COORDINATION COMPOUNDS

Coordination compounds are a special class of compounds in which the central metal atom is surrounded by ions or molecules beyond their normal valency. These compounds are widely present in the minerals, plants and animals and play many important functions. Many biologically important compounds are Coordination compounds in which complicated organic species are bound to metal ions. The common examples are: **Haemoglobin** which is a Coordination compound of **Iron**, **Chlorophyll** which is a Coordination compound of **Magnesium** and **Vitamin B_{12}** which is a Coordination compound of **Cobalt** etc. The Coordination compounds are also finding extensive applications in metallurgical processes, analytical chemistry, industrial catalysts, textile dyeing, electroplating and medicinal chemistry.

Coordination compounds are molecular compounds which are formed from the combination of two or more simple stable compounds and retain their identity in the solid as well as in the dissolved state. For example, when aqueous ammonia is added to green solution of nickel chloride, $NiCl_2$, the colour changes to $[Ni\ (NH_3)_6]\ Cl_2$ purple crystals. Such a compound is called Coordination compounds.

$NiCl_2$ (Green) + $6NH_3$ ----> $[Ni\ (NH_3)_6]\ Cl_2$ (Purple)

When the compound $[Ni\ (NH_3)_6]\ Cl_2$ is dissolved in water it ionizes to give a new species. Such an ion is called complex ion $[Ni\ (NH_3)_6]^{2+}$.

$[Ni\ (NH_3)_6]\ Cl_2$ -----> $[Ni\ (NH_3)_6]^{2+} + 2Cl^-$

Coordination compounds are the compounds in which the central metal atom is bound to a number of anions or neutral molecules by coordinate bonds.

Coordination entity and Coordination sphere:

Coordination entity: A coordination entity constitutes a central metal atom or ion bounded to a fix number of oppositely charged ions or neutral molecules. For example, $[Co\ Cl_3\ (NH_3)_3]$

Coordination sphere: The central metal atom or ion and the molecules or ions bonded to it are enclosed in a square bracket and a collectively called the **Coordination sphere.**

Central atom or ion and Ligands:

Central atom or ion: The atom or ion to which a fixed number of neutral molecules or ions are attached in the coordination entity is called **Central atom or ion.**

Ligands: The neutral molecules or ions bonded to the central atom or ion in the coordination entity are called **ligands.** For example,

$[Ni\ (NH_3)_6]^{2+}$: Central atom = Ni^{2+}, ligands = NH_3 molecules

Types of ligands:

(i) **Unidentate or monodentate ligands:** When a ligand is bound to a metal ion through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be **Unidentate ligands**.

(ii) **Didentate** or Bi**dentate ligands:** When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1, 2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be **Didentate ligands.**

(iii) **Polydentate ligands:** Ligands having more the two donor atoms present in the **molecule,** the ligands are said to be **Polydentate ligands**.
Diethylene triamine acts as **tridentate ligand** having three donor N atoms.

Triethylene tetra amine acts as **tetradentate ligand** having four donor N atoms.
Ethylenediamine triacetate ion acts as **Pentadentate ligand** having two N atoms and three O atoms.
Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important **hexadentate ligand**. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

When a di- or Polydentate ligand uses its two or more donor atoms simultaneously to bind a single metal ion, it is said to be a **chelate ligand**. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing Unidentate ligands.

Ligand which has two different donor atoms and either of the two ligates in the complex is called **ambidentate ligand.**
Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.
Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.

Coordination number: The total number of ligands attached to a central metal atom or ion is called the Coordination number of that metal atom or ion. For example,
$[Ni(NH_3)_4]^{2+}$: C.N. of $Ni^{2+} = 4$
$[CoCl_3(NH_3)_3]$: C.N. of $Co^{3+} = 6$

IUPAC nomenclature of coordination compounds: Write the IUPAC names of the following coordination compounds:
(a) $[Pt(NH_3)_2Cl(NO_2)]$
(b) $K_3[Cr(C_2O_4)_3]$
(c) $[CoCl_2(en)_2]Cl$
(d) $[Co(NH_3)_5(CO_3)]Cl$
(e) $Hg[Co(SCN)_4]$
(f) $[Cr(NH_3)_3(H_2O)_3]Cl_3$
(g) $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$
(h) $[Ag(NH_3)_2][Ag(CN)_2]$
(a) Diamminechloridonitrito-N-platinum (II)
(b) Potassium trioxalatochromate (III)
(c) Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride
(d) Pentaamminecarbonatocobalt (III) chloride
(e) Mercury (I) tetrathiocyanato-S-cobaltate (III)
(f) Triamminetriaquachromium (III) chloride
(g) Tris (ethane-1,2–diamine)cobalt(III) sulphate
(h) Diamminesilver (I) dicyanidoargentate (I)

Werner's theory: Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds such as $CrCl_3$, $CoCl_2$ or $PdCl_2$ have primary valence of 3, 2 and 2 respectively.

