COORDINATION COMPOUNDS

- TARGET 100
- these notes have been verified by top faculties of India & CBSE Science Toppers 2020
- Previous Year Qs have been integrated

COMPLETE NCERT
- No syllabus deduction

APNI KAKSHA

Raman Dattarwal
HOW TO STUDY THE NOTES?

Apni Kaksha

- Coloured and double sided print
- Revise the notes at least 3-4 time
- Write to revise | 10% rule
- Keep track of previous year qs
- See the marking scheme
Flow Chart Of Complete Chapter (NCERT)

IUPAC Nomenclature

- Octahedral
- Tetrahedral
- Square planar

Coordination Compounds

Addition Comp.

Double Comp.

Complex Comp.

Terminology related to Coordination Compounds

Co-ordination entity | Wavelength of light absorbed (nm) | Colour of light absorbed | Colour of coordination entity
--- | --- | --- | ---
\(\text{[Cu(NH}_3\text{)}_4\text{NO}_3\text{]}^2+\) | 535 | Yellow | Violet
\(\text{[Cu(NH}_3\text{)}_4\text{Cl}_2\text{]}^+\) | 500 | Blue Green | Red
\(\text{[Ni(NH}_3\text{)}_6\text{]}^2+\) | 475 | Blue | Yellow Orange
\(\text{[Cu(NO}_3\text{)}_4\text{]}^2+\) | 475 | Ultraviolet | Yellow Orange
\(\text{[Co(NH}_3\text{)}_6\text{]}^3+\) | 310 | Ultraviolet | Pale Yellow
\(\text{[CuCl}_4\text{]}^2-\) | 600 | Red | Blue
\(\text{[CuCl}_4\text{]}^2-\) | 498 | Blue Green | Purple

Isomerism

- Structural Isomerism
  - Geometrical
  - Optical

Bonding in Coordination Compounds

- Woman's Theory
- Valence Bond Theory
- Crystal Field Theory

Bonding in Metal Carbonyl

Synergetic bonding
Addition Compound :- They are formed by the combination of two or more stable compounds in stoichiometric ratio.

Double Salts

Compounds which lose their identity in solution are called double salts.

\[ \text{K}_2\text{SO}_4 + \text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O} \]

\[ \rightarrow \text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O} \text{ [A lotion]} \]

\[ \sqrt{3}\text{H}_2\text{O (Aqueous)} \]

\[ 2\text{K}^+ (aq.) + 2\text{Al}^{3+} (aq.) + 8\text{SO}_4^{2-} (aq.) \]

Coordination Compounds

Compounds which do not lose their identity in solution are called coordinate compounds.

\[ \text{Fe(CN)}_2^+ + \text{KCN} \rightarrow \text{K}_4[\text{Fe(CN)}_6] \]

\[ \rightarrow 4\text{K}^+ (aq.) + 4[\text{Fe(CN)}]_4^{3-} (aq.) \]

Terminology related to Coordination Compounds :-

9. Co-ordination Entity :- The central atom or ion and the ligands attached to it are enclosed in square brackets and are collectively known as Co-ordination entity or Co-ordination sphere.

For example :- \[ \text{[Fe(CN)}_6]^{3-}, \text{[Co(NH}_3)_6]^{2+} \]

Here Fe is a central metal and CN\(^{-}\) is a ligand.

Ligand :- The donor atoms, ions or molecules which donate a pair of electrons to the central metal atom or ion are called ligands.
b) Denticity: The no. of donor atoms present in a ligand, is called denticity of ligand.

→ Unidentate: Only one donor atom [Cl⁻ | NH₃ | H₂O etc.]

→ Bidentate / Didentate: When a ligand can bind through two donor atoms.

For example → Ethane-1,2-diamine \( \text{[NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{]} \)

or

Ethylenediamine \([\text{en}]\)

→ Polydentate: More than two donor atoms.

For example → Ethylene diamine tetra-azacate ion 

\( [\text{EDTA}]^{4-} \)

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→ It can bind through two nitrogen and four oxygen atoms to a central metal ion.

c) Ambidentate ligand: Unidentate ligands containing more than one co-ordinating atoms are ambidentate ligands.

For example → \( M \rightleftharpoons \text{N} \rightleftharpoons \text{O} \)

nitrito-N nitrito-O thiocyanato isothiocyanato

d) Co-ordination Number: The no. of ligand donor atoms to which the metal is directly bonded.

For example → \( [\text{PtCl}_6]^{2-} \): C.N. \( \Rightarrow 6 \)

\( [\text{Ni(NH}_3)_4 ]^{2+} \): C.N. \( \Rightarrow 4 \)

Octahedral Tetrahedral Square planar

e) Co-ordination Polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom (ion) defines a co-ordination polyhedron about the central atom.

