UNIT 5 - COORDINATION CHEMISTRY

Textual Questions:

Answer the following questions:

1. Write the IUPAC names for the following complexes.

i. $Na_2[Ni(EDTA)]$ - Sodium 2,2’,2”2’” (ethane 1,2diyl dinitrito)tetra acetato nickelate(III)

ii. $[Ag(CN)_2]$ - Dicynaido argentate (I) ion

iii. $[Co(en)_3]_2(SO_4)_3$ - Tris(ethane 1,2 –diammine) cobalt (III) chloride

iv. $[Co(ONO)(NH_3)_5]^{+2}$ – Pent ammine nitrito-κ-O cobalt (III)ion

v. $[Pt(NH_3)\ Cl\ (NO_2)]$ Diammine chloridonitrito -κ-N platinum (II)

2. Write the formula for the following coordination compounds.

a) potassiumhexacyanidoferrate(II) - $K_4[Fe(CN)_6]$

b) petacarbonyliron(0) - $[Fe(CO)_5]$

c) pentaamminenitrito - κ– N-cobalt(III)ion - $[Co(NH_3)_5NO_2]^{+2}$

d) hexaamminecobalt(III)sulphate - $[Co(NH_3)_6]$

e) sodiumtetrafluoridodihydroxidochromate(III) - $Na_3[Cr(F)_4(OH)_2]$

3. Arrange the following in order of increasing molar conductivity

i) $Mg[Cr(NH_3)(Cl)_5]$ ii) $[Cr(NH_3)_5Cl]\ [Co(F)_6]$ iii) $[Cr(NH_3)_3Cl_3]$

$[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]\ [Co(F)_6] < Mg[Cr(NH_3)(Cl)_5]$

4. Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction.

$Ni[ONC(CH_3)C(CH_3)NOH]_2$

5. $[CuCl_4]^{-2}$ exists while $[CuI_4]^{-2}$ does not exist why?

In $[CuCl_4]^{-2}$ complex the size of chlorine atoms is less hence exist. But in $[CuI_4]^{-2}$ the bigger iodine atom makes the compound unstable.

6. Calculate the ratio of $\dfrac{Ag^+}{[Ag(NH_3)_2]^+}$ in 0.2 M solution of NH_3. If the stability constant for the complex $[Ag(NH_3)_2]^+$ is 17×10^7.

Given :

$[NH_3]$ = **0.2 M**

stability constant (α) = 17×10^7 .

Consider the dissociation of complex **$[Ag(NH_3)]^+$**

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$\alpha = \frac{[Ag^+]\ [NH_3]^2}{[Ag(NH_3)_2]^+}$$

$$= 17 \times 10^7 = \frac{[Ag^+]\ [NH_3]^2}{[Ag(NH_3)_2]^+}$$

On substituting the concentration of NH_3

$$= 17 \times 10^7 = \frac{[Ag^+]\ [0.2]^2}{[Ag(NH_3)_2]^+}$$

$$\text{The ratio} = \frac{[Ag^+]}{[Ag(NH_3)_2]^+} = \frac{17 \times 10^7}{[0.2]^2} = \frac{17 \times 10^7}{[2 \times 10^{-1}]^2} = \frac{17 \times 10^7}{4 \times 10^{-2}} = \frac{17}{4} \times 10^9$$

$$= 0.425 \times 10^9 = 4.25 \times 10^8$$

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

- A red blood corpuscles (RBC) is composed of heme group, which is $Fe2^+$- Porphyrin complex.

  .It carries oxygen from lungs to tissues and carbon dioxide from tissues to lungs.
- Vitamin B12 (cyanocobalamine) is a complex in which the central metal ion is Co+

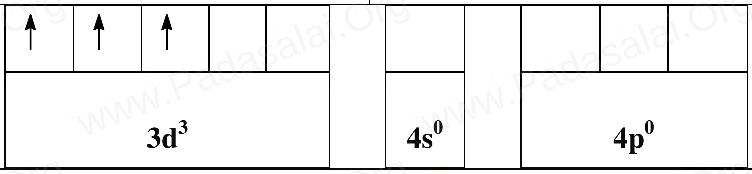
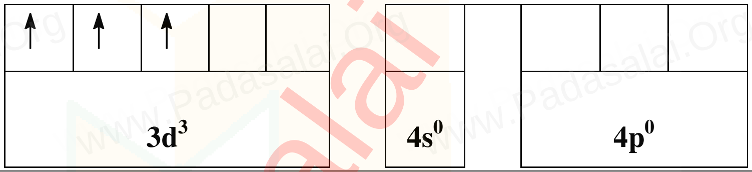
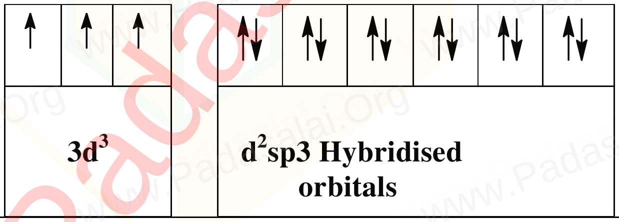
  It is surrounded by Porphyrin like ligand.

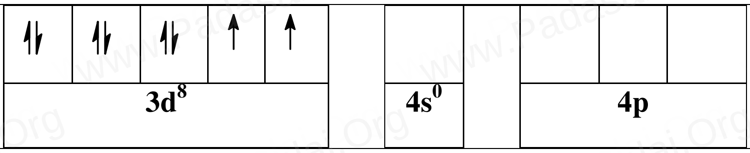
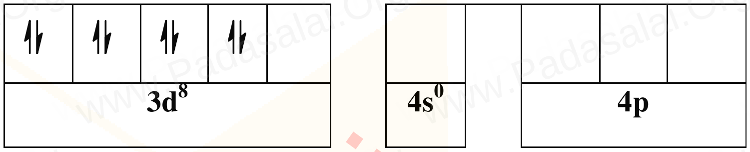
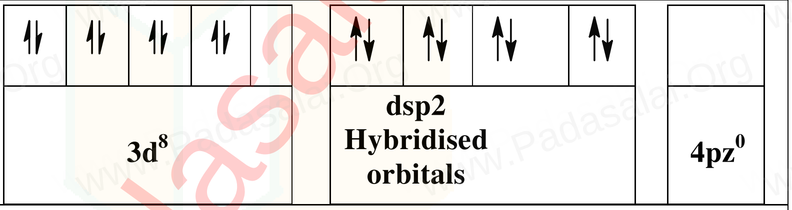
08. Give one test to differentiate $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$

An aquous solution of $[Co(NH_3)_5Cl]SO_4$ gives white precipitate with a solution of $BaCl_2$

A aquous solution of $[Co(NH_3)_5SO_4]Cl$ gives white precipitate with a solution of $AgNO_3$

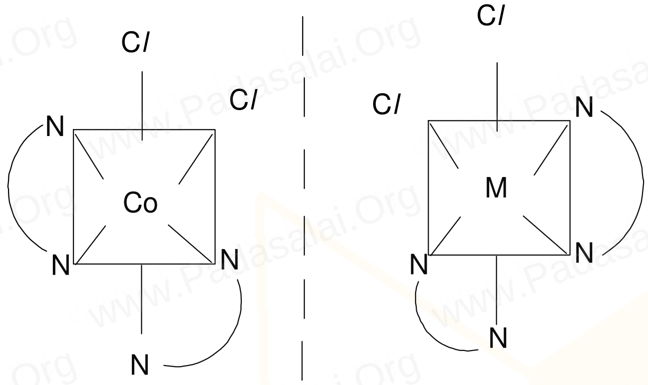
9. Based on VB theory explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ is diamagnetic.

COMPLEX	$[Cr(NH_3)_6]^{3+}$	
Central metal atom/ion and its outer electronic configuration	**Cr : $3d^5\ 4s^1$**	**Cr^{3+} : $3d^3\ 4s^0$**
Outer orbitals of metal atom/ion		
Nature of ligand	NH_3 weak field ligand for Cr^{3+} hence no pairing of 3d electrons in the metal	
Outer orbitals of metal atom/ion in presence of ligands		
Hybridisation	Coordination number - 6 Hybridisation – d^2sp^3	
Hybridised orbitals of the metal atom in the complex		
Geometry	Square planar	
Magnetic property	No. of unparied electrons = 3; Hence paramagnetic	
Magnetic moment (Using spin only formula)	$\mu s = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.87$	

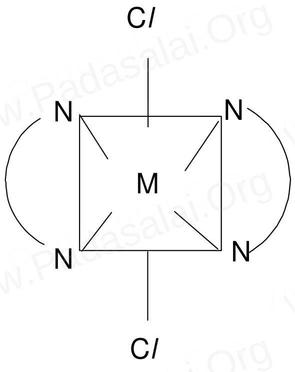
COMPLEX	$[Ni(CN)_4]^{2-}$
Central metal atom/ion and its outer electronic configuration	Ni^{2+} : $3d^8 4s^0$
Outer orbitals of metal atom/ion	
Nature of ligand	CN^- Strong field ligand causes the pairing of 3d electrons in the metal
Outer orbitals of metal atom/ion in presence of ligands	
Hybridisation	Coordination number - 4 Hybridisation - dsp2
Hybridised orbitals of the metal atom in the complex	
Geometry	Square planar
Magnetic property	No. of unparied electrons = 0; Hence **diamagnetic**
Magnetic moment (Using spin only formula)	$\mu s = \sqrt{n(n+2)} = 0$

9. Draw all possible geometrical isomers of the complex $[Co(en)_2Cl_2]^+$ and identify the optically active isomer.

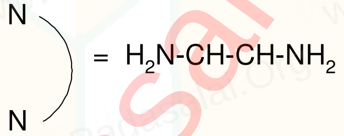
The coordination complex $[CoCl_2(en)_2]^+$ has three isomers, two optically active cis forms and one optically inactive trans form. These structures are shown below.



optically active cis forms



optically inactive trans form



10. [Ti $(H_2O)_6$ $]^{3+}$ is coloured, while $[Sc(H_2O)_6]^{3+}$ is colourless- explain.

$[Ti(H_2O)_6]^{3+}$ is colored due to presence of unpaired electrons while is colorless due to the absence of unpaired electrons.

Explanation:

- **$[Ti(H_2O)_6]^{3+}$** has titanium in +3 oxidation state as water is a neutral ligand.

Atomic number of titanium is 22

The electronic configuration of Ti^{3+} is, [Ar] $3d^1$ $4s^0$

As it contains unpaired electrons in d orbitals, there is a transition between orbitals and thus produce color.

- **$[Sc(H_2O)_6]^{3+}$** has scandium in +3 oxidation state as water is a neutral ligand.

Atomic number of scandium is 21

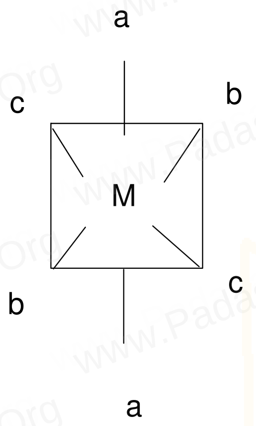
The electronic configuration of Sc^{3+} is, [Ar] $3d^0$ $4s^0$

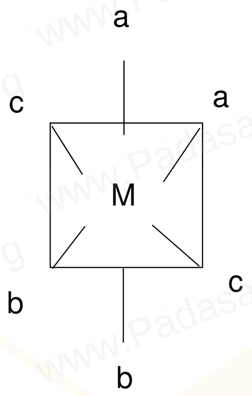
As it contains no unpaired electrons, they do not show any color.

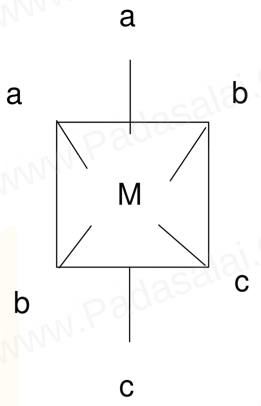
11. Give an example for complex of the type M $[a_2 b_2 c_2]$ where a, b, c are monodentate ligands and give the possible isomers.

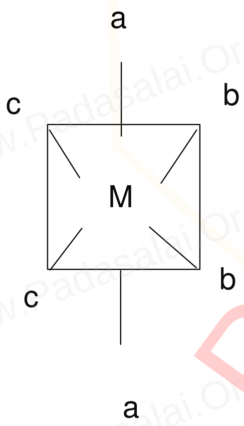
For the octahedral structure of the compound the combination are as follows for ($Ma_2b_2c_2$)
1.(a,a)(b,b),(c,c) 2. (a,b)(a,b)(c,c) 3. (a,c)(a,c)(b,b) 4. (b,c)(b,c)(a,a) 5. (a,c)(b,c)(a,b)

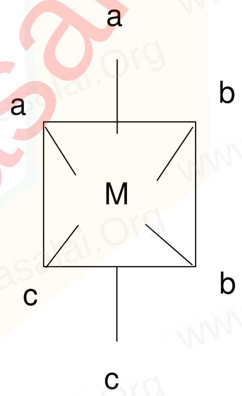
These are the five possible geometrical isomers. 5th isomer shows optical isomerism too and hence total number of isomers is 6.





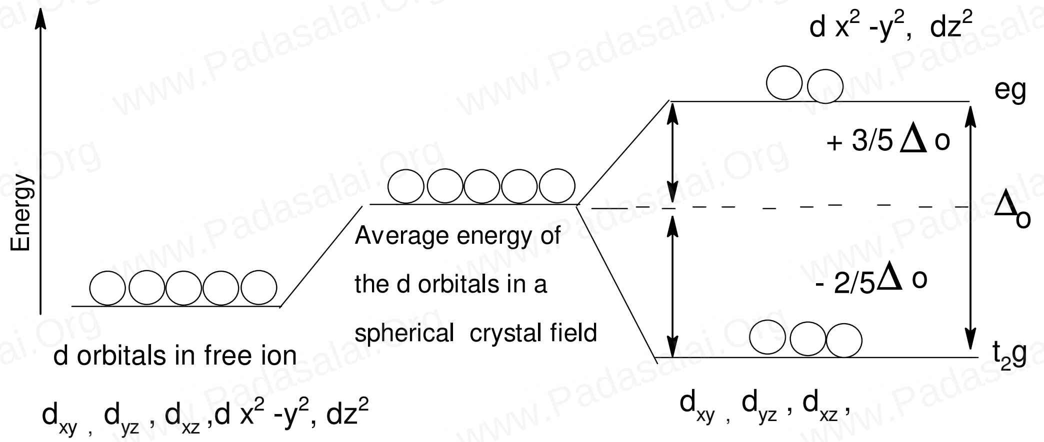




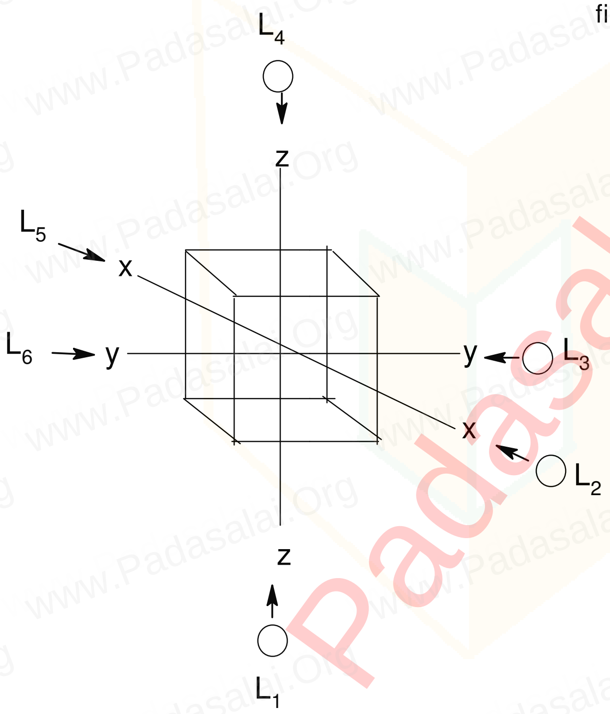


13. In an octahedral crystal field, draw the figure to show splitting of d orbitals.

- 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 eg orbitals) are increased by 3/5Δo while that of the other three orbitals dxy, dyz and dzx (represented as t_{2g} orbitals) are decreased by 2/5Δo.
- Here, Δo represents the crystal field splitting energy in the octahedral field.



Splitting of d orbitals in an octahedral crystal field

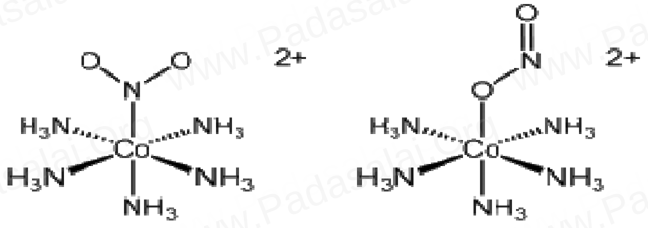


14. What is linkage isomerism? Explain with an example.

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.

In the 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.

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



15. Write briefly about the applications of coordination compounds in volumetric analysis.

16. Classify the following ligand based on the number of donor atoms.

a) NH_3 - **monodentate ligand**

b) en - **bidentate ligand.**

c) ox $^{2-}$ - **bidentate ligand.**

d) triaminotriethylamine - **tetradentate ligand**

e) pyridine - **monodentate ligand**

17. Give the difference between double salts and coordination compounds.

- Double salts lose their identity and dissociates into their constituent simple ions in solutions , whereas the complex ion in coordination compound, does not lose its identity and never dissociate to give simple ions.

18. Write the postulates of Werner's theory.

Werner postulated his theory as follows

1. Most of the elements exhibit, two types of valence namely primary valence and secondary valence and each element tend to satisfy both the valences.

primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number.

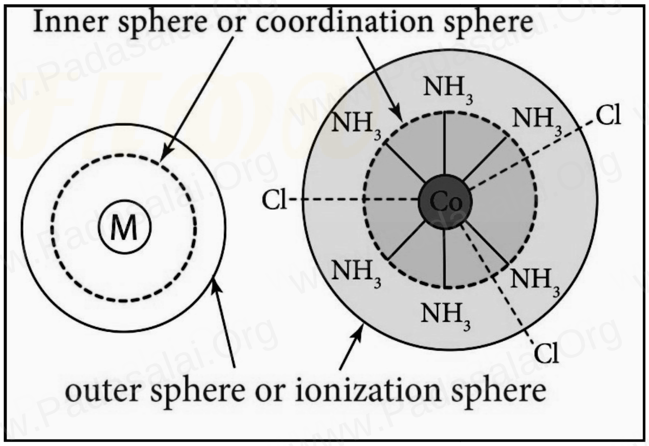
2. The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions.

3.The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these.

4. 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.



5. The primary valences are non-directional while the secondary valences are directional.

The geometry of the complex is determined by the spacial arrangement of the groups which satisfy the secondary valence.

Ex. **$CoCl_3.6NH_3$**

Limitations of Werner's theory:

It does not explain their colour and the magnetic properties.

19. $[Ni(CN)_4\ ]^{2-}$ is diamagnetic, while $[NiCl_4]^{2-}$ is paramagnetic, explain using crystal field theory.

In $[Ni(CN)_4]^{2-}$ CN^- is a strong field ligand.

Therefore, it causes the pairing of unpaired 3d electrons. Since no unpaired electrons are present in this case, [Ni(CO)4] is diamagnetic.

In **$[NiCl_4]^{2-}$** Cl^- is a weak field ligand.

It does not cause the pairing of unpaired 3d electrons.

Hence, $[NiCl_4]^{2-}$ is paramagnetic.

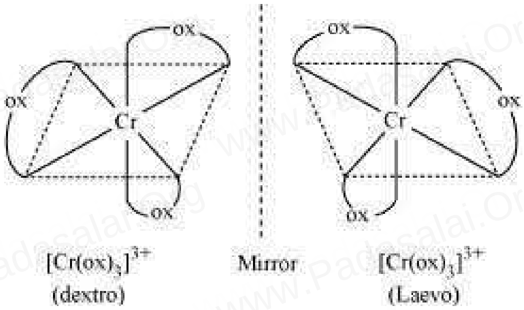
20. Why tetrahedral complexes do not exhibit geometrical isomerism.

Tetrahedral complexes do not show geometrical isomerism because the relative position of unidentate ligand attached with Central metal atom are same with respect to each other

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

- Coordination compounds which possess chairality 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

Structures of optical isomers of: **$[Cr(C_2O_4)_3]^{3-}$**



22. What are hydrate isomers? Explain with an example.

The exchange of free solvent molecules such as water , ammonia, alcohol in the crystal lattice with a ligand in the coordination entity gives different isomers.

These type of isomers are called solvate isomers.

If the solvent molecule is water, then these isomers are called hydrate isomers.

$CrCl_3.6H_2O$ has three hydrate isomers

$[Cr(H_2O)_6]Cl_3$	a violet colour compound and gives three chloride ions in solution,
$[Cr(H_2O)_5Cl]Cl_2.H_2O$	a pale green colour compound and gives two chloride ions in solution and,
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	dark green colour

23. What is crystal field splitting energy?

- The degenerate d-orbitals (in a spherical field environment) split into two levels i.e., eg and t_2g in the presence of ligands.
- The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting.
- The energy difference between the two levels (eg and t_2g) is called the crystal-field splitting energy.
- It is denoted by Δ.
- the crystal field splitting energy (Δ) and is given by the following expression,
  $$\Delta = hv = hc\,\lambda = hcv$$
- where h is the Plank' s constant; c is velocity of light, **υ** is the wave number of absorption maximum which is equal to 1/λ

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

The crystal field stabilisation energy is the energy difference of electronic configurations in the ligand filed (ELF) and the isotropic field/barycentre (Eiso).

CFSE (ΔE_o) = {ELF } - {Eiso } = {[**nt_2g** (-0.4)+ **neg** (0.6)] Δo + **np**P} - {**n'p** P}

Here, n **t_2g** is the number of electrons in **t_2g** orbitals**;** **neg** is number of electrons in **eg** orbitals; **np** is number of electron pairs in the ligand field; & **n'p** is the number of electron pairs in the isotropic field (barycentre).

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

In $[Ni(H_2O)_6]^2$ Ni is in **+2** state with the configuration of **$3d^8$** it has two unpaired electrons which do not pair up in the presence of the weak ligand **H_2O.** Hence it is coloured.

For d- d transition red light is absorbed and complementary colour light emitted is green.

In the case of **$[Ni(CN)_4]^{-2}$** Ni is again in **+2** state with the configuration $3d^8$ but in presence of strong CN^- ligand the two unpaird electrons in the 3d orbitals are pair up thus there in no unpaired electron present, hence it is colouless

26. Discuss briefly the nature of bonding in metal carbonyls.

Metal carbonyls are the transition metal complexes of carbon monoxide, containing Metal-Carbon bond.

In these complexes CO molecule acts as a neutral ligand.

The first homoleptic carbonyl $[Ni(CO)_4]$ nickel tetra carbonyl was reported by Mond.

These metallic carbonyls are widely studied because of their catalytic properties and their ability to release carbon monoxide.

Depending upon the number of metal atoms present in a given metallic carbonyl, they are classified as a. Mononuclear carbonyls b. Poly nuclear carbonyls

Based on the structure it is classified as a. Non-bridged metal carbonyls b. Bridged carbonyls

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

- When small amounts of Ammonium Hydroxide is added to copper sulphate solution a blue precipitate of Copper Hydroxide is formed.
- When we continue to add more drops of Ammonium hydroxide solution, the blue precipitate dissolves to form a deep blue solution..
- This deep blue solution is due to the formation of complex ion of copper and ammonia.

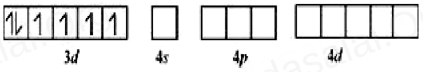
$$CuSO_4 + 2NH_4OH \longrightarrow (NH_4)_2SO_4 + Cu(OH)_2$$

$$(NH_4)_2SO_4 + Cu(OH)_2 + 2NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$

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

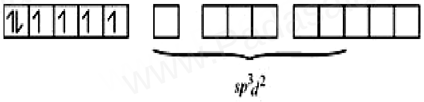
$[Co(C_2O_4)_3]^{3-}$ Cobalt exists in the +3 oxidation state in the given complex.

Orbitals of Co^{3+} ion:

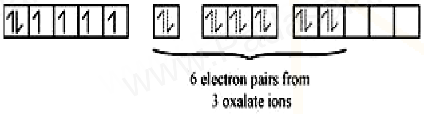


Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3*d* orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.

sp^3d^2 hybridization of Co^{3+}:



The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.



29. What are the limitations of VB theory?

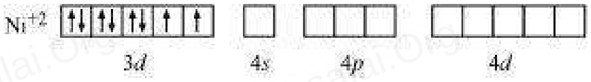
1. It does not explain the colour of the complex
2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal. For example, [Fe(CN)6]4- is diamagnetic (low spin) whereas [FeF6]4- is paramagnetic (high spin).

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

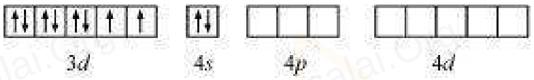
1	Oxidation state	**+2**
2	Coordination number	6
3	Nature of ligand	negative
4	Magnetic property	Magnetic moment, $\mu = \sqrt{n(n+2)}$ $= \sqrt{1(1+2)}$ $= \sqrt{3}$ $= 1.732$ BM
5	Electronic configuration in Octahedral crystal field	**$d^5 = t_2g\ 5$**

31. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

Though both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ are tetrahedral, their magnetic characters are different. This is due to a difference in the nature of ligands. Cl^- is a weak field ligand and it does not cause the pairing of unpaired 3d electrons. Hence, $[NiCl_4]^{2-}$ is paramagnetic.



In $Ni(CO)_4$, Ni is in the zero oxidation state i.e., it has a configuration of $3d^8\ 4s^2$.



But CO is a strong field ligand. Therefore, it causes the pairing of unpaired 3d electrons. Also, it causes the 4s electrons to shift to the 3d orbital, thereby giving rise to sp^3 hybridization. Since no unpaired electrons are present in this case, $[Ni(CO)_4]$ is diamagnetic.

32. State the Main assumptions of VB Theory

1.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.

2. Each ligand should have at least one filled orbital containing a lone pair of electrons.

3. In order to accommodate the electron pairs donated by the ligands the central metal ion present in a complex provides required number of vacant orbitals.

4. These vacant orbitals of central metal atom undergo hybridisation.

The process of mixing of atomic orbitals of comparable energy to form equal number of new orbitals called hybridised orbitals.

5. The vacant hybridised orbitals of the central metal ion, linearly overlap with filled orbitals of the ligands to form coordinate covalent sigma bonds between the metal and the ligand.

6. The hybridised orbitals are directional and their orientation in space gives a definite geometry to the complex ion.

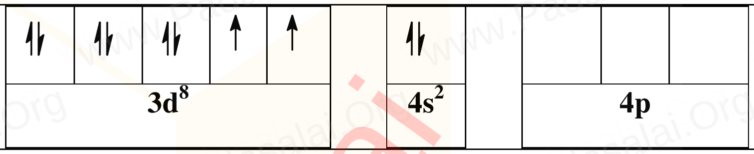
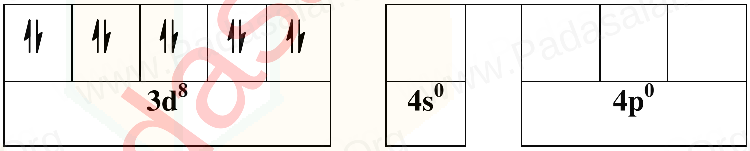
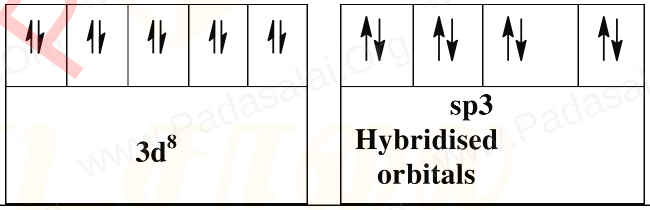
7.In the octahedral complexes, if the (n-1) d orbitals are involved in hybridisation, then they are called inner orbital complexes or low spin complexes or spin paired complexes. If the nd orbitals are involved in hybridisation, then such complexes are called outer orbital or high spin or spin free complexes. Here n represents the principle quantum number of the outermost shell.

8. The complexes containing a central meal atom with unpaired electron(s) are paramagnetic. If all the electrons are paired, then the complexes is diamagnetic.

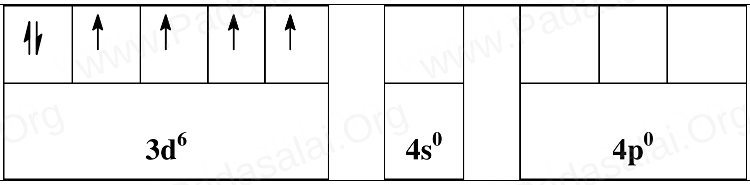
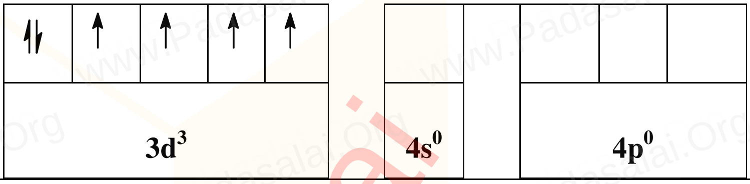
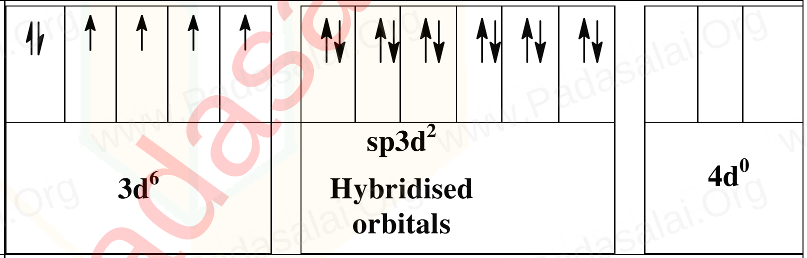
9. Ligands such as CO, CN-, en, and NH_3 present in the complexes cause pairing of electrons present in the central metal atom. Such ligands are called strong field ligands.

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

33. Based on VB theory explain the geometry of $[Ni(CO)_4]$.

COMPLEX	$[Ni(CO)_4]$
Central metal atom/ion and its outer electronic configuration	Ni^0 : $3d^8 4s^2$
Outer orbitals of metal atom/ion	
Nature of ligand	CN- Strong field ligand causes the pairing of 4s electrons with 3d electrons in the metal
Outer orbitals of metal atom/ion in presence of ligands	
Hybridisation	Coordination number - 4 Hybridisation – sp3
Hybridised orbitals of the metal atom in the complex	
Geometry	Tetrahedral
Magnetic property	No. of unparied electrons = 0; Hence **diamagnetic**
Magnetic moment (Using spin only formula)	$\mu s = \sqrt{n(n+2)} = 0$

34. Explain $[Co F_6]^{3-}$ is paramagnetic

COMPLEX	$[CoF_6]^{3-}$
Central metal atom/ion and its outer electronic configuration	Co^{3+} : $3d^6 4s^0$
Outer orbitals of metal atom/ion	
Nature of ligand	F^- weak field ligand and hence no pairing of 3d electrons in the metal
Outer orbitals of metal atom/ion in presence of ligands	
Hybridisation	Coordination number - 6 Hybridisation – $sp^3 d^2$
Hybridised orbitals of the metal atom in the complex	
Geometry	Octahedral In this complex outer d orbitals are involved in the hybridisation and hence the complex is called outer orbital complex
Magnetic property	No. of unparied electrons = 4; Hence paramagnetic
Magnetic moment (Using spin only formula)	$\mu s = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.899$

35. In a tetrahedral crystal field, draw the figure to show splitting of d orbitals.

The approach of ligands in tetrahedral field can be visualised as follows.

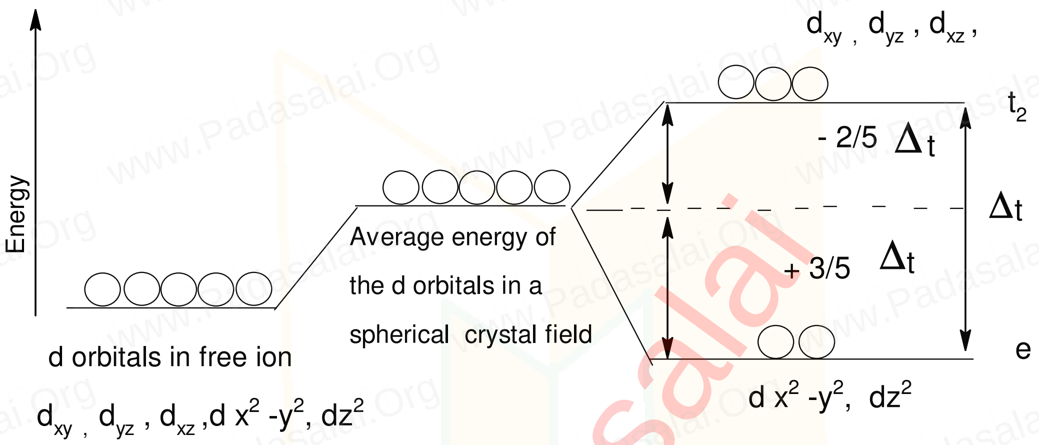
Consider a cube in which the central metal atom is placed at its centre

The four ligands approach the central metal atom along the direction of the leading diagonals drawn from alternate corners of the cube.

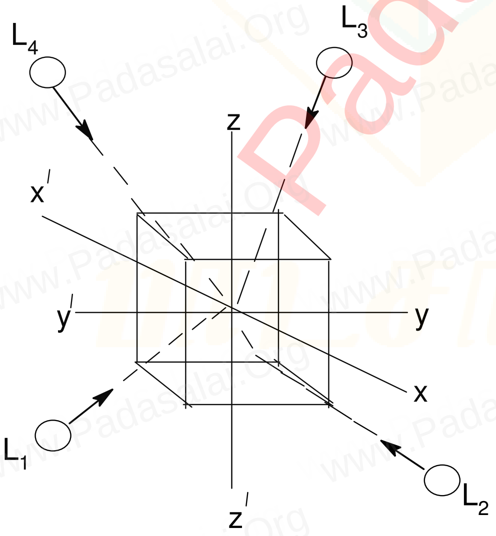
In this field, the t_2g orbitals (dxy, dyz and dzx) are pointing close to the direction in which ligands are approaching than the eg orbitals (dx2-y2 and dz^2).

As a result, the energy of **t_2** orbitals increases by $2/5\Delta t$ and that of **e** orbitals decreases by $3/5\Delta t$ as shown below.

This splitting is inverted when compared to the octahedral field.



Splitting of d orbitals in an tetrahedral crystal field



36. What are labile and inert complexes.

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

37. Write note on Stability and instability constants.

The stability of a complex is the degree of association between two species involved in an equilibrium. Let us consider the following complex formation reaction

$$Cu^{+2} + 4\,NH_3 \rightleftharpoons [Cu\,(NH_3)_4\,]^{+2}$$

$$\beta = \frac{[Cu\,(NH_3)_4\,]^{+2}}{[Cu^{+2}\,]\;[NH_3\;]^{4}}$$

- ✓ If the concentration of complex increases the value of stability complexes also increases. Therefore the greater the value of stability constant greater is the stability of the complex.
- ✓ Generally coordination complexes are stable in their solutions
- ✓ The complex ion can undergo dissociation to a small extent.
- ✓ Extent of dissociation depends on the strength of the metal ligand bond.
- ✓ Thus Stronger the M ← L, lesser is the dissociation.

- ✓ The stability of the metal complex can also be expressed in terms of dissociation equilibrium constant or instability constant.

- ✓ For example let us consider the dissociation of Cu NH3 in aqueous solution.

$$[Cu\,(NH_3)_4\,]^{+2} \rightleftharpoons Cu^{+2} + 4\,NH_3$$

$$\alpha = \frac{[Cu^{+2}\,]\;[NH_3\;]^{4}}{[Cu\,(NH_3)_4\,]^{+2}}$$