

9. CO-ORDINATION COMPOUNDS

Ligands The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

Unidentate:-When a ligand is bound to a metal ion through a single donor atom, the ligand is said to be unidentate. Example Cl^- , H_2O , NH_3 etc.,

Didentate :- When a ligand can bind through two donor atoms as in the ligand is said to be didentate

Example $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethane-1,2-diamine) or $\text{C}_2\text{O}_4^{2-}$ (oxalate),

Polydentate:-when several donor atoms are present in a single ligand the ligand is said to be polydentate.

Example $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$,

Note:- Ethylenediaminetetraacetate ion (EDTA^{4-}) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

Nomenclature of Mono nuclear co-ordination compounds (IUPAC)

Write the formulas for the following coordination compounds:

- | | |
|---|--|
| (a) tetraammineaquachloridocobalt(III)chloride | $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ |
| (b) potassiumtetrahydroxidozincate(II) | $\text{K}_2 [\text{Zn}(\text{OH})_4]$ |
| (c) potassiumtrioxalatoaluminate(III) | $\text{K}_3 [\text{Al}(\text{C}_2\text{O}_4)_3]$ |
| (d) dichloridobis(ethane-1,2-diamine)cobalt(III)ion | $[\text{CoCl}_2(\text{en})_2]^+$ |
| (e) tetracarbonylnickel(0) | $[\text{Ni}(\text{CO})_4]$ |

Write the IUPAC names of the following coordination compounds:

- | | |
|--|--|
| (a) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ | pentaamminechloridocobalt(III)chloride |
| (b) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ | hexaaquachromium(III)chloride |
| (c) $\text{K}_3[\text{Fe}(\text{CN})_6]$ | potassiumhexacyanidoferrate(III) |
| (d) $[\text{NiCO}_4]$ | tetracarbonylnickel(0) |
| (e) $[\text{Cr}(\text{en})_3]^{3+}$ | tris(ethylene diamine)chromium(III) ion |
| (f) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$ | diamminechloridonitrito-N-platinum(II) |
| (g) $\text{K}_3 [\text{Cr}(\text{C}_2\text{O}_4)_3]$ | potassiumtrioxalatochromate(III) |
| (h) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ | dichloridobis(ethane-1,2-diamine)cobalt(III)chloride |
| (i) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$ | pentaamminecarbonatocobalt(III)chloride |
| (j) $\text{Hg}[\text{Co}(\text{SCN})_4]$ | mercurytetrathiocyanato-S-cobaltate(III) |

2. Isomerism in coordination compounds:- Compounds which have same molecular formula, but different structures and therefore different physical and chemical properties are called isomers.

Depending upon the position and arrangement of ligands around the central metal atom several types of isomerism are possible. Isomerism are broadly classified into two.

A. Structural isomerism

These are isomers which have different structural arrangement around the central metal atom. The various structural isomers are.

a. Ionisation isomerism These type of isomerism arises because of the capability of coordination compounds to produce different ions in solution.

Eg:- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$

b. Hydrate isomerism or solvate isomerism This type of isomerism arises because of the capability of water molecule to appear in a variety of ways inside and outside the coordination sphere.

Eg:- Three hydrate isomerism are possible for the molecular formulae $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

Eg:- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

c. Linkage isomerism : It is shown by the complex containing ambidentate ligand with more than one donor atom. Eg:- when NO_2^- is bonded to the metal through nitrogen the ligand is named as **nitrito-N** and if it is bonded to the metal through oxygen (ONO^-) the ligand is named as **nitrito-O**.

Eg:- $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$

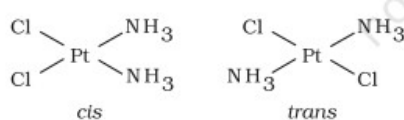
d. Coordination isomerism This type of isomerism arises from the interchange of ligands between cationic and anionic entities in the complex..