\( [\text{Ni(CO)}_4] \)

\( [\text{Co(NH}_3)_6 ]^{3+} \)
Homoleptic and Heteroleptic Complexes:

- Complexes in which a metal is bound to only one kind of donor groups are known as homoleptic.
  - For example: \([\text{Co(NH}_3\text{)}_6]^{3+}\)

- Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic complex.
  - For example: \([\text{Co(NH}_3\text{)}_4\text{C}_2\text{H}_2\text{J}^+\]

### Formula | IUPAC Name
---|---
\(\text{C}_5\text{H}_5\text{N}\) or Pyridine | NO | Nitrosyl
\(\text{NH}_3\) | \(\text{NO}_2^-\)| Nitro
\(\text{H}_2\text{O}\) | \(\text{ONO}^-\)| Nitrito-0
CO | \(\text{NH}_2^-\)| Amido
\(\text{R-NH}_2\) | Alkylamine | Oxalato [OX]
\(\text{Cl}^-\) | Chlorido | Hydroxo-
\(\text{Br}^-\) | bromido |
\(\text{CN}^-\) | Cyanido | Cyanide
\(\text{CO}_3^-\) | Carbonato |
\(\text{SCN}^-\) | thiocyanato |
\(\text{NCS}^-\) | isothiocyanato |

### Oxidation No. of Central Atom:

\(\text{oxidation no. of central atom} = \frac{\text{oxidation no. of central atom} + \text{sum of charge on total ligands}}{\text{co-ordination sphere}}\)
$\text{Cu(NH}_3\text{)}_4^{2+}$ : Oxidation no. of Cu ??

$x + 4 $ (charge on NH$_3$) $= 2$

$x + 4 \times 0 = 2$ then $x = +2$

Nomenclature of Co-ordination Compounds

Rule for writing formula of mononuclear co-ordination complexes :-

a) Formula of Cation [simple or complex] is written first.

b) Co-ordination entity is enclosed in square bracket.

c) In coordination sphere, metal atom is written first, followed by ligands in alphabetical order of their names.

d) In abbreviated ligands [like en, ox] → first letter of abbreviation is considered.

e) When ligands are polyatomic, their formulas are enclosed in parenthesis.

   for example → (SCN), (PPh$_3$) etc.

f) There should be no space between the ligands and the metal.

g) For charged coordination entity → charge is indicated outside the square brackets as a right superscript with the no. before the sign.

   for example → [Co(CN)$_6$]$^{3-}$, [Cr(H$_2$O)$_6$]$^{3+}$ etc.

h) The charge of the cation is balanced by the charge of anion.

   for example:- $\left[ \text{Cr(H}_2\text{O)}_5\text{CH}_3 \right]\text{Cl}_2 \cdot \text{H}_2\text{O}$

   Alphabetical: Aqua > Chloro
Rules for naming of mononuclear Co-ordination Compounds →

1. Complex Cation is named first followed by anion (if present).
2. The ligands are named in alphabetical order before the name of metal atom(s).
3. Names of anionic ligands end in -o. [For example → cyano | chlorido].
   Neutral ligands have no special ending [H₂O → Aqua, NH₃ → ammine].
   Positive ligands end in -ium. [Not: Nitrosium]
4. Prefixes mono, di, tri... are used to indicate the number of the individual ligands.
   → When the names of ligands include a numerical prefix, then terms, bis, tris, tetrakis are used; the ligand to which they refer being placed in parenthesis.
5. Oxidation state of metal is indicated by Roman numerical in parenthesis.
6. If complex ion is a cation, the metal is named same as the element.
   → If complex ion is an anion, the name of the metal ends with suffix -ate.
   → The neutral complex molecule is named similar to that of the complex cation.

(i) [Cr(NH₃)₃(H₂O)₃]Cl₃ : triamminetriaquachromium(III) chloride

   Oxidation no. of Cr + 3 (charge on NH₃) = 3 (charge on H₂O) = 3 (charge on Chlorine)
   = 0
   → Oxidation no. of Cr = +3

(ii) [Co(C(NH₂)₂CH₂NH₂)₃]₄(SO₄)₃ : tetrakis (ethane-1,2-diamine)cobalt(III) Sulphate

   4(x + 3 × 0 + 3 × 0 + 3 × -1) = 0
   → x = +3

(iii) [Ag(NH₃)₂] [Ag(CN)₂] : diammine silver(I) dicyanoargentate(I)
\[ \text{Ni(CO)}_{4} \rightarrow \text{TetraCarbonyl nickel (0)} \rightarrow \text{K}_4[\text{Fe(CN)}_6] \]

\[ x + 4 (0) = 0 \quad \text{then} \quad x = 4 \]

