

COORDINATION COMPOUNDS

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CO-ORDINATION COMPOUNDS

C1 Double Salts and Co-ordination Compounds

Double Salts : are those which lose their identity in solution as alum. $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$

Co-ordination Compounds (Complexes) : Those which retain their identity in solution (complexes) as potassium ferrocyanide, $K_4[Fe(CN)_6]$.

A complex (or co-ordination compound) is a compound consisting either complex ions with other ions of opposite charge.

$K_4[Fe(CN)_6]$ K^+ is other ion
complex anion

$[Pt(en)_3]Cl_4$ Cl^- is other ion
complex cation

$[Pt(en)_2Cl_2]$
neutral complex

Ligands : A Ligand is a species that is capable of donating an electron pair(s) to a central ion. It is a Lewis base. In accepting electron pairs, the central ion acts as a Lewis acid.

Ligand can be (a) unidentate
(b) bidentate, tridentate, tetradentate etc.
(c) Ambident

Unidentate Ligand : Ligand is said to be unidentate if it has only one pair of electrons that it can donate.

Polydentate Ligand : Ligand is said to be bidentate, tridentate, tetradentate etc. depending on the number of electron pairs that it can donate.

(a) $:NH_3$; one electron pair available for donation unidentate.

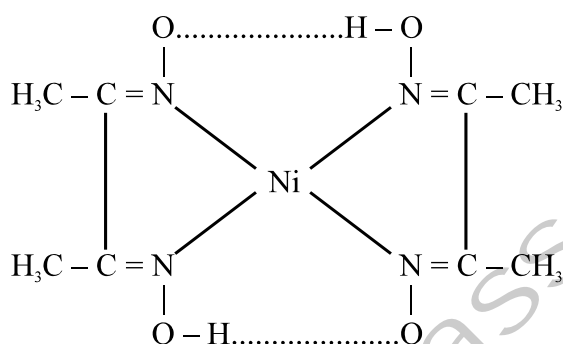
(b) $\begin{array}{c} \ddot{C}H_2\ddot{N}H_2 \\ | \quad \ddot{C} \\ \ddot{C}H_2\ddot{N}H_2 \end{array}$ two electron pairs available for donation bidentate

Some common Multidentate Ligands (Chelating Agents)

Abbreviation	Multi	Name	Formulae	Charge
en	bidentate	ethylenediamine	$\begin{array}{c} CH_2NH_2 \\ \\ CH_2NH_2 \end{array}$	0
ox	bidentate	oxalate	$\begin{array}{c} COO^- \\ \\ COO^- \end{array}$	-2
gly	bidentate	glycinate	$\begin{array}{c} CH_2NH_2 \\ \\ COO^- \end{array}$	-1

DMG	bidentate	dimethyl glyoximate	$\begin{array}{c} \text{CH}_3 - \text{C} = \text{NO}^- \\ \\ \text{H}_3\text{C} - \text{C} = \text{NOH} \end{array}$	-1
EDTA	hexadentate	ethylenediamine tetraacetate	$\begin{array}{c} ^-\text{OOCCH}_2\text{C} \\ \\ \text{N} - \text{CH}_2 - \text{CH}_2 - \text{N} \\ \qquad \qquad \qquad \\ ^-\text{OOCCH}_2\text{C} \qquad \qquad \text{CH}_2\text{COO}^- \\ \qquad \qquad \qquad \qquad \qquad \\ \qquad \qquad \qquad \qquad \qquad \text{CH}_2\text{COO}^- \end{array}$	-4

Chelates : Some ligands are capable of donating more than a single electron pair, from different atoms in the ligand and to different sites in the geometric structure of a complex. These are called as multidentate ligands. When the bonding of a multidentate ligand to metal ion produces a ring (usually five or six membered) we refer to the complex as a chelate. The multidentate ligand is called a **chelating agent** and the process of chelate formation is called chelation



Nickel (II) dimethylglyoximate (chelate)

[bis-(dimethylglyoximate) nickel (II)]

Co-ordination Number : The co-ordination number of a metal atom in a complex is the total number of bonds the metal atom forms with Ligands.

C2A Nomenclature : Following rules are adopted for naming a complex ion.

