.
3. Werner gave the concept of two valences-
 - (a) Primary or ionisable valences. (b) Secondary or non ionisable valences.
4. The oxidation number of a metal is the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the metal atom or ion.
5. 2
6. Examples of complexes in biological system.-
 1. Chlorophyll is a complex of Mg.
 2. Haemoglobin is a complex of iron.
 3. Cyanocobalamine , Vit , is a complex of cobalt.
7. $[\text{Co}(\text{NH}_3)_6]$ $[\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6]$ $[\text{Co}(\text{CN})_6]$
8. It shows ionisation isomerism and linkage isomerism.
9. $[\text{Co}(\text{en})_3]^{3+}$ is more stable complex than $[\text{Co}(\text{NH}_3)_6]^{3+}$ because of chelate effect.
10. Low spin tetrahedral complexes are rarely observed because orbital splitting energies for tetrahedral complexes are sufficiently large for forcing pairing.
- 11.

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

Orbitals of Co^{3+} ion :

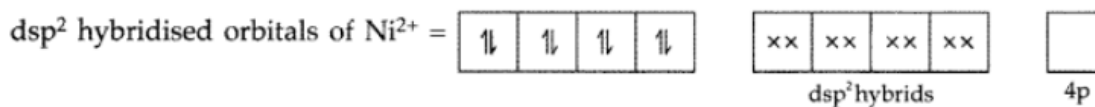
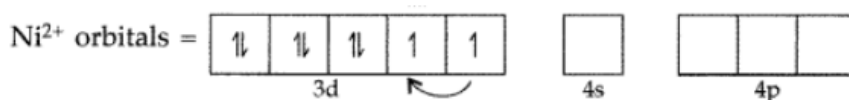


• d^2sp^3 hybridised orbitals of Co^{3+} :



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)

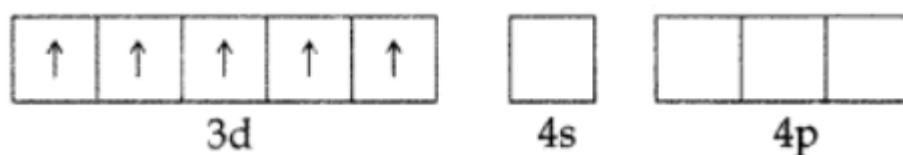
12. Stability of a complex in solution means the measure of resistance to the replacement of a ligand by some other ligand. This stability can be expressed in terms of equilibrium constant.

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.

13. In both the cases, Fe is in oxidation state +3. Outer electronic configuration of Fe³⁺ is :

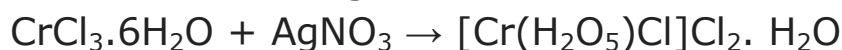


In the presence of CN⁻, the 3d electrons pair up leaving only one unpaired electron. The hybridisation involved is d²sp³ forming inner orbital complex which is weakly paramagnetic. In the presence of H₂O (a weak ligand), 3d electrons do not pair up. The hybridisation involved is sp³d² forming an outer orbital complex. As it contains five unpaired electrons so it is strongly paramagnetic. .

13. In [Co(NH₃)₆]³⁺, the d-electrons of Co³⁺ ([Ar]3d⁶ 4s⁰) get paired leaving behind two empty d-orbitals and undergo d²sp³ hybridization and hence inner orbital complex, while in [Ni(NH₃)₆]²⁺ the d-electrons of Ni²⁺ ([Ar]3d⁸ 4s⁰) do not pair up and use outer 4d subshell hence outer orbital complex.

14. IUPAC name : Tetraamine dichlorido chromium (III) ion. It exhibits geometrical isomerism.

16. (i) The complex formed on mixing a coordination compound CrCl₃.6H₂O with AgNO₃ is as follows



(ii) Pentaquachloridochromium (III) chloride monohydrate

17. (i) Complex so formed is:



