CHAPTER - 8

CO-ORDINATION COMPOUNDS

1. Define ligand.

Ligand is an atom or molecule or ion which is capable of donating a pair of electrons to the central metal or ion and forms a co-ordinate bond with it.

2. What do you mean by unidentate ligand?

Ligands which can coordinate to the central ion through only one donor atom are known as unidentate ligand.

Ex- NH_3, H_2O, Cl^-, CN^-, OH^-.

3. Define bidentate ligand / didentate?

Ligands which have two donor atoms and therefore can coordinate to the central ion at two positions are called bidentate ligands.

Ex- Oxalate ion $(C_2O_4)^{2-}$, en (Ethane-1,2-diamine)

4. What are polydentate ligand?

Ligand having more than two donor atoms present in the molecule are called polydentate ligand

Ex- (EDTA) (Ethylenediaminetetraacetate)

5. What do you mean by chelation or chelate complex?

When a di or polydentate ligand uses its two or more donor atoms to bind to the same central metal atom or ion forming a ring structure is called chelation and the complex is called chelate complex.

Ex- $[Cu(en)_2]^{2+}$

6. Define ambidentate ligand ?

The monodentate ligands which can co-ordinate with the central atom through more than one site are called ambidentate~~den~~ ligand.

Ex -

$M \leftarrow NO_2$ (Nitrito-N) $M \leftarrow SCN$ (thiocyanato)

$M \leftarrow ON_2O$ (Nitrito-O) $M \leftarrow NCS$ (isothiocyanato)

$M \leftarrow CN$ (cyanide)

$M \leftarrow NC$ (isocyanide)

7. How to calculate coordination number of the complex?

Total number of ligands attached to the central metal atom is called coordination number.

Note - One bidentate ligand should be counted as two

Ex - $[Co(en)_3]^{3+}$ CN of Co^{3+} = 6 = 2×3

Coordination number is determined by the number of sigma bonds formed.

8. What are homoleptic and heteroleptic complexes. Give examples.

Homoleptic complexes are the complexes in which metal atom is bound by only one kind of donor atom.

Ex - $[Co(NH_3)_6]^{3+}$, $[Ni(NH_3)_6]^{3+}$

Heteroleptic complexes are the complexes in which metal atom is bound to more than one kind of donor atom.

Ex - $[Co(NH_3)_4Cl_2]Cl$

Rules for writing names of the complex

1. Cation named first and then anion
2. Name of ligand first then central atom
3. Name of anionic ligands end with -o
   Name of positive ligands end in -ium
   Neutral as such

	Negative ligands	Neutral ligand
1.	F^- (Fluorido)	CH_3NH_2 methylamine
2.	NO_2^- (Nitrito-N)	(en) Ethane-1,2-diamine
3.	ONO^- (Nitrito-O)	(PH_3) phosphine
4.	SO_4^{2-} (sulphato)	H_2O aqua
5.	OH^- (hydroxo)	NH_3 ammine
6.	CO_3^{2-} (carbonato)	NO Nitrosyl
7.	$S_2O_3^{2-}$ (thiosulphato)	CO carbonyl
8.	CN^- (cyano)	(PPh_3) Phenyl phosphine
9.	Cl^- (chlorido)	

4. Ligands are named in alphabetical order
5. di, tri, tetra etc are used to indicate their number.
   If ligand include numerical prefix (di-, tri, tetra-) then bis-( ), tris-( ) etc.
6. If the complex is anionic the name of central metal atom ends with -ate.