Potassium hexacyanoferrate (II).

\[ 4 (+1) + x + 6 (-1) = 0 \quad \text{then} \quad x = +2 \]

\[ \text{chlo}r/o \text{h}l/o\text{nido} \rightarrow u. \]

\[ \text{Pt(en)}_{2}U_2^{2+} \rightarrow \text{dichloro(bis(ethane-1,2-diamine)} \text{platinum (IV) ion} \]

\[ \text{Ni(NH}_3)_6 U_4 \rightarrow \text{hexaamine nickel (II) chloride} \]

\[ \text{PtU(NH}_3CH}_3(NH}_3)_2 \rightarrow \text{diamin chloride methylamine platinum (II) chloride} \]

\[ \text{Pt(NH}_3)_4 U_2 \rightarrow \text{tetraamine dichloro platinum (IV) chloride} \]

\[ \text{Cr(NH}_3)_6 \rightarrow \text{Co(CN)}_6 \rightarrow \text{hexaamine chromium (III) hexacyanocobaltate (III)} \]

\[ \text{Cr(NH}_3)_5 \rightarrow \text{Co(NH}_3)_6 \rightarrow \text{Pentaamine dicyano cobalt (III) chloride} \]

\[ \text{Cr(NH}_3)_5 \rightarrow \text{ZnU}_4 \rightarrow \text{Pentaamine thiocyanato chromium (III) tetrachloro zincate (II)} \]

\[ \text{Co(NH}_3)_5 \rightarrow \text{Cu}_2 \rightarrow \text{Pentaamine chloride cobalt (III) chloride} \]

\[ \text{Cr(NH}_3)_2 \rightarrow \text{Cu(en)} \rightarrow \text{Diamine dichloro (ethane-1,2-diamine) chromium (III) chloride} \]

\[ \text{K}_3[\text{Fe(CN)}_6] \rightarrow \text{Potassium hexacyanoferrate (III)} \]

\[ \text{Co(NH}_3)_6 \rightarrow \text{U}_3 \rightarrow \text{Hexaamine cobalt (III) chloride} \]

\[ \text{Co(en)}_3^{3+} \rightarrow \text{Tri's (ethane-1,2-diamine) cobalt (III) ion} \]
\[
\text{[Ni(II)]}^{2+} : \text{Tetrachlorido nickelate (II) ion.} \\
\text{[Co(NH}_3\text{)}_5(\text{NO}_2\text{)}]^{2+} : \text{Pentaamminenitrito-N cobalt (III) ion.} \\
\text{[Pt(NH}_3\text{)}_2\text{U}_2\text{]} : \text{Diammine dichlorido platinum (II).} \\
\rightarrow \text{Co-ordination No} \rightarrow 4 \\
\rightarrow \text{oxidation State} \rightarrow +2 \\
\text{[Co(C}_2\text{O}_4\text{)}_3]^{3-} : \text{Trioxalatocobaltate (III) ion.} \\
\text{[Cr(CO)}_6\text{]} : \text{Hexacarbonyl chromium (0).} \\
\text{[PtU}_3\text{(C}_2\text{H}_4\text{)}\text{]} : \text{Trichlorido ethene platinum (IV)} \\
\text{[CoBr}_2\text{(en)}_2\text{]}^{+} : \text{Dibromido bis (ethane -1,2 - diamine) cobalt (III) ion.} \\
\text{[K}_3\text{[Fe(C}_2\text{O}_4\text{)}_3\text{]} : \text{Potassiumtrioxalato ferrate (III) ion.} \\
\text{[Pt(NH}_3\text{)}_4\text{U}_4\text{]} : \text{Hexaammine platinum (IV) chloride.} \\
\text{[Cr(C}_2\text{O}_4\text{)}_3]^{3-} : \text{Trioxalatocromate (III) ion} \\
\text{[Co(en)}_2\text{U}_2\text{]}^{+} : \text{Dichlorido bis (ethane -1,2 - diamine) cobalt (III) ion} \\
\rightarrow \text{Hexaammine cobalt (III) sulphate : [Co(NH}_3\text{)}_6\text{]}_2(\text{SO}_4\text{)}_3 \rightarrow \text{[Deli 2013]} \\
\text{Potassiumtrioxalatocromate (III) : K}_3\text{[Cr(C}_2\text{O}_4\text{)}_3\text{]} \\
\text{Potassiumtrioxalato aluminate (III) : K}_3\text{[Al(C}_2\text{O}_4\text{)}_3\text{]} \\
\text{Dichlorido bis (ethane -1,2 - diamine) cobalt (III) ion : [CoU}_2\text{(en)}_2\text{]}^{+} \rightarrow \text{[CBSE 2017]}
Werner's Theory: Werner was the first to formulate his idea about the structures of coordination compounds. The main postulates are:

1. In coordination compounds metals show two types of valency - 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.
4. The ions/groups bound by secondary valency to metal have spatial arrangements corresponding to different coordination numbers.

