S.SHANMUGAM **UNIT- 5** **St.John's M.H.S.S porur Chennai -116**
COORDINATION CHEMISTRY **Mob: 9841945665**

1. **Write the IUPAC names for the following complexes.**

   i) $Na_2[Ni(EDTA)]$ ii) $[Ag(CN)_2]^-$ iii) $[Co(en)_3]_2(SO_4)_3$
   iv) $[Co(ONO)(NH_3)_5]^{2+}$ v) $[Pt(NH_3)_2Cl(NO_2)]$
   Ans:

   i) $Na_2[Ni(EDTA)]$ - Sodium 2,2',2'',2'''-(ethane-1,2- diamminetetraacetate)nickelate(II)

   ii) $[Ag(CN)_2]^-$ - Dicyanidoargentate(I) ion

   iii) $[Co(en)_3]_2(SO_4)_3$ - tris (ethylenediamine)cobalt(III)sulphate.

   iv) $[Co(ONO)(NH_3)_5]^{2+}$ - pentaammine (nitrito κ -O) cabalt (III) sulphate

   v) $[Pt(NH_3)_2Cl(NO_2)]$ - diamminechloridonitrito κ -N- platinum(II)

2. **Write the formula for the following coordination compounds.**

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

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

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

   d) hexaamminecobalt(III)sulphate - $[Co(NH_3)_6]_2(SO_4)_3$

   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) $[Cr(NH_3)Cl]_3[CoF_6]_2$ iii) $[Cr(NH_3)_3Cl_3]$

   i) $Mg[Cr(NH_3)(Cl)_5] \rightarrow Mg^{2+} + [Cr(NH_3)(Cl)_5]^{2-}$ Total no of ions = 2

   ii) $[Cr(NH_3)Cl]_3[CoF_6]_2 \rightarrow 3[Cr(NH_3)_5Cl]^{2+} + 2[CoF_6]^{3-}$ Total no of ions = 5

   iii) $[Cr(NH_3)_3Cl_3] \rightarrow$ no dissociation occurs Total no of ions = 0

   More the number of ions given out by the complex on dissociation and their molar conductivity also increases

   increasing order of molar conductivity

   $[Cr(NH_3)_3Cl_3] < Mg[Cr(NH_3)(Cl)_5] < [Cr(NH_3)Cl]_3[CoF_6]_2$
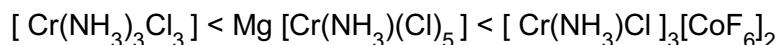
4. **Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction**

   Addition of an alcoholic solution of dimethylglyoxime to an ammoniacal solution of Ni(II) gives a rose-red precipitate, abbreviated **$Ni(dmg)_2$:**

   $[Ni(NH_3)_6]^{2+}{}_{(aq)} + 2(CH_3CNOH)_2(alc) \rightleftharpoons$ **$Ni[ONC(CH_3)C(CH_3)NOH]_2$**(s) + $2NH_4^+{}_{(aq)} + 4NH_{3\ (aq)}$

5. **$[CuCl_4]^{2-}$ exists while $[Cu I_4]^{2-}$ does not exist why?**

   Both the species contains Cu^{2+} ions but only iodide ion (not chloride ion) reduces Cu^{2+} to cuprous iodide and I_2. Hence, $[CuI_4]^{2-}$ does not exist.

   In $[CuI4]2-$complex iodide ion reduces Cu2+ to Cu+ therefore the complex is unstable.

   so , $2CuI_2 \rightarrow Cu_2I_2 + I_2$
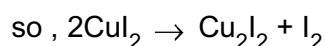
6 **Calculate the ratio of** $\dfrac{[Ag^+]}{[Ag(NH_3)_2]^+}$ **in 0.2 M solution of** NH_3. **If the stability constant for the**

complex $[Ag(NH_3)_2]^+$ **is 1.7 x10^7**

$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$ $(\beta) = 1.7 \times 10^7$, $[NH_3] = 0.2M$

i) **(β)** $= \dfrac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$, $\dfrac{[Ag(NH_3)_2]^+}{[Ag^+]} = \beta \times [NH_3]^2 = 1.7 \times 10^7 \, (0.2)^2 = 6.8 \times 10^5$

ii) $\dfrac{[Ag^+]}{[Ag(NH_3)_2]^+} = \dfrac{1}{\beta [NH_3]^2} = \dfrac{1}{6.8 \times 10^5} = 1.47 \times 10^{-5}$ **ratio =** 1.47×10^{-5}