In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol $CoCl_3.6NH_3$ (Yellow)	gave	3 mol AgCl
1 mol $CoCl_3.5NH_3$ (Purple)	gave	2 mol AgCl
1 mol $CoCl_3.4NH_3$ (Green)	gave	1 mol AgCl
1 mol $CoCl_3.4NH_3$ (Violet)	gave	1 mol AgCl

Werner proposed the term secondary valence for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

Formulation of Cobalt (III) Chloride-Ammonia Complexes:

Colour	Formula	Solution conductivity corresponds to
Yellow	$[Co (NH_3)_6]^{3+} 3Cl^-$	1:3
Purple	$[Co Cl (NH_3)_5]^{2+} 2Cl^-$	1:2
Green	$[Co Cl_2 (NH_3)_4]^+ Cl^-$	1:1
Violet	$[Co Cl_2 (NH_3)_4]^+ Cl^-$	1:1

The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

Valence Bond Theory (VBT) for bonding in Coordination Compounds:

The main assumptions of this theory are listed below:

1. The central metal ion in the complex makes available a number of empty orbitals for the formation of coordination bonds with suitable ligands.
2. The number of empty orbitals made available for this purpose is equal to coordination number of the central metal ion. For example, if coordination number is 6, six empty orbitals are made available and if coordination number is 4, four empty orbitals are made available in the central metal ion.
3. The appropriate atomic orbitals (s, p and d) of the metal hybridize to give a set of equivalent orbitals of definite geometry such as square planar, tetrahedral and octahedral and so on.
4. The d-orbitals involved in the hybridization may be either inner d-orbitals i.e. (n-1) d or outer d-orbitals i.e. nd. For example, in case of octahedral hybridization. The orbitals may be two 3d, one 4s and three 4p (d^2sp^3) or one 4s, three 4p and two 4d (sp^3d^2)
5. Each ligand has at least one orbital (of donor atom)) containing a lone pair of electrons.
6. The empty hybrid orbitals of metal ion overlap the filled orbitals of the ligand to form metal-ligand coordinate covalent bonds.

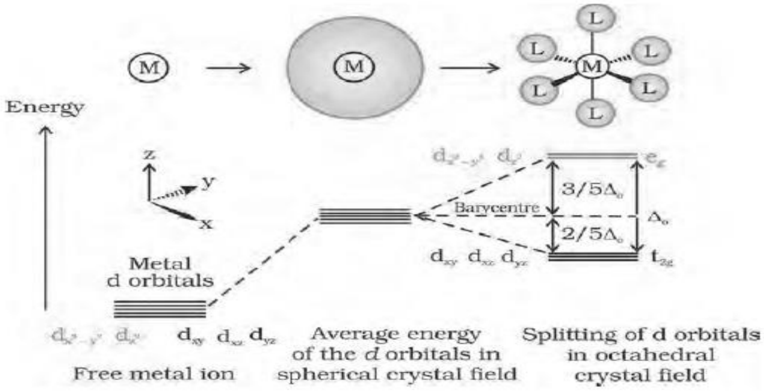
Number of Orbitals, Types of Hybridizations and Magnetic Properties of Coordination Compounds:

Coordination number	**Type of hybridization**	**Complex/ion**	**Geometry**	**No. of unpaired electrons**	**Magnetic Character**
4	sp^3	$[NiCl_4]^{2-}$	Tetrahedral	2	Paramagnetic
4	dsp^2	$[Ni(CN)_4]^{2-}$	Square planar	0	Diamagnetic
6	sp^3d^2	$[CoF_6]^{3-}$	Octahedral	4	Paramagnetic
6	d^2sp^3	$[Co(NH_3)_6]^{3+}$	Octahedral	0	Diamagnetic

CRYSTAL FIELD THEORY (CFT): The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules. The five *d* orbitals in an isolated gaseous metal atom/ion have same energy, *i.e.*, they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the *d* orbitals is lifted. It results in splitting of the *d* orbitals. The pattern of splitting depends upon the nature of the crystal field.

The conversion of five degenerate d-orbitals of the metal ion into different sets of orbitals having different energies in the presence of electric field of ligand is called **crystal field splitting**.