   Ex

Fe	Ferrate	Ag -	Argentate	Sn -	Stannate
Cu	Cuprate	Au -	Aurate	Pd -	Palladate

7. O.N of central metal atom is written in Roman numerals

$[Co(en)_2(NO_2)Cl]^+$

Chlorido bis-(ethane-1,2-diamine) Nitrito-N Cobalt (III) ion

$[Pt(NH_3)_2Cl(NO_2)]$

diamminechloridonitrito-N platinum (II)

$K_3[Cr(C_2O_4)_3]$

Potassium trioxalatochromate (III)

$Hg[Co(SCN)_4]$

Mercury tetrathiocyanato cobaltate (III)

$K_2[PdCl_4]$

Potassium tetrachloridopalladate (II)

$[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

diammine chlorido methyl amine platinum (II) chloride

$[Ni(CO)_4]$ $[Ag(NH_3)_2][Ag(CN)_2]^-$

tetracarbonyl Nickel (0) diamminesilver (I) dicyanoargentate(I)

Rules for writing formula of the complex

1. Cation 1st then anion.
2. 1st symbol of central metal atom, followed by ligands in alphabetical order of their first symbol.
3. When two ligands have same defining atom ligand with fewer atom is cited first followed by ligand with more atom.
4. For abbreviated symbol first character is used. (Abbreviation are written in small
5. Polydentate ligands are written is small bracket.
6. If neutral then total charge should balance out.
7. If charge is to be written then numerical value come before (+) or (−).

Hexaaquachromium (III) chloride

$[Cr(H_2O)_6]Cl_3$

Sodium trioxalatoferrate (III)

$Na_3[Fe(C_2O_4)_3]$

Tetraamminediaquacobalt (III) chloride

$[Co(H_2O)_2(NH_3)_4]Cl_3$

Dibromido bis (ethane-1,2-diamine) platinum (IV) nitrate

$[PtBr_2(en)_2](NO_3)_2$

Potassium tri (oxalato) chromate (III)

$K_3[Cr(C_2O_4)_3]$

Hexaaquamanganese (II) sulphate, Hexaamminecobalt (III) sulphate

$[Mn(H_2O)_6](SO_4)$ $[Co(NH_3)_6]_2(SO_4)_3$

Tetraammine dichloridonitrito-N cobalt (III)

$[CoCl_2(NO_2)(NH_3)_4]$

1. Ionization isomers - Give different ions in solutions

Ex- Structure $[CoBr(NH_3)_5]SO_4$

Ionization isomers are

$[CoBr(NH_3)_5]SO_4$ - Gives precipitate with $BaCl_2$

pentaammine bromido cobalt (III) sulphate

$[CoSO_4(NH_3)_5]Br$ - Does not give precipitate with $BaCl_2$

pentaammine sulphato cobalt (III) bromide

Ex.

$[CoCl(NO_2)(NH_3)_4]Cl$ and $[CoCl_2(NH_3)_4]NO_2$

2. Solvate or hydrate isomers - Differs in number of water molecules present as ligands

Ex -

$[CoCl(en)_2(H_2O)]Cl_2$ and $[CoCl_2(en)_2]Cl \cdot H_2O$

3. Coordination isomers - Occur in compound containing both cationic and anionic coordination entity.

Ex -

$[Cr(NH_3)_6][Co(CN)_6]$

$[Co(NH_3)_6][Cr(CN)_6]$

4. Linkage isomers - Differ in mode of attachment of the ligand to metal atom.

Ex.

$[Co(NH_3)_5(ONO)]Cl_2$ and $[Co(NH_3)_5(NO_2)]Cl_2$

5. Geometrical isomers ((cis form

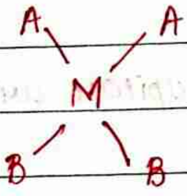
a) Arises in heteroleptic complexes

b) cis - form (ligands occupy adjacent position)

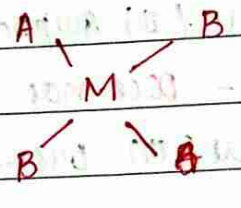
trans- form (ligands occupy opposite position)

