

UNIT – V – COORDINATION CHEMISTRY | Mr.S.JOHNSON., M.Sc., M.Sc., B.Ed.,

UNIT – 5 – COORDINATION CHEMISTRY

II. Answer the following questions:

1. Write the IUPAC names for the following complexes.

- (i) $\text{Na}_2[\text{Ni}(\text{EDTA})]$ [QY-19, SMT-22] (ii) $[\text{Ag}(\text{CN})_2]^-$ (iii) $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ [QY-19]
 (iv) $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$ (v) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO})_2]$ [QY-19]

(i) Sodium 2,2',2'',2'''-(ethane-1,2-diyl)dinitrilo tetraacetato)nickelate (II)

(ii) Dicyanidoargentate (I) ion

(iii) Tris(ethane-1,2-diamine)cobalt(III)sulphate

(iv) Pentaamminenitrito-kO cobalt(III)ion

(v) Diamminechloridonitrito-kN platinum(II)

2. Write the formula for the following coordination compounds.

a) potassiumhexacyanidoferrate(II) [FRT24] b) pentacarbonyliron(0) [FRT-24]

c) pentamminenitrito-kN cobalt(III)ion d) hexaamminecobalt(III)sulphate [FRT24]

e) sodiumtetrafluoridodihydroxidochromate(III)

a) $\text{K}_4[\text{Fe}(\text{CN})_6]$ b) $[\text{Fe}(\text{CO})_5]$ c) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ d) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ e) $\text{Na}_3[\text{CrF}_4(\text{OH})_2]$

3. Arrange the following in order of increasing molar conductivity

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

Molar conductivity increases as the number of ions increases.

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

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

✚ Cis-platin is used as an antitumor drug in cancer treatment.

✚ Ca-EDTA chelate, is used in the treatment of lead and radioactive poisoning. That is for removing lead and radioactive metal ions from the body.

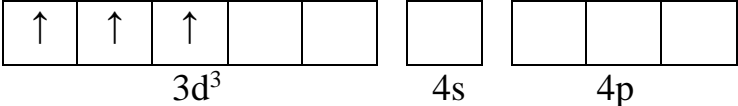
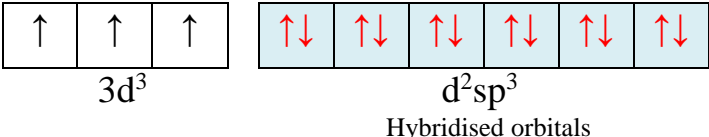
✚ A red blood corpuscles (RBC) is composed of heme group, which is Fe^{2+} - Porphyrin complex.it plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.✚ Chlorophyll, a green pigment present in green plants and algae, is a coordination complex containing Mg^{2+} as central metal ion surrounded by a modified Porphyrin ligand called corrin ring. It plays an important role in photosynthesis, by which plants converts CO_2 and water into carbohydrates and oxygen.✚ Vitamin B_{12} (cyanocobalamine) is the only vitamin consist of metal ion. It is a coordination complex in which the central metal ion is Co^+ surrounded by Porphyrin like ligand.

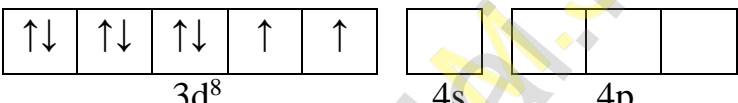
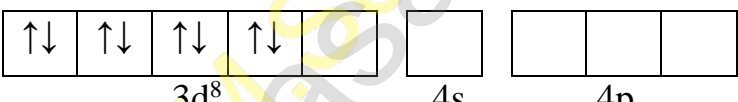
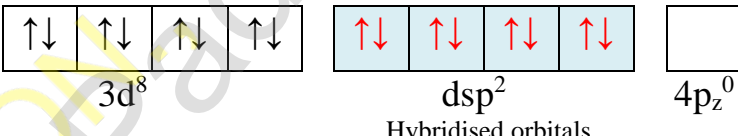
✚ Many enzymes are known to be metal complexes, they regulate biological processes. For example, Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein.

5. Based on VB theory explain why $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is paramagnetic, while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic. [AUG-21]

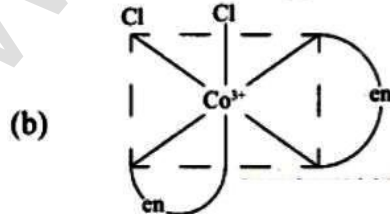
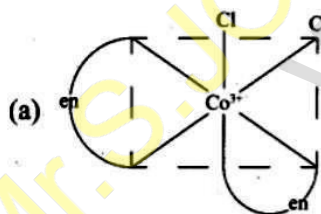
Complex	$[\text{Cr}(\text{NH}_3)_6]^{3+}$																			
Central metal ion and its electronic configuration	$\text{Cr}^{3+} : 3d^3 4s^0$																			
Outer orbitals of metal atom/ion	<table style="display: inline-table; border-collapse: collapse; text-align: center;"> <tr> <td style="border: 1px solid black; width: 20px; height: 20px;">↑</td> <td style="border: 1px solid black; width: 20px; height: 20px;">↑</td> <td style="border: 1px solid black; width: 20px; height: 20px;">↑</td> <td style="border: 1px solid black; width: 20px; height: 20px;"></td> <td style="border: 1px solid black; width: 20px; height: 20px;"></td> <td style="border: 1px solid black; width: 20px; height: 20px;"></td> <td style="border: 1px solid black; width: 20px; height: 20px;"></td> <td style="border: 1px solid black; width: 20px; height: 20px;"></td> <td style="border: 1px solid black; width: 20px; height: 20px;"></td> <td style="border: 1px solid black; width: 20px; height: 20px;"></td> </tr> <tr> <td colspan="3" style="text-align: center;">$3d^3$</td> <td colspan="2" style="text-align: center;">$4s$</td> <td colspan="4" style="text-align: center;">$4p$</td> </tr> </table>	↑	↑	↑								$3d^3$			$4s$		$4p$			
↑	↑	↑																		
$3d^3$			$4s$		$4p$															
Nature of ligand	NH_3 is weak field ligand. So no pairing of 3d electrons in the metal.																			

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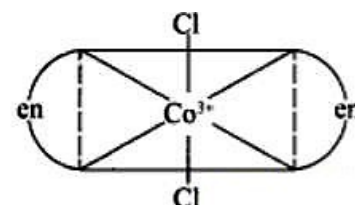
Outer orbital of metal atom/ion in presence of ligand	
Hybridisation	Coordination number – 6 Hybridisation – d^2sp^3
Hybridised orbitals of the metal atom in the complex	
Geometry	Octahedral
Magnetic property	No of unpaired electron = 3, Hence paramagnetic
Magnetic moment	$\mu_s = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.872 \text{ BM}$

Complex	$[\text{Ni}(\text{CN})_4]^{4-}$
Central metal ion and its electronic configuration	$\text{Ni}^{2+} : 3d^8 4s^0$
Outer orbitals of metal atom/ion	
Nature of ligand	CN is strong field ligand causes the pairing of 3d electrons in the metal.
Outer orbital of metal atom/ion in presence of ligand	
Hybridisation	Coordination number – 4 Hybridisation – dsp^2
Hybridised orbitals of the metal atom in the complex	
Geometry	Square planar
Magnetic property	No of unpaired electron = 0, Hence diamagnetic
Magnetic moment	$\mu_s = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0$

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



Two cis $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ isomers (optically active)

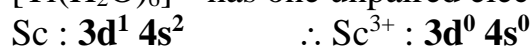


One trans $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ isomers (optically inactive)

7. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured, while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless – explain. [MAR-20]



$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ has one unpaired electron so it is coloured.