NOTE: In modern formulation -> Primary valency corresponds to oxidation state of metal.

Secondary valency corresponds to coordination number of central metal.

Spatial arrangements are called coordination polyhedra.
Experiments: 1. In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of chloride ions could be precipitated as AgCl on adding excess AgNO₃ solution but some remained in solution.

\[
\text{CoCl}_2 \cdot 6\text{NH}_3 \xrightarrow{\text{AgNO}_3 \text{ Excess}} 3\text{ mol AgCl}
\]

\[
\text{[Co(NH}_3)_6]\text{Cl}_2 \xrightarrow{\text{AgNO}_3 \text{ Excess}} 3\text{ AgCl + [Co(NH}_3)_6\text{Cl}^{3+}} \quad \text{GNH}_3 \quad 3\text{Cl}^-
\]

\[
\text{CoCl}_2 \cdot 5\text{NH}_3 \xrightarrow{\text{AgNO}_3 \text{ Excess}} 2\text{ mol AgCl}
\]

\[
\text{[Co(NH}_3)_5\text{Cl}]\text{Cl}_2 \xrightarrow{\text{AgNO}_3 \text{ Excess}} 2\text{ AgCl + [Co(NH}_3)_5\text{Cl}^{2+}} \quad 5\text{NH}_3 \quad 1\text{Cl}^-
\]

\[
\text{CoCl}_2 \cdot 4\text{NH}_3 \xrightarrow{\text{AgNO}_3 \text{ Excess}} 1\text{ mol AgCl}
\]

\[
\text{[Co(NH}_3)_4\text{Cl}_2]\text{Cl} \xrightarrow{\text{AgNO}_3 \text{ Excess}} \text{[Co(NH}_3)_4\text{Cl}_2]^{3+} + \text{AgCl} \quad 4\text{NH}_3 \quad 2\text{Cl}^-
\]

→ As we know conductivity of a solution depends on no. of ions present in solution.

Experimental order of conductivity: \text{CoCl}_2 \cdot 6\text{NH}_3 > \text{CoCl}_2 \cdot 5\text{NH}_3 > \text{CoCl}_2 \cdot 4\text{NH}_3

No. of ions in their solution:

\[
\begin{align*}
1 \quad \text{[Co(NH}_3)_6\text{Cl}^{3+} & 3\text{Cl}^- \\
1 \quad \text{[Co(NH}_3)_5\text{Cl}^{2+} & 2\text{Cl}^- \\
1 \quad \text{[Co(NH}_3)_4\text{Cl}_2]^{3+} & 1\text{Cl}^-
\end{align*}
\]

→ When a coordination compound \text{CrCl}_3 \cdot \text{CH}_2\text{O} is mixed with AgNO₃, 2 moles of AgCl are precipitated per mole of compound.

\[
\text{CrCl}_3 \cdot \text{CH}_2\text{O} \xrightarrow{\text{AgNO}_3} 2\text{ AgCl l } \text{ means that } 2\text{Cl}^- \text{ is ionisable.}
\]

Write structural formula:

\[
\text{[Cr(H}_2\text{O})_5\text{U}]\text{Cl}_2 \cdot \text{H}_2\text{O}
\]

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Valence Bond Theory

According to this theory, the metal ion or atom under the influence of ligand can use its \((n-1)d\), ns, np, nd orbitals for hybridisation to give a set of equivalent orbitals of definite geometry.

These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Type of hybridisation</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>(sp^3)</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td>(dsp^2)</td>
<td>Square Planar</td>
</tr>
<tr>
<td>6</td>
<td>(sp^3d^2)</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td>(d^2sp^3)</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>

It is possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of VB.T.

Magnetic moment \(n = \sqrt{n(n+2)}\)

- \(n\) = No. of Unpaired electrons.

Example: \([\text{Co}(\text{NH}_3)_6]^{3+}\) : Diamagnetic in nature.