Geometrical isomers in C.N 4 :- Square planar

i) MA_2B_2

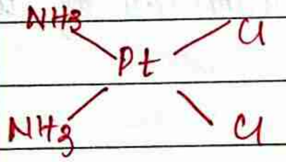


cis -

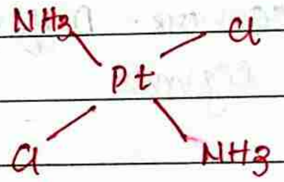


trans -

Ex- $[Pt(NH_3)_2Cl_2]$

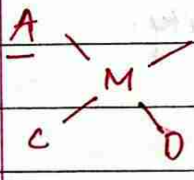


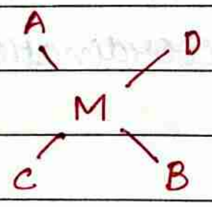
cis -

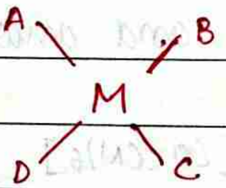


trans -

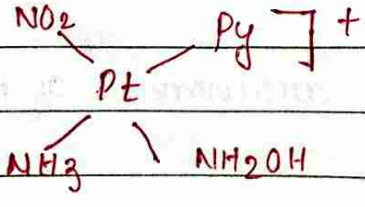
ii) MABCD

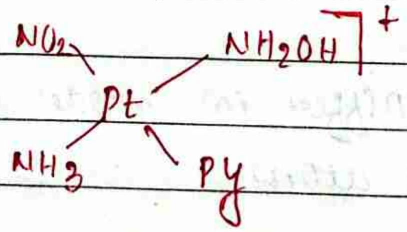


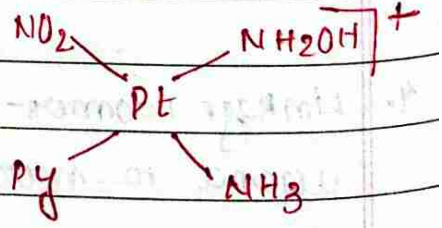




Ex- $[Pt(NO_2)(Py)(NH_2OH)(NH_3)]^+$

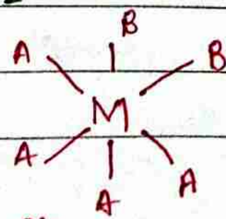




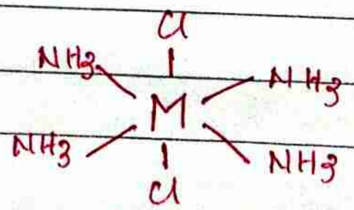


Geometrical isomers in C.N 6 - Octahedral

i) MA_4B_2

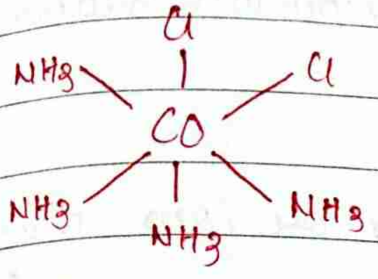


cis -

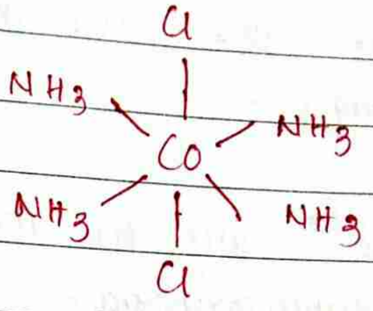


trans -

Ex- $[CO(NH_3)_4Cl_2]^+$

