

9. Coordination Compounds

Coordination compounds are complex compounds in which transition metal atoms are bound to a number of anions or neutral molecules.

- **Coordination entity:** A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. Example: in $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ represents coordination entity.
Counter ions: The ions present outside the coordination sphere are called counter ions. For example: in the complex $K_4[Fe(CN)_6]$, K^+ is the counter ion.

Postulates of Werner's theory of coordination compounds:

- In coordination compounds, there are two types of linkages (valences) – primary and secondary.
- The primary valences are ionisable and are satisfied by negative ions.
- The secondary valences are non-ionisable and are satisfied by negative ions or neutral molecules. The secondary valence is equal to the coordination number of a metal and remains fixed for a metal.
- Different coordination numbers have characteristic spatial arrangement of the ions or groups bound by the secondary linkages.

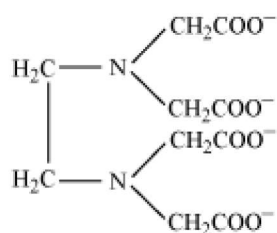
Difference between a double salt and a complex:

- In water, a double salt dissociates completely to give simpler ions. Examples of double salt: carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), Mohr's salt [$FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O$]
- Complex ions do not dissociate further to give simpler ions. For example, $[Fe(CN)_6]^{4-}$, $[Fe(C_2O_4)_3]^{3-}$

Ligands:

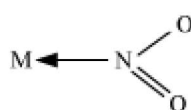
Ions or molecules bound to the central metal atom or ion in the coordination entity

- **Denticity:** The number of donor atoms present in ligand
- Didentate –
 $H_2N - CH_2 - CH_2 - NH_2$ $C_2O_4^{2-}$
Ethane-1,2-diamine Oxalate
- Polydentate –

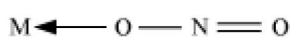


Ethylenediaminetetraacetate (EDTA^{4-})

- Ambidentate –
(Can bind through two different atoms)



Nitrito – N



Nitrito – O



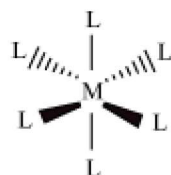
Thiocyanato



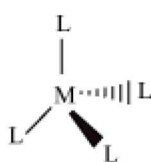
Isothiocyanato

Coordination number: Number of ligand donor atoms bonded directly to the metal

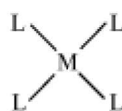
Coordination polyhedral:



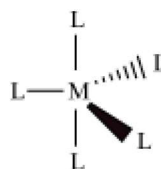
Octahedral



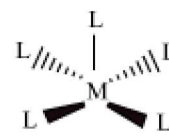
Tetrahedral



Square
planar



Trigonal
bipyramidal



Square
pyramidal

Homoleptic and heteroleptic complexes:

- Homoleptic complexes: In which metal is bound to only one kind of donor groups, e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Heteroleptic complexes: In which metal is bound to more than one kind of donor groups, e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

Naming of mononuclear coordination compounds:

- The cation is named first in both physically and negatively charged coordination entities.

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- The ligands are named in alphabetical order, before the name of the central atom/ion.
 - Names of the anionic ligands end in $-o$.
[Exceptions: aqua (H_2O), ammine (NH_3), carbonyl (CO), nitrolyl (NO)]
 - To indicate the number of the individual ligands, the prefixes mono-, di-, tri-, etc., are used. If these prefixes are present in the names of ligands, then the terms bis-, tris-, tetrakis-, etc., are used.
 - Oxidation state of the metal is indicated in Roman numerals, in parentheses.
 - If the complex ion is cation, then the metal is named as the element.
If the complex ion is anion, then the metal is named with ‘-ate’ ending.
 - The neutral complex molecule is named as the complex cation.
 - 1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is named as:
 - triamminetriaquachromium(III) chloride
 - 2. $[Co(H_2NCH_2CH_2NH_2)_2(SO_4)_3]$ is named as:
 - tris(ethane-1,2-diammine)cobalt(III) sulphate
 - 3. $[Ag(NH_3)_2][Ag(CN)_2]$ is named as:
 - diamminesilver(I) dicyanoargentate(I)
 - 4. $K_2[Zn(OH)_4]$
 - Potassium tetrahydroxozincate(II)
 - 5. $[Co(NH_3)_4(H_2O)Cl]Cl_2$
 - Tetraammineaquachloridocobalt(III) chloride
 - 6. $Hg[Co(SCN)_4]$
 - Mercury tetrathiocyanatocobaltate(III)
 - 7. $[Pt(NH_3)_2Cl(NO_2)]$
 - Diamminechloridonitrito-N-platinum(II)
 - 8. $K_3[Cr(C_2O_4)_3]$
 - Potassium trioxalatochromate(III)