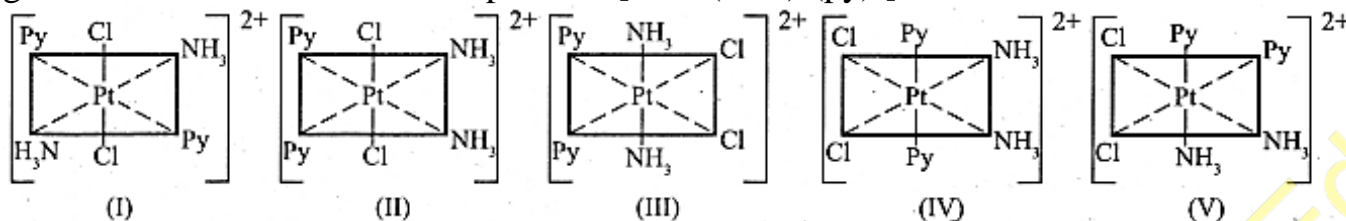


$[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ has no unpaired e^- so it is colourless.

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8. Give an example for complex of the type $[Ma_2b_2c_2]$ where a, b, c are monodentate ligands and give the possible isomers.

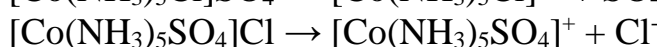
The octahedral complexes of $[Ma_2b_2c_2]$ type can exist in five geometrical isomers. The five geometrical isomers for the complex ion $[PtCl_2(NH_3)_2(py)_2]^{2+}$ are shown below.



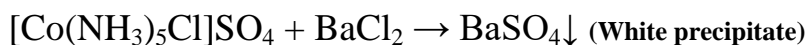
9. Give one test to differentiate $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$. [QY-19]

$[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionization isomers.

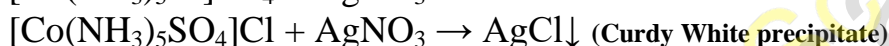
When these isomers are dissolved in water, they ionise to give different ions in solution which react differently with different reagents.



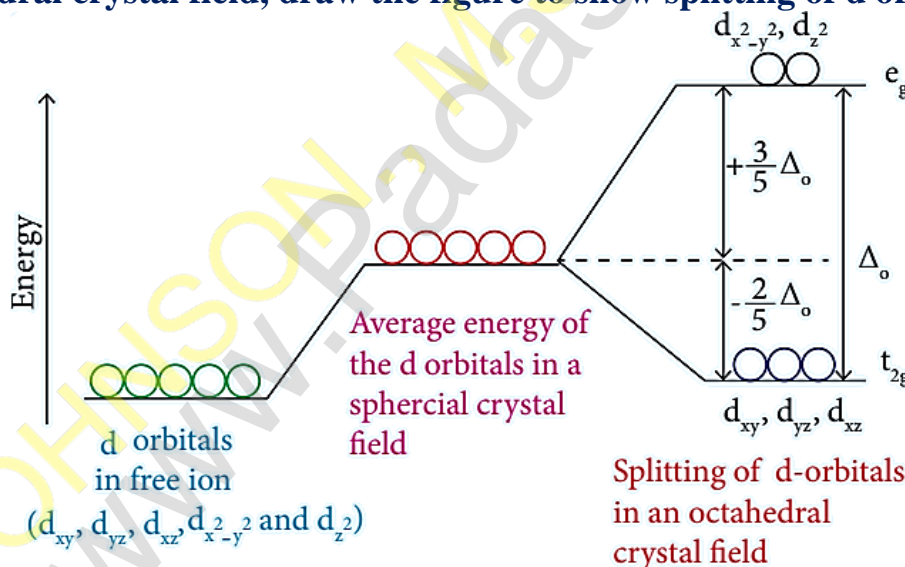
For Ex.1: Barium Chloride test



For Ex.2: Silver nitrate test

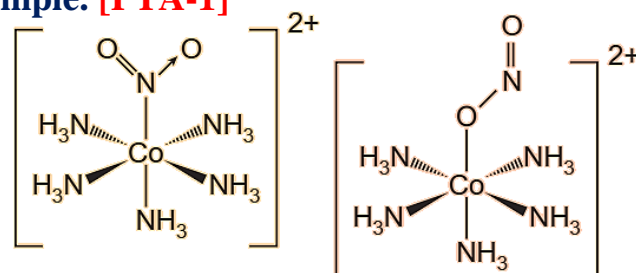


10. In an octahedral crystal field, draw the figure to show splitting of d orbitals.



11. What is linkage isomerism? Explain with an example. [PTA-1]

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms. In the below mentioned examples, the nitrite ion is bound to the central metal ion Co^{3+} through a nitrogen atom in one complex, and through oxygen atom in other complex.



Ex: $[Co(NH_3)_5(NO_2)]^{2+}$

12. Classify the following ligands based on the number of donor atoms.

- | | | | |
|--|-------|--------------|-----------------------------|
| a) NH_3 | b) en | c) ox^{2-} | d) pyridine |
| a) NH_3 - monodentate (N-Donor atom) | b) en | | - bidentate (2N-Donor atom) |

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c) ox^{2-} - bidentate (2O-Donor atom) d) pyridine - monodentate (N-Donor atom)
13. Give the difference between double salts & coordination compounds. [AUG21, MAR24]

	Double salts	Co-ordination compound
1	Double salts contain two simple salt in equimolar proportion.	The simple salts from which they are formed may or may not be in equimolar proportion.
2	These exist only in solid state and dissociate into consistent species in their solutions	They retain their identity in solid as well as in solution state.
3	They lose their identity in dissolved state	They do not lose their identity in dissolved state
4	Their properties essential the same as those of constituent species.	Their properties different from their constituents for <i>ex:</i> $K_4[Fe(CN)_6]$ does not show the test of the Fe^{2+} and CN^- ions.
5	In double salts the metal atom/ion exhibit normal valency	The metal ion exhibits two types of valencies – Primary and secondary

14. Write the postulates of Werner's theory. [SEP-20, MAY-22]

- ✚ Most of the elements exhibit, two types of valence namely primary valence and secondary valence and each element tend to satisfy both the valences. In modern terminology, the primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number. **For example**, according to Werner, the primary and secondary valences of cobalt are 3 and 6 respectively.
- ✚ The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions. **For example** in the complex $CoCl_3.6NH_3$, The primary valence of Co is +3 and is satisfied by $3Cl^-$ ions.
- ✚ The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these.
For example, in $CoCl_3.6NH_3$ the secondary valence of cobalt is 6 and is satisfied by six neutral ammonia molecules, whereas in $CoCl_3.5NH_3$ the secondary valence of cobalt is satisfied by five neutral ammonia molecules and a Cl^- ion.
- ✚ According to Werner, there are two spheres of attraction around a metal atom/ion in a complex. The inner sphere is known as coordination sphere and the groups present in this sphere are firmly attached to the metal. The outer sphere is called ionisation sphere. The groups present in this sphere are loosely bound to the central metal ion and hence can be separated into ions upon dissolving the complex in a suitable solvent.
- ✚ The primary valences are non-directional while the secondary valences are directional. The geometry of the complex is determined by the special arrangement of the groups which satisfy the secondary valence.
For example, if a metal ion has a secondary valence of six, it has an octahedral geometry. If the secondary valence is 4, it has either tetrahedral or square planar geometry.