- \(\text{Co}^{3+}\) Ion: \(3d^6\) 

Hybridisation: \(d^2sp^3\)

- Inner orbital: \(d^2\) 
- Outer orbital: \(sp^3\) 

Complex: \(\text{NH}_3\) 

6 ligands: Octahedral

[Delhi 2013] [2M]
→ Inner Orbital Complex : d^2sp^2 : Low spin complex : spin paired complex.

\[
\text{Co}^3+ \text{ Ion} : \quad (3d^6) \quad \text{Hybridisation} : \quad \text{Sp}^3d^2 \text{ Hybrid}
\]

\[\text{Co}_6^3^- : \quad \text{Paramagnetic Octahedral complex.} \quad \text{Presence of unpaired electrons.} \]

\[\text{Co}_6^3^- : \quad \text{Paramagnetic in nature.} \quad \text{[CSE 2017]} \]

\[\text{Ni}^{2+} \text{ Ion} : \quad (3d^8) \quad \text{Hybridisation} : \quad \text{Sp}^3 \text{ Hybrid} \]

\[\text{NiCl}_4^{2-} : \quad \text{Diamagnetic in nature.} \quad \text{[DETH 2012]} \]

\[\text{Ni}^{(0)} : \quad (3d^8 4s^2) \quad \text{Hybridisation} : \quad \text{Sp}^3 \text{ Hybrid} \]

\[\text{Ni(CO)}_4 : \quad \text{Diamagnetic in nature.} \]

\[\text{Ni}^{(0)} : \quad \text{Hybridisation} : \quad \text{Sp}^3 \text{ Hybrid} \]
\([\text{Ni}^+ (\text{CN})_4]^{3-}\): Square Planar Complex: Diamagnetic.

\(\text{Ni}^{+2}\) Ion: 

\(|\text{3d}^8\rangle\)

Hybridisation: 

\(|\text{d}^2\text{sp}^2\rangle\): Square Planar

\([\text{Ni}^+ (\text{CN})_4]^{3-}\):

\(|\text{CN}^-\rangle\)

**Note:**

- For octahedral complex: Always \(d^2\text{sp}^3\)
- 2 Inner d orbitals are always available for hybridisation.
- Always \(sp^3d^2\)
- Because inner d orbitals are not available.

\([\text{Mn}(\text{CN})_6]^{3-}\): Magnetic moment of 2 electrons: \(d^2\text{sp}^3\): Paramagnetic

\([\text{Mn}^2+ (\text{CN})_6]^{3-}\): Magnetic moment of 4 electron: \(sp^3d^2\)

\([\text{Fe}(\text{CN})_6]^{3-}\): \(M = \sqrt{n(n+1)} = \sqrt{5(5+1)}\): 1 unpaired electron: \(d^2\text{sp}^3\)

\([\text{Fe}^2+ (\text{CN})_6]^{3-}\): \(M = \sqrt{s(5+2)}\): 5 unpaired electrons: High Spin Complex \([sp^3d^2]\)

\([\text{Co}^2+ (\text{CN})_6]^{3-}\): Paramagnetic: \(d^2\text{sp}^3\): Inner orbital complex \([3d^6]\)

\([\text{CoF}_6]^{3-}\): Paramagnetic with four unpaired electron: \(sp^3d^2\)

**Limitation of VBT:**

(i) It involves no. of assumptions.

(ii) It does not explain colour of coordination compounds.

(iii) It does not give explanation of kinetic and thermodynamic stabilities of complex.
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 ligand.

→ Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules (H₂O, NH₃ etc.)

↓
[O⁻, O²⁻, OH⁻ etc.]

Crystal Field Splitting in Octahedral Complexes:

→ Under the influence of 6 ligands field, degeneracy of d orbitals has been removed due to ligand-metal electron repulsions in octahedral complex.

→ Removal of degeneracy gives three orbitals [dₓ²-y², dₓz, dᵧz] of lower energy (t₂g) and two orbitals of higher energy [dₓ²+y², dₓz, dᵧz = eg set].

→ dₓ²-y² and dₓz orbitals point towards the axles along the direction of the ligand, will experience more repulsion and will raise in energy.

→ dₓz, dᵧz, dₓz orbitals are directed between axes, will be lowered in energy (relative to average energy (in the spherical crystal field).

→ Splitting of degenerate levels due to the presence of ligands in a definite geometry is called **crystal field splitting** and the energy separation is denoted by Δₑ [crystal field splitting energy].

[Delhi 2011c/11]
The extent of splitting depends upon the field produced by ligand and charge on metal ion.

\[ \text{d}^1 \rightarrow \text{t}_{2g}^2 \text{eg} \]

\[ \text{d}^2 \rightarrow \text{t}_{2g}^2 \text{eg} \]

\[ \text{d}^3 \rightarrow \text{t}_{2g}^2 \text{eg} \]

\[ \text{d}^4 \rightarrow \text{eg} \]

Spectrochemical Series:

- If ligands are arranged in a series in the order of increasing field strength, then that series is called spectrochemical series.