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

18. (i) [Fe(en)₂Cl₂] Cl or x + 0 + 2 (-1) + (-1) = 0

$$x + (-3) = 0 \text{ or } x = +3$$

∴ Oxidation number of iron, x = +3

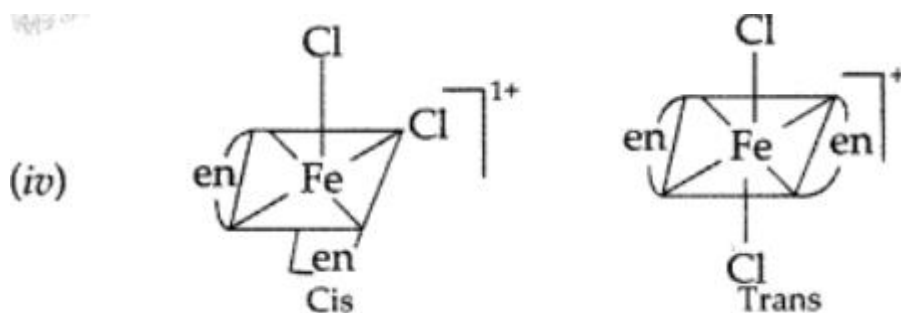
(ii) The complex has two bidentate ligands and two

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

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

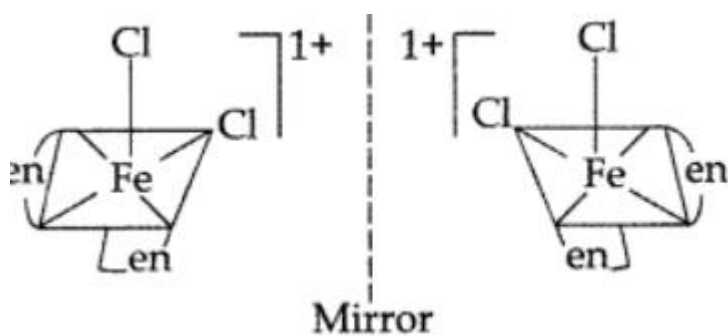


Due to presence of one unpaired electrons in d orbitals the complex is paramagnetic.

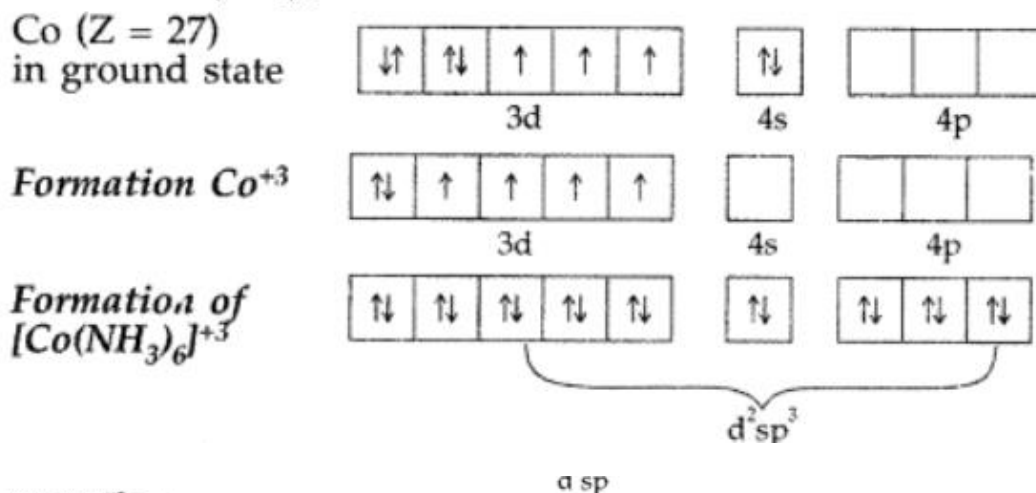


The number of geometrical isomers are two.

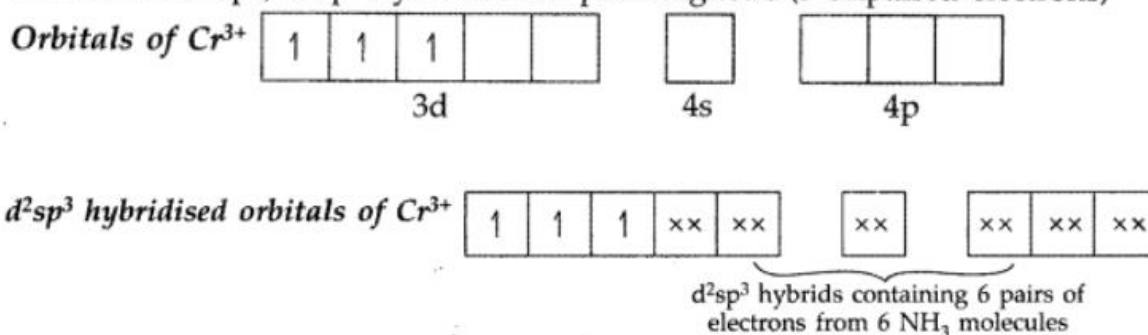
(v) In coordination complex of $[\text{Fe}(\text{en})_2\text{Cl}_2]^+$, only cis-isomer shows optical isomerism.