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The following table illustrates the Werner's postulates.

Complex	Groups satisfy the secondary valence (non-ionisable, inner coordination sphere)	No. of ionisable Cl ⁻ ions in the complex (outer coordination sphere)	No. of moles of AgCl formed = No. of moles of ionisable Cl ⁻
CoCl ₃ .6NH ₃	6NH ₃	3Cl ⁻	3AgCl
CoCl ₃ .5NH ₃	5NH ₃ & Cl ⁻	2Cl ⁻	2AgCl
CoCl ₃ .4NH ₃	4NH ₃ & 2Cl ⁻	Cl ⁻	AgCl
CoCl ₃ .3NH ₃	3NH ₃ & 3Cl ⁻	-	-

15. Why tetrahedral complexes do not exhibit geometrical isomerism? [SRT-23]

Tetrahedral complexes do not show geometrical isomerism because

- ✚ The relative position of unidentate ligands attached with central metal atom are same with respect each other.
- ✚ All the four ligands are adjacent or equidistant to one another.
- ✚ It has plane of symmetry.

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

Coordination compounds which possess chirality exhibit optical isomerism similar to organic compounds. The pair of two optically active isomers which are mirror images of each other are called enantiomers. Their solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called 'd' (dextro rotatory) and 'l' (levo rotatory) forms respectively. The octahedral complexes of type [M(xx)₃]^{n±}, [M(xx)₂AB]^{n±} and [M(xx)₂B₂]^{n±} exhibit optical isomerism.

Examples: The optical isomers of [Co(en)₃]³⁺ are shown in figure (1) and The coordination complex [CoCl₂(en)₂]⁺ has three isomers, two optically active cis forms and one optically inactive trans form. These structures are shown in figure (2)

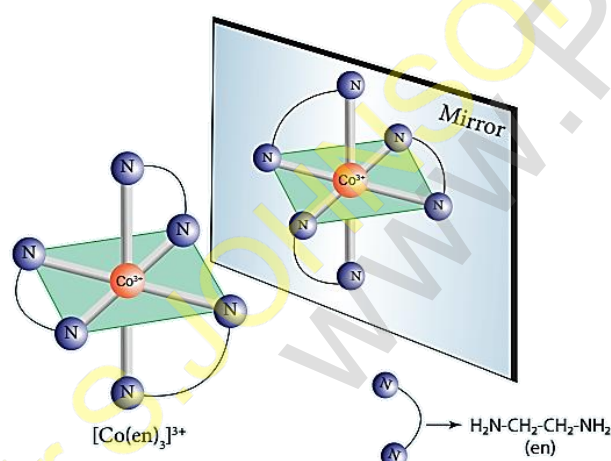


Figure (1) – Optical isomer

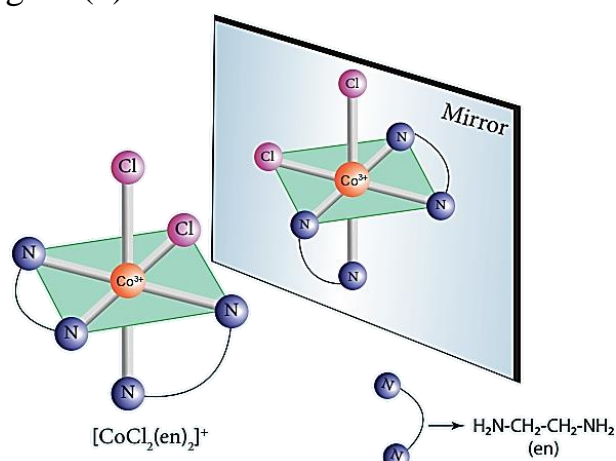


Figure (2) – Optical isomer

17. What are hydrate isomers? Explain with an example. [MAR-20]

The exchange of free solvent molecules such as water, ammonia, alcohol etc., in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called solvate isomers. If the solvent molecule is water, then these isomers are called hydrate isomers. For example, the complex with chemical formula CrCl₃.6H₂O has three hydrate isomers as shown below.

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$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	a violet colour compound and gives three chloride ions in solution
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	a pale green colour compound and gives 2 chloride ions in solution
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$	dark green colour compound and gives one chloride ion in solution

18. What is crystal field splitting energy? [HY-22]

✚ The orbitals lying along the axes $d_{x^2-y^2}$ and d_{z^2} orbitals will experience strong repulsion and raise in energy to a greater extent than the orbitals with lobes directed between the axes (d_{xy} , d_{yz} and d_{zx}). Thus the degenerate d orbitals now split into two sets and the process is called crystal field splitting.

✚ In an octahedral complex, the d – orbitals of the central metal ion divide into two sets of different energies. The separation in energy is the crystal field splitting energy.

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

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

$$\text{CFSE} (\Delta E_o) = \{E_{LF}\} - \{E_{iso}\} = \{[n_{t_{2g}}(-0.4) + n_{e_g}(0.6)] \Delta_o + n_p P\} - \{n'_p P\}$$

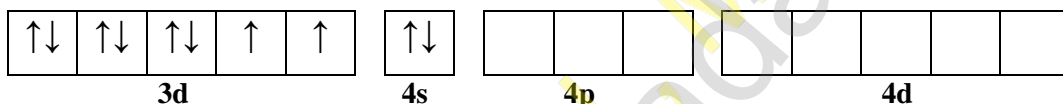
Here, $n_{t_{2g}}$ is the number of electrons in t_{2g} orbitals; n_{e_g} is number of electrons in e_g orbitals; n_p is number of electron pairs in the ligand field; & n'_p is the number of electron pairs in the isotropic field (barycentre).

20. A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green, whereas a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless – Explain.

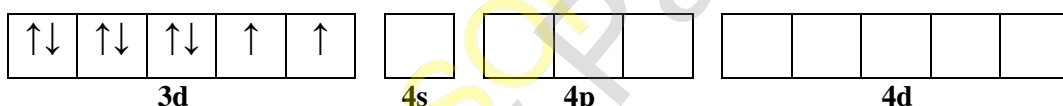
Complex I: $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

The outer electronic configuration of Ni is $3d^8 4s^2$

Ni atom

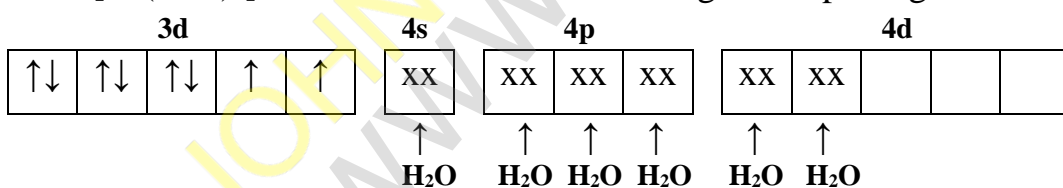


Ni^{2+} ion $3d^8 4s^0$



Ni in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

H_2O is weak field ligand so pairing does occur.