Eg:- $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
 $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

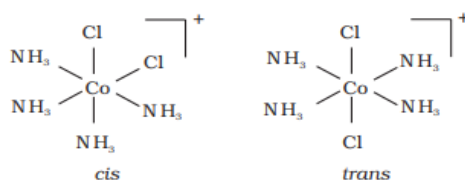
B. Stereo isomerism Isomers are those which contain same atom or group but they differ in the spatial arrangement around the central atom. They are of two types.

a. Geometrical isomerism Also known as cis-trans isomerism. These types of isomerism arises due to different spatial arrangements of ligands..

C.N 4 Square planar complex of formula $[\text{MX}_2\text{L}_2]$ In a square planar complex of formula $[\text{MX}_2\text{L}_2]$ (X and L are unidentate), Here the two identical ligands either occupy adjacent positions to each other (cis isomer) or opposite to each other (trans-isomer).



C.N 6 Octahedral complexes of formula $[\text{MX}_2\text{L}_4]$ In octahedral complexes of formula $[\text{MX}_2\text{L}_4]$ two ligands X may be oriented cis or trans to each other



Complexes of formula $[MX_2(L-L)_2]$

This type of isomerism also arises when didentate ligands $L-L$ [e.g., $NH_2CH_2CH_2NH_2$ (en)] are present in complexes of formula $[MX_2(L-L)_2]$

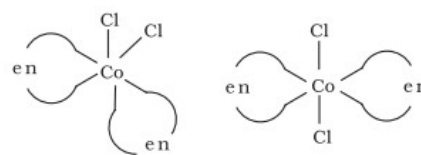
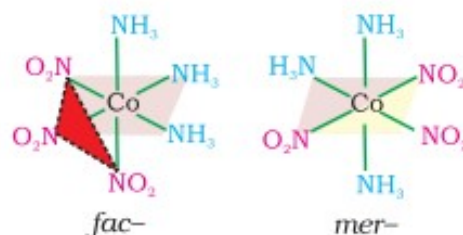


Fig. 9.4: Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

Facial and Meridional isomerism $[MA_3B_3]$

Ex $[Co(NH_3)_3(NO_2)_3]$.

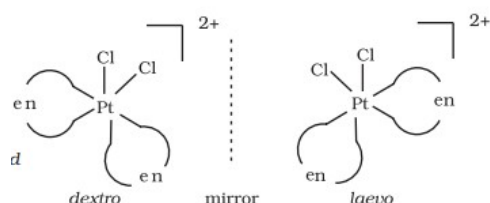
If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial (fac) isomer**. And if the positions are around the meridian of the octahedron, we get the **meridional (mer) isomer**



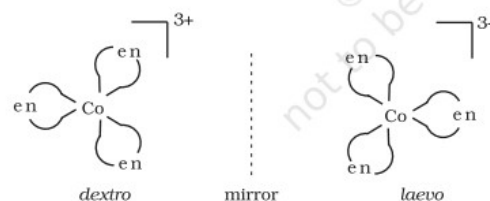
b. Optical Isomerism

Optical isomers which are mirror images to each other and cannot be superimposed on one another are called as **enantiomers**. Such molecules or ions that cannot be superimposed are called **chiral**. The enantiomers are called **dextro (d)** and **laevo (l)** depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates plane polarised light to the right direction, whereas l to the left).

Optical isomerism is common in octahedral complexes involving didentate ligands. In a coordination entity of the type $[PtCl_2(en)_2]^{2+}$, only the cis-isomer shows optical activity



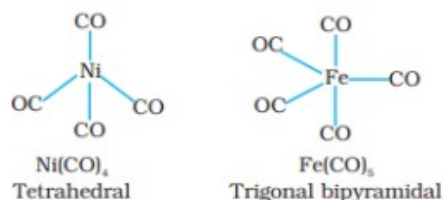
Another Example
 $[Co(en)_3]^{2+}$



Bonding in metal carbonyls (synergic bonding)

Metal carbonyls are formed between metal and carbon monoxide ligands. It possesses both **sigma and pi bond**.

Metal carbon sigma bond is formed by the donation of lone pair of electrons from carbonyl carbon to vacant orbital of metal.



The **metal carbon pi bond** is formed by the donation of a pair of electrons from the filled d orbital of metal into vacant anti bonding orbital of carbon monoxide