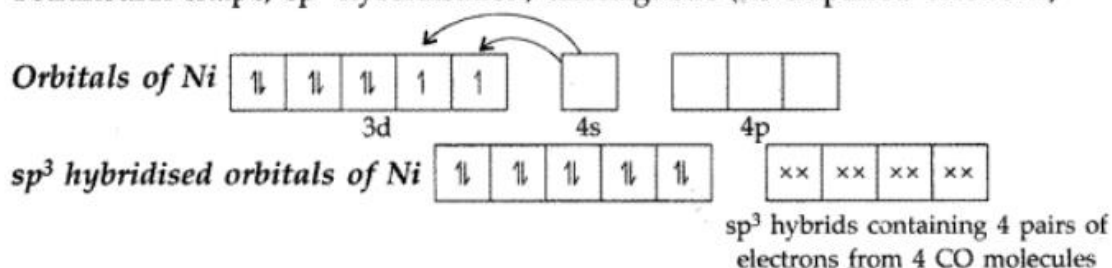
(i) $[\text{Co}(\text{NH}_3)_6]^{+3} \rightarrow$ Octahedral shape, d^2sp^3 hybridisation, diamagnetic
 Formation of $[\text{Co}(\text{NH}_2)_6]^{+3} \rightarrow$ oxidation state of Co is +3.



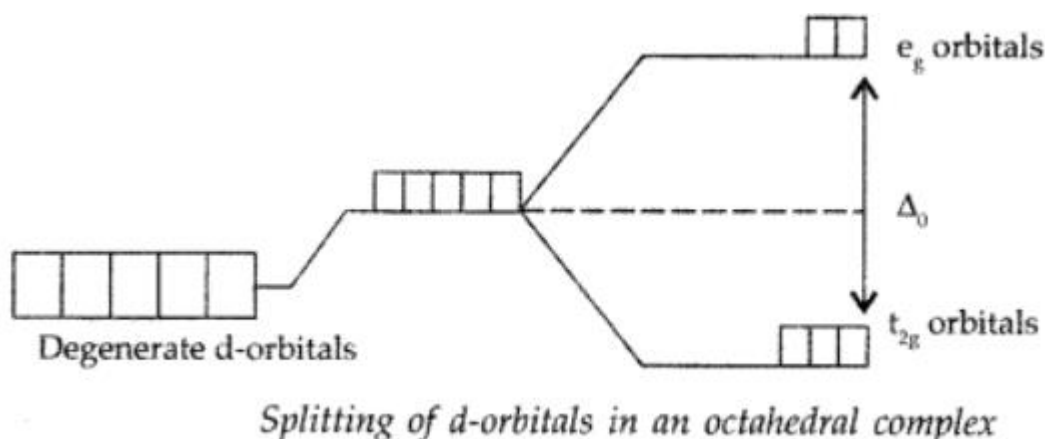
(ii) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 Octahedral shape, d^2sp^3 hybridisation paramagnetic (3 unpaired electrons)



(iii) $[\text{Ni}(\text{CO})_4]$
 Tetrahedral shape, sp^3 hybridisation, diamagnetic (no unpaired electrons)



20. (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)



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.

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

21. (i) The electronic configuration of Ni is $[Ar] 3d^8 4s^2$ 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 n electrons and hence can form π -back-bonding complexes.

Example : ligands like C_5H_5 , C_6H_6 etc.

(iii) Due to greater magnitude of Δ_0 , CO produces strong fields

which cause more splitting of d-orbitals and moreover it is also able to form π bond due to back bonding.