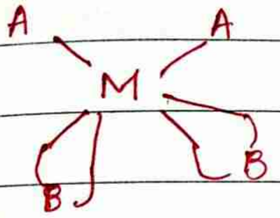


cis-

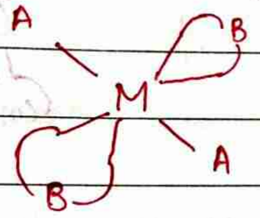


trans-

ii) MA_2B_2 where B is didantate ligand

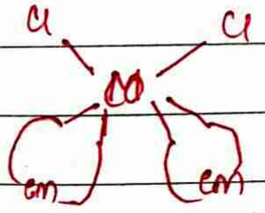


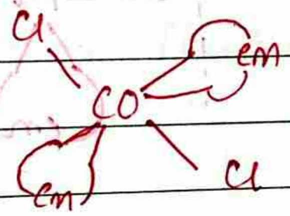
cis-



trans-

Ex- $[COCl_2(en)_2]$

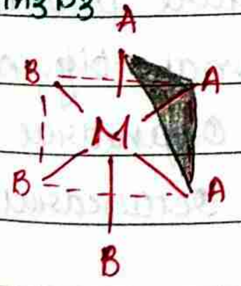


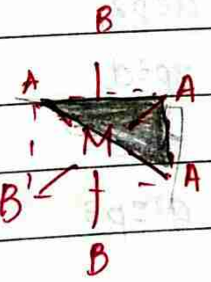


trans-

cis-

iii) MA_3B_3

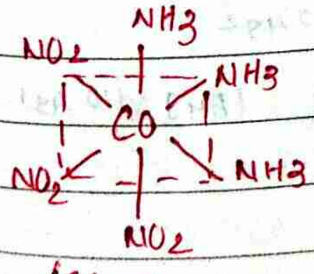




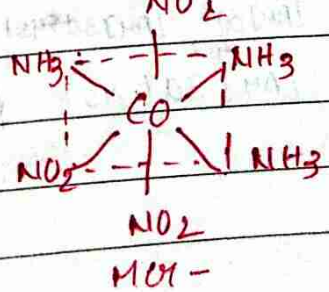
facial (fac-)

Meridonidal (Mer-)

Ex- $[CO(NH_3)_3(NO_2)_3]$



fac-



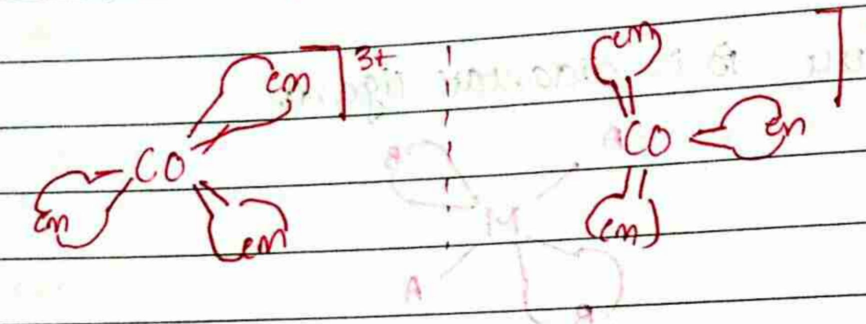
Mer-

9. What are enantiomers?

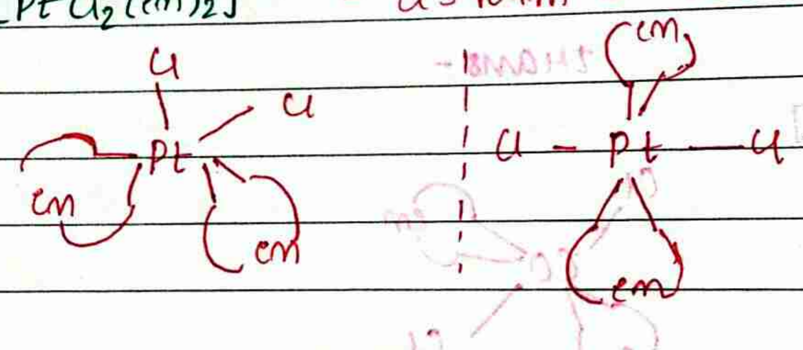
Enantiomers are the non superimposable mirror images.

Chiral molecules are the molecules or ions that cannot be superimposed.

