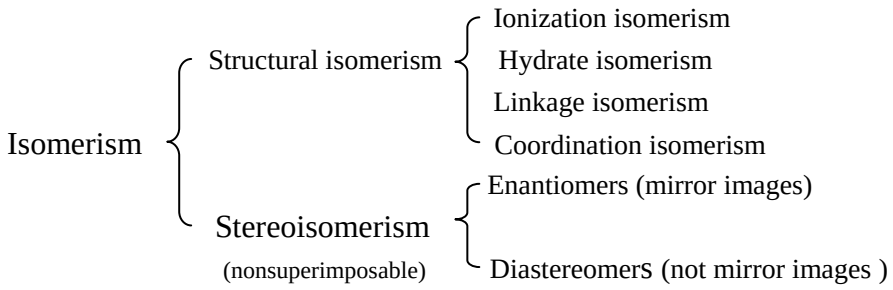
Isomerism of Coordination Compound

Isomerism of complexes: For simple molecules, a molecular formula is sufficient to identify a molecule. However, as a coordination compound is much more complicated, the formulas are not always adequate: the ligands could change their positions and/or arrangements, leading to different molecules/ions which have the same chemical formula. Isomers have different chemical/physical properties, such as color or optical activity.



1. Structural isomers:

Have the same chemical formula, but differences in connectivity between the atoms.

1). Ionization isomerism: ligand(s) and counterion(s) are exchanged (same sum formula!).
e.g. $[Pt(NH_3)_4\underline{Cl_2}]\underline{Br_2}$ and $[Pt(NH_3)_4\underline{Br_2}]\underline{Cl_2}$

2). Hydrate isomerism: A kind of ionization isomerism, but one of the ligands is water.
e.g. $CrCl_3 \cdot 6H_2O$: $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

3). Linkage isomerism: a ligand connects with the central metal atom through different atoms. e.g. the NO_2 group can be bonded either through the nitrogen or through one of the oxygen atoms, so that a formula like $[Co(NO_2)(NH_3)_5]^{2+}$ might correspond to two molecules (here: nitro or nitrito complex).

4). Coordination isomerism: the metal ions in a compound with two comlex ions exchange their places. e.g. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

2. Stereoisomerism

Have the same molecular formula and connective sequence of the atoms, but differ in spatial arrangements of their atoms. The most typical character of them is ‘nonsuperimposable’.

1). Enantiomers: are a pair of stereoisomers that are related to each other by reflection. Enantiomerism could result from the chirality of the central metal, chirality of the ligand and/or chirality of the metal/ligand system. Pure enantiomers are optically active: that the plane of polarized light rotates in different directions when the light goes through them.

2). Diastereomers: are stereoisomers which are not enantiomers. There are two pairs of terms for identifying diastereomers.

a) cis-*trans*: When a pair of identical ligands are arranged in opposing directions, the isomer is referred as *trans*, on the contrary, the isomer is referred as *cis*,.

b) *fac-mer*: When three identical ligands occupy the vertices of one face of an octahedron, the isomer is referred as *fac(ial)*. If these three ligands together with the metal ion form a plane in the octahedron, the isomer is referred as *mer(idional)*.

Reference:

1. Inorganic Chemistry, 4th edition by Shriver Atkins.
2. Inorganic Chemistry, by Holleman-Wiberg
3. http://en.wikipedia.org/wiki/complex_(chemistry)
4. http://en.wikipedia.org/wiki/isomer

Questions:

1. Give examples for four different types of structural isomers.
2. How can you distinguish a pair of linkage isomers containing a nitro group and a nitroto group respectively?
3. Sketch *cis-trans* and *fac-mer* isomers.