Using IUPAC norms write the formulas for the following:

(i) Potassium tetracyanonickelate(II)

(ii) Pentaamminenitrito-O-cobalt(III)

(iii) Hexaamminecobalt(III) sulphate

(iv) $K_2[Ni(CN)_4]$

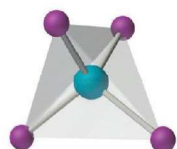
(v) $[Co(ONO)(NH_3)_5]^{2+}$

(vi) $[Co(NH_3)_6]_2(SO_4)_3$

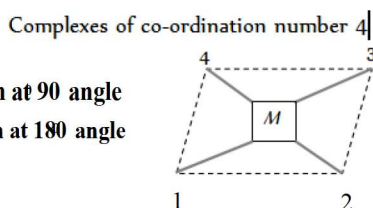
Isomerism in coordination compounds:

Geometric isomers, Cis and trans positions

Two Cis positions:- position at 90 angle
Two trans positions:- position at 180 angle



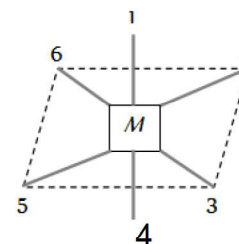
Tetrahedral and square planar ML_4



Complexes of co-ordination number 6

Cis-Positions : 1-2, 2-3, 3-4, 4-5

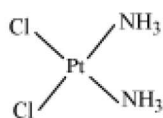
Trans - position : 1-4, 2-5, 3-6



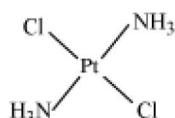
In Tetrahedral geometry : In this case all the four ligands are symmetrically arranged with respect to one another as such geometrical isomerism is not possible.

• Stereoisomerism –

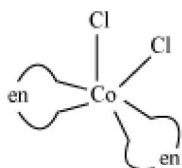
➤ Geometrical isomerism:



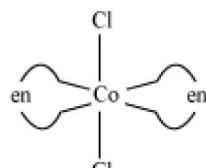
Cis



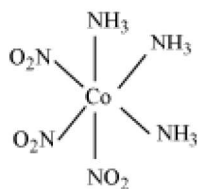
Trans



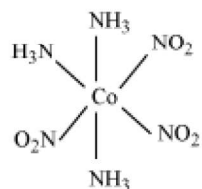
Cis



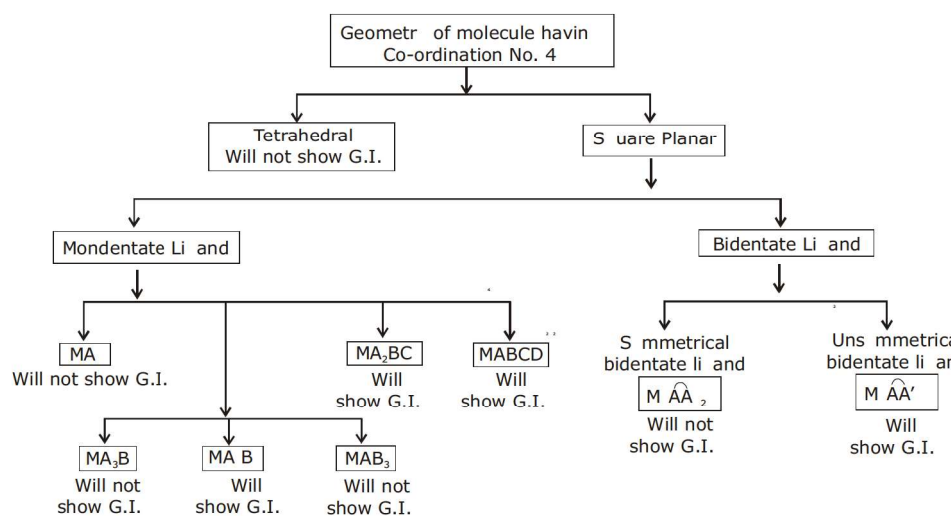
Trans



facial (fac-)



meridional (mer-)



