Stereochemistry of complex combinations

1. Stereochemistry or structural chemistry studies the geometrical configurations of complex combinations in close correlation with the electronic structure.

2. The geometrical configuration of a complex combination depends on the number and orientation of the covalent bonds σ made by the central atom, the nature of the ligands, and the number of non-participating electron pairs in the outer shell of the central atom.

3. Although to date no unified theory has been developed to predict the geometric shape of molecules, a number of empirical and semi-empirical models have been established that establish the dependence between electronic structure and geometric configuration.

Isometrism of complex combinations

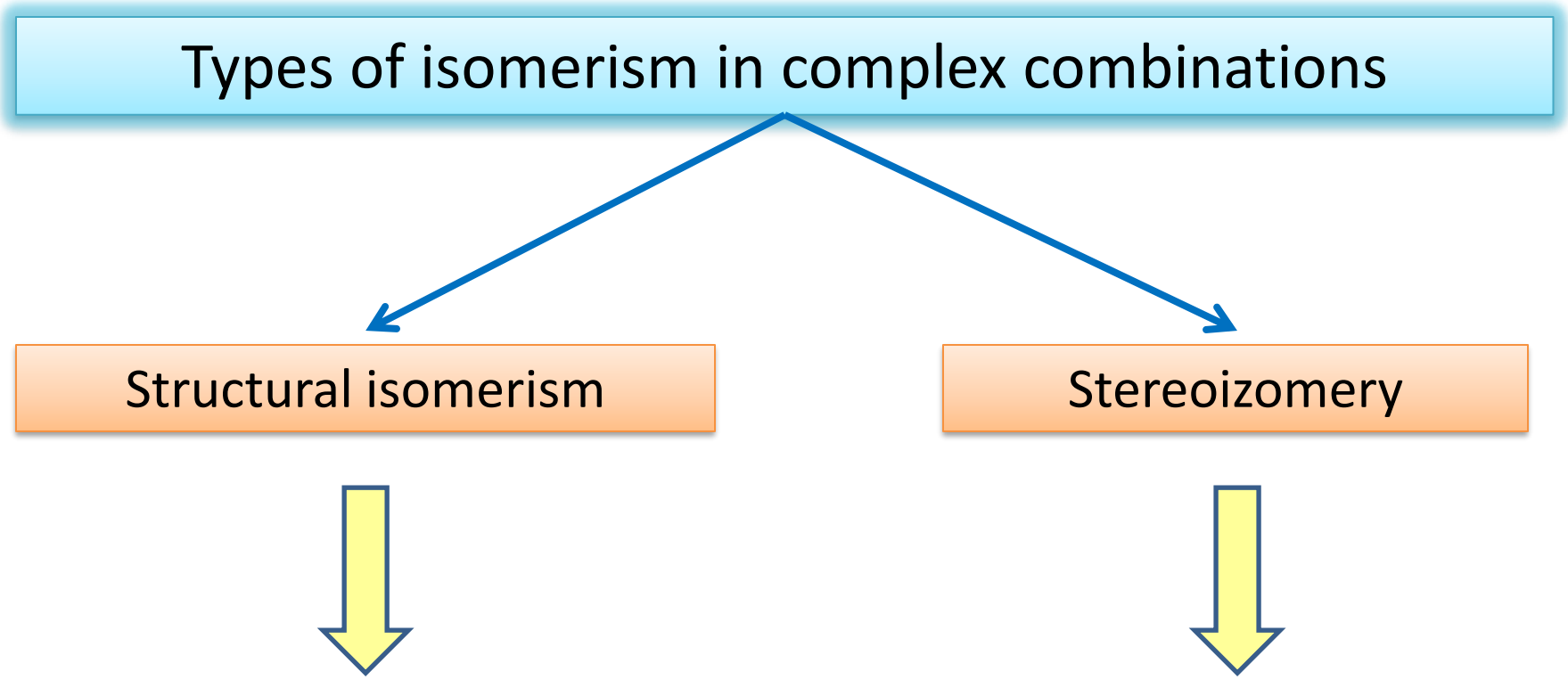
- Isomerism is a phenomenon specific to stable chemical combinations which, although having the same chemical composition, may be present in the form of several structures characterised by different physical and chemical properties.

- The properties of the different isomers are maintained both in solution and in crystalline form, especially in the case of kinetically stable complex combinations, the labile ones forming by rearrangement (isomerisation) only the most stable isomer.

- Among the factors that can influence the production of an isomer: synthesis routes, working conditions (especially temperature), the nature of the solvent and the physical state of the compound itself.

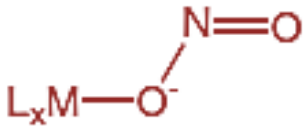
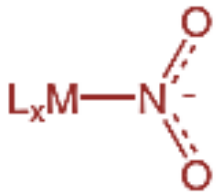
- These factors depend on the electronic structure of the central ion, the nature and geometry of the ligands, including neighbouring ligands in the case of small complexes, and sometimes even the nature of the ions in the outer coordination sphere.

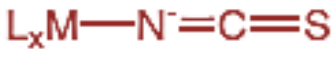
Isometrism of complex combinations

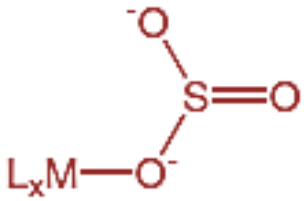
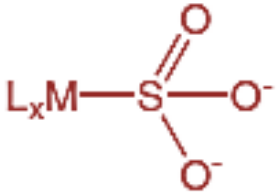


Binding isomerism

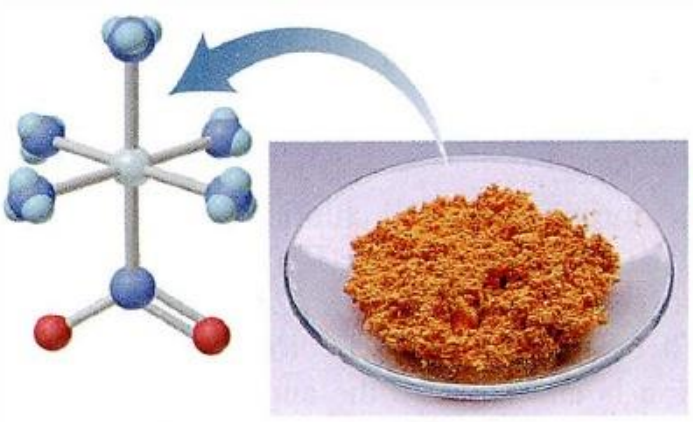
Binding isomerism occurs in complex combinations in which ambidentate (bifunctional) ligands can coordinate to the metal ion either through one donor atom or the other donor atom.

NO_2^-  ***nitrito***  ***nitro***

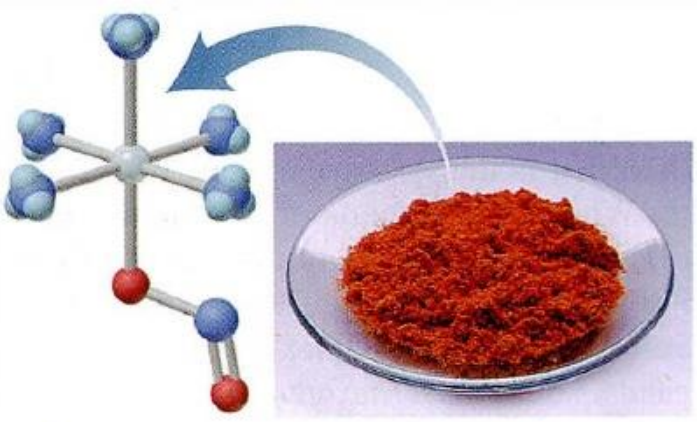
SCN^-  ***thiocyanate***  ***isothiocyanate***

SO_3^{2-}  ***O-sulphite***  ***S-sulphite***

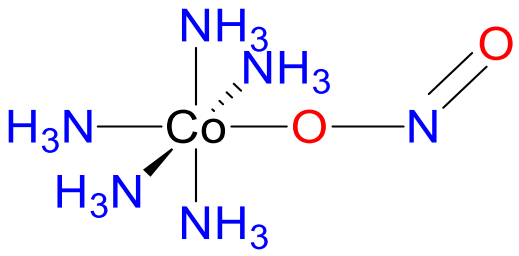
Binding isomerism



Nitro isomer, $[Co(NH_3)_5(NO_2)]Cl_2$

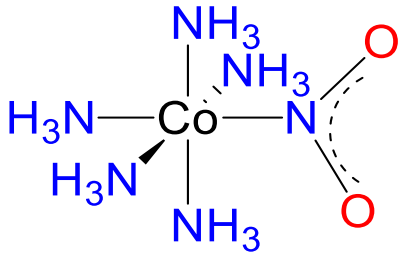


Nitrite isomer, $[Co(NH_3)_5(ONO)]Cl_2$



ligand nitrito

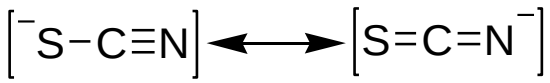
RED



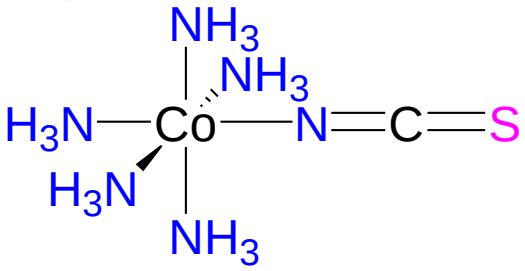
ligand nitro

ORANGE

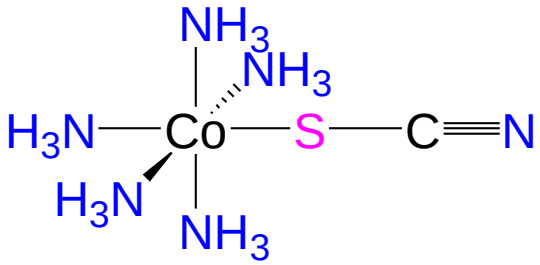
Binding isomerism



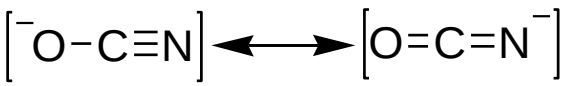
The ambidentate ligand SCN- can generate two binding isomers.



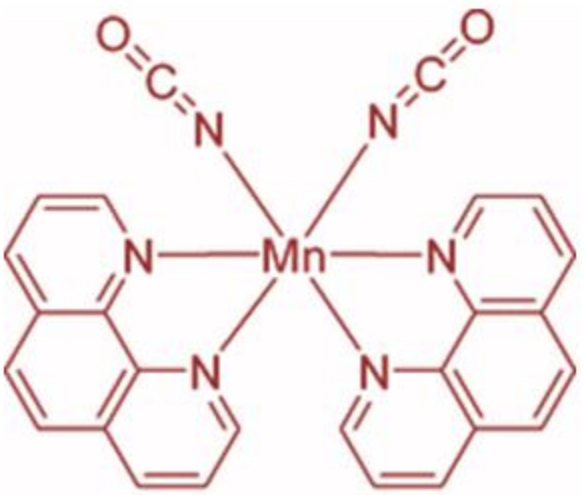
izotiocianat



tiocianat



...as well as the cyanated ambidentate ligand OCN^-

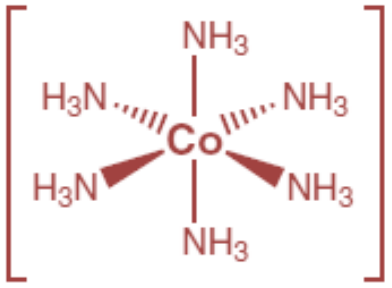


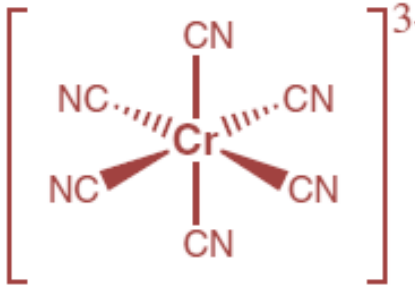
Coordination isomerism

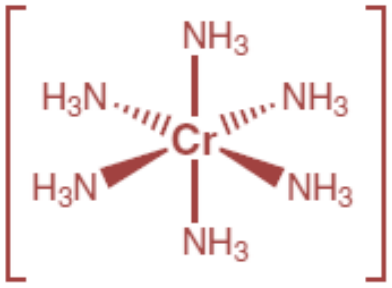
Coordination isomerism occurs in complex combinations where both the anion and the cation are complex ions. This type of isomerism is due to the different distribution of ligands between the two coordination spheres.

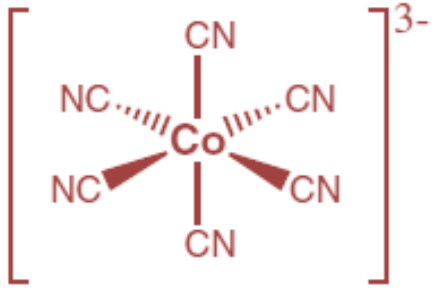
ligand exchange between cation and anion

- $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$;
- $[Co(NH_3)_6][Co(NO_2)_6]$ and $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$;
- $[Pt^{II}(NH_3)_4][Pt^{IV}Cl_6]$ and $[Pt^{IV}(NH_3)_4Cl_2][Pt^{II}Cl_4]$.



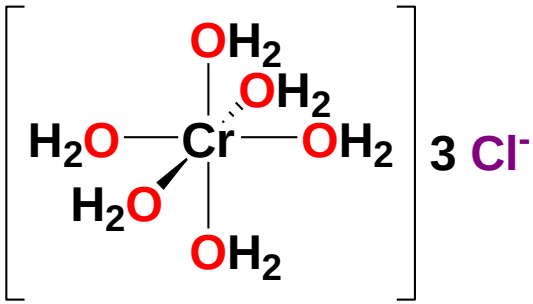




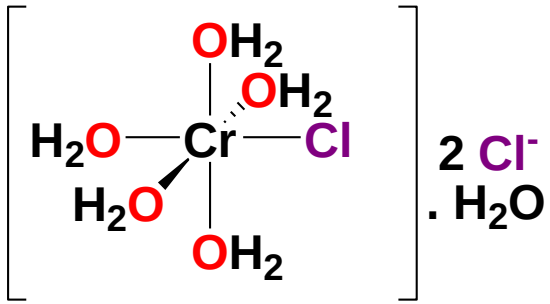


Solvation isomerism

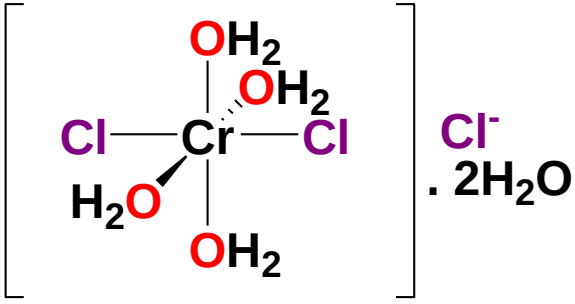
Solvation isomers differ from each other in the way they bind solvent molecules. When the solvent is water, this is the case of hydration isomers.



$[Cr(H_2O)_6]Cl_3$
violet

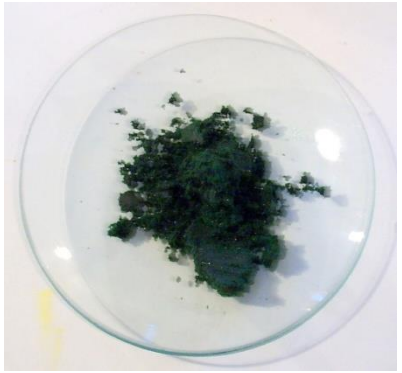


$[Cr(H_2O)_5Cl]Cl_2 . H_2O$
light green



$[Cr(H_2O)_4Cl_2]Cl.2H_2O$
dark green

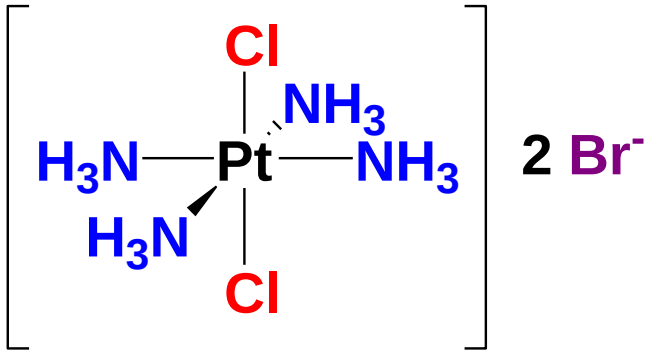
interchange of water molecules with anionic ligands

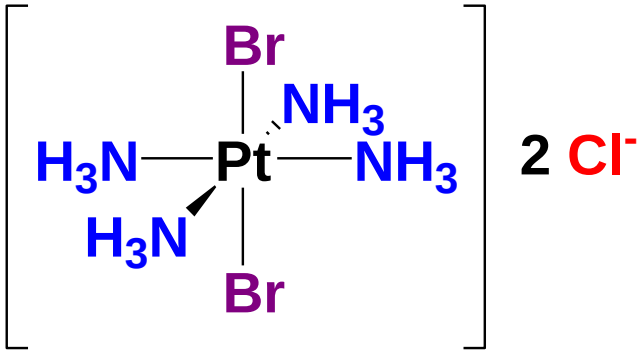


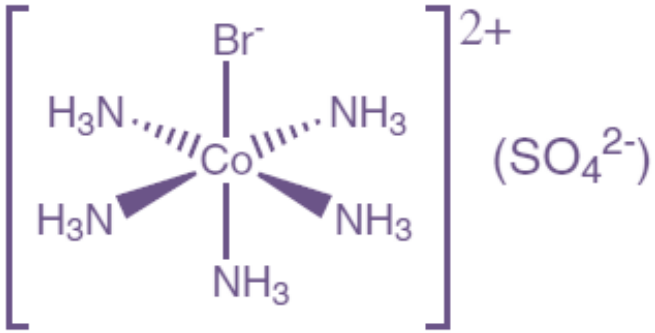
Ionisation isomerism

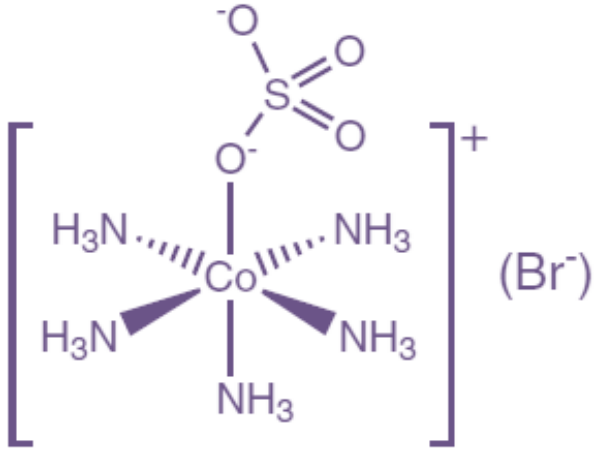
Ionization isomerism is determined by the property of complex combinations of the same composition to form different ions in solution.

interchange of internal and external anionic ligands

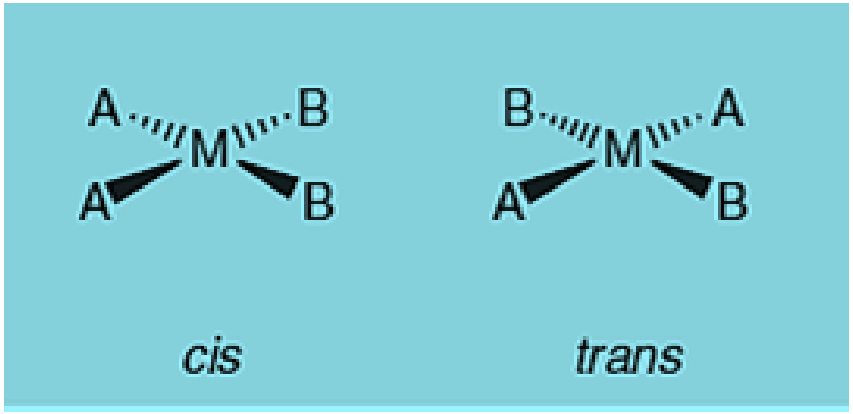






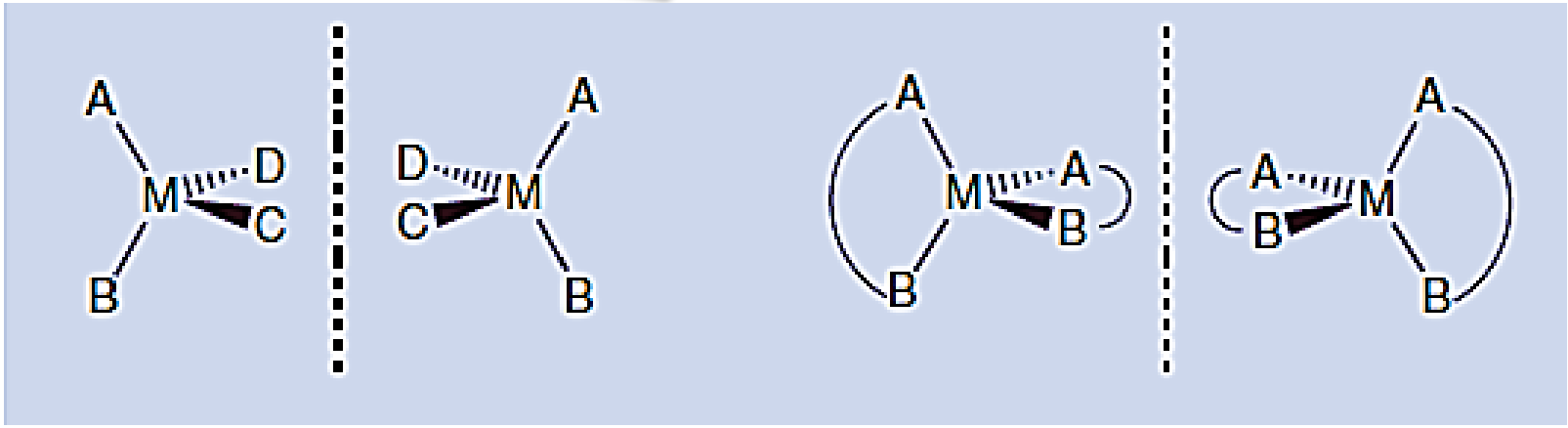


Stereoisomerism in hexacoordinate combinations



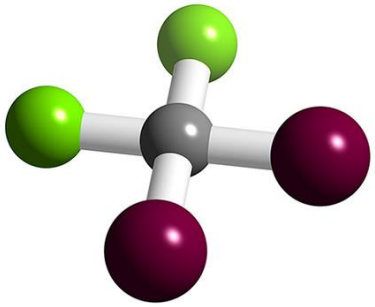
Complex tetracoordinate combinations with square-planar geometry have two geometric isomers.

Complex tetracoordinate combinations with tetrahedral geometry cannot have geometric isomerism, but they can have optical isomerism.

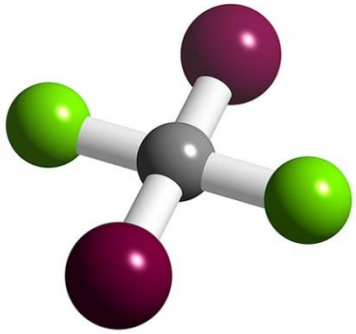


Stereoisomerism in hexacoordinate combinations

Square-planar complexes



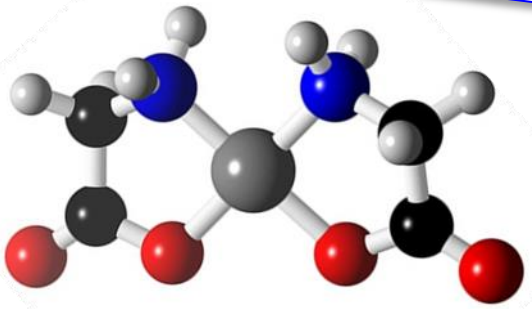
cis - MA_2B_2



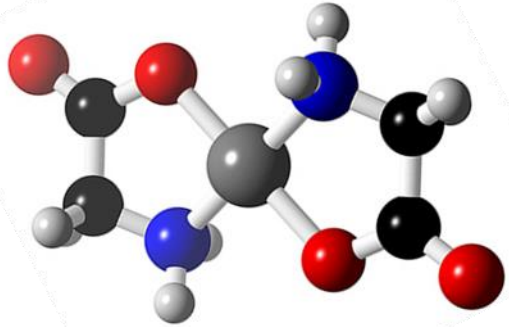
trans - MA_2B_2

The only isomers are *cis* and *trans*

Chelated bidentate ligands, as in **$[M(AB)_2]$** combinations, can generate *cis* and *trans*geometric isomers.



cis–$[Pt(O_2C\text{-}CH_2NH_2)_2]$

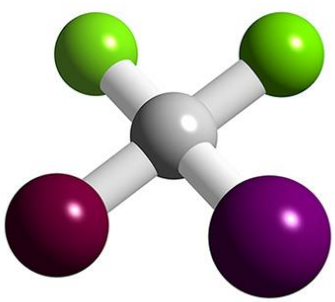


trans–$[Pt(O_2C\text{-}CH_2NH_2)_2]$

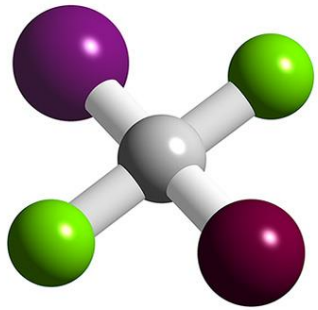
Stereoisomerism in hexacoordinate combinations

Square-planar complexes

Even with three different types of ligands *cis* and *trans* isomers can be obtained.

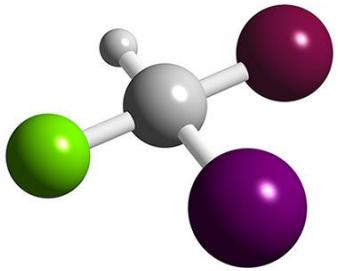


cis - MA_2BC

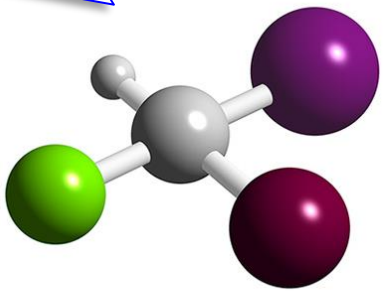


trans - MA_2BC

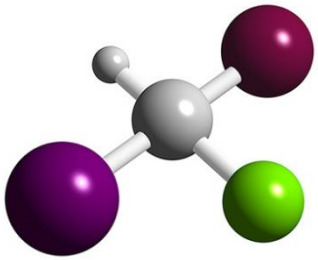
Instead, for the **MABCD** complexes with four different types of ligands, three geometric isomers are obtained.



A *trans* D



A *trans* C

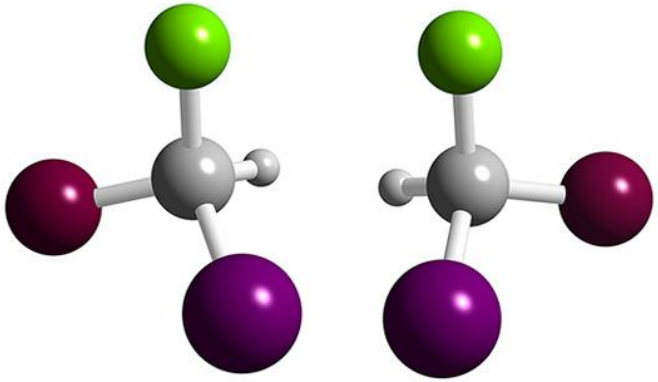


A *trans* B

Stereoisomerism in hexacoordinate combinations

Tetrahedral complexes

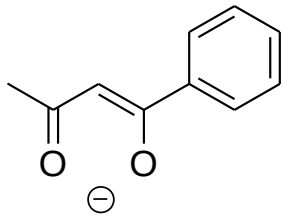
When all four ligands are different → *chiral* molecules



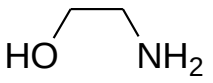
MABCD Enantiomers

The only possible isomers are the ***optical***ones.

Or when there are two non-symmetric chelate bidentate ligands → *chiral*molecules

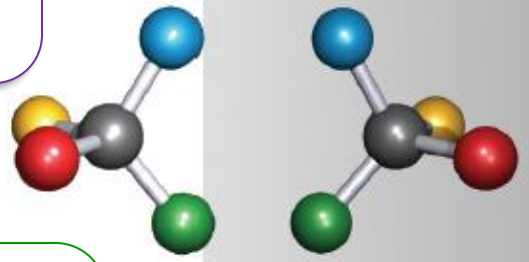


benzoilacetona



etanolamina

Two (non-superposable) optical isomers constitute an enantiomer pair.

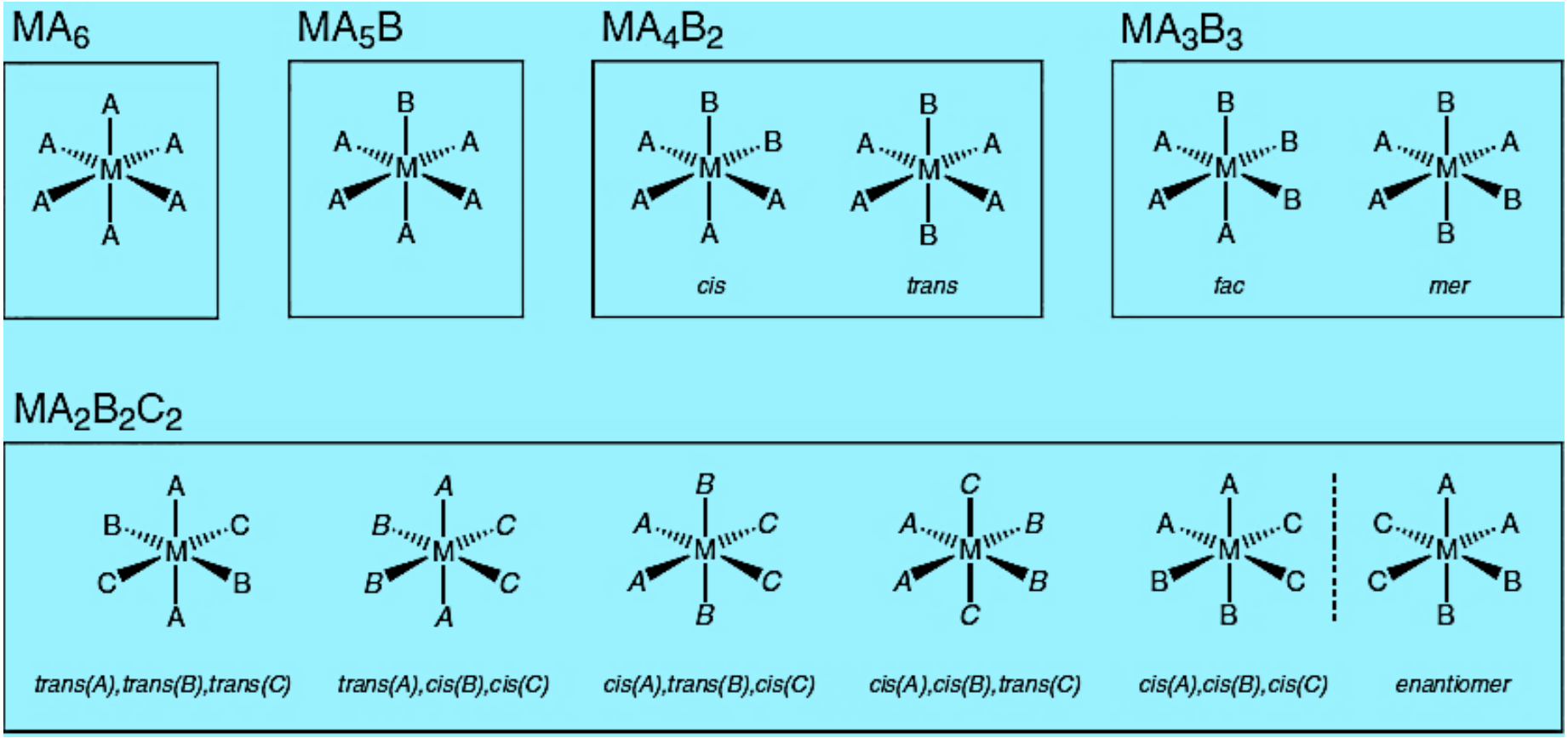


The mixture of the two enantiomers in equal amounts is called a ***racemic mixture***.

Chirality in architecture

Stereochemistry of complex combinations

Stereoisomerism in hexacoordinate combinations

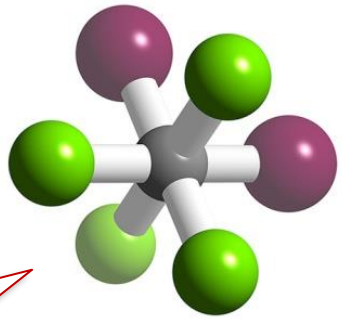


Stereoisomerism in hexacoordinate combinations

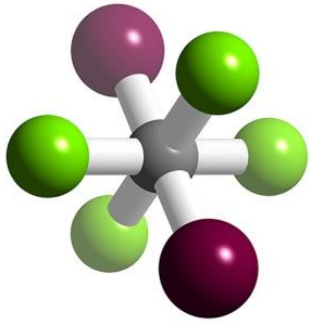
Octahedral complexes

The $[MA_6]$ and $[MA_5B]$ complexes have no isomers, while the $[MA_4B_2]$ complexes have geometric isomerism.

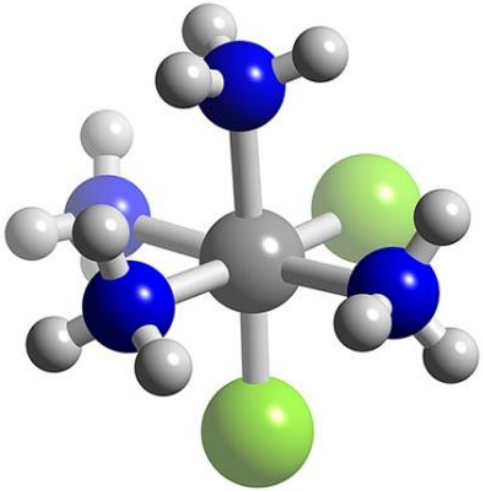
Isomers *cis* and *trans* for **$[MA_4B_2]$** type complexes



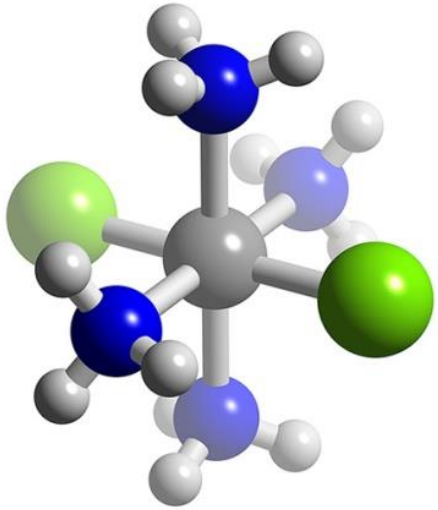
cis-MA_4B_2



trans-MA_4B_2



cis-$[Co(NH_3)_4Cl_2]$



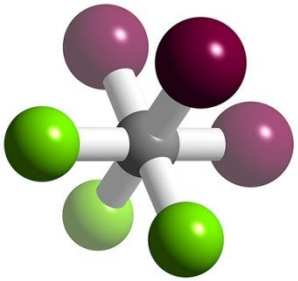
trans-$[Co(NH_3)_4Cl_2]$

Stereoisomerism in hexacoordinate combinations

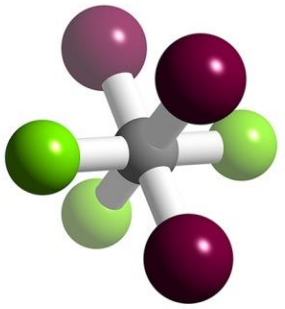
Octahedral complexes

Geometric isomerism is also shown by $[MA_3B_3]$-type complexes:

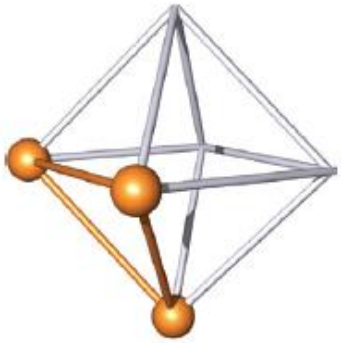
Isomers ***fac*** and ***mer*** for $[MA_3B_3]$ type complexes



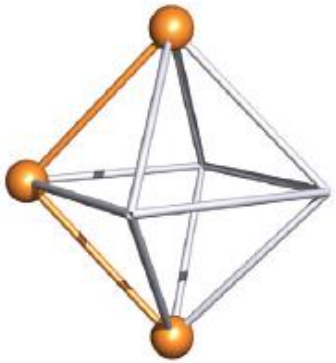
fac-MA_3B_3



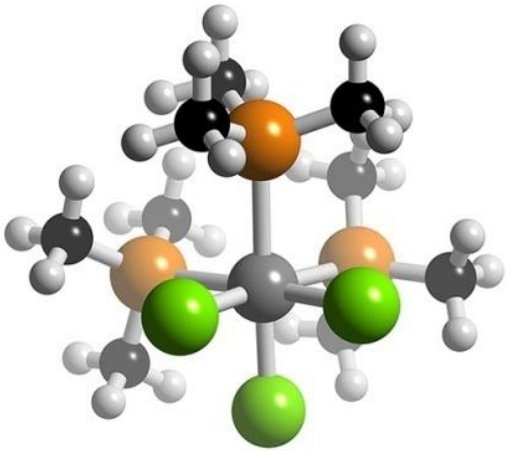
mer-MA_3B_3



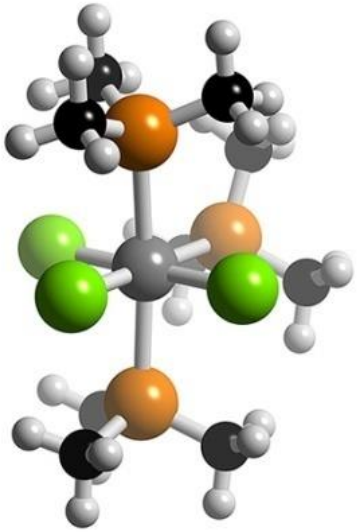
facial arrangement
isomer *fac*



meridian arrangement
izomer *mer*



fac-$[IrCl_3(PMe_3)_3]$

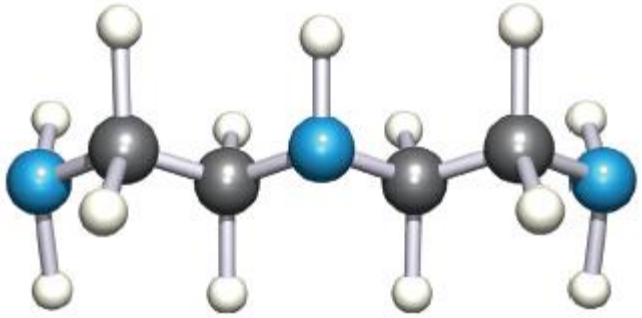


mer-$[IrCl_3(PMe_3)_3]$

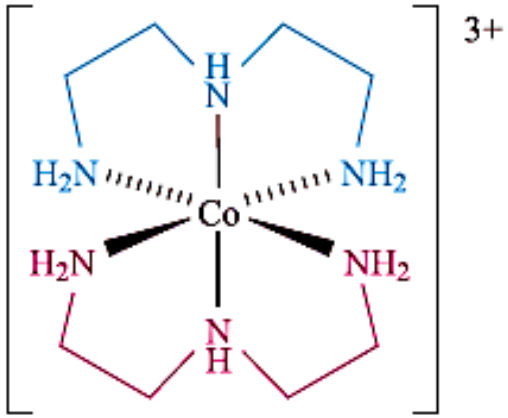
Stereoisomerism in hexacoordinate combinations

Octahedral complexes

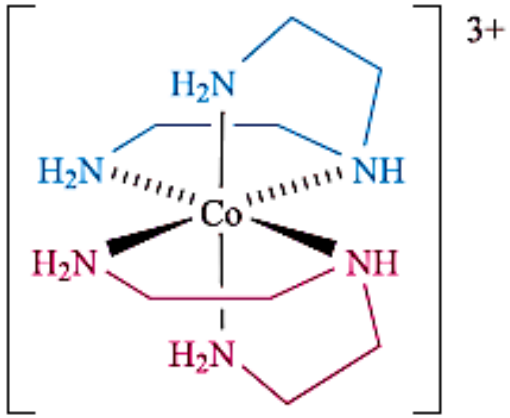
The $[M(L\text{-}L\text{-}L_{)2}]$ complexes have three geometric isomers.



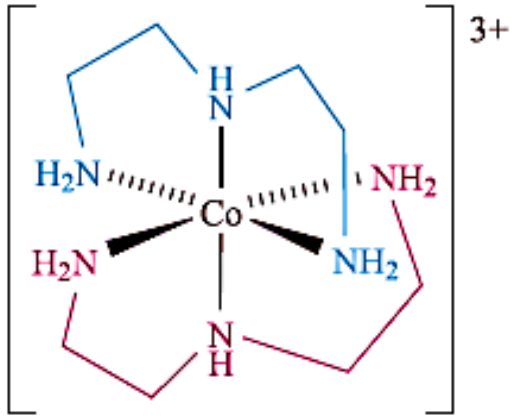
The tridentate ligand "dien" in extended conformation



isomer *fac*
symmetric



isomer *fac*
asymmetric

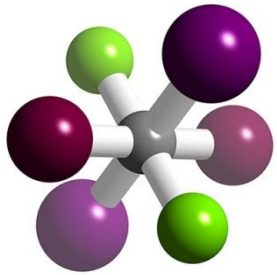


isomer *mer*

Stereoisomerism in hexacoordinate combinations

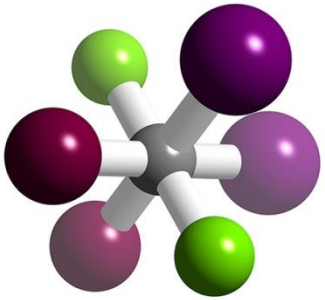
Octahedral complexes

Five different isomers exist for $[MA_2B_2C_2]$ type complexes:

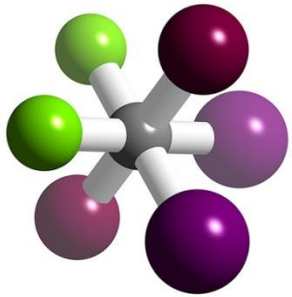


$MA_2B_2C_2$ – all the *trans* ligands

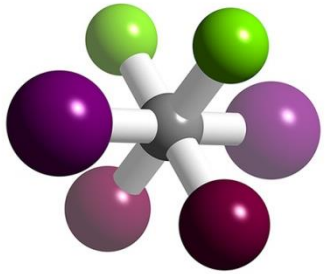
three different isomers with one pair of *trans* and one pair of *cis* ligands



$MA_2B_2C_2$-*trans, cis, cis*

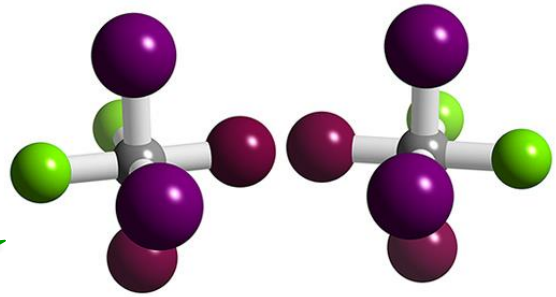


$MA_2B_2C_2$-*cis, trans, cis*



$MA_2B_2C_2$-*cis, cis, trans*

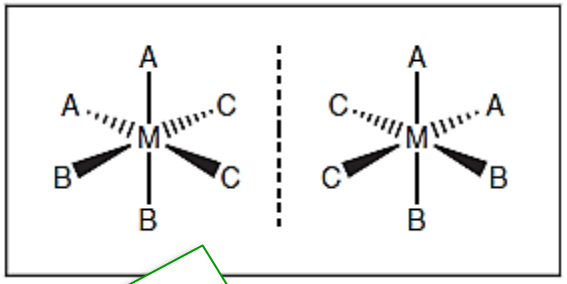
an enantiomeric pair of the isomer with all *cis* ligands **(optical isomerism)**



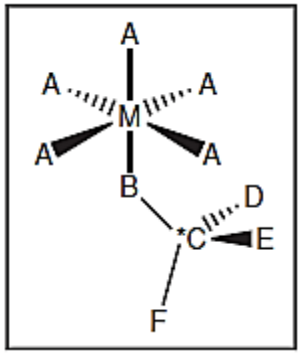
$MA_2B_2C_2$-*cis, cis, cis*

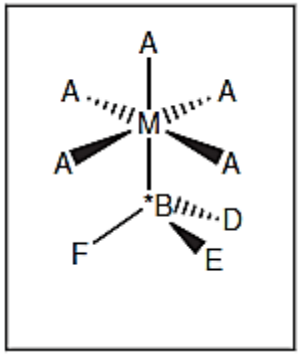
Stereoisomerism in hexacoordinate combinations

Octahedral optical isomers



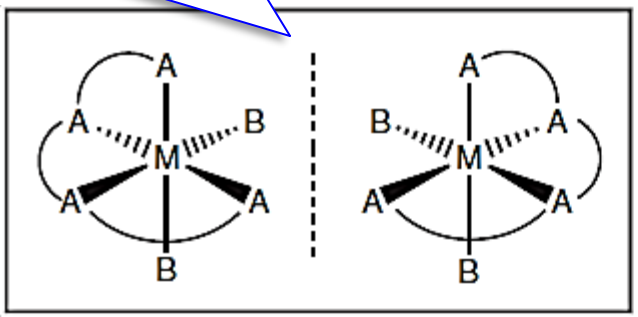
Chirality arises from the different distribution of monodentate ligands around the metal centre.

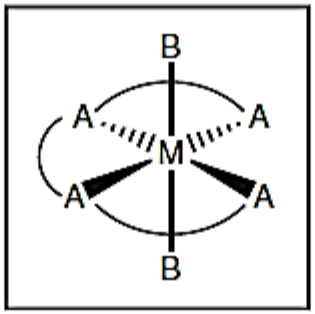


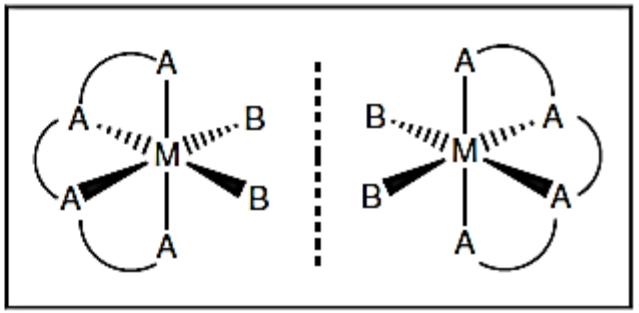


Chirality also arises from the coordination of an organic ligand that is asymmetric, hence chiral, or with the asymmetric centre attached to the metal centre

three geometric isomers (diastereoisomers) for $[M(AAAA)B_2]$ complexes





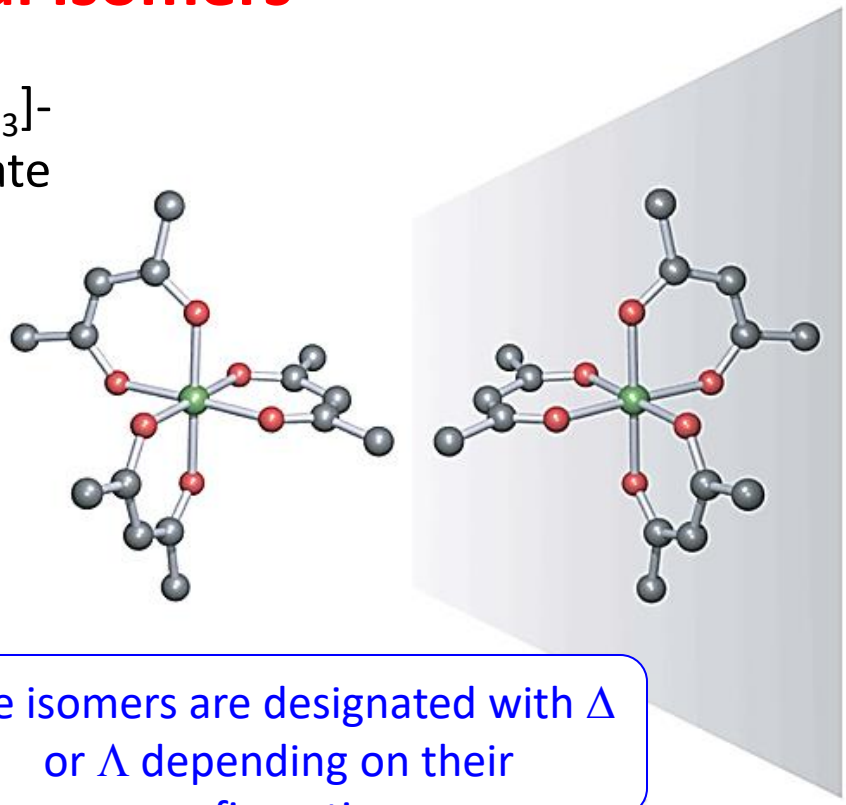


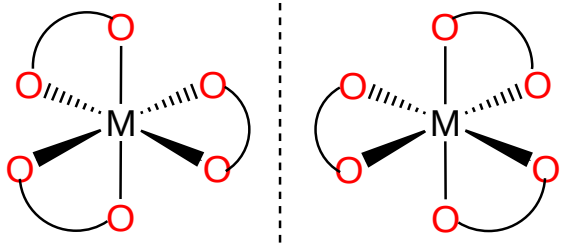
Stereoisomerism in hexacoordinate combinations

Octahedral optical isomers

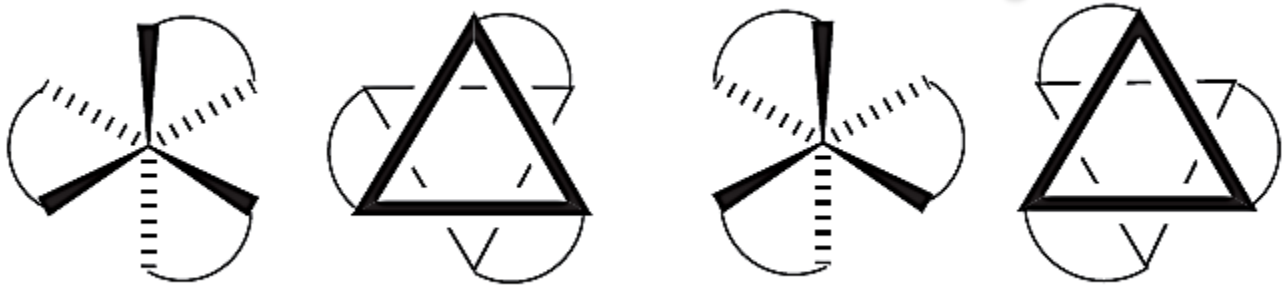
Optical isomerism occurs in simple $[M(L\text{-}L)_3]$-type complexes containing chelate bidentate ligands.

The $[M(acac)_3]$ complexes exist as a pair of enantiomers.





The isomers are designated with Δ or Λ depending on their configuration.

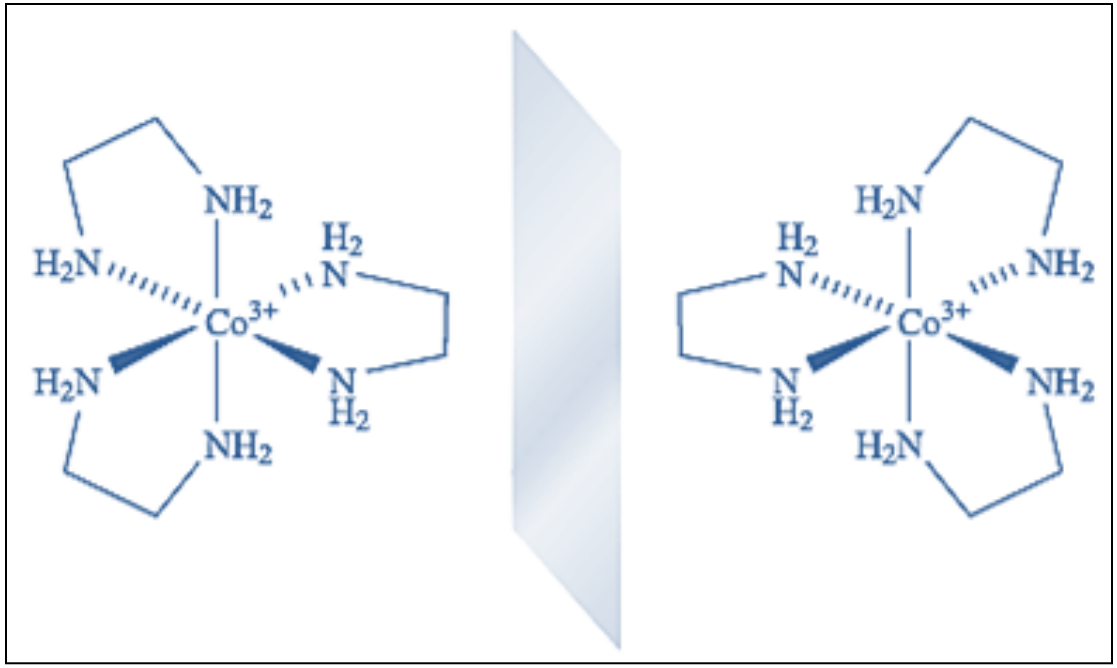


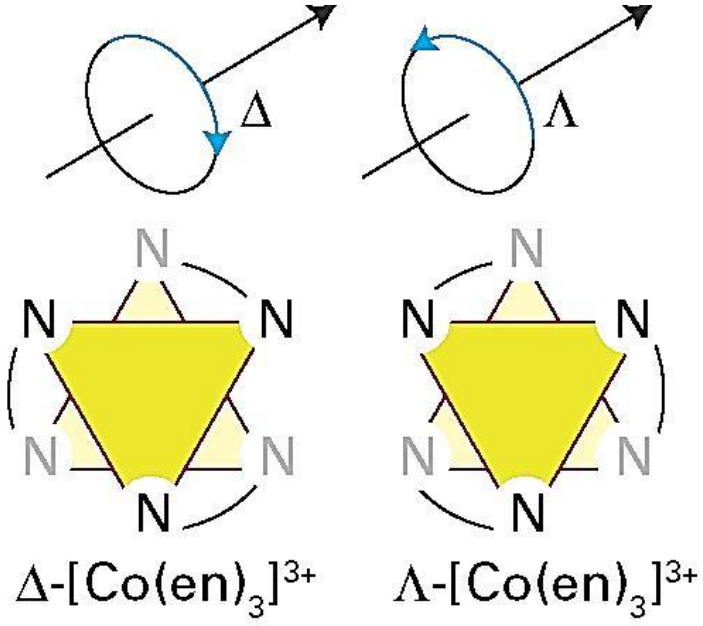
Δ Λ

Stereoisomerism in hexacoordinate combinations

Octahedral optical isomers

Prefixes Δ and Λ: enantiomers of octahedral complexes containing three equivalent bidentate ligands are distinguished using the prefixes Δ and Λ. The octahedron is viewed along an axis, and the chelae then define a helix oriented to the right (Δ) or left (Λ).



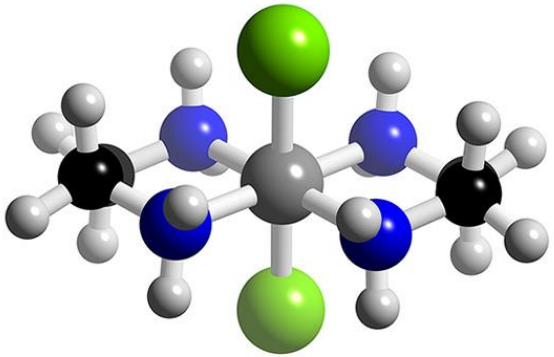


Stereoisomerism in hexacoordinate combinations

Octahedral optical isomers

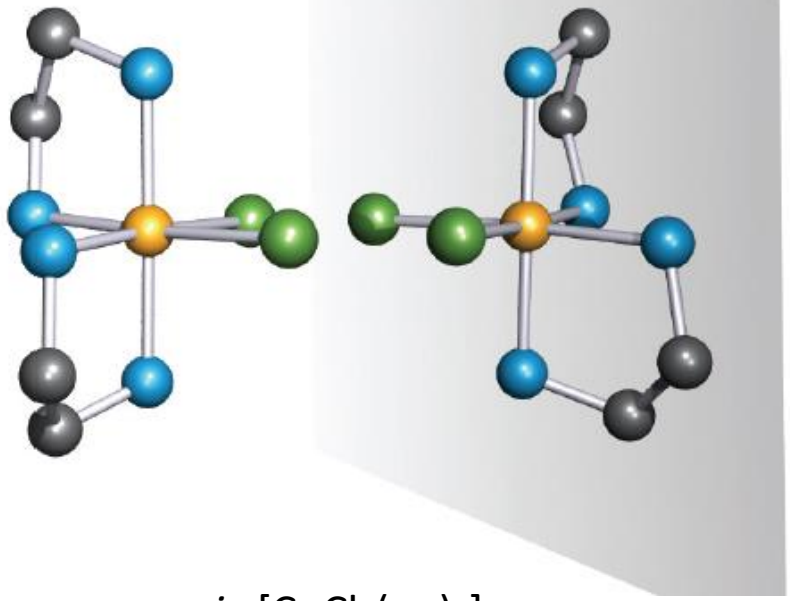
Complexes of the type [MA2(L-L$_{)2}$] also exhibit **optical isomers** when the two A ligands are in *cis*, but not when they are in *trans* to each other.

achiral isomer, optically inactive



trans – $[CoCl_2(en)_2]$

optical isomers

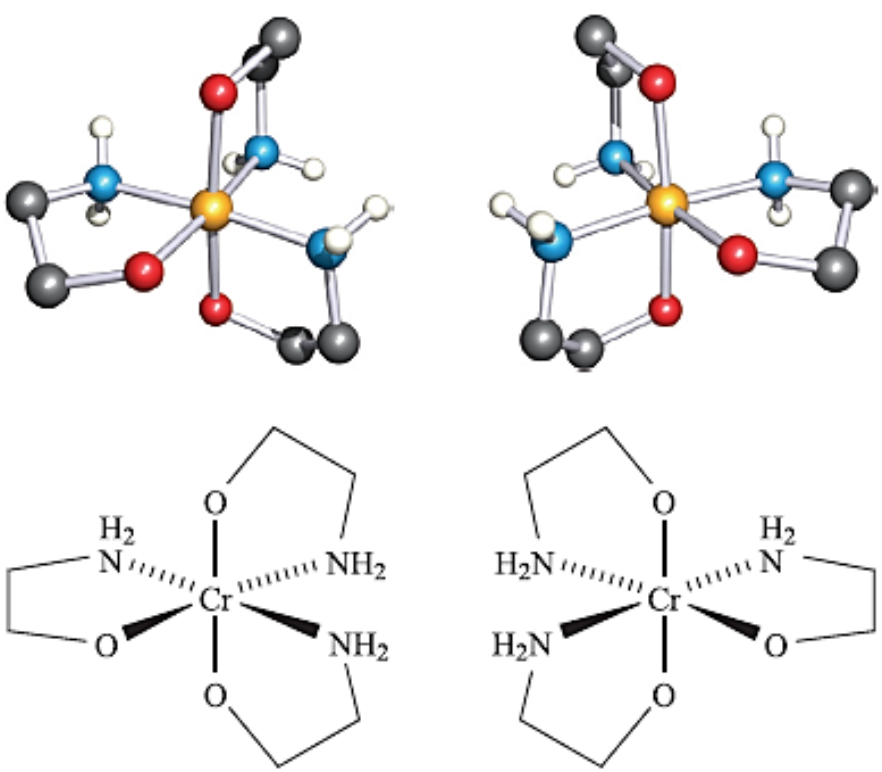


cis-$[CoCl_2(en)_2]$

Stereoisomerism in hexacoordinate combinations

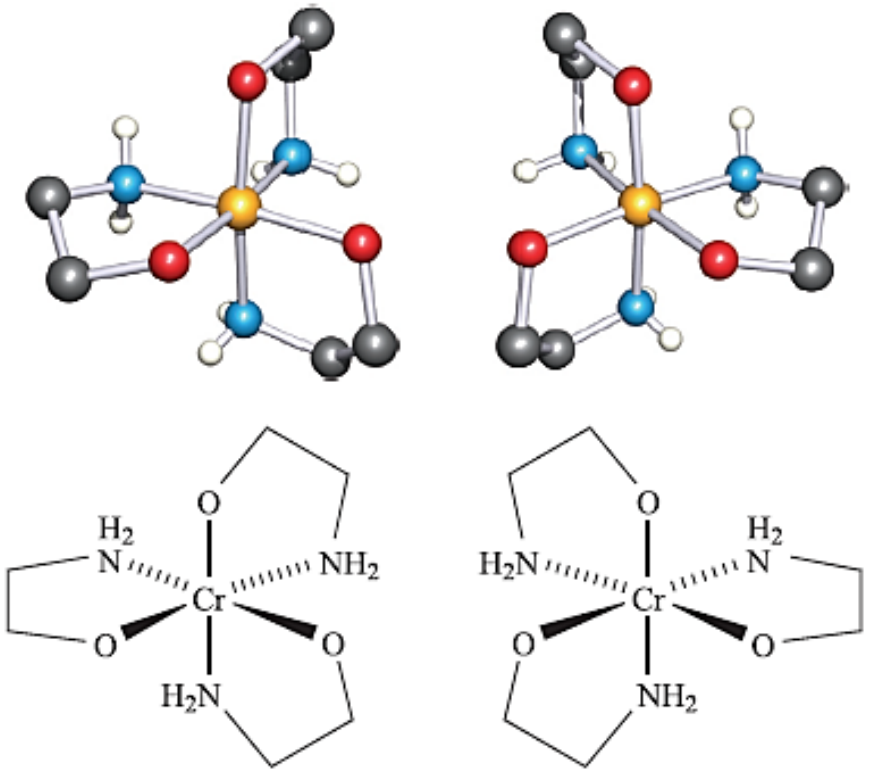
Octahedral optical isomers

The $[M(L\text{-}L'_{)3}]$ complexes can also have two pairs of **optical isomers**.



mer arrangement (O atoms and NH_2 groups)

enantiomers



fac arrangement (O atoms and NH_2 groups)

enantiomers