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

Used in medicine

(1) Ca-EDTA chelate, is used in the treatment of lead and radioactive poisoning

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

Biologically important coordination compounds.

i) (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.

ii) Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein

8. **Based on VB theory explain why $[Cr(NH_3)_3]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ diamagnetic.**

i) Cr is in the +3 oxidation state i.e., d^3 configuration. Also,

NH$_3$ is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.
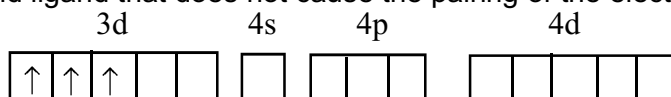
Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, **it is paramagnetic in nature.**

ii) In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d^8 configuration.
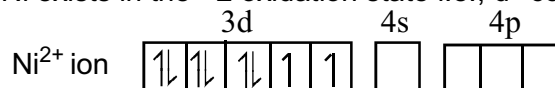
CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons.

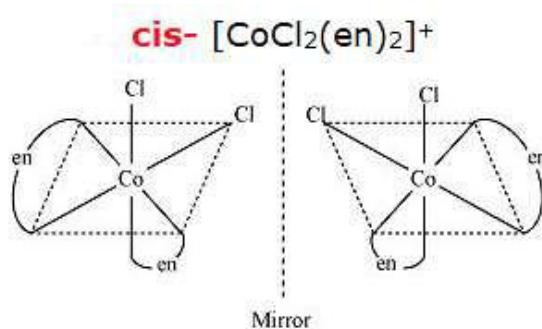Then, Ni^{2+} under goes dsp^2 hybridization.
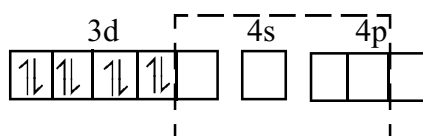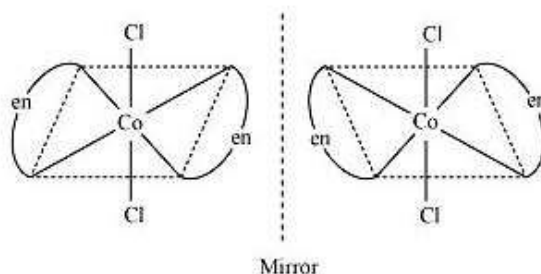
As there are **no unpaired electrons, it is diamagnetic.**

9. **Draw all possible geometrical isomers of the complex [Co(en)$_2$Cl$_2$]$^+$ and identify the optically active isomer.**

Cis - [Co(en)$_2$Cl$_2$]$^+$ is shows both geometrical as well as optical isomerism.

Its cis form is unsymmetrical,

cis- [CoCl$_2$(en)$_2$]$^+$

Mirror

Cis-[Co(en)$_2$Cl$_2$]$^+$ - **optically active** [Non - superimposable mirror image]

Mirror

trans- [CoCl$_2$(en)$_2$]$^+$

trans-[Co(en)$_2$Cl$_2$]$^+$ is symmetrical because it contains a **plane of symmetry**

Hence, *optically in active*

In total , Three isomers are possible

10. **[Ti(H$_2$O)$_6$]$^{3+}$ is coloured, while [Sc(H$_2$O)$_6$]$^{3+}$ is colourless- explain .**

i) **[Ti(H$_2$O)$_6$]$^{3+}$ is coloured because of** configuration is Ti^{3+} - 3d^1
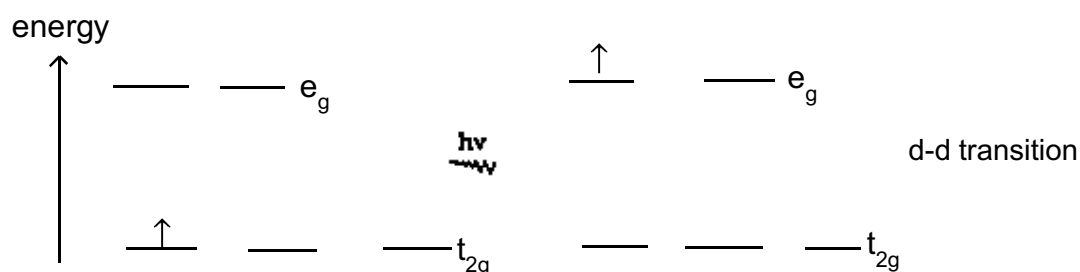
has one unpaired electron for d-d transition, hence it is coloured

i) **[Sc(H$_2$O)$_6$]$^{3+}$ is colourless because of** configuration is Configuration Sc^{3+} - 3d^0