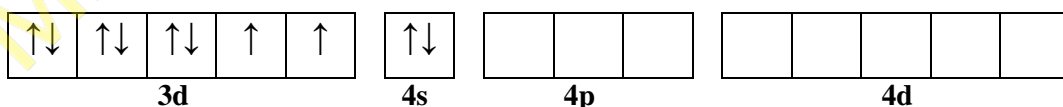


Hybridisation is sp^3d^2 . Two unpaired electrons so coloured and paramagnetic in nature.

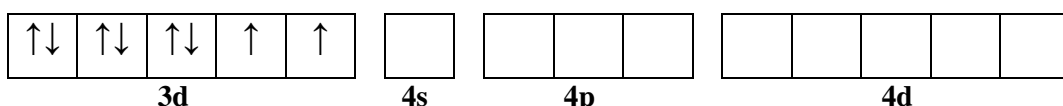
Complex II: $[\text{Ni}(\text{CN})_4]^{2-}$

The outer electronic configuration of Ni is $3d^8 4s^2$

Ni atom

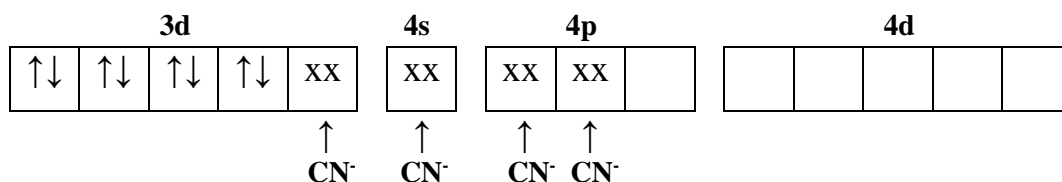


Ni^{2+} ion $3d^8 4s^0$



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

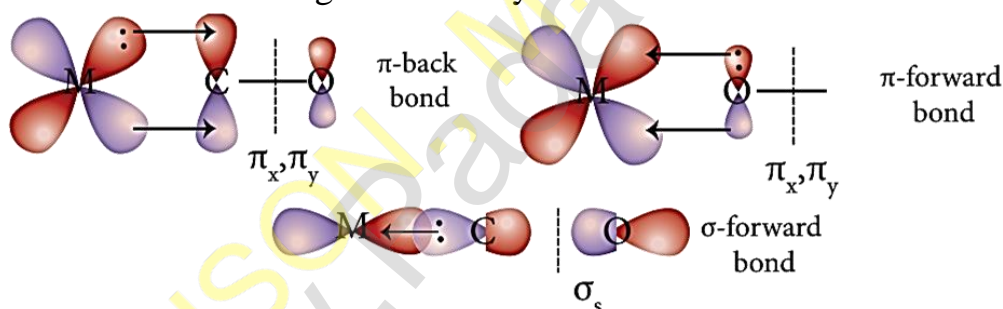
CN is strong field ligand so pairing occur.

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Hybridisation is dsp^2 . No unpaired electrons so colourless and diamagnetic in nature.

21. Discuss briefly the nature of bonding in metal carbonyls. [SRT-23]

- ✚ In metal carbonyls, the bond between metal atom and the carbonyl ligand consists of two components.
- ✚ The first component is an electron pair donation from the carbon atom of carbonyl ligand into a vacant d-orbital of central metal atom.
- ✚ This electron pair donation forms $M \xleftarrow{\sigma \text{ bond}} CO$ sigma bond.
- ✚ This sigma bond formation increases the electron density in metal d orbitals and makes the metal electron rich.
- ✚ In order to compensate for this increased electron density, a filled metal d-orbital interacts with the empty π^* orbital on the carbonyl ligand and transfers the added electron density back to the ligand.
- ✚ This second component is called π -back bonding. Thus in metal carbonyls, electron density moves from ligand to metal through sigma bonding and from metal to ligand through pi bonding, this synergic effect accounts for strong $M \leftarrow CO$ bond in metal carbonyls.
- ✚ This phenomenon is shown diagrammatically as follows.


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

The coordination complex formed when excess of liquid ammonia is added to an aqueous solution of copper sulphate is $[Cu(NH_3)_4]SO_4$ – Tetraamminecopper(II)sulphate

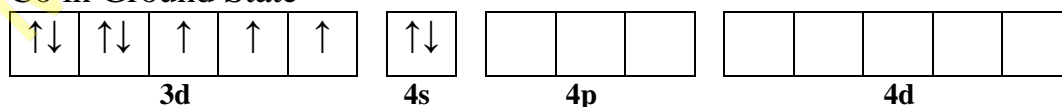


So, the coordination entity is $[Cu(NH_3)_4]^{2+}$

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

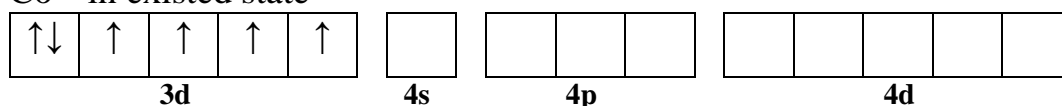
$[Co(C_2O_4)_3]^{3-}$ Outer electronic configuration – $3d^7 4s^2$

Co in Ground State



Cobalt exists in +3 oxidation state in the given complex.

Co^{3+} in existed state



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

- Central metal atom/ion**
- Ligands(s) and their types**
- Coordination entity**
- Oxidation number of the central metal ion**
- Coordination number**

- Central metal ion – Pt^{2+}
- Ligands and their types – NO_2 – Negative monodentate ligand, H_2O and NH_3 – neutral monodentate ligand
- Coordination entity – $[\text{Pt}(\text{NO}_2)(\text{H}_2\text{O})(\text{NH}_3)_2]^{3+}$
- Oxidation number of the central metal ion
 $-x + 1(-1) + 1(0) + 1(0) = +1 \Rightarrow x - 1 = +1 \Rightarrow x = +2$
- Coordination number – 4

3. Write the IUPAC name for the following compounds.

- $\text{K}_2[\text{Fe}(\text{CN})_3(\text{Cl})_2(\text{NH}_3)]$
- $[\text{Cr}(\text{CN})_2(\text{H}_2\text{O})][\text{CO}(\text{ox})_2(\text{en})]$
- $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2]$
- $[\text{Cr}(\text{NH}_3)_3(\text{NC})_2(\text{H}_2\text{O})]^+$
- $[\text{Fe}(\text{CN})_6]^{4-}$

- Potassium amminedichloridotricyanidoferrate (III)
- Tetraaquadicyanidochromium (II) mono(ethylene diamine) dioxalato cobalate (IV)
- Diamminedichloro copper (II)
- Triammineaquodicyanido – kN Chromium (III)ion
- Hexacyanidoferrate (II) ion

4. Give the structure for the following compounds.

- diamminesilver (I) dicyanidoargentate(I)
- Pentaammine nitrito-kN-cobalt (III) ion
- hexafluorido cobaltate (III) ion
- dichloridobis(ethylenediamine) Cobalt (III) sulphate
- Tetracarbonylnickel (0)

- $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$
- $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$
- $[\text{CoF}_6]^{3-}$
- $[\text{Co}(\text{en})_2\text{Cl}_2]_2\text{SO}_4$
- $[\text{Ni}(\text{CO})_4]$

5. A solution of $[\text{Co}(\text{NH}_3)_4\text{I}_2]\text{Cl}$ when treated with AgNO_3 gives a white precipitate. What should be the formula of isomer of the dissolved complex that gives yellow precipitate with AgNO_3 . What are the above isomers called?