- cations are named before anions.
- oxidation state (O.S.) of the central metal ion is denoted by Roman numeral

Cation O.S. Anion



Copper (II) chloride



Iron (III) chloride

- The names of ligands are given first followed by the name of central metal ion.
- The names of ligands that are anions and ending with
 - ‘ide’ changed to ‘o’
 - ‘ite’ changed to ‘ito’
 - ‘ate’ changed to ‘ato’

(e) **Some Common Unidentate Ligands**

Neutral		Anions (replacing 'ide' by 'o')	
Formula	Names as Ligand	Formula	Name as Ligand
H ₂ O	aqua	F ⁻ (Fluoride)	Fluorido
NH ₃	ammine	Cl ⁻	Chlorido
CO	Carbonyl	S ⁻²	sulphido
NO	nitrosyl	H ⁻	hydrido
CH ₃ NH ₂	methyl amine	O ⁻² (oxide)	oxo
C ₅ H ₅ N or Py	Pyridine	OH ⁻ (hydroxide)	hydroxo
(C ₂ H ₅) ₃ N	Triethylamine	CN ⁻ (cyanide)	cyano*
(C ₆ H ₅) ₃ N	Triphenyl amine	NC	isocyano*

[* marked are ambident)

Replacing 'e' by 'o'

SO ₄ ²⁻	sulphato
S ₂ O ₃ ²⁻	thiosulphato
CO ₃ ²⁻	carbonato
NO ₂ ⁻	nitro*
ONO ⁻	nitrito*
SCN ⁻	thiocyanato*
NCS ⁻	isothiocyanato*

(e) Positive groups end in -ium

NH₂ – NH₃⁺ hydrazinium

(f) When there are several ligands of the same kind we normally use the prefix di, tri, tetra soon. If the name of ligand includes a number e.g. ethylenediamine (en). To avoid confusion in such cases, bis, tris and tetrakis are used.

e.g. bis (ethylenediamine)

(g) If anion is a complex then metal ends with 'ate' [Ni(CN)₄]²⁻**tetracyanonickelate (II) ion**

lead – plumbate

gold – Aurate

tin – stannate

silver – argentate

iron – ferrate

copper – cuprate

(h) If the complex contain two or more metal atoms, it is termed polynuclear. The bridging ligands which link the two metal atoms together are indicated by the prefix

- (c) $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$ Sodium bis (thiosulphato) argentate (I)
 (d) $\text{Na}_2[\text{OSCl}_5\text{N}]$ sodium pentachloronitrido osmate (VI)
 (e) $\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)\text{NH}_3]$ Potassium amminedicyanodioxo peroxochromate (VI)

7. Organic Ligands have been used :-

- (a) $[\text{Pt}(\text{Py})_4][\text{PtCl}_4]$ Tetrapyridineplatinum (II) tetrachloroplatinate (II)
 (b) $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ Bis (benzene) chromium (0)
 (c) $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ Bis (cyclopentadienyl) iron (II)

C2C (EAN) Effective Atomic Number :

Each ligand donates an electron pair to the metal ion, thus forming a co-ordinate bond

$$\text{EAN} = Z - \text{O.N.} + 2 (\text{C.N.})$$

ON \rightarrow oxidation number

or C.N. \rightarrow co-ordination number

$$\text{EAN} = Z - \text{O.N.} + 2 (\text{Ligands})$$

(assuming that each ligand is unidentate)

C3 Isomerism in Complexes :-

Compounds having same chemical formulae but differ structural arrangements are called isomers.

Structural isomerism :-

Differ from each other. How the atoms are joined together that is in the order in which the atoms are bonded to each other.

$\text{H} - \text{N} = \text{C} = \text{O}$ and $\text{N} \equiv \text{C} - \text{O} - \text{H}$ are structural isomer.

Ionisation Isomerism :-

This type of isomerism occurs when there is an interchange of groups between the co-ordination sphere of the metal ion and the ions outside this sphere. Examples are :



[give yellow ppt. with Ag^+]
 [give white ppt. with Ba^{2+} as SO_4^{2-} being ion as Br⁻ outside the bracket ionisable]
 is ionisable]

Co-ordination isomerism :-

When both positive and negative ions are complex ions. Isomerism may be caused due to interchange of ligands between anion and cation. This arises only when cation and anion have same C.N. and charge



&



Linkage Isomerism :-

- (i) $[\text{CO}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{CO}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$
 (ii) $[\text{Mn}(\text{CO})_5(\text{SCN})]^+$ $[\text{Mn}(\text{CO})_5(\text{NCS})]^+$

Hydrate Isomerism :-

Hydrate isomers of a complex that differ in the placement of water molecules in the complex $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ can be written as

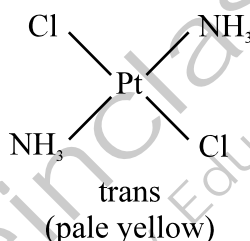
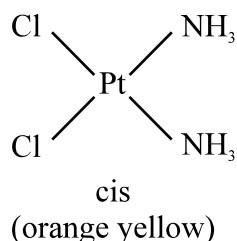
**Stereo Isomers :-**

1. Geometrical
2. Optical

Geometrical :- are isomers in which the atoms are joined to one another in the same way but differ because some atom occupy different relative position in space.