No unpaired electron, so d-d transition is not possible hence it is not coloured

11. Give an example for complex of the type [Ma₂b₂c₂] where a, b, c are monodentate ligands and give the possible isomers.

The combination are as follows for **[Ma₂b₂c₂] are (a,a)(b,b),(c,c)** - this means in the octahedral structure of the compound a lies directly opposite of **a** ,and **b** lies opposite of **b** , same followed for **c**. these are the five possible combination e**g) [Cr((NH₃)₂(H₂O)₂(Br)₂]⁺**

a-a trans   b-b trans   c-c trans
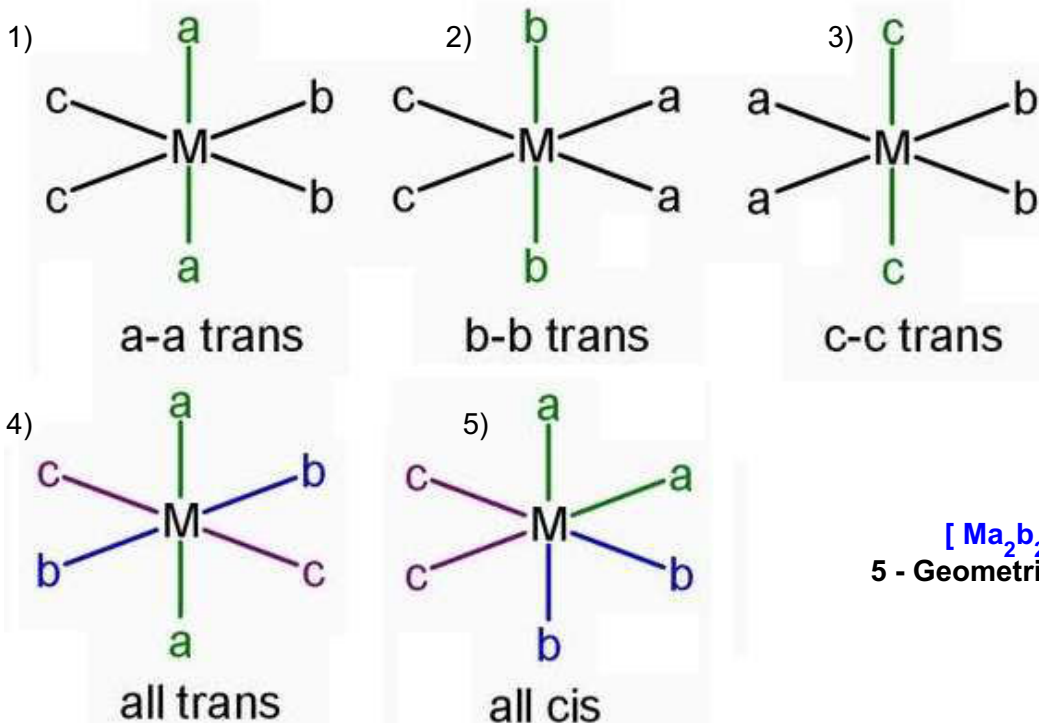
all trans   all cis

[Ma₂b₂c₂]
5 - Geometrical isomers

1. (a,a)(b,c)(b,c) -trans   2. (b,b) (a,c) (a,c) -trans   3. (c,c) (a,b) (a,b)- trans
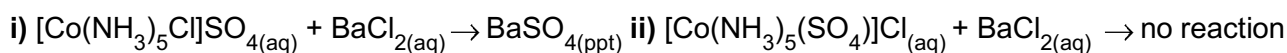4.(a,a)(b,b),(c,c) -all trans   5. (a,c)(a,b) (b,c) - all cis
(5th , isomer - shows optical isomerism d and l form)
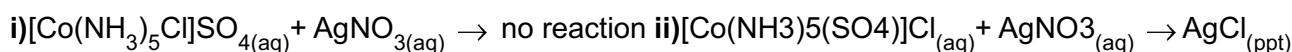**7- isomers out of which 5 are geometrical and 2 are optical isomers.**