✚ A solution of $[\text{Co}(\text{NH}_3)_4\text{I}_2]\text{Cl}$ when treated with AgNO_3 gives a white precipitate, because Cl^- ion is counter ion.

✚ Formula of isomer of the dissolved complex that gives yellow precipitate with AgNO_3 is, $[\text{Co}(\text{NH}_3)_4\text{Cl I}]\text{I}$ because I is counter ion

✚ $[\text{Co}(\text{NH}_3)_4\text{I}_2]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl I}]\text{I}$ both are ionisation isomers.

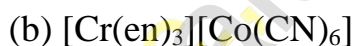
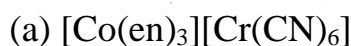
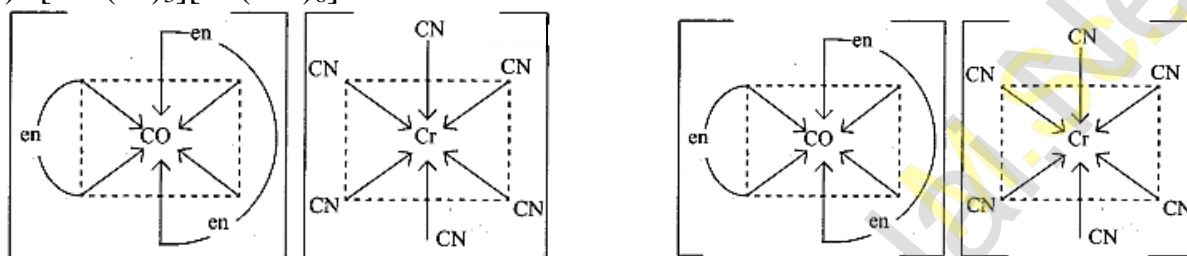
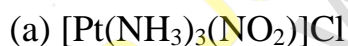
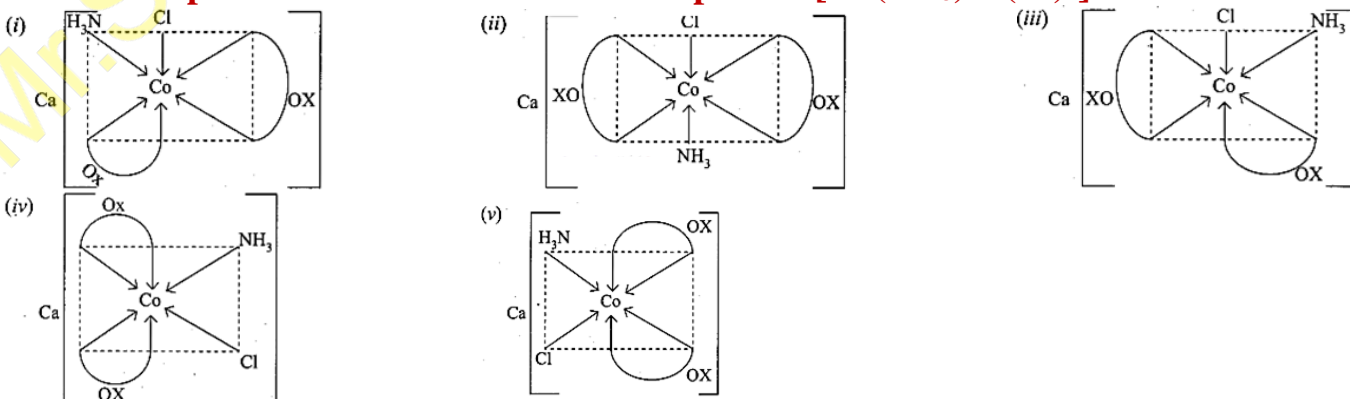
6. Three compounds A, B and C have empirical formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. they are kept in a container with a dehydrating agent and they lost water and attaining constant weight as shown below.

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

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

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

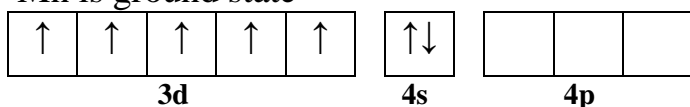
i) $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$ – Exhibits coordination isomerismii) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ – Exhibits linkage isomerismiii) $[\text{Pt}(\text{NH}_3)_3(\text{NO}_2)]\text{Cl}$ – Exhibits ionisation isomerismHere Cl⁻ is counter ionHere NO₂⁻ is counter ion8. Draw all possible stereo isomers of a complex $\text{Ca}[\text{Co}(\text{NH}_3)\text{Cl}(\text{ox})_2]$ 

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9. The spin only magnetic moment of Tetrachloridomanganate(II) ion is 5.9 BM. On the basis of VBT, predict the type of hybridisation and geometry of the compound.

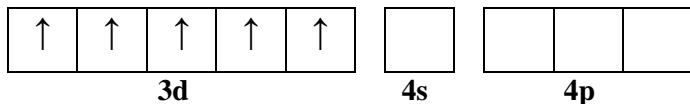
$[\text{MnCl}_4]^{2-}$ Electronic configuration of Mn ($z=25$) is $3d^5 4s^2$

Mn is ground state



Manganese exists in +2 oxidation state in the given complex.

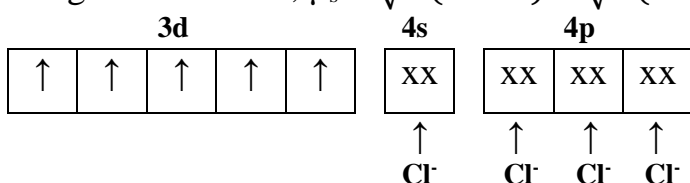
Mn^{2+} in existed state



Mn^{2+} in the complex $[\text{MnCl}_4]^{2-}$

Cl^- is weak field ligand so no pairing occurs. It has 5 unpaired electrons. Hence paramagnetic.

Magnetic moment, $\mu_s = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.9 \text{ BM}$



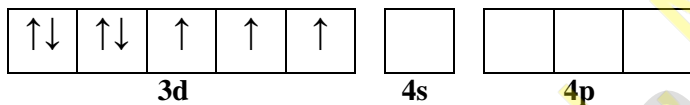
\therefore Hybridisation is sp^3 . So the geometry of the complex is tetrahedral.

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

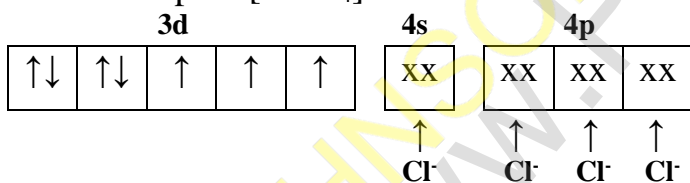
Central metal atom and its outer electronic configuration: Co: $3d^7 4s^2$

Cobalt exists in +2 oxidation state in the given complex.

