

Student Corner

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Isomerism in Coordination Compounds

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Isomers (compounds with the same chemical formula) can be broadly classified into (i) **stereoisomers** (e.g. geometrical and optical) with the same connectivity but having different spatial arrangements and (ii) **structural isomers** with different connections between atoms. We are quite familiar with the geometrical (*cis* and *trans*) and optical isomers (e.g. enantiomers) of organic molecules where the valency of carbon is **four**. Coordination compounds can form several different types of isomers because metal centres, often, can have coordination numbers higher than four and can adopt different geometries. The following are the common structural isomers of coordination compounds: **ionization, hydrate, linkage and coordination**.

Ionization isomers

Ionization isomers have the same **empirical formula** but differ in the **coordinated anion(s)** thus, yielding different ions **when dissolved in a solution**. Furthermore, ionization isomerism is shown by salts, often involves the exchange of an **anionic ligand** (e.g. halide, sulphate, etc) between the complex ion (**coordination-sphere**) and the remainder of the salt (**ionization-sphere**). For example, $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ are such isomers. They have the same **chemical composition**, $\text{CoBrSO}_4(\text{NH}_3)_5$, but differ in ions present in an aqueous solution. In water, $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ produces sulphate ions whilst $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ gives bromide ions.

Hydrate isomers

This is analogous to ionization isomerism except that **water molecule(s)** (a **neutral ligand**) replaces the **ionic ligand**, bromide. For example, there are **four** different **octahedral Cr(III)** compounds with the **composition**

$\text{CrBr}_3 \cdot 6\text{H}_2\text{O}$. They are given below.

Compound	No. of Br ions
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$	3
$[\text{CrBr}(\text{H}_2\text{O})_5]\text{Br}_2 \cdot \text{H}_2\text{O}$	2
$[\text{CrBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$	1
$[\text{CrBr}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$	0

Linkage isomers

Some ligands can bind in **more than one way** hence they are called **ambidentate** ligands (e.g. NCS and SCN; thiocyanate and isothiocyanate). Complexation of these ligands can result in isomeric compounds, known as **linkage isomers**, with different modes of bonding to the metal centre. For example, the coordination compound with the empirical formula $\text{MnNCS}(\text{CO})_5$ shows two linkage isomers $[\text{MnNCS}(\text{CO})_5]$ with a Mn-N bond and $[\text{MnSCN}(\text{CO})_5]$ with a Mn-S bond. The NO_2 ligand is also an ambidentate ligand and can use either N or O as the donor atom.

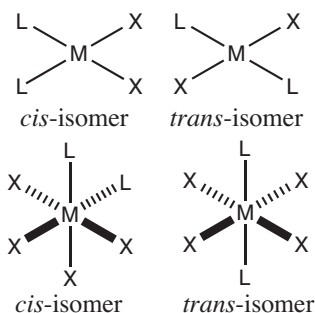
Coordination isomers

When both the **cation** and the **anion** are of complex ions of two different metal centres (e.g. Co and Cr), the distribution of ligands can vary between the two metal centres giving rise to isomers. This isomerism can be considered as an extreme case of ionization isomerism. e.g. $[\text{Co}(\text{NH}_3)_6][\text{CrBr}_6]$, $[\text{Cr}(\text{NH}_3)_6][\text{CoBr}_6]$ are **coordination isomers** with the same empirical formula, $\text{CoCrBr}_6(\text{NH}_3)_6$.

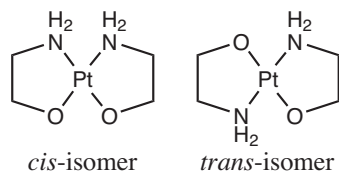
Geometric isomers

Geometric isomers (or *cis*- and *trans*- isomers) occur when the relative positions of ligands in a **disubstituted**

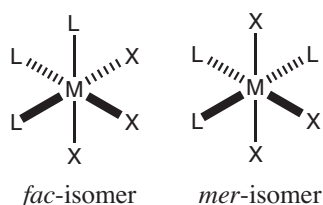
compound are different. This is commonly found in square-planar complexes of type $[MX_2L_2]$ and $[MXYL_2]$; and octahedral complexes of the type $[MX_4L_2]$.