12. Give one test to differentiate [Co(NH₃)₅Cl]SO₄ and [Co(NH₃)₅SO₄]Cl.

This can be tested by using AgNO₃solution and BaCl₂

Barium chloride test

i) $[Co(NH_3)_5Cl]SO_{4(aq)} + BaCl_{2(aq)} \rightarrow BaSO_{4(ppt)}$ **ii)** $[Co(NH_3)_5(SO_4)]Cl_{(aq)} + BaCl_{2(aq)} \rightarrow$ no reaction

Silver nitrate test

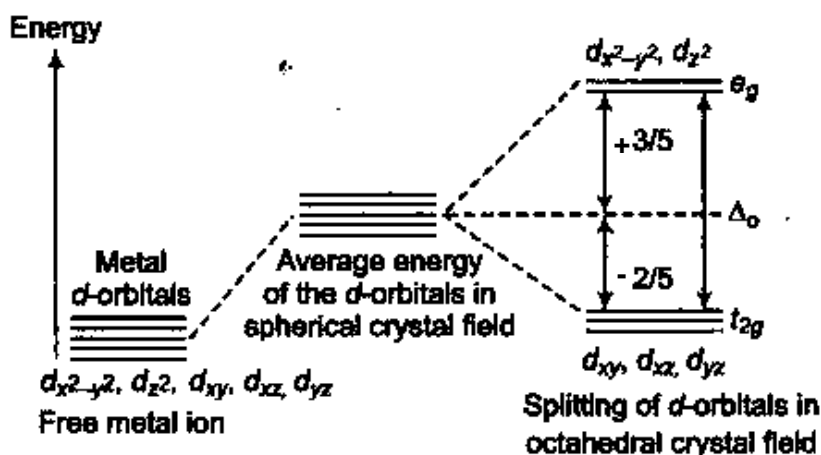**i)**$[Co(NH_3)_5Cl]SO_{4(aq)} + AgNO_{3(aq)} \rightarrow$ no reaction **ii)**$[Co(NH3)5(SO4)]Cl_{(aq)} + AgNO3_{(aq)} \rightarrow AgCl_{(ppt)}$

Hence they give different precipitates with different solutions. Thus they are ionisation isomers.

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

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.

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

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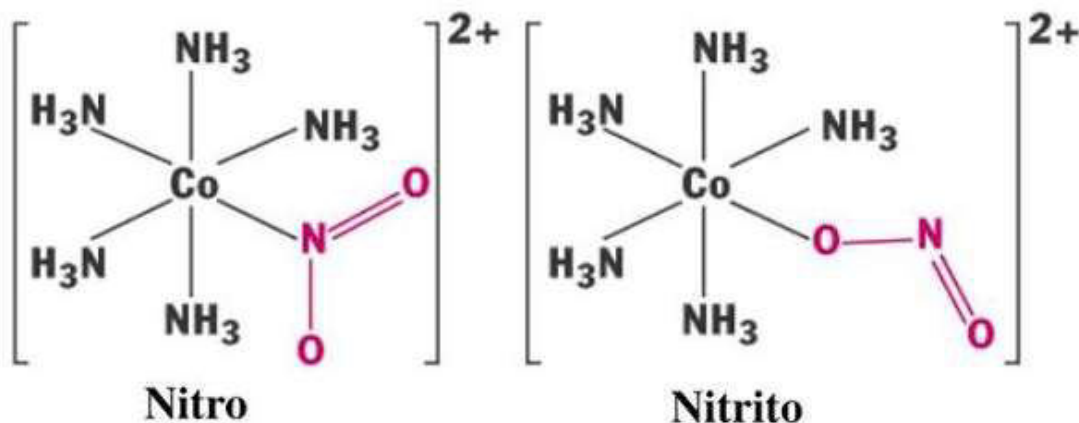
15. Write briefly about the applications of coordination compounds in volumetric analysis.

a) Colour Tests :

Since many complexes are highly coloured they can be used as colourimetric reagents

e.g. formation of red 2,2'-bipyridyl and 1,10-phenanthroline complexes as a test for Fe^{2+}

b) Gravimetric Analysis : Here chelating ligands are often used to form insoluble complexes

e.g.Ni(DMG)$_2$ and Al(oxine)$_3$.

c) Complexometric Titrations and Masking Agents :

An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution,

e.g. Zn^{2+}, Pb^{2+},Ca^{2+},Co^{2+},Ni^{2+},Cu^{2+}, etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+} in the presence of Pb^{2+}.

Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

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

a) NH$_3$ **b) en**   **c) ox^{2-}**   **d) triaminotriethylamine**   **e) pyridine**

a) **NH$_3$ - Monodentate** : The ligands which have only one donor atom.

b) **en   - Bidentate ligands :** H$_2$N- CH$_2$-CH$_2$- NH$_2$ **ethane-1,2-diamine**

Bidentate ligands have two lone pairs and both of which can bond to the central metal ion. Bidentate ligands may be neutral molecules or anions

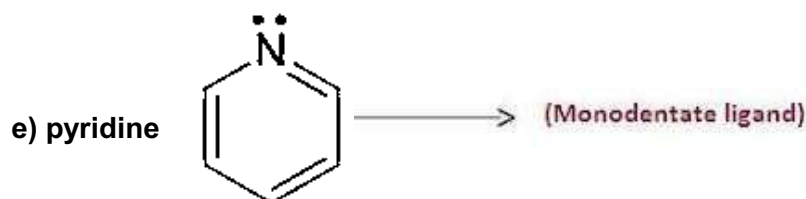c) **ox^{2-} - Bidentate ligands**

oxalato

d) triaminotriethylamine - Tetradentate ligands :

Tetradentate ligands have two lone pairs and the four lone pair can bond to the central metal ion.

$\longrightarrow$ (Tetradentate ligand)
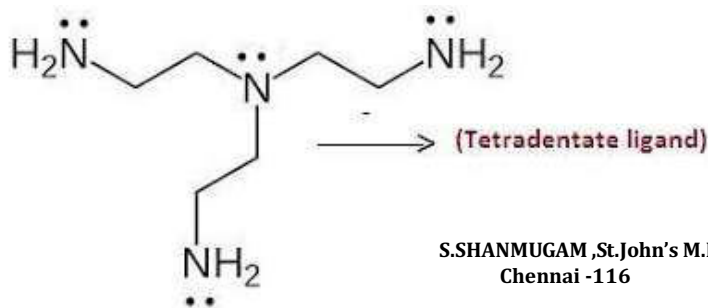
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e) pyridine

$\longrightarrow$ (Monodentate ligand)

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

i) **Double salts** are molecular compounds which are formed by the evoporation of solution containing 2 or more salts in stoichiometric proportions. They dissociate into their constituent ions in solution

eg: $K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow 2K+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$
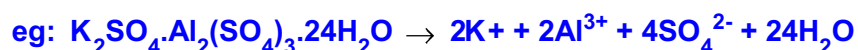
ii) **A complex compound** is a compound formed from a lewis acid and a lewis base.

They do not dissociate into its constituent ions in solutions

eg: $Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$

$K_4[Fe(CN)_6]$ on dissociation gives $4K+ + [Fe(CN)_6]^{4-}$ In $K_4[Fe(CN)_6]$ the individual components lose their identity. The metal of the complex ion is not free in solution unlike the metal in double salt solution.

18. Write the postulates of Werner's theory.

i) Most of the elements exhibit, two types of valence namely primary valence and secondary valence

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

iii) 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.

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

v) Two spheres of attraction around a metal atom/ion in a complex.

1) The inner sphere is known as coordination sphere

2) The outer sphere is called ionisation sphere.

Inner sphere or coordination sphere

outer sphere or ionization sphere
two sphere of attraction of metal
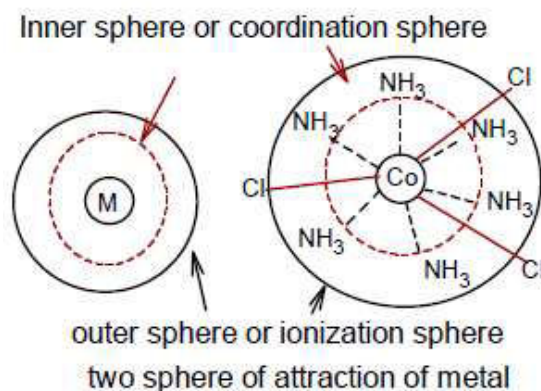
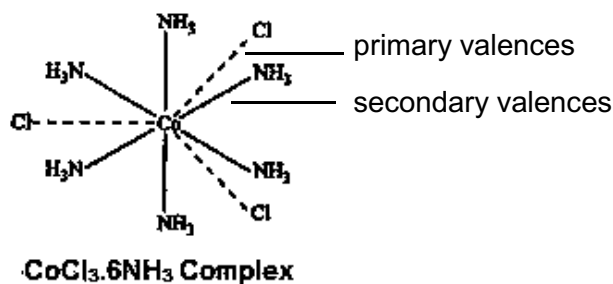vi) i) The primary valences - non-directional

    ii) Secondary valences - directional

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

      6 - octahedral geometry.   4 - either tetrahedral or square planar geometry.

Werner's representation

$CoCl_3.6NH_3$ **Complex**

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

The $[Ni(CN)_4]^{2-}$ is a low-spin square planar complex, since it contains the strong-field CN– ligand in it.

The oxidation state number of Ni in the complex +2 and the electronic configuration of Ni^{2+} is $3d^8$.

In the splitting pattern for a square-planar complex, the orbital possess the highest energy,

followed by the dxy and orbitals. **The dxz and dyz are symmetrically equivalent.**

All the eight electrons will enter these five orbitals, such that no electron remains unpaired.

This makes the complex diamagnetic
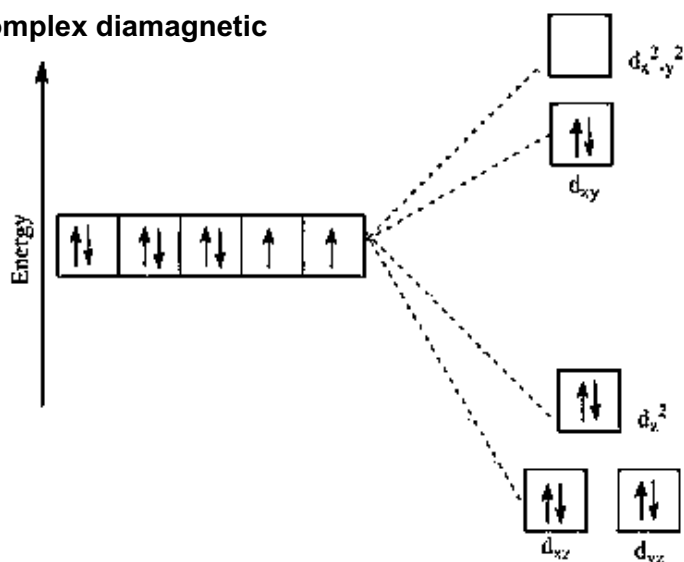
[NiCl4]2-: Splitting in the tetrahedral field
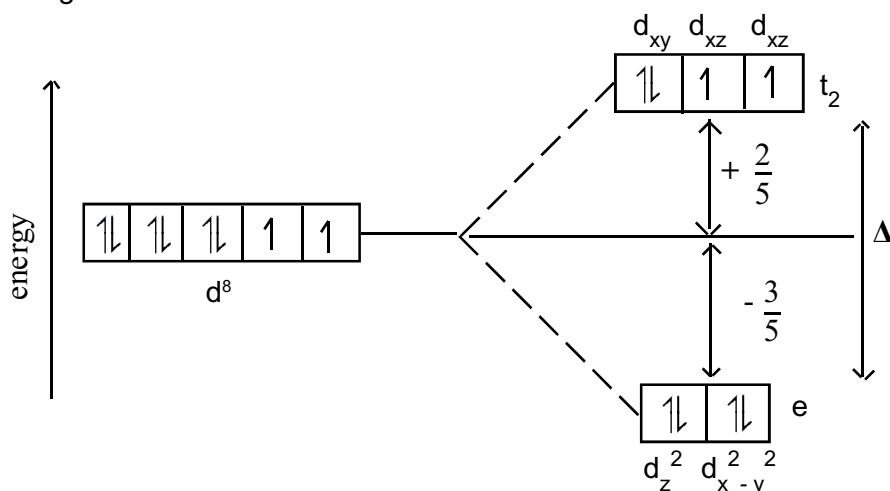
The d orbitals here fill with
8 electrons, but instead, high spin.