Geometrical Isomers of C.N. – 4

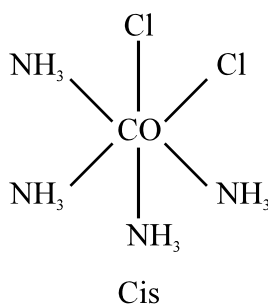
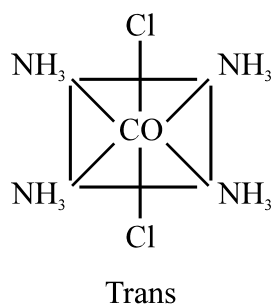
- (a) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

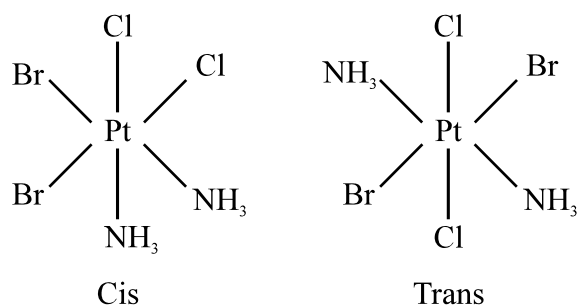
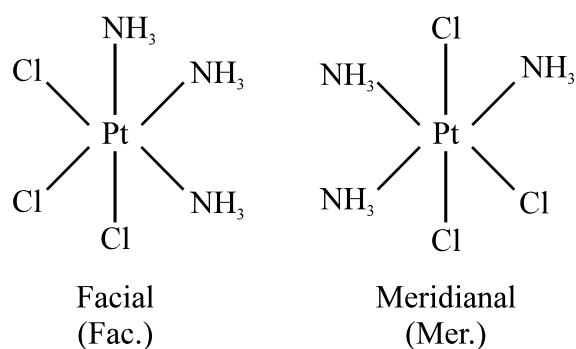


- (b)
-
- (cis)
-
- (Trans)