Geometric isomerism can also occur in square-planar *bis*-chelate complexes if the chelating group is **not symmetrical**. For example, $[Pt(NH_2CH_2CH_2O)_2]$ can have two *cis-trans* isomers.



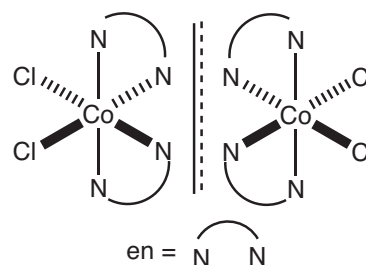
Trisubstituted octahedral complexes of the type $[MX_3L_3]$ can exist in two forms; (i) *facial* isomer or *fac*-isomer and (ii) *meridional* isomer or *mer*-isomer. Note that $[MX_3L_3]$ does not show *cis-trans* isomerism.



Optical isomers

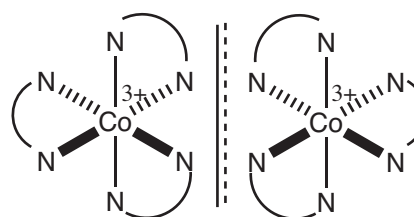
Optical isomers exist when the mirror image of one isomer is **not superimposable** on the other. Such a pair of isomers is called **enantiomers**. The isomers are prefixed either *dextro* or *laevo* (often abbreviated to *d* or *l*) depending on the direction they rotate the plane of polarized light. **These compounds do not possess either a plane of symmetry or a centre of symmetry.** Optical isomerism is found mainly in octahedral complexes with chelating bidentate ligands, and to a lesser extent in tetrahedral and square-planar compounds.

The octahedral complex *cis*- $[CoCl_2(en)_2]$ has two optical isomers, where $en =$ ethylenediamine $= H_2NCH_2CH_2NH_2$.

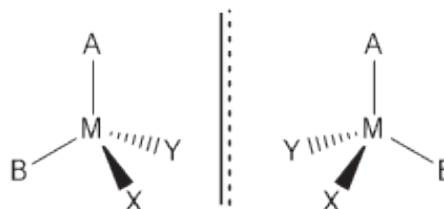


trans- $[CoCl_2(en)_2]$ is **optically inactive** because it has a plane of symmetry.

The cation $[Co(en)_3]^{3+}$ exists in two isomeric forms, which are **non-superimposable** mirror images. Therefore, they are enantiomers.



Optical isomers in tetrahedral complexes are more common. If the complex is of the type $[MX_2YAB]$, where X, Y, A and B are different ligands, the compound is capable of existing in two optically active forms.



Generally, square-planar complexes of the type $[MX_2YAB]$ **do not exhibit** optical isomerism because the **plane of the molecule acts as a plane of symmetry.**

Optical isomerism is also possible when the tetrahedral complex contains two **asymmetrical bidentate** ligands. Complexes containing hexadentate ligands can show optical isomerism, e.g. the Co(III) complex $[Co(EDTA)]^-$ forms two optical isomers.

Problems

- How can you distinguish $[CoBr(NH_3)_5]SO_4$ from $[Co(SO_4)(NH_3)_5]Br$?
- Draw and identify the three geometrical isomers

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- of $[\text{FeBr}_2(\text{CO})(\text{NH}_3)_3]$ (**A**). Does (**A**) show optical isomerism?
3. Draw the **geometrical** and **optical** isomers of $[\text{NiBrCl}(\text{CO})(\text{NH}_3)]$.
4. $[\text{FeBr}_2(\text{acac})(\text{NH}_3)_2]$ shows **two** geometrical isomers (**B**) and (**C**). (**C**) shows optical isomerism. Draw and identify the structures of (**B**) and (**C**). Draw the optical isomer of (**C**). ($\text{acac}^- = \text{acetylacetonate ion}$)