So, the dz^2 and dx^2-y^2 fill with one electron each, then the dxy, dxz, and dyz with one electron each, and then pairing occurs only after that, filling the dz^2, dx^2-y^2, and dxy completely. This leaves two unpaired electrons in the t2 orbitals, and thus this complex is **paramagnetic** with two unpaired electrons, as expected

20. Why tetrahedral complexes do not exhibit geometrical isomerism.

In tetrahedral complex metal atom or ion is at the Centre of a tetrahedron and four ligands are at four corners of tetrahedron this type of complex does not exhibit geometrical isomerism since all four ligands are at the equidistance having bond angle $109^o28'$

OR

Tetrahedral complexes do not show geometrical isomerism because the relative positions of unidentate ligands attached to the central atom are same with respect to each other

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

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 .

Examples:

The optical isomers of $[Co(en)_3]^{3+}$

l-form　　　　　　*d*-form
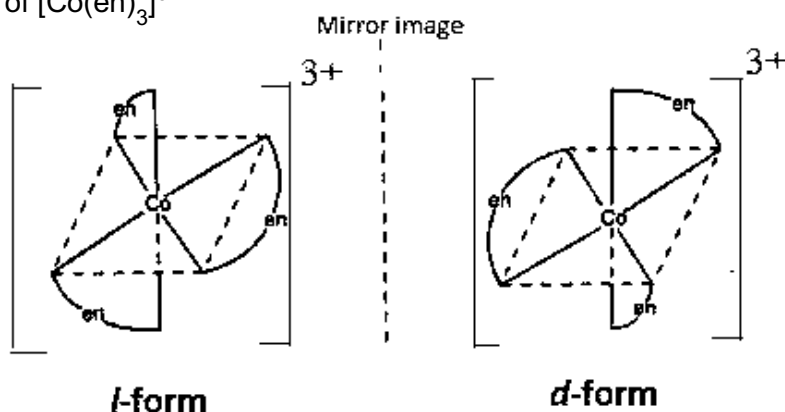
The octahedral complexes of type $[M(xx)_3]^{n\pm}$, $[M(xx)_2AB]^{n\pm}$ and $[M(xx)_2B_2]^{n\pm}$ exhibit optical isomerism

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

The exchange water molecules in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called hydrate isomers.

For example

$[Cr(H_2O)_6] Cl_3$ - is a violet colour compound and gives $3Cl^-$ ions in solution

$[CrCl(H_2O)_5] Cl_2.H_2O$ - is a pale green colour compound and gives $2Cl^-$ ions in solution

$[CrCl_2(H_2O)_4]Cl. 2H_2O$ is a dark green colour compound and gives one Cl^- ion in solution

23. What is crystal field splitting energy?

The degenerate d-orbitals (in a spherical field environment) split into two levels i.e., e_g 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 while the energy difference between the two levels (e_g and t_{2g}) is called the crystal-field splitting energy. It is denoted by Δo.

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

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

CFSE ($.\Delta E_o$) = {E_{LF}} - {E_{iso}}

= { [$nt_{2g}(-0.4) + n_{eg}(0.6)$] $\Delta o + n_p P$} - {$n'_p P$}

nt_{2g} - is the number of electrons in t_{2g} orbitals

n_{eg} - is number of electrons in eg 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).

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 +2 state with the configuration is $3d^8$ i.e it has two unpaired electrons which do not pair up in the presence of the week H_2O ligand. Hence, it is coloured, For d-d transition, red is absorbed and complementary light emitted is green

In case $[Ni(CN)_4]^{2-}$ Ni is again in + 2 state with with the configuration is $3d^8$ but in the presence of the strong CN- ligand , the two unpaired electrons in the 3d orbitals pair up.Thus, there is no unpaired electron present. Hence, it is colourlesss (no d-d transition)

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

The metal-carbon bonds in metal carbonyls have both σ and π characters.

A σ bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal.

A π bond is formed by the donation of a pair of electrons from the filled metal d orbital into the vacant anti- bonding π orbital (also known as back bonding of the carbonyl group).