(a) Crystal field splitting in octahedral coordination entities:



d orbital splitting in an octahedral crystal field (fig. 9.8 ncert)

Spectrochemical series: ligands can be arranged in a series in the order of increasing field strength as given below:

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4{}^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

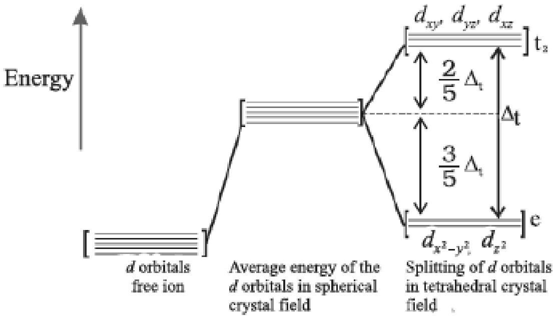
For d^4 ions, two possible patterns of electron distribution arise:

(i) The fourth electron could either enter the t_{2g} level and pair with an existing electron, or

(ii) It could avoid paying the price of the pairing energy by occupying the e_g level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δo and the pairing energy, P (P represents the energy required for electron pairing in a single orbital).
The two options are:
(i) If $\Delta o < P$, the fourth electron enters one of the *e*g orbitals giving the configuration $t_{2g}^3\ e_g^1$. Ligands for which $\Delta o < P$ are known as *weak field ligands* and form high spin complexes.

(ii) If $\Delta o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4\ e_g^0$. Ligands which produce this effect are known as *strong field ligands* and form low spin complexes.

(b) Crystal field splitting in tetrahedral coordination entities:



d orbital splitting in a tetrahedral crystal field (fig.9.9 ncert)

In tetrahedral coordination entity formation, the *d* orbital splitting (Fig. 9.9) is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\ \Delta_o$.

Colour in Coordination Compounds: The crystal field theory attributes the colour of the coordination compounds to *d-d* transition of the electron.
Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities:

Coordination entity	**Wavelength of light absorbed (nm)**	**Colour of light absorbed**	**Colour of coordination entity**
$[Co(CN)_6]^{3-}$	310	Violet	Pale Yellow
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Ti(H_2O)_6]^{3+}$	510	Blue Green	Purple
$[Co\ Cl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue

Isomerism in Coordination Compounds:

Two or more compounds having the same molecular formula but different arrangement of atoms are called **isomers** and the phenomenon is called **Isomerism**
Two types of isomerism are: (a) Structural isomerism (b) Stereoisomerism

(a) Structural isomerism: The isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called **structural isomers.**

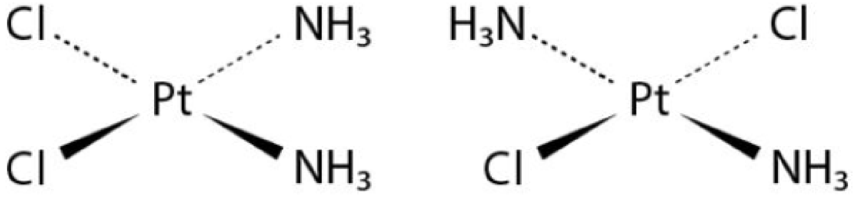
(i) Ionization isomerism: The compounds which have same molecular formula but give different ions in solution are called ionization isomers. For example:
$[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

(ii) Solvate isomerism: The compounds which have same molecular formula but differ in the number of solvent molecules present as ligands and as free solvent molecules in the crystal lattice are called solvate isomers. This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. For example:
$[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

(iii) Coordination isomerism: This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. For example: $[Co(NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}.

(iv) Linkage isomerism: The compounds which have same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers. Linkage isomerism arises in a coordination compound containing ambidentate ligand. For example: Complexes containing the thiocyanate ligand, which may bind through sulphur to give M–SCN. Isothiocyanate ligand through the nitrogen to give M–NCS.
$[Co(NH_3)_5(NO_2)]Cl_2$ the ligand is bound through nitrogen ($–NO_2$).
$[Co(NH_3)_5(ONO)]Cl_2$ the ligand is bound through oxygen (–ONO).

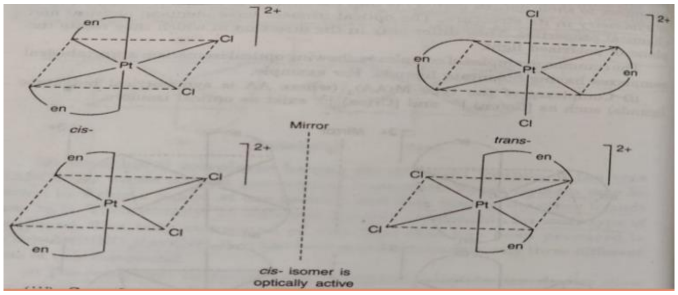
(b) Stereoisomerism: Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement of atoms.
Two types of isomerism are: (a) Geometrical isomerism (b) Optical isomerism
(a) Geometrical isomerism: This type of isomerism arises in heteroleptic complexes due to ligands occupying different positions around the central ion. The ligands occupy positions either adjacent to one another or opposite to one another. These are referred to cis- form (ligand occupy adjacent position) and trans-form (ligand occupy opposite position). For example:
Geometrical isomers (cis and trans) of Pt $[NH_3]_2Cl_2$]



Cis- trans-

(b) Optical isomerism: Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers.

