

Concepts and Formulas to Remember

9.3.2 Naming of Mononuclear Coordination Compounds

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers. The following rules are used when naming coordination compounds:

- The cation is named first in both positively and negatively charged coordination entities.
- The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).
- Names of the anionic ligands end in -o, those of neutral and cationic ligands are the same except aqua for H_2O , ammine for NH_3 , carbonyl for CO and nitrosyl for NO . While writing the formula of coordination entity, these are enclosed in brackets ().
- Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used, the ligand to which they refer being placed in parentheses. For example, $[\text{NiCl}_2(\text{PPh}_3)_2]$ is named as dichloridobis(triphenylphosphine)nickel(II).
- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
- If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix -ate. For example, Co in a complex anion, $[\text{Co}(\text{SCN})_4]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g., ferrate for Fe.
- The neutral complex molecule is named similar to that of the complex cation.

Note: The 2004 IUPAC draft recommends that anionic ligands will end with -ido so that chloro would become chlorido, etc.

9.4 Isomerism in Coordination Compounds

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

(a) Stereoisomerism

- Geometrical isomerism
- Optical isomerism

(b) Structural isomerism

- Linkage isomerism
- Coordination isomerism
- Ionisation isomerism
- Solvate isomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds. A detailed account of these isomers are given below.

9.4.1 Geometric Isomerism

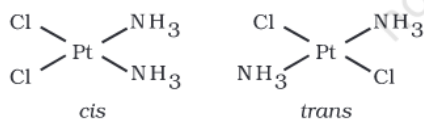


Fig. 9.2: Geometrical isomers (*cis* and *trans*) of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[\text{MX}_2\text{L}_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans* isomer as depicted in Fig. 9.2.

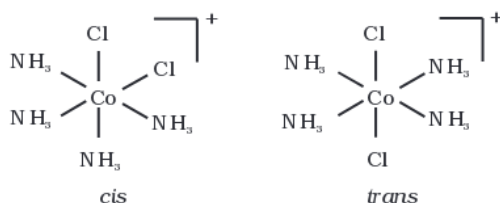


Fig. 9.3: Geometrical isomers (*cis* and *trans*) of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

Other square planar complex of the type MABXL (where A, B, X, L are unidentates) shows three isomers—two *cis* and one *trans*. You may attempt to draw these structures. Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula $[\text{MX}_2\text{L}_4]$ in which the two ligands X may be oriented *cis* or *trans* to each other (Fig. 9.3).

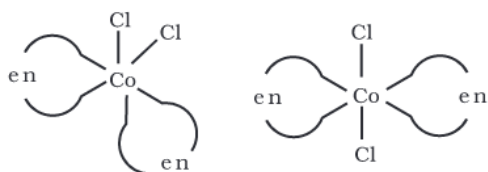
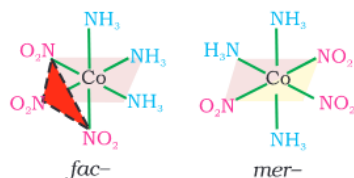


Fig. 9.4: Geometrical isomers (cis and trans) of $[\text{CoCl}_2(\text{en})_2]$

This type of isomerism also arises when didentate ligands $L-L$ [e.g., $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (en)] are present in complexes of formula $[\text{MX}_2(\text{L}-\text{L})_2]$ (Fig. 9.4).

Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[\text{Ma}_3\text{b}_3]$ like $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial (fac) isomer**. When the positions are around the meridian of the octahedron, we get the **meridional (mer) isomer** (Fig. 9.5).

Fig. 9.5
The facial (fac) and meridional (mer) isomers of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$



9.4.3 Linkage Isomerism

Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^- , which may bind through the nitrogen to give $\text{M}-\text{NCS}$ or through sulphur to give $\text{M}-\text{SCN}$. Jørgensen discovered such behaviour in the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen ($-\text{ONO}$), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-\text{NO}_2$).

9.4.4 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. An example is provided by $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+} . In its coordination isomer $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+} .

9.4.5 Ionisation Isomerism

This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$.

9.4.6 Solvate Isomerism

This form of isomerism is known as '**hydrate isomerism**' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet) and its solvate isomer $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (grey-green).