Geometrical isomers of C.N. – 6

- (a) $[\text{CO}(\text{NH}_3)_4\text{Cl}_2]^+$

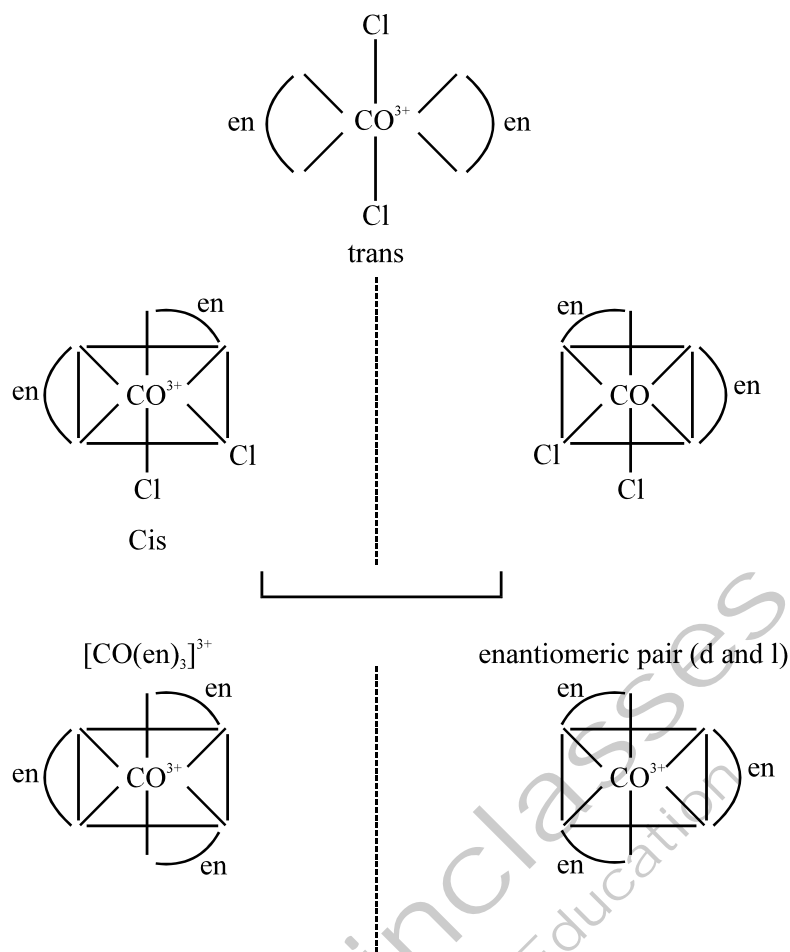


(b) $[\text{Pt}(\text{NH}_3)\text{Cl}_2\text{Br}_2]$ (c) $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]$ 

Optical Isomerism :- If a molecule is asymmetric that it cannot superimposed on its mirror image. The two forms have the same type of symmetry shown by the left and right hands and are called enantiomeric pair. The two forms are called optical isomers. They are called either dextro or leavo (dor l).

Optical isomerism is common in octahedral complexes involving bidentate ligands.

$[\text{CO}(\text{en})_2\text{Cl}_2]$ exists as cis and trans but cis-form can have optical isomerism.



C4A Werner's theory of co-ordination compounds :

- There are two types of valency shown by central metal atom/metal ion in a compound
 - Primary
 - Secondary
 - Primary Valency** corresponds to oxidation number and **secondary valency** corresponds to co-ordination number.
 - In the complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, primary valency is satisfied by three Cl, secondary valency is six.
 - In $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$, four NH_3 and two H_2O (ligands) satisfy secondary valency.
 - One SO_4^{2-} satisfy primary valency.
 - Primary valency is ionisable.
 - The secondary valencies are directional and are responsible for isomerism in complexes.
 - The primary valencies are non-directional and is represented by and secondary valency by _____

- In all cases, metal or metal ions should satisfy primary and secondary valency both. Some negative ions can satisfy primary as well as secondary valency both.

e.g. $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ satisfy both primary and secondary valency.

Practice Problems :

1. Explain the bonding in coordination compounds in terms of Werner's postulates.

C4B Bonding in complexes

- The metal m loses required no. of electrons to form cation. No. of electrons lost correspond to O.N.
- The metal ion makes available a no. of empty orbitals equal to its co-ordinates number for the formation of co-ordinates bonds with the Ligand Orbitals.
- A weak ligand like (H_2O , halide) will not affect the electronic configuration of the metal/metal ion.
- A strong ligand like (NH_3 , CN^- , CO) affect the electronic configuration of the metal/metal ion. They make unpaired electrons paired.
- The metal ion orbitals hybridise to form a new set of equivalent hybridised orbitals.
- If there are unpaired electrons in the complex it is called paramagnetic.

$$\text{Magnetic moment} = \sqrt{N(N+2)} \text{ B.M.}$$

$N \rightarrow$ no. of unpaired electrons.

- The complex with so many unpaired electrons is **high spin complex** and that with paired electrons is **low spin complex**.
- If inner d-orbital is used for hybridisation it is called inner d complex. e.g. d^2sp^3 $[\text{Fe}(\text{CN})_6]^{4-}$
- If outer d-orbital is used is called outer d-complex. sp^3d^2

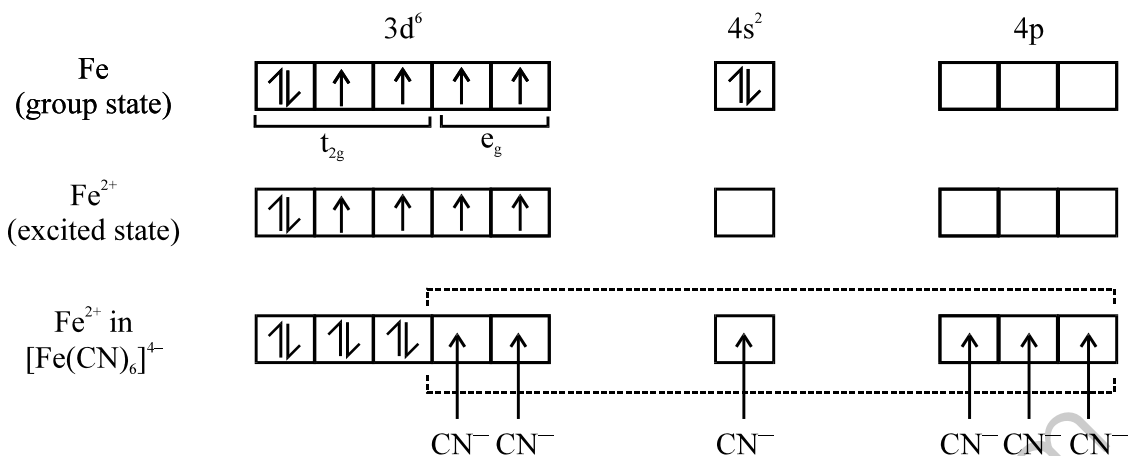
Weak field ligand $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