Ex- $[Co(en)_3]^{3+}$



$[PtCl_2(en)_2]^{2+}$ - cis form is active



C.N	Type of hybridisation	Shape
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

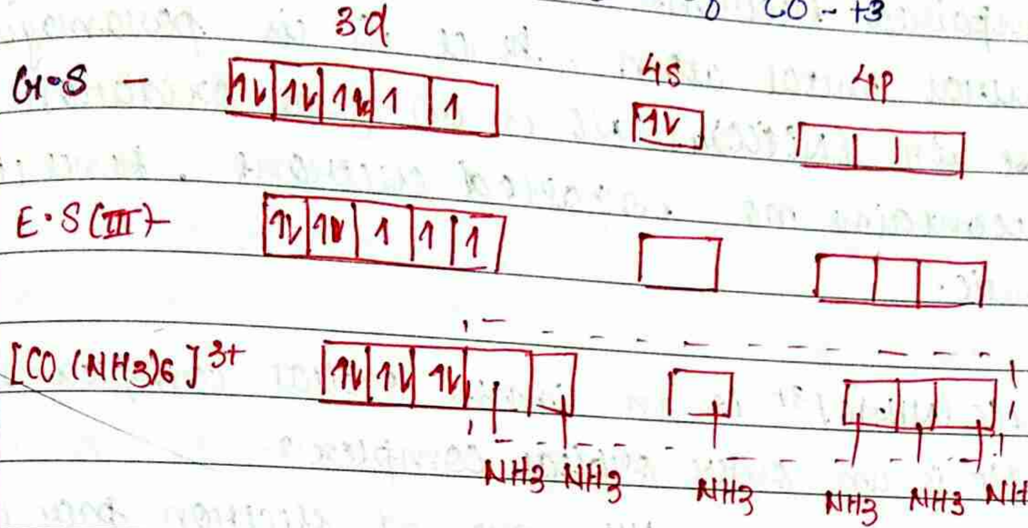
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30

[Ar]$3d^1 4s^2$ [Ar]$3d^2 4s^2$ [Ar]$3d^3 4s^2$ [Ar]$3d^5 4s^1$ [Ar] $3d^5 4s^2$

[Ar] $3d^6 4s^2$ [Ar] $3d^7 4s^2$ [Ar]$3d^8 4s^2$ [Ar]$3d^{10} 4s^1$ [Ar]$3d^{10}4s^2$

10. Describe the structure of $[Co(NH_3)_6]^{3+}$ according to VBT?

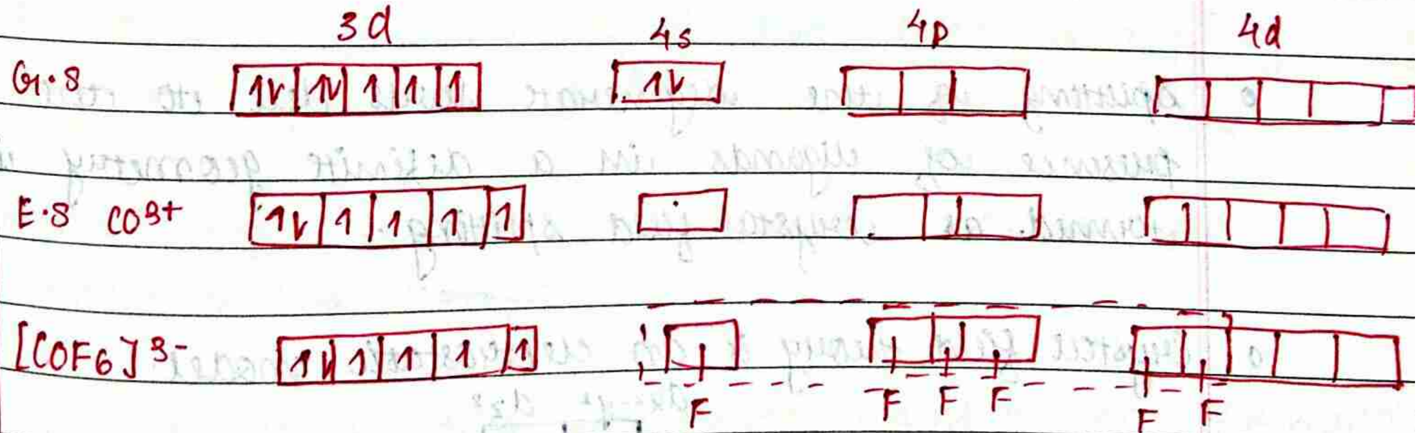
Co_{27} – [Ar] $3d^7 4s^2$ O.S of Co – +3