The molecules or ions that cannot be superimposed are called chiral.
The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarized light in a polarimeter (d rotates to the right, l to the left).
Optical isomerism is common in octahedral complexes involving Didentate ligands.
Optical isomers of $[PtCl_2\,(en)_2]^{2+}$



Importance and Applications of Coordination Compounds:
The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analyses. Examples of such reagents include EDTA, DMG (dimethylglyoxime), etc.
Ni2+ ions are detected by adding DMG (dimethylglyoxime) in the presence of NH_4OH to nickel salt solution, red precipitates are formed.
- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au\,(CN)_2\,]^-$ in aqueous solution
- Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.
For example, impure nickel is converted to $[Ni\,(CO)_4\,]$, which is decomposed to yield pure nickel.
- Biological importance: Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron.
Vitamin B12, cyanocobalamine, the anti– pernicious anaemia factor, is a coordination compound of cobalt.
- In catalyst: Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3\,Rh\,Cl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag\,(CN)_2]^-$ and $[Au(CN)_2\,]^-$ than from a solution of simple metal ions.

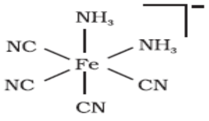
- In black and white photography: The developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- In medicine: Complexing agents are used for removal of metal poisoning. A platinum complex, $[Pt\,Cl_2(NH_3)_2]$ known as cis-platin has been used in cancer therapy.

ASSIGNMENTS:

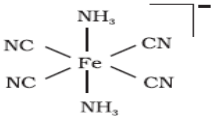
Q1. Write the formulas for the following coordination compounds:
(a) Tetraammineaquachloridocobalt (III) chloride
(b) Potassium tetrahydroxidozincate (II)
(c) Potassium trioxalatoaluminate (III)
(d) Dichloridobis (ethane-1, 2-diamine) cobalt (III) ion
(e) Tetracarbonylnickel (0)
(a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(b) $K_2[Zn(OH)_4]$
(c) $K_3[Al(C_2O_4)_3]$
(d) $[Co\,Cl_2(en)_2]^+$
(e) $[Ni(CO)_4]$

Q2. Write the IUPAC names of the following coordination compounds:
(a) $[Pt(NH_3)_2Cl(NO_2)]$
(b) $K_3[Cr(C_2O_4)_3]$
(c) $[Co\,Cl_2(en)_2]Cl$
(d) $[Co(NH_3)_5(CO_3)]Cl$
(e) $Hg[Co(SCN)_4]$
(a) Diamminechloridonitrito-N-platinum (II)
(b) Potassium trioxalatochromate (III)
(c) Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride
(d) Pentaamminecarbonatocobalt (III) chloride
(e) Mercury (I) tetrathiocyanato-S-cobaltate (III)

Q3. Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$
Ans.



cis



trans

Q4. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:
- (i) $K[Cr(H_2O)_2(C_2O_4)_2$
- (ii) $[Co(en)_3]Cl_3$
- (iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$
- (iv) $[Pt(NH_3)(H_2O)Cl_2]$

Ans. (i) Both geometrical (cis and trans) and optical isomers for cis.

(ii) Two optical isomers
(iii) Geometrical, ionization and linkage isomers.
(iv) Geometrical (cis and trans)

Q5. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionization isomers.
Ans. $[Co(NH_3)_5Cl]SO_4 + BaCl_2 \longrightarrow BaSO_4$ (white ppt)
$[Co(NH_3)_5(SO_4)]Cl + AgNO_3 \longrightarrow AgCl$ (white ppt)

Q6. The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?
Ans. Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridization) or square planar (dsp^2 hybridization). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the *d* orbitals.

Q7. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.
Ans. Pt = $5d^9\ 6s^1$
Pt (II) = $5d^8$, square planar geometry and dsp^2 hybridization.

Q8. Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.
Ans. $[Ni(CN)_4]^{2-}$ square planar geometry and dsp^2 hybridization.
$[NiCl_4]^{2-}$ Tetrahedral geometry and sp^3 hybridization.

Q9. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.
Ans. In both the complexes, Fe is in +3 oxidation state.
CN^- is strong field ligand, inner d-orbitals are involved, d^2sp^3 hybridization, one unpaired electron, weakly paramagnetic.
H_2O is weak field ligand, outer d-orbitals are involved, sp^3d^2 hybridization, five unpaired electrons, strongly paramagnetic.

Q10. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.
Ans. $[Co(NH_3)_6]^{3+}$ is an inner orbital complex, d^2sp^3 hybridization.
$[Ni(NH_3)_6]^{2+}$ is an outer orbital complex, sp^3d^2 hybridization.