- $\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{oxalate} < \text{H}_2\text{O} < \text{EDTA} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- < \text{CO}$

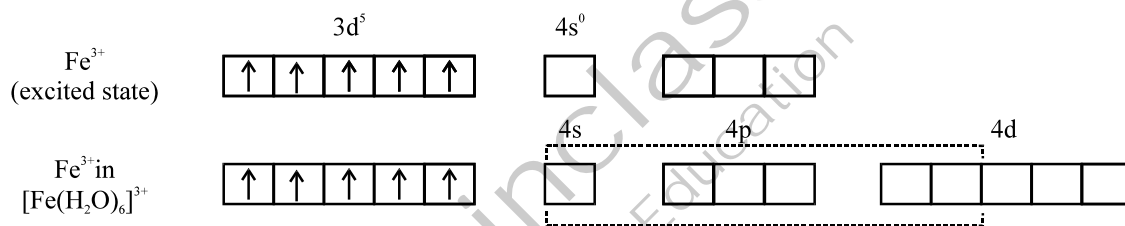
Examples : $[\text{Fe}(\text{CN})_6]^{4-}$ O.N. = +2

C.N. = 6

[six empty orbitals are required by six CN^- ligands] $t_2g \rightarrow d_{xy}, d_{yz}, d_{zx}$ **e.g.** $dx^2 - y^2, dz^2$



- Complex ion is d^2sp^3 hybridised
- Diamagnetic
- Octahedral geometry
- Inner d-complex
- Magnetic moment = 0



(H₂O is weak ligand)

- Hybridisation – sp^3d^2
- Paramagnetic (High spin complex)
- Outer-d-complex
- Octahedral geometry

State of Hybridisation and Magnetic Behaviour of some co-ordination complex

Metal Complex	Metal Ion	Configuration of metal ion	Hybridisation of metal ion orbitals for ligand bonds	No. of unpaired electrons	Magnetic Behaviour
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	V^{3+}	d^2	sp^3d^2	2	Paramagnetic
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	Cr^{3+}	d^3	d^2sp^3	3	Paramagnetic
$[\text{MnF}_6]^{3-}$	Mn^{3+}	d^4	sp^3d^2	4	Paramagnetic
$[\text{Mn}(\text{CN})_6]^{3-}$	Mn^{3+}	d^4	d^2sp^3	2	Paramagnetic
$[\text{Fe}(\text{CN})_6]^{3-}$	Fe^{3+}	d^5	d^2sp^3	1	Paramagnetic
$[\text{Fe}(\text{F}_6)]^{3-}$	Fe^{3+}	d^5	sp^3d^2	5	Paramagnetic
$[\text{Fe}(\text{Cl}_4)]^{2-}$	Fe^{2+}	d^6	sp^3	4	Paramagnetic
$[\text{COF}_6]^{3-}$	CO^{3+}	d^6	sp^3d^2	4	Paramagnetic
$[\text{CO}(\text{CN})_6]^{3-}$	CO^{3+}	d^6	d^2sp^3	0	Diamagnetic
$[\text{Ni}(\text{Cl})_4]^{2-}$	Ni^{2+}	d^8	sp^3	2	Paramagnetic
$[\text{Ni}(\text{CN})_4]^{2-}$	Ni^{2+}	d^8	dsp^2	0	Diamagnetic
$[\text{COCl}_4]^{2-}$	CO^{2+}	d^9	sp^3	1	Diamagnetic
$[\text{Zn}(\text{NH}_3)_4]^{2+}$	Zn^{2+}	d^{10}	sp^3	0	Diamagnetic