S.No.	Complex having Co-ordination No. 6	Number of Geometrical isomers
1.	MA_6	0
2.	MA_5B	0
3.	MA_4B_2	2
4.	MA_3B_3	2
5.	$MA_2B_2C_2$	5
6.	$MABCDEF$	15

Octahedral complexes of general formulae show optical isomer

(i) $[Ma_2b_2c_2]^{n\pm}$

(ii) $[Mabcdef]$

(iii) $[M(AA)_3]^{n\pm}$

(iv) $[M(AA)_2a_2]^{n\pm}$ (where AA = symmetrical bidentate ligand)

(v) $[M(AA)_2ab]^{n\pm}$

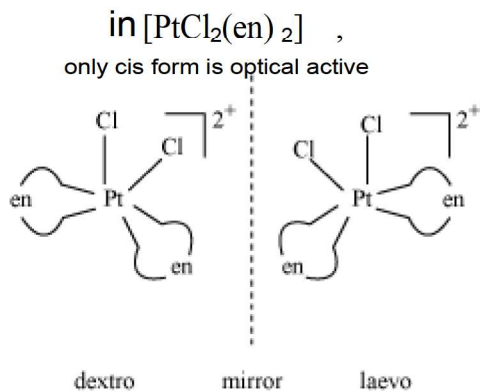
(vi) $[M(AB)_3]^{n\pm}$ (where AB = unsymmetrical bidentate ligand)

➤ Optical isomerism:

Optical isomers (enantiomers) are mirror images which cannot be superimposed on one another.

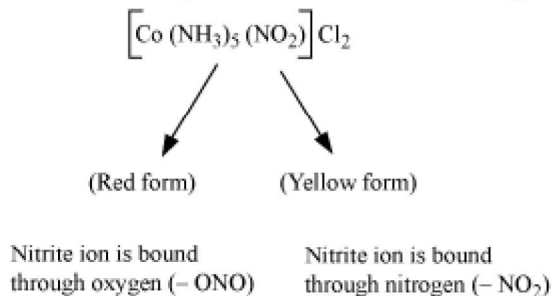
➤ The molecules or ions which cannot be superimposed are called chiral.

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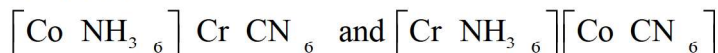
- Structural isomerism –
 - Linkage isomerism:

Arises due to the presence of ambidentate ligand



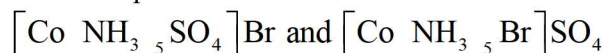
- Coordination isomerism:

Arises due to the interchange of ligands between cationic and anionic entities of different metal ions



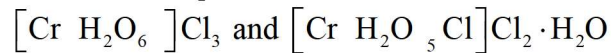
- Ionisation isomerism:

Arises due to the interchange of ligands between the inside and the outside of the coordination sphere



- Solvate isomerism (Hydrate isomerism when solvent is water):

Arises depending upon whether a solvent molecule is directly bonded to the metal ion or is present as a free solvent molecule.