22. (i) $[\text{CoCl}_2]^-$:

Name – Tetra chlorido Cobalt (II) ion

Shape = Tetrahedral

Hybridization = sp^3

Magnetic property = Paramagnetic

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

Name = Diaquabis (oxalato) chromium (III) ion

Shape = Octahedral

Hybridization = d^2sp^3

Magnetic property = Paramagnetic

23. (i) $\text{K}_4[\text{Mn}(\text{CN})_2]$: IUPAC name : Potassium Hexacyano manganate (II)

Geometry : Octahedral

Magnetic behaviour: Paramagnetic (one unpaired electron)

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

Name : Pentaammine chlorido cobalt (III) chloride

Shape : Octahedral (\because Coordination number = 6)

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

(iii) $\text{K}_2 [\text{Ni}(\text{CN})_4]$:

Name : Potassium tetracyanonickelate (II)

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

Hybridization : dsp^2 Magnetic behaviour : Diamagnetic

24. (i) 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

(ii) Denticity of a ligand: The number of donor atoms in a ligand which forms coordinate bond with the central metal atom are called denticity of a ligand.

Example : If donor atom is one then it is called Monodentate ligand, if it is two, then it is called Bidentate and so on.

(iii) 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)

25. i) $[\text{Co}(\text{en})_3]\text{Cl}_3$

Name ; Tris (ethane -1,2-diamine cobalt (III) chloride)

Hybridization : d^2sp^2 (\because Coordination number = 6)

Shape : Octahedral

Magnetic behaviour : Diamagnetic

(ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

Name : Diammine dichlorido platinum (II) ion

Hybridization : dsp^2 (\because Coordination number = 4)

Shape : Square planar

Magnetic behaviour : Diamagnetic

(iii) $[\text{Fe}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Name : Tetraammine dichlorido Iron (III) chloride

Hybridization : d^2sp^3 (\because Coordination number = 6)

Shape : Octahedral

Magnetic behaviour diamagnetic

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

$$\text{or } \mu = \sqrt{1(1+2)} \text{ BM} = \sqrt{3} \text{ BM}$$

$$\therefore \mu = 1.73 \text{ BM}$$

26. (i) $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$: amminechloridobis (ethane-1,2-diamine) cobalt (II), "diamagnetic"

(ii) $[\text{Ni}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{-2}$: diaquadioxalatonickelate (II),
"paramagnetic"

27. i) Because in the presence of strong ligands, the crystal field splitting energy is more than the energy required to oxidise Co^{2+} .

(ii) This is due to the formation of π – bond by back donation of electrons from metal to carbon of CO or due to synergic bonding.

(iii) CO is a stronger field ligand than CN. Ni is in zero oxidation state in $\text{Ni}(\text{CO})_4$ and has tetrahedral geometry. But, Ni is in +2 oxidation state in $[\text{Ni}(\text{CN})_4]^{2-}$ and has dsp^2 hybridization (different geometry than tetrahedral sp^3).

28. (i) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$

Name : Diamine chloridonitroplatinum II

Magnetic behaviour: paramagnetic

(ii) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Name : Tetraamminedichloridocobalt (III) chloride

Structure : octahedral

Magnetic behaviour : diamagnetic

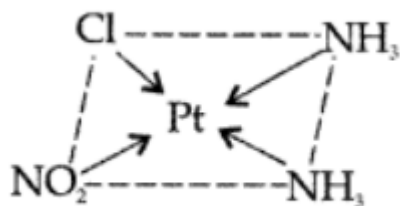
(iii) $\text{Ni}(\text{CO})_4$

Name : Tetracarbonylnickel (0)

Structure : tetrahedral

Magnetic behaviour : diamagnetic

Structure :



Square-planar

29. a) (i) Cis – platin[Pt(NH₃)₂Cl₂] is used in the treatment of cancer.

(ii) EDTA is used in the treatment of lead poisoning.

(b) [Ni(CN)₄]⁻² The electronic configuration of Ni is 3d⁸4s² dsp² hybridisation. The complex has square planar geometry and is diamagnetic in nature due to absence of unpaired electrons.

30. Crystal field splitting energy : When ligands approach the central metal ion, the degenerate d-orbitals split into two sets, one with lower energy (t_{2g}) and the other with higher energy (e_g). The difference of energy between these two sets of orbitals is called crystal field splitting energy. (Δ₀ for octahedral complexes).

The magnitude of Δ₀ decides the actual configuration of d-orbitals by the help of mean pairing energy.