It is diamagnetic, low spin complex and have octahedral geometry, its an inner complex

11 Describe the structure of $[CoF_6]^{3-}$ according to VBT?

Co_{27} – [Ar] $3d^7 4s^2$ O.S of Co – +3



It is paramagnetic, high spin complex and have octahedral geometry, it is an outer complex

Decreasing order of strong field ligand

CO > CN^- > en > NH_3 > edta4- > NCS^- > H_2O > $C_2O_4^{2-}$ > OH^- > F^- >
S^{2-} > Cl^- > SCN^- > Br^- > I^-

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

$[NiCl_4]^{2-}$ is a high spin complex and there are two unpaired electrons with $3d^8$ electronic configuration of central metal atom, hence it is paramagnetic. whereas in $[Ni(CO)_4]$ Ni is in zero oxidation state and contains no unpaired electrons, hence it is diamagnetic.

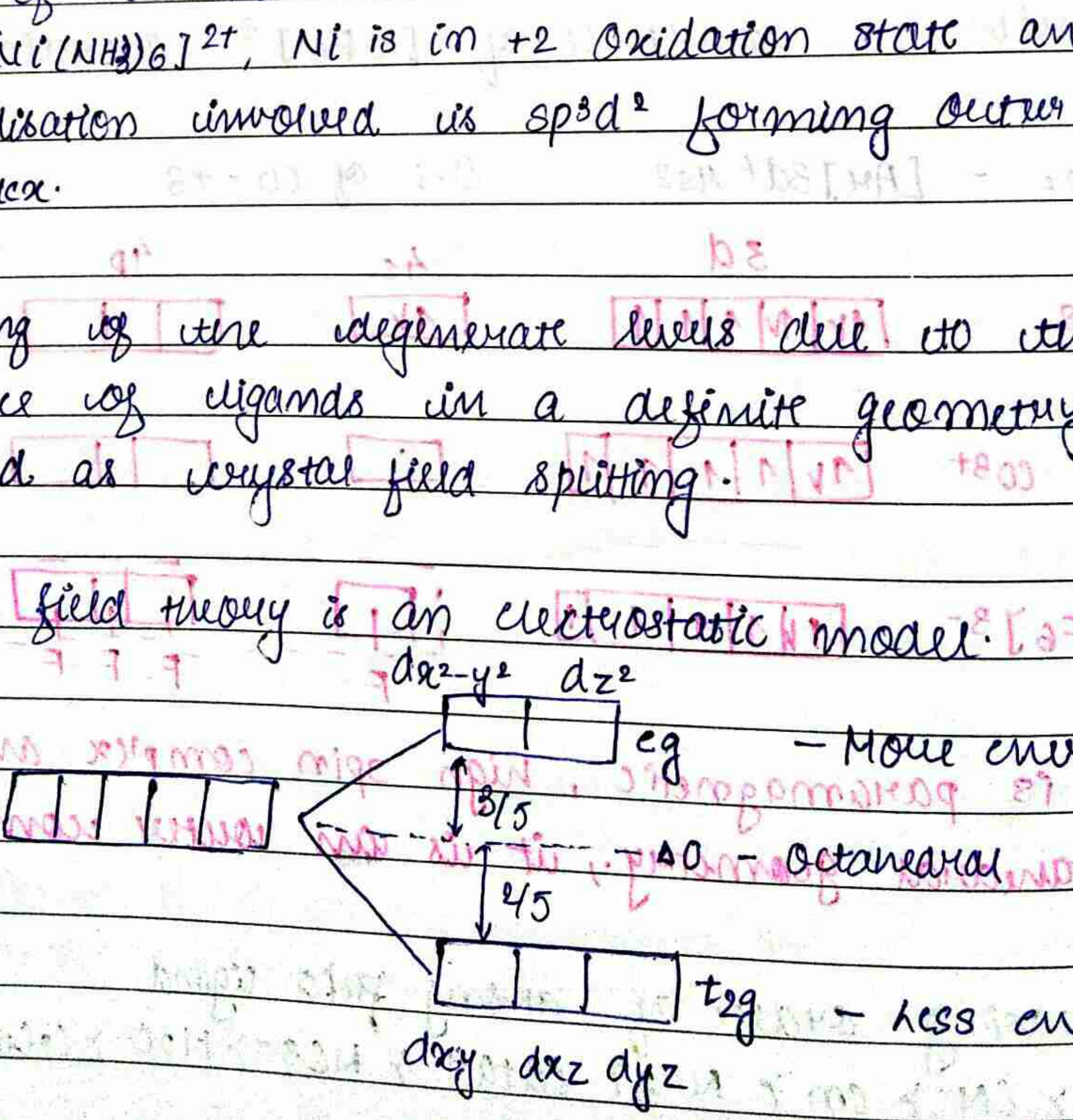
13. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex?

