

2.5: Isomerism

Here, we will apply isomerism to coordination chemistry. Some forms of isomerism in organic and coordination chemistry are the same, but there are some forms of isomerism that only occur in coordination chemistry.

Let us first briefly review the definition of isomerism: Isomerism is when two or more compounds have identical empirical formulas but different structures.

Definition: Isomerism

When two or more compounds have identical empirical formulas but different structures they are called isomers.

We distinguish between two basic types of isomerisms: constitutional isomerism and stereoisomerism. Remember, constitutional isomerism the bonds are not between the same atoms.

Definition: Constitutional Isomers

In constitutional isomers the bonds are not between the same atoms.

In stereoisomerism, the bonds are between the same atoms, but ligands are at different coordination sites.

Definition: Stereoisomers

In stereoisomers, the bonds are between same atoms, but the ligands are at different coordination sites.

Forms of Constitutional Isomerism

Ionization Isomerism

One form of isomerism is the ionization isomerism. In this case one or more anionic ligand(s) and counterion(s) switch places.

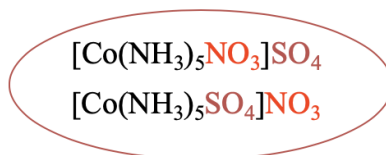


Figure 2.5.1. Two ionization isomers of the complex $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$

For example, in the compound $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$ there is a nitrate ion acting as a ligand, and a sulfate ion in acting as a counterion (Figure 2.5.1). There is an ionization isomer to this compound, in which the sulfate ion is now in the first coordination sphere, and the nitrate is in the second coordination sphere.

Coordination Isomerism

Another form of constitutional isomerism is coordination isomerism. In this isomerism, ligands are bound to different metal ions. Naturally, this implies that this form of isomerism can only exist if at least one isomer has two distinguishable metal ions.

For example, the compound $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ has two different coordination isomers. At first glance, they do not seem to be isomers at all. However, we can verify that they have the same empirical formula than the first compound (Figure 2.5.2).

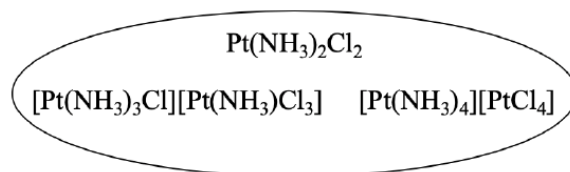


Figure 2.5.2. Two different coordination isomers for the complex $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

$[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$ has two Pt atoms, four NH_3 units and four Cl atoms. That makes $\text{Pt}_2(\text{NH}_3)_4\text{Cl}_4$. This formula can be divided by 2 to to give $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. We can now easily see that the two compounds are isomers. The third isomer also has two Pt

atoms, four NH_3 units, and four chloro atoms, so it must be an isomer as well.

Linkage isomerism

Linkage isomerism, also called ambidentate isomerism, is an isomerism that can be observed for ligands that have more than one reactive end. In two linkage isomers, the ligands will bind with different ends to the metal.

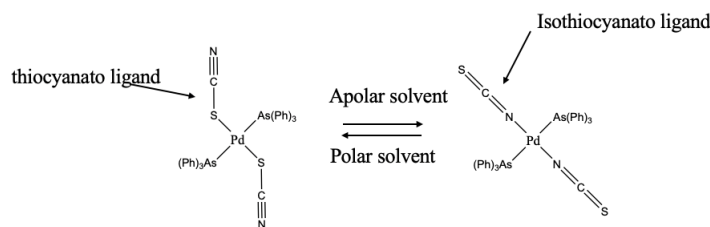


Figure 2.5.3. Two ambidentate isomers of thiocyanate

An example of an ambidentate ligand is the thiocyanate anion (Figure 2.5.3). It can bind either with the sulfur or with the nitrogen end to a metal ion. When it binds with the S-end it is called the thiocyanato ligand, when it binds with the N-end it is called the isothiocyanato ligand. Which atom binds to the metal can depend on the solvent. It is even possible that two, same ambidentate ligands bind with opposite ends to the metal in one and the same molecule. An example is the complex shown (Figure 2.5.4). In this molecule, there is a thiocyanato and an isocyanato ligand binding to Pd.

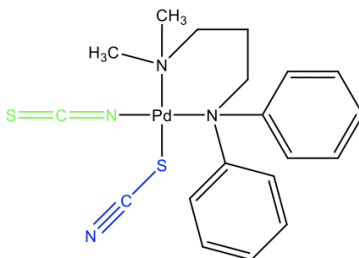


Figure 2.5.4. An example of two, same ambidentate ligands binding with opposite ends to the metal in one and the same molecule.

Thio- and isothiocyanato ligands are not the only examples of ambidentate ligands.

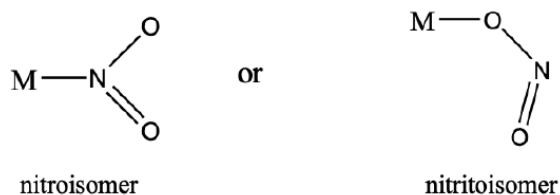


Figure 2.5.5. Two linkage isomers of the nitrite anion

Another example is the nitrite anion. It can either bind with the N- end or the O-end to a metal. In the first case it is called a nitroisomer, in the latter it is called a nitrito isomer (Figure 2.5.5). Nitritoisomers are usually more stable.

Stereoisomers (Configuration Isomers)

Now let us discuss the second major type of isomerism: stereoisomerism. As mentