Coordination Complex Isomerism

Reference:
Miessler, G. L., Tarr, D. A., Inorganic Chemistry, 2^{nd} Ed., Prentice-Hall, Toronto, p. 286 – 300.

Isomers

Isomers are 2 or more compounds that have the same stoichiometry (elemental composition), but differ in their structure.

In coordination chemistry, this can be caused by:

- the type of coordination
- the donor atom
- difference in symmetry
- difference in conformation

We will break isomerisation down into two broad categories:

- Constitutional Isomers – Isomers that bonds to the metal center.
- Configurational Isomers – Isomers that differ in geometry, but not connectivity.

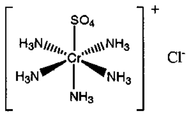
Constitutional Isomers

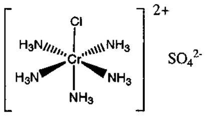
Constitutional isomers are also called structural isomers. There are three 3 types:

- Ionisation isomers – Ionisation isomers have the same formula but result in different isomers when dissolved in a solvent.
- Coordination isomers – Coordination Isomers have different groupings of the same ligands bonded to a metal centre.
- Linkage isomers – Linkage isomers have ambidentate ligands that can coordinate through different donor atoms to the metal centre.

Ionisation Isomers

Ionization isomers are compounds that have the same formula but produce different ions in solution. They have different ligands in their 1^{st} and 2^{nd} coordination spheres:





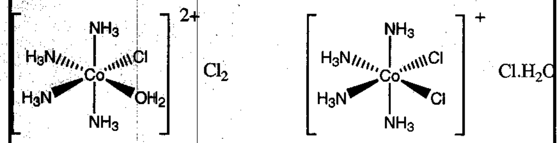
Notice that there can be very obvious differences in these isomers:

- Different bonds at the metal centre result in a different stabilisation and possibly charge of the complex ion, and can thus affect reactivity.
- Likewise, the free anion can be different and also affect reactivity, as well as solubility.

Solvation Isomers

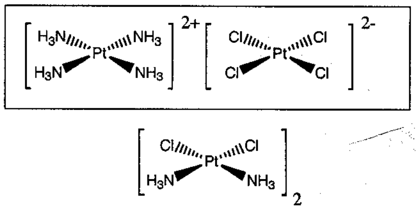
A specific form of ionisation isomers exist when the solvent participates in inner shell coordination.

Solvent can sometimes be included in the extended crystal structure. These are called solvent of crystallization. They behave very differently than solvent coordinated to the metal centre.



Coordination Isomers

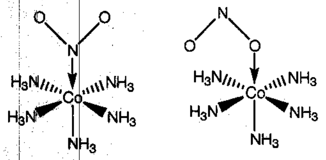
2. Coordination isomers have different groupings of the same ligands bonded directly to the metal center:



These are related to ionisation isomers, and this isomerisation can affect the chemistry in a similar manner.

Linkage Isomers

Linkage isomers have a ligand with two different atoms through which it binds (ambidentate ligand):



These isomers are usually governed by hard/soft acid/base interactions, but solvent and other subtle effects can cause isomersation:

The above isomerisation goes to products in a solvent with low dielectric constant, and to reactants in a solvent with high dielectric constant.

Configurational Isomers (Stereoisomers)

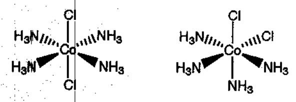
<u>Stereoisomers</u>: have all the same bonds, but differ by some aspect of symmetry.

Diastereomers : Stereoisomers that differ spatially, but are not mirror images. These are also called geometric isomers.

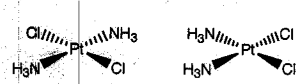
Enantiomers : Pairs of isomers that are mirror images of each other and non-superposable. These are also called optical isomers.

Diastereomers (Geometric Isomers)

In transition metal complexess, cis/trans isomerism exists for both the octahedral and square planar geometries:

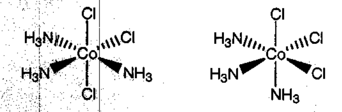


trans cis

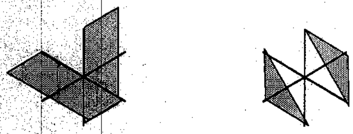


trans cis

As well, there are mer/fac (meridional/facial) isomers for octahedral complexes:

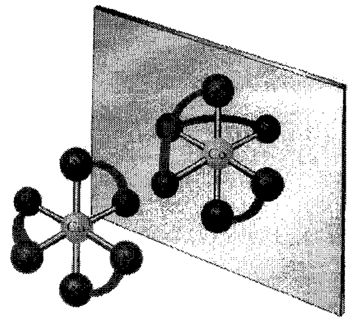


mer **fac**



Entantiomers (Optical Isomers)

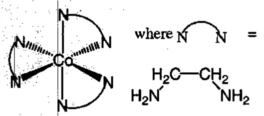
Enantiomers can be difficult to see from a 2D depiction. They are mirror images of each other, and the two forms cannot be superimposed.

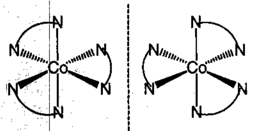


Octahedral Entantiomers

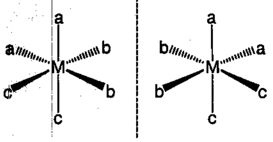
There are many types of octahedral enantiomers, two prime examples are the trischelate structures and $Ma_2b_2c_2$ (all *cis*) complexes:

Trischelate Structures



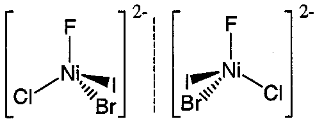


MA$_2$B$_2$C$_2$ (all *cis*) Complexes



Tetrahedral Enantiomers

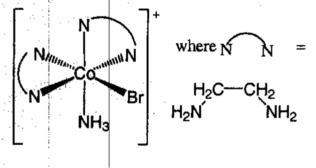
Tetrahedral enantiomers occur when there are four different groups around the central atom. This enentiomerism is seen in coordination chemistry, but plays a much larger role in organic chemistry:

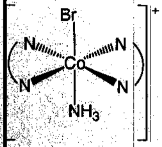


Typically, a tetrahedral complex with four different ligands is too unstable.

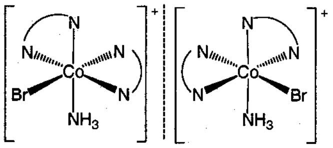
Diastereomeric and Enantiomeric Behavior in the Same Compound

The compound $Co(en)_2NH_3Br$ (en = ethylenediamine) displays both diastereomerism and enantiomerism:





trans isomer
(diastereomer)



cis isomer
(pair of enantiomers)

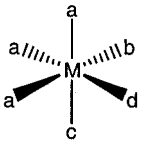
Number of Octahedral Isomers

The octahedral case can be very complex, depending on the number of different ligands and whether or not they chelate.

A systematic approach is to consider ligands that lie trans to each other, and write out a table of possible isomers:

- Keep one pair constant
- Alter the second pair by keeping one ligand constant and changing the second ligand
- Let the third pair be whatever is left over

Consider the complex Ma_3bcd, where a, b, c, and d are different ligands:



Systematic Isomerisation Analysis

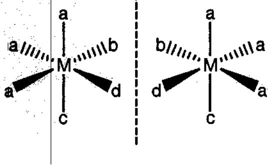
Octahedron Only

Consider the complex Ma_3bcd, where a, b, c, and d are different ligands:

Isomer	1	2	3	4
Trans pair 1	aa	aa	aa	ab
Trans pair 2	ab	ac	ad	ac
Trans pair 3	cd	bd	bc	ad

Any other sets of pairs are repetitions of these four structures.

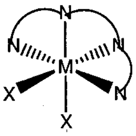
Now each needs to be drawn and checked for chirality. Since having the same ligand trans to itself ruins chirality, the only possible chiral isomer is isomer 4. Thus, there are five isomers::



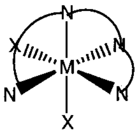
Orientation of Chelate Rings

In an octahedral complex, the relationship of the chelate rings to each other can cause isomerisation.

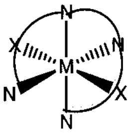
If there are three rings, there are three possible arrangements:



no coplanar rings
α

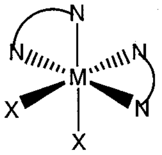


2 coplanar rings
β

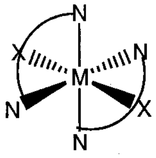


all coplanar rings
trans

It is easier to consider with just two, unconnected rings:



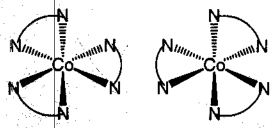
no coplanar rings
α



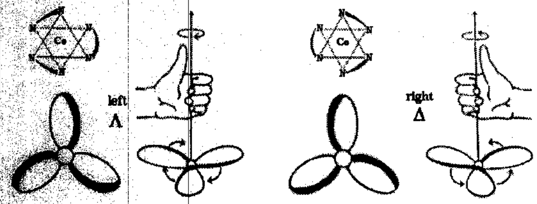
all coplanar rings
trans

Combinations of Chelate Rings

In the case of three bidentate ligands in an octahedral arrangement, we have seen that there are two chiral isomers:



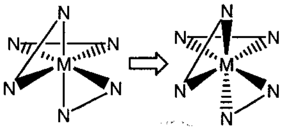
These are called propellar molecules, because of their three-dimensional shape.



The *handedness* (either Λ or Δ) is determined by which way the helix defined by the isomer is twisted. It can be easily discerned

Λ vs. Δ

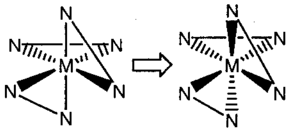
Turn the molecule so that one triangular face is pointed frontwards, with one ring at the back and horizontal.



Lambda Λ

Now consider that the bidentate ligand in the front used to be parallel with the rear ring.

If it had to be rotated counterclockwise (to the left) to achieve its present orientation, then the complex is the *levo* complex, and is labelled lambda Λ.



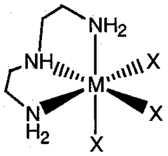
Delta Δ

If it had to be rotated clockwise (to the right) to be in its present orientation, then the complex in the *dextro* complex, and is labelled delta Δ.

Systems With Two Rings

This labelling system also works for octahedral chelates with only two rings, as long as the rings are in the same plane or adjacent to each other.

They are adjacent to each other in systems where the two rings are defined by a tridentate ligand.

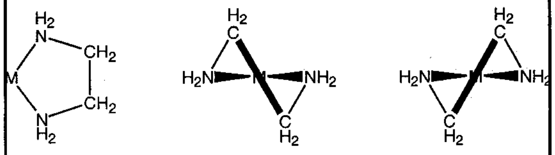


λ vs. δ

The same analysis can be performed on chelate rings within an octhedral complex.

Since many rings are not perfectly planar it is necessary to differentiate their twists, also labelled lambda and delta, but now in lowercase.

We consider two lines again, but now it is one line joining the donor atoms of the ligand. If we consider the ethylenediamine case, it would connect the two nitrogen.



δ λ

The second line connects the two carbons.

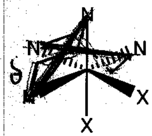
Like before, we put the first line to the back and horizontal.

We then consider that the other line used to be parallel with it, and determine its handedness by which way the line would have to be rotated in order to achieve the present configuration.

Labelling Octahedral Isomers

Since an octahedral complex can have up to 3 rings, and each ring can have its own chirality, the labeling of the complex can be quite complex.

Label this compound:



- It has no coplanar rings, so it is α.
- The front ring had to be twisted left with respect to the back ring, so it is Λ.
- The rear ring is λ.
- The front ring is δ.

Overall, this is the α isomer, $\Lambda\lambda\delta$.

turn so it's in front.