In the presence of NH_3 the 3d electron pair up leaving two d orbitals empty to be involved in d^2sp^3 hybridisation forming inner orbital complex in case of $[Co(NH_3)_6]^{3+}$.

In $[Ni(NH_3)_6]^{2+}$, Ni is in +2 oxidation state and the hybridisation involved is sp^3d^2 forming outer orbital complex.

- Splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting.

- Crystal field theory is an electrostatic model.



0. For d^4 ions, the e^- can either i) pair up with t_{2g} electrons ii) enter into e_g level. the discision depends on two factors a) magnitude of crystal field splitting Δ_o
b) pairing energy, P.

i) if $\Delta_o < P$ - 4th e^- enters one of the e_g orbitals ligands are known as weak field ligands and form high spin complexes.

ii) if $P < \Delta_o$ - 4th e^- occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands are known as strong field ligands and form low spin complexes.

14. Write the electronic configuration of d^6 on the basis of field theory when
i) $\Delta_o < P$ and
ii) $\Delta_o > P$.

i) electronic configuration of d^6 when $\Delta_o < P$ is $t_{2g}^4 e_g^2$
$d_{xy}^2 d_{xz}^1 d_{yz}^1 d_{x^2-y^2}^1 d_{z^2}^1$

ii) electronic configuration of d^6 when $\Delta_o > P$ is $t_{2g}^6 e_g^0$
$d_{xy}^2 d_{xz}^2 d_{yz}^2 d_{x^2-y^2}^0 d_{z^2}^0$

0 Number of unpaired electron present decides the colour of the complex.

15. Why are low spin tetrahedral complex not formed?
In tetrahedral complex, the d-orbital splitting is too small as compared to octahedral. For same metal and same ligand $\Delta_t = \frac{4}{8}\Delta_o$. Hence the orbital splitting energies are not enough to force pairing. As a result low spin complexes are rarely observed.

16. Why $CuSO_4 \cdot 5H_2O$ is blue in colour while $CuSO_4$ is colourless?

In $CuSO_4 \cdot 5H_2O$ water acts as ligand and causes crystal field splitting. Hence d-d transition is possible thus $CuSO_4 \cdot 5H_2O$ is coloured.

In anhydrous $CuSO_4$ due to absence of ligand crystal field splitting is not possible and hence it is colourless.

Dissociation constant/ Instability constant = $\frac{1}{\text{Formation constant } \beta_4}$.

17. **Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion?**

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