- Halogen donors < oxygen donors < nitrogen donors < carbon donors

- I^- < Br^- < SCN^- < CN^- < S^2- < P^- < OH^- < C_2O_4^{2-} < H_2O < NCs^- < EDTA^- < NH_3 < en < CN^- < CO

- Generally, CN^- & CO are SFL with M^2+ and most ligands are WFL.

- CN^-, CO, en, NH_3 & H_2O are SFL with M^3+

**Question:**

a. \([\text{CoFe}_2]^{3-}\)  

b. \([\text{Co(en)}_3]^{3+}\)  

c. \([\text{Co(NH}_3)_6]^{3+}\)

- f^- as WFL  
- en as SFL  
- NH_3 as SFL
Crystal Field Splitting in Tetrahedral Complexes:

- In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

- For some metal and ligand: \( \Delta_t = \frac{g - 3}{g} \Delta_o \)

\[
\begin{align*}
[M\ell_6] & \rightarrow \Delta_o \\
[M\ell_4] & \rightarrow \Delta_t
\end{align*}
\]

\[d^4\]

\[t_{2g}^2 \epsilon_g^2\]

\[\epsilon_g\]

\[t_{2g} \epsilon_g^2\]

\[\Delta_t < \epsilon_g\]

\[\text{For tetrahedral complex:}\]

\[\Delta_t < \epsilon_g\]

\[\text{Always}\]

\[\text{Abhi Kaksha}\]

**Colour in Coordination Compounds**

- When light of certain frequency falls on the complex, it absorbs light from the visible range for transition of electrons from lower d-energy level to higher d-energy level. This transition is called d-d transition of electron.

- Colour of the compound is the complementary colour of absorbed light. For example, if green is absorbed by the complex, it appears red.

\[[\text{Ti(H}_2\text{O)}_6]^{2+}\]: violet in colour.

\[d^1\]

\[t_{2g}^1 \epsilon_g^0\]

Transition: \(t_{2g}^1 \epsilon_g^0 \rightarrow t_{2g}^0 \epsilon_g^1\)

- In absence of ligand, crystal field splitting does not occur and hence the substance is colourless.

- \([\text{Ti(H}_2\text{O)}_6]^{3+}\) violet → \([\text{Ti(H}_2\text{O)}_6]^{2+}\) Colourless.

- \([\text{CuCl}_2]^{2+}\) blue → \([\text{CuCl}_2]^{+}\) Colourless.
### Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

<table>
<thead>
<tr>
<th>Coordination entity</th>
<th>Wavelength of light absorbed (nm)</th>
<th>Colour of light absorbed</th>
<th>Colour of coordination entity</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CoCl(NH₃)₆]²⁺</td>
<td>535</td>
<td>Yellow</td>
<td>Violet</td>
</tr>
<tr>
<td>[Co(NH₃)₅(H₂O)]³⁺</td>
<td>500</td>
<td>Blue Green</td>
<td>Red</td>
</tr>
<tr>
<td>[Co(NH₃)₆]³⁺</td>
<td>475</td>
<td>Blue</td>
<td>Yellow Orange</td>
</tr>
<tr>
<td>[Co(CN)₆]³⁻</td>
<td>310</td>
<td>Ultraviolet</td>
<td>Pale Yellow</td>
</tr>
<tr>
<td>[Cu(H₂O)₄]²⁺</td>
<td>600</td>
<td>Red</td>
<td>Blue</td>
</tr>
<tr>
<td>[Ti(H₂O)₆]³⁺</td>
<td>498</td>
<td>Blue Green</td>
<td>Purple</td>
</tr>
</tbody>
</table>

**Shapes of different coordination polyhedra.** M represents the central atom/ion and L, a unidentate ligand.

**d orbital splitting in a tetrahedral crystal field.**
Limitations of CFT: From the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. But it is not true because anionic ligands are found at the low end of spectrochemical series.