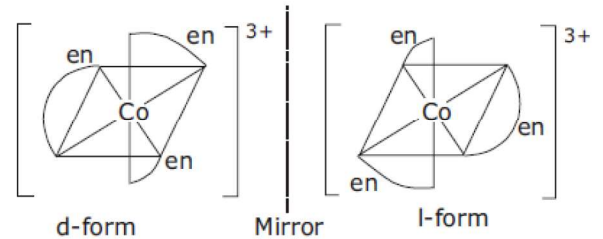
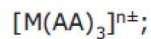


violet (grey – green)

Valence bond theory:

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral

optical isomerism in complex with three bidentate ligand



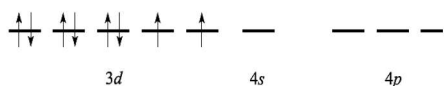
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

- Inner-orbital or low spin or spin-paired complexes: Complexes that use inner d -orbitals in hybridisation, e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Outer-orbital or high spin or spin-free complexes: Complexes that use outer d -orbitals in hybridisation, e.g., $[\text{CoF}_6]^{3-}$

Limitations of valence bond theory:

- A number of assumptions are involved.
- Quantitative interpretation of magnetic data is not given.
- The exhibition of colour by coordination compounds is not explained.
- The thermodynamic or kinetic stabilities of coordination compounds are not quantitatively interpreted.
- Whether a complex of coordination number 4 is tetrahedral or square planar cannot be exactly predicted.
- Weak and strong ligands cannot be distinguished.

illustration of Effect of ligand on Ni^{2+} ion in co No=4



in both complex Ni is same with +2 state in but in 1st Cl^- is weak ligand and can not force pairing of e so 3d orbital can be made vacant so it use 4s, 4p to have sp^3 hybrid but in 2nd case CN^- do forced pairing and creat vacant d orbital in 3d subshell and can hve dsp^2 hybridisation

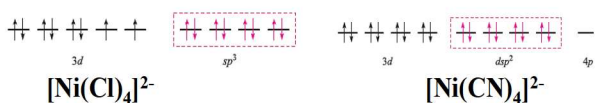


illustration of Effect of ligand on Fe^{3+} ion in co No=6

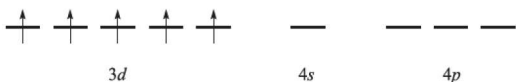


The electronic configuration of the free Fe^{3+} ion is:



Requirement of vacant orbital =6, $[sp^3d^2 \text{ or } d^2sp^3]$
two d, one s, three p

Vacant orbital available in 3d = zero



State of Hybridisation and Magnetic Behaviour of Some Co-ordination Complex

Metal complex	Metal ion	Con. of M^+	Orbital used	Hyb.	No unpaired e-	Nat
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	V^{3+}	d^2		d^2sp^3	2	P
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	Cr^{3+}	d^3		d^2sp^3	3	P.
$[\text{MnF}_6]^{3-}$	Mn^{3+}	d^4		sp^3d^2	4	P.
$[\text{Mn}(\text{CN})_6]^{3-}$	Mn^{3+}	d^4		d^2sp^3	2	P.
$[\text{Fe}(\text{CN})_6]^{3-}$	Fe^{3+}	d^5		d^2sp^3	1	P.
$[\text{FeF}_6]^{3-}$	Fe^{3+}	d^5		sp^3d^2	5	P.
$[\text{FeCl}_4]^{2-}$	Fe^{2+}	d^6		sp^3	4	P.
$[\text{CoF}_6]^{3-}$	Co^{3+}	d^6		sp^3d^2	4	P.
$[\text{Co}(\text{CN})_6]^{3+}$	Co^{3+}	d^6		d^2sp^3	0	D.
$[\text{Ni}(\text{Cl})_4]^{2-}$	Ni^{2+}	d^8		sp^3	2	P.
$[\text{Ni}(\text{CN})_4]^{2-}$	Ni^{2+}	d^8		dsp^2	0	D.
$[\text{CuCl}_4]^{2-}$	Cu^{2+}	d^9		sp^3	1	P.
$[\text{Zn}(\text{NH}_3)_6]^{2+}$	Zn^{2+}	d^{10}		sp^3	0	D.

$[\text{Fe}(\text{CN})_6]^{3-}$: The electronic configuration of the free Fe^{3+} ion



Requirement of vacant orbital =6, $[sp^3d^2 \text{ or } d^2sp^3]$

two d, one s, three p Vacant orbital available in 3d = zero

CN^- force e- in 3d to give two d orbital vacant