The σ bond strengthens the π bond and vice-versa.

Thus, a synergic effect is created due to this metal-ligand bonding.

This synergic effect strengthens the bond between CO and the metal.
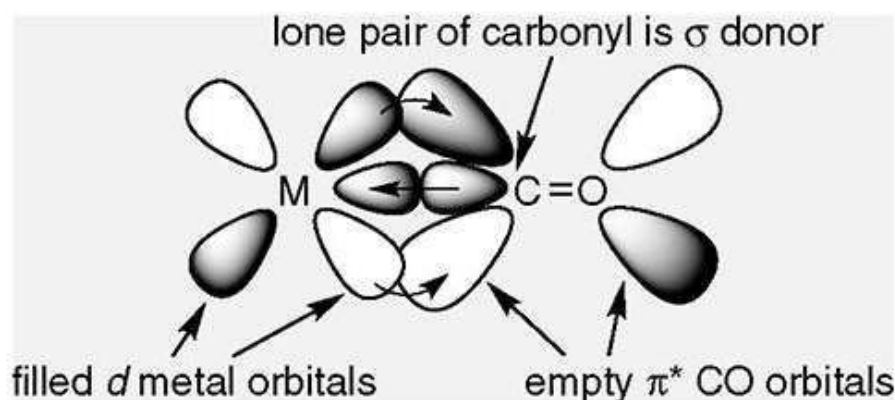
27. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution of copper sulphate?

When excess of liquid ammonia is added to an aqueous solution of copper sulphate it gives tetraammine copper (II) sulphate.
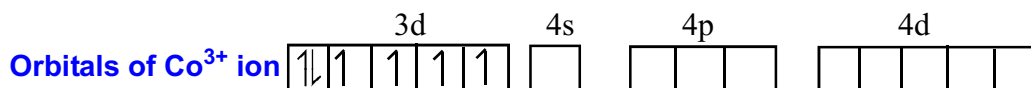
$$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$$
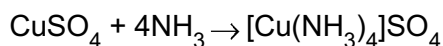
Thus, the coordination entity formed in the process is $[Cu(NH_3)_4]SO_4$ is a very stable complex, which does not ionize to give Cu^{2+} ions when added to water

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

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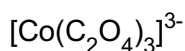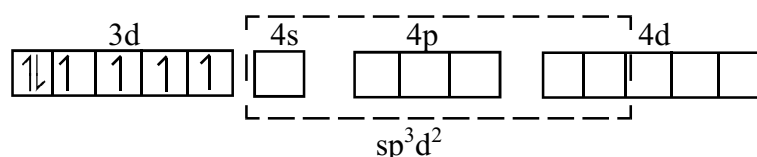
Cobalt exists in the +3 oxidation state in the given complex.

Orbitals of Co^{3+} ion

| 3d	4s	4p	4d
↑↓ ↑ ↑ ↑ ↑	□	□□□	□□□□

Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d 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+}:

3d	4s	4p	4d
↑↓ ↑ ↑ ↑ ↑	□	□□□	□□□□

sp^3d^2

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

3d	4s	4p	4d
↑↓ ↑ ↑ ↑ ↑	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ □□

6 electron pairs from 3 oxalate ions
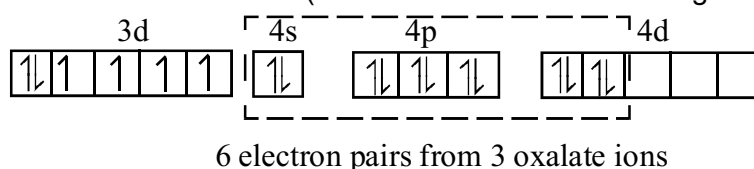
Hence, the geometry of the complex is found to be octahedral.

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.

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

$K_4[Mn(CN)_6]$ - Potassium hexacyanomanganate(II)

Oxidation state of manganese = +2 { $4(+1) + x + 6(-1) = 0$; $x = +2$ }

Coordination number - 6

Nature of ligand - CN^- Monodentate ligand

Magnetic property : Paramagnetic

$$\text{Magnetic moment. } \mu = \sqrt{n(n+2)}$$
$$= \sqrt{1(1+2)}$$
$$= \sqrt{3}$$
$$= 1.732 \text{ BM}$$

Electronic configuration - d5$^+$: t_{2g}^5