Co^{2+} in existed state



Nature of ligand: Cl^- is weak field ligand so no pairing occurs. Hybridise orbitals of the Co^{2+} in the complex $[\text{CoCl}_4]^{2-}$



Unpaired electrons: 3

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

Compound A - pale yellow precipitate - counter ion Br^-	Compound B - white precipitate - counter ion Cl^-
$[\text{Co}(\text{en})_2\text{Cl}_2]\text{Br}$	$[\text{Co}(\text{en})_2\text{Cl Br}]\text{Cl}$

12. The mean pairing energy and octahedral field splitting energy of $[\text{Mn}(\text{CN})_6]^{3-}$ are $28,800 \text{ cm}^{-1}$ and 38500 cm^{-1} respectively. Whether this complex is stable in low spin or high spin?

Mean pairing energy = $28,800 \text{ cm}^{-1}$
 $[\text{Mn}(\text{CN})_6]^{3-}$ Mn = $3d^5 4s^2$

Octahedral field splitting energy = $38,500 \text{ cm}^{-1}$
 $\text{Mn}^{3+} = 3d^4$

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High Spin Complex	Low Spin Complex
Electronic Configuration of isotropic fields d^6 $\uparrow\downarrow \uparrow \uparrow \uparrow \uparrow$ Number of paired electrons(n_p^1) = 1 $\therefore E_{iso} = 1$	
Ligand field electronic configuration : $t_{2g}^4 e_g^2$ CFSE = $\{[4(0.4)+2(0.6)]\Delta_o + 1p\} - \{1\}$ $= \{-1.6+1.2\}\Delta_o + p - \{1\}$ $= \{-0.4 \Delta_o + p\} - \{1\}$ $= \{-0.4 \times 13000\} + 21,000 - 1$ $= -5200 + 21000 - 1$ $= 15799 \text{ cm}^{-1}$	Ligand field electronic configuration : $t_{2g}^6 e_g^0$ CFSE = $\{[6(-0.4)+0(0.6)]\Delta_o + 3p\} - \{1\}$ $= -2.4\Delta_o + 3p - 1$ $= \{-2.4 \times 13000\} + (3 \times 21000) - 1$ $= -31200 + 63000 - 1$ $= 31799 \text{ cm}^{-1}$
High positive CFSE, value indicates that high spin complex is favoured.	High positive CFSE, value indicates that low spin complex is not favourable one.

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



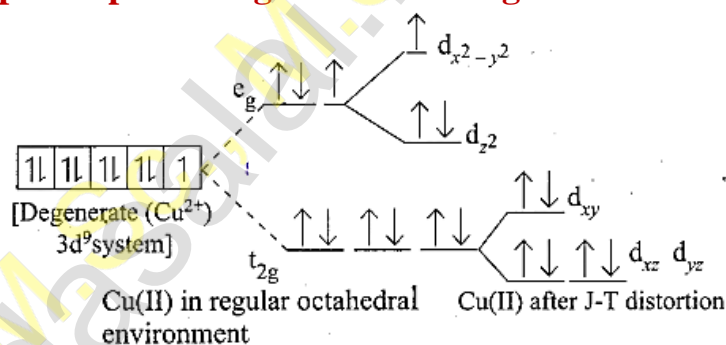
Central metal ion is Cu^{2+}

Electronic Configuration is $2d^9 4s^0$

$n_{t_{2g}} = 6e^-$

$n_{e_g} = 3e^-$

Since one unpaired electron is present, the complex is paramagnetic and C.N is 6 the geometry is Octahedral.



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

Mean pairing energy = $21,000 \text{ cm}^{-1}$

$\Delta_o = 13000 \text{ cm}^{-1}$.

$[\text{CoF}_6]^{3-}$, $\text{Co} = 3d^7 4s^2$; $\text{Co}^{3+} = 3d^6$

High Spin Complex	Low Spin Complex
Electronic Configuration of isotropic fields d^4 $\uparrow \uparrow \uparrow \uparrow$ Number of paired electrons(n_p^1) = 0 $\therefore E_{iso} = 0$	
Ligand field electronic configuration : $t_{2g}^3 e_g^1$ CFSE = $\{[3(-0.4)+1(0.6)]\Delta_o + 0 \times p\} - \{0\}$ $= [-1.2+0.6]\Delta_o$ $= (-0.6) \Delta_o$ $= -0.6 \times 38,500$ $= -23100 \text{ cm}^{-1}$	Ligand field electronic configuration : $t_{2g}^4 e_g^0$ CFSE = $\{[4(-0.4)+0(0.6)]\Delta_o + 2p\} - \{0\}$ $= [-1.6]\Delta_o + 2p$ $= \{-1.6 \times 38,500\} + (2 \times 28,800)$ $= -61600 + 57600$ $= -4000 \text{ cm}^{-1}$

GOVERNMENT EXAM QUESTION PAPER

1. What are Ionisation isomers? [GMQ-19]

Ionisation isomers arises when an ionisable counter ion (simple ion) itself can act as a ligand. The exchange of such counter ions with one or more ligands in the coordination entity will

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result in ionisation isomers. Its will give different ions in solution. For example, $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Br}_2$.

2. Define Co-ordination number. [MAY-22]

The number of ligand donor atoms bonded to a central metal ion in a complex is called the coordination number of the metal. In other words, the coordination number is equal to the number of σ -bonds between ligands and the central atom.

3. In the complex $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$, mention the (i) Hybridisation (ii) Nature of ligand (iii) Geometry. [HY-19]

i) Hybridisation : sp^3d^2 ii) Nature of ligand : Oxalato is a negative weak field ligand (oxalate anion is a bidentate ligand) iii) Geometry : Octahedral

4. Arrange the following ligands in the ascending order on the basis of crystal field splitting power H_2O , CO , Br^- , CN^- [HY-19]

Spectrochemical series: $\text{Br}^- < \text{H}_2\text{O} < \text{CN}^- < \text{CO}$

5. Mention the metal complexes and its metal ions are used in biological system. [SEP20] (or) Give an example of Coordination compound used in medicine and a biologically important Coordination compound. [MAR-24]

✚ A red blood corpuscles (RBC) is composed of heme group, which is Fe^{2+} - Porphyrin complex. It plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.

✚ Chlorophyll, a green pigment present in green plants and algae, is a coordination complex containing Mg^{2+} as central metal ion surrounded by a modified Porphyrin ligand called corrin ring. It plays an important role in photosynthesis, by which plants converts CO_2 and water into carbohydrates and oxygen.

✚ Vitamin B_{12} (cyanocobalamine) is the only vitamin consist of metal ion. It is a coordination complex in which the central metal ion is Co^+ surrounded by Porphyrin like ligand.

✚ Many enzymes are known to be metal complexes, they regulate biological processes. For example, Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein.

✚ Many complexes are used as medicines for the treatment of various diseases. For example, (1) **Ca-EDTA chelate**, is used in the treatment of lead and radioactive poisoning. That is for removing lead and radioactive metal ions from the body. (2) **Cis-platin** is used as an antitumor drug in cancer treatment.