**Bonding in metal carbonyls**

- Compounds which have at least one metal-carbon bond are called organometallic compounds.
- The metal-carbon bond in metal carbonyl possesses both $\sigma$ and $\pi$ character.
- The $\sigma$ bond is formed by the donation of a lone pair of electrons on the carbonyl carbon into a vacant orbital of metal.
- The $\pi$ bond is formed by the donation of a pair of electrons from a filled d-orbital of metal into a vacant $\pi^*$ orbital of CO.
- The metal-to-ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

**Stability of Coordination Compounds**

- The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium.
- Equilibrium constant for the association expresses the stability.

$$M + 4L \rightleftharpoons ML_4$$

- Value of equilibrium constant $K \Rightarrow [ML_4]^+$$

**Stepwise Stability Constant:** The equilibrium constant of each step of a complex reaction is called stepwise stability constant ($k_1, k_2, \ldots$) [CBE 2011c] ($2M$)

**Overall Stability Constant:** The equilibrium constant for the reaction.

$\beta_+$

**Abni Kaksha:**
\[ \begin{align*}
(i) \quad M + L \rightleftharpoons ML & \quad k_1 = \frac{[ML]}{[M][L]} \\
(ii) \quad ML + L \rightleftharpoons ML_2 & \quad k_2 = \frac{[ML_2]}{[ML][L]} \\
(iii) \quad ML_2 + L \rightleftharpoons ML_3 & \quad k_3 = \frac{[ML_3]}{[ML_2][L]} \\
(iv) \quad ML_3 + L \rightleftharpoons ML_4 & \quad k_4 = \frac{[ML_4]}{[ML_3][L]}
\end{align*} \]

\[ M + 4L \rightleftharpoons ML_4 \quad \beta_4 = \frac{[ML_4]}{[M][L]^4} \]

Then, \[ \beta_4 = k_1 \cdot k_2 \cdot k_3 \cdot k_4 \]

**Important Previous Year Questions:**

1. **What is meant by chelate effect?** [CSE\,2015] 1M

   When a denticulate or polydentate ligand containing donor atoms positioned in such a way that, they coordinate with the central metal ion forming a five or six membered ring. The effect is called chelate effect.

2. **As a result of chelate effect, the stability of the complex increases.**

3. **Stability of complex:** \([\text{Co(CN)}_6]^{3-} < [\text{Co(NH}_3)_3]^{3+} \]

   due to chelate effect

   \( \rightarrow \) More stable

4. **[CSE\,2012] 1M**

   \([\text{III}] \) CO is a stronger complexing agent than NH\(_3\). Why?

   \( \rightarrow \) There exist a backbonding in CO complexes in which CO accepts electron density from the filled d orbitals of metal atom into their \( \pi^* \) orbitals. So, there are \( \sigma \) as well as \( \pi \) interaction with metal in case of CO. But NH\(_3\) makes only \( \sigma \) bond with metal. Therefore CO is a stronger complexing agent than NH\(_3\).
Write the state of hybridisation, the shape and the magnetic behaviour of following complex entities.

\[ [\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+ \rightarrow [\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^{+1} \rightarrow \text{Cr}^{3+} \rightarrow d^3 \]

No pairing happens.

\[ \downarrow \]

\[ \text{Paramagnetic} \]

in nature due to unpaired electrons.

\[ [\text{Cr}(\text{NH}_3)_2\text{Cl}_2]^+: \]

\[ d^2sp^3: \text{Hybridisation} \]

octahedral

\[ [\text{Co}(\text{en})_3]^3+ \rightarrow [\text{Co}(\text{en})_3]^{+3} \rightarrow \text{Co}^{3+} \rightarrow d^6 \]

\[ \text{Paring happens due to presence of 3d} \]

\[ \text{Co}^{3+} \text{Ion:} \]

\[ d^6 \]

\[ \text{Octahedral} \]

\[ [\text{Co}(\text{en})_2]^{3+}: \]

\[ d^2sp^3: \text{Hybridisation} \]

\[ \text{Octahedral} \]

\[ [\text{Ni}(\text{CN})_4]^2- \rightarrow [\text{Ni}(\text{CN})_4]^{2+} \rightarrow \text{Square planar} \]

\[ \text{Diagonalistic} \]

\[ d^8 \text{Hybridisation} \]

\[ \text{K}_4[\text{Mn}(\text{CN})_6] \]

\[ \text{U} \text{P} \text{AC} \text{ Name:} \text{ Potassium hexacyano manganate (III)} \]

\[ +1 + x + 6(-1) = 0 \]

\[ \text{Then} \ x = +2 \]

\[ \text{K}_4[\text{Mn}(\text{CN})_6] \rightarrow [\text{Mn}(\text{CN})_6]^{4-} \rightarrow \text{Mn}^{2+} \rightarrow [\text{Ar}]3d^5 \]

\[ \text{Paramagnetic} \]

\[ \text{One unpaired electron} \]
Isomerism in Coordination Compounds

Isomerism arises due to different structural arrangements or special arrangements of compounds having same formula.

**Structural Isomerism:**

1. **Ionisation Isomerism:** When the complexes with same composition give different ions in solution.