6. Write the following for the complex $[\text{Ag}(\text{NH}_3)_2]^+$. [MAY-22]

(i) Ligand (ii) Central Metal ion (iii) IUPAC name

i) Ligand – NH_3 ii) Central Metal ion – Ag^+ iii) IUPAC name – diamminesilver(I)ion

7. Write the IUPAC ligand for the following: (i) $\text{C}_2\text{O}_4^{2-}$ (ii) H_2O (iii) Cl^- [JUL-22]

i) Oxalato ii) Aqua iii) Chlorido

8. Write the IUPAC name of the following:

i) $[\text{Ag}(\text{NH}_3)_2]^+$ ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ [MAR-20]

i) Diamminesilver(I)ion ii) Pentaamminechloridocobalt(III)ion

9. Calculate the magnetic moment and magnetic property of $[\text{CoF}_6]^{3-}$ [MAR-20]

Magnetic moment of $[\text{CoF}_6]^{3-}$ $\mu_s = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.89 \text{ BM}$

Magnetic property of $[\text{CoF}_6]^{3-}$ = No. of unpaired electrons = 4. Hence **paramagnetic**.

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10.Explain $[\text{Fe}(\text{CN})_6]^{3-}$ is paramagnetic, using Crystal Field theory. [GMQ-19]

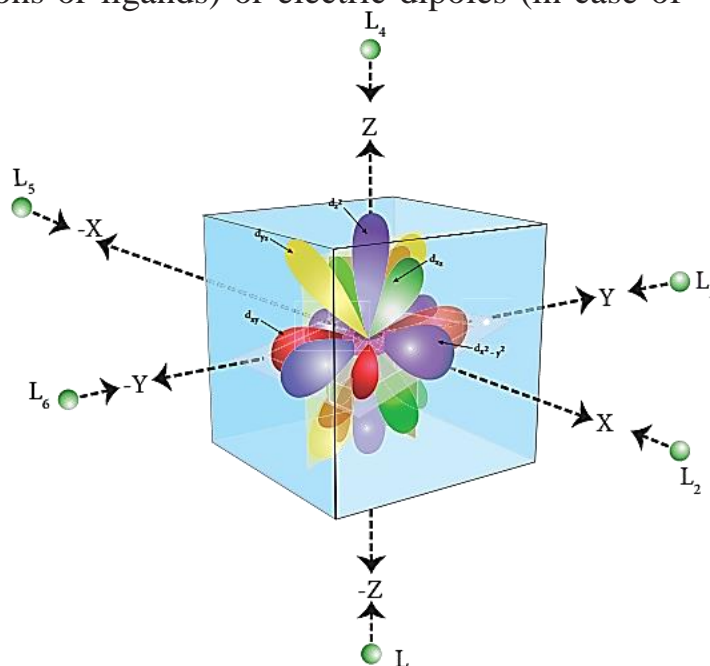
High Spin Complex	Low Spin Complex
Electronic configuration in isotropic field : d^5	$\uparrow \uparrow \uparrow \uparrow \uparrow$
No. of paired electrons ($n'p$) = 0; Therefore, $E_{\text{iso}} = 0$	
Ligand field: Electronic configuration : $t_{2g}^3 e_g^2$ CFSE = $\{[3(-0.4)+2(0.6)] \Delta_o + 0 \times P\} - \{0\}$ = 0	Ligand field: Electronic configuration : $t_{2g}^5 e_g^0$ CFSE = $\{[5(-0.4)+0(0.6)] \Delta_o + 2 \times P\} - \{0\}$ = $-2 \Delta_o + 2P$ = $(-2 \times 35000) + (2 \times 30000)$ = -10000 cm^{-1} Negative CFSE value indicates that low spin complex is favoured
Nature of the complex	Low spin (Spin paired)
Electronic configuration of central metal ion	$t_{2g}^5 e_g^0$
Magnetic property	No. of unpaired electrons = 1; Hence paramagnetic
Magnetic moment (Using spin only formula)	$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)}$ = $\sqrt{3} = 1.732 \text{ BM}$

11. Write the postulates of Crystal Field theory. [QY-19]

Valence bond theory helps us to visualise the bonding in complexes. However, it has limitations as mentioned above. Hence Crystal Field Theory to explain some of the properties like colour, magnetic behaviour etc., This theory was originally used to explain the nature of bonding in ionic crystals. Later on, it is used to explain the properties of transition metals and their complexes. The salient features of this theory are as follows.

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

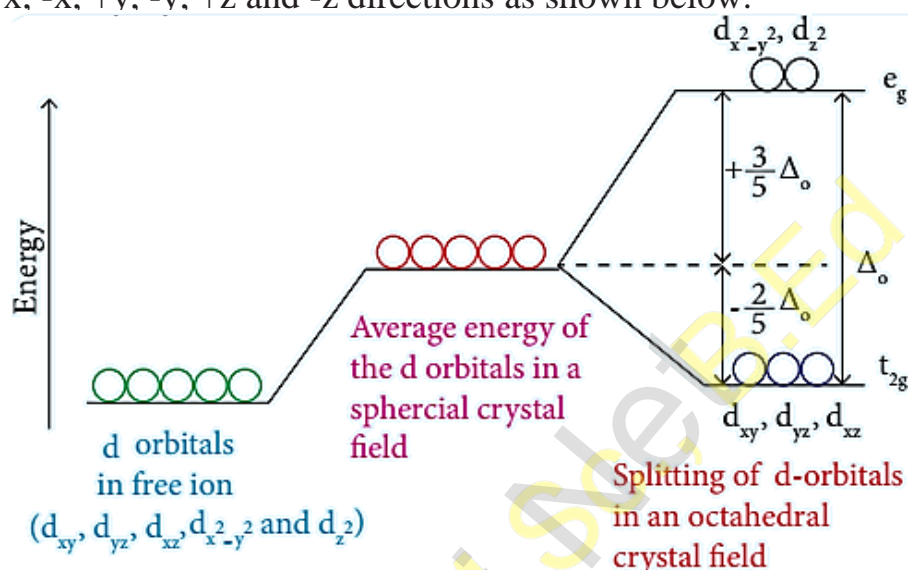
Step 1: In an isolated gaseous state, all the five d orbitals of the central metal ion are degenerate. Initially, the ligands form a spherical field of negative charge around the metal. In this field, the energies of all the five d orbitals will increase due to the repulsion between the electrons of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



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Step 2: The ligands are approaching the metal atom in actual bond directions. To illustrate this let us consider an octahedral field, in which the central metal ion is located at the origin and the six ligands are coming from the +x, -x, +y, -y, +z and -z directions as shown below.

As shown in the figure, the orbitals lying along the axes $d_{x^2-y^2}$ and d_{z^2} orbitals will experience strong repulsion and raise in energy to a greater extent than the orbitals with lobes directed between the axes (d_{xy} , d_{yz} and d_{zx}). Thus the degenerate d orbitals now split into two sets and the process is called crystal field splitting.



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

Crystal field splitting in octahedral complexes:

During crystal field splitting in octahedral field, in order to maintain the average energy of the orbitals (barycentre) constant, the energy of the orbitals $d_{x^2-y^2}$ and d_{z^2} (represented as e_g orbitals) will increase by $3/5\Delta_o$ while that of the other three orbitals d_{xy} , d_{yz} and d_{zx} (represented as t_{2g} orbitals) decrease by $2/5\Delta_o$. Here, Δ_o represents the crystal field splitting energy in the octahedral field.

12. Give the main assumptions of Valence Bond Theory? [HY-22, HY-23]

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

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

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3	sp^2	Trigonal planar	$[\text{HgI}_3]^-$
4	sp^3	Tetrahedral	$[\text{Ni}(\text{CO})_4]$, $[\text{NiCl}_4]^{2-}$
4	dsp^2	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$
5	dsp^3 ($d_{x^2-y^2}$ orbital is involved)	Trigonal bipyramidal	$\text{Fe}(\text{CO})_5$
6	d^2sp^3 (d_{z^2} and $d_{x^2-y^2}$ orbitals of inner shell are involved)	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ (Inner orbital complexes)
6	sp^3d^2 (d_{z^2} and $d_{x^2-y^2}$ orbitals of the outer shell are involved)	Octahedral	$[\text{FeF}_6]^{4-}$, $[\text{CoF}_6]^{4-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (Outer orbital complexes)

- In the octahedral complexes, if the $(n-1)d$ orbitals are involved in hybridisation, then they are called inner orbital complexes or low spin complexes or spin paired complexes. If the nd orbitals are involved in hybridisation, then such complexes are called outer orbital or high spin or spin free complexes. Here n represents the principal quantum number of the outermost shell.
- The complexes containing a central metal atom with unpaired electron(s) are paramagnetic. If all the electrons are paired, then the complexes will be diamagnetic.
- Ligands such as CO , CN^- , en , and NH_3 present in the complexes cause pairing of electrons present in the central metal atom. Such ligands are called strong field ligands.
- Greater the overlapping between the ligand orbitals and the hybridised metal orbital, greater is the bond strength.

13. What is facial isomer? [SMT-22]

Octahedral complex of the type $[\text{MA}_3\text{B}_3]^{n\pm}$ also shows geometrical isomerism.

If the three similar ligands (A) are present in the corners of one triangular face of the octahedron and the other three ligands (B) are present in the opposing triangular face, then the isomer is referred as a facial isomer (fac isomer).

14. How will you differentiate primary and secondary valencies? [SMT-22]

- Most of the elements exhibit, two types of valence namely primary valence and secondary valence and each element tend to satisfy both the valences. The primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number.

For example, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ – according to Werner, the primary and secondary valences of cobalt are 3 and 6 respectively.

- The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions.

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✚ The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these (No. of ligand).

15. In the complex, $[\text{Co}(\text{CN})_2\text{Cl}_2]\text{Cl}$ $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, identify the following, i) IUPAC name, ii) Central metal ion and iii) Co-ordination number [MAR-24]

i) Dichloridobis(ethane-1,2-diamine)cobalt(III)chloride ii) Co^{3+} iii) 6

16. Mention any three applications of coordination complexes? [SRT-24]

✚ Phthalo blue – a bright blue pigment is a complex of Copper (II) ion and it is used in printing ink and in the packaging industry.

✚ Purification of Nickel by Mond's process involves formation $[\text{Ni}(\text{CO})_4]$, which Yields 99.5% pure Nickel on decomposition.

✚ EDTA is used as a chelating ligand for the separation of lanthanides, in softening of hard water and also in removing lead poisoning.

✚ Coordination complexes are used in the extraction of silver and gold from their ores by forming soluble cyano complex. These cyano complexes are reduced by zinc to yield metals. This process is called as Mac-Arthur –Forrest cyanide process.

✚ Some metal ions are estimated more accurately by complex formation. For example, Ni^{2+} ions present in Nickel chloride solution is estimated accurately for forming an insoluble complex called $[\text{Ni}(\text{DMG})_2]$.

✚ Many of the complexes are used as catalysts in organic and inorganic reactions. For example,

(i) Wilkinson's catalyst – $[(\text{PPh}_3)_3 \text{RhCl}]$ is used for hydrogenation of alkenes.

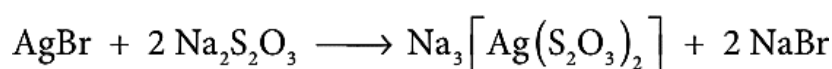
(ii) Ziegler-Natta catalyst - $[\text{TiCl}_4] + \text{Al}(\text{C}_2\text{H}_5)_3$ is used in the polymerization of ethene.

✚ In order to get a fine and uniform deposit of superior metals (Ag, Au, Pt etc.,) over base metals, Coordination complexes $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$ etc., are used in electrolytic bath.

✚ Many complexes are used as medicines for the treatment of various diseases. For example, (1) Ca-EDTA chelate, is used in the treatment of lead and radioactive poisoning. That is for removing lead and radioactive metal ions from the body.

(2) Cis-platin is used as an antitumor drug in cancer treatment.

✚ In photography, when the developed film is washed with sodium thio sulphate solution (hypo), the negative film gets fixed. Undecomposed AgBr forms a soluble complex called sodiumdithiosulphatoargentate(I) which can be easily removed by washing the film with water.



17. In the complex, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, mention i) Ligands, ii) Central Metal atom/ion and iii) Co-ordination number [SRT-24]

i) NH_3 – neutral ligand, Cl – negative ligand ii) Co^{3+} iii) 6

18. For the complex, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, mention i) Nature of the complex, ii) Shape of the complex and iii) IUPAC name [HY-23]

i) Its entity is $[\text{Cu}(\text{NH}_3)_4]^{2+}$. So, its **cationic complex** ii) Co-ordination number is 6. **Square planar** iii) **Tetraamminecopper(II)sulphate**

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19. Calculate CFSE value for the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ complex. [SRT-23]

High Spin Complex	Low Spin Complex
Electronic configuration in isotropic field : d ⁵	$\uparrow \uparrow \uparrow \uparrow \uparrow$
No. of paired electrons (n'p) = 0; Therefore, $E_{\text{iso}} = 0$	
Ligand field: Electronic configuration : $t_{2g}^3 e_g^2$ CFSE = $\{[3(-0.4)+2(0.6)] \Delta_o + 0 \times P\} - \{0\}$ = 0	Ligand field: Electronic configuration : $t_{2g}^5 e_g^0$ CFSE = $\{[5(-0.4)+0(0.6)] \Delta_o + 2 \times P\} - \{0\}$ = $-2 \Delta_o + 2P$ = $(-2 \times 14000) + (2 \times 30000)$ = 32000 cm^{-1} High positive CFSE value indicates that low spin complex is not a favourable one.
Nature of the complex	High spin (Spin free)
Electronic configuration of central metal ion	$t_{2g}^5 e_g^2$
Magnetic property	No. of unpaired electrons = 5; Hence paramagnetic
Magnetic moment (Using spin only formula)	$\mu_s = \sqrt{n(n+2)} = \sqrt{5(5+2)}$ = $\sqrt{35} = 5.916 \text{ BM}$

20. Define the term central atom in co-ordination compounds. [MAR-23]

The central atom/ion is the one that occupies the central position in a coordination entity and binds other atoms or groups of atoms (ligands) to itself, through a coordinate covalent bond. For example, in $\text{K}_4[\text{Fe}(\text{CN})_6]$, the central metal ion is Fe^{2+} .