   Example: \[ \text{[Co(NH}_3\text{)}_5 \text{NO]} \text{SO}_4 \quad \text{and} \quad \text{[Co(NH}_3\text{)}_5 \text{SO}_4]Br} \]

   \[ \downarrow \quad \downarrow \]

   \[ \text{[Co(NH}_3\text{)}_5 \text{Br]}^{2+} + \text{SO}_4^{2-} \quad \text{[Co(NH}_3\text{)}_5 \text{SO}_4]^{4+} + \text{Br}^- \]

2. **Solvate / Hydrate Isomerism:** When complex differs in the number of water (solvent) molecules present as ligand.

   Example: \[ \text{[Cr(H}_2\text{O)}_6\text{]}\text{Cl}_3 \quad \text{and} \quad \text{[Cr(H}_2\text{O)}_5\text{Cl]H}_2\text{O and [Cr(H}_2\text{O)}_4\text{Cl}_2\text{H}_2\text{O}} \]

3. **Linkage Isomerism:** When complexes differ only in the point of attachment of the ambidentate ligand with central metal atom.

   Example: \[ \text{[Co(NH}_3\text{)}_5\text{(NO)}_2\text{]} \text{U}_2 \quad \text{and} \quad \text{[Co(NH}_3\text{)}_5\text{(ONO)}\text{]} \text{U}_2 \]

4. **Coordination Isomerism:** When the interchange of the ligands take place between ionic and anionic entities of different metal ions present in a complex.

   Example: \[ \text{[Co(en)}_3\text{]} \quad \text{[Cr(en)}_6\text{]} \quad \text{and} \quad \text{[Co(en)}_3\text{]} \quad \text{[Co(CN)}_6\text{]} \]

   \[ \rightarrow \quad \text{[Pt(NH}_3\text{)}_4\text{]} \quad \text{[CuCl}_4\text{]} \quad \text{and} \quad \text{[Cu(NH}_3\text{)}_4\text{]} \quad \text{[PtCl}_4\text{]} \]

   \[ \rightarrow \quad \text{[CGSE 2018]} \quad \text{[1M]} \]

**Stereo-Isomerism:**

5. **Geometrical Isomerism:** When similar groups are present in adjacent position, it is cis. When they are present in opposite position, it is trans.

   It occurs in square planar compounds and octahedral compounds.
Geometrical Isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$:

Geometrical Isomers of $[\text{Co(NH}_3)_2\text{Cl}_2]^+$:

Geometrical Isomers of $[\text{CoCl}_2(\text{en})_2]$:

Geometrical Isomers of $[\text{Mn}_3\text{by}_3]$:

- Facial [fac]
- Meridional [mer]

Example: $[\text{Co(NH}_3)_3(\text{NO}_2)_3]$  

Optical Isomerism: This is shown by complexes whose mirror images are non-superimposable. Such complexes are called optical isomers.

Optical Isomers (d and l) of $[\text{Co(en)}_2]^{3+}$:

Optical Isomers (d and l) of cis $[\text{PtCl}_2(\text{en})_2]^{2+}$:

From $[\text{PtCl}_2(\text{en})_2]^{2+}$ is optically inactive.
Example

Draw structures of geometrical isomers of \([\text{Fe(NH}_3\text{)}_2\text{(CN)}_4^-]\)

Solution

\[
\begin{align*}
&\text{cis} & &\text{trans} \\
&\begin{array}{c}
\text{Fe} \\
\text{NC} \\
\text{NC} \\
\text{CN} \\
\text{NH}_3 \\
\end{array} & &\begin{array}{c}
\text{Fe} \\
\text{NC} \\
\text{NC} \\
\text{CN} \\
\text{NH}_3 \\
\end{array}
\end{align*}
\]

Example

Out of the following two coordination entities which is chiral (optically active)?
(a) \(\text{cis-}[\text{CrCl}_2(\text{ox})_2]^{3-}\)  
(b) \(\text{trans-}[\text{CrCl}_2(\text{ox})_2]^{3-}\)

Solution

The two entities are represented as

\[
\begin{align*}
&\text{cis} & &\text{trans} \\
&\begin{array}{c}
\text{ox} \\
\text{Cl} \\
\text{Cl} \\
\text{ox} \\
\text{ox} \\
\end{array} & &\begin{array}{c}
\text{ox} \\
\text{Cl} \\
\text{Cl} \\
\text{ox} \\
\text{ox} \\
\end{array}
\end{align*}
\]

Out of the two, (a) \(\text{cis - [CrCl}_2(\text{ox})_2]^{3-}\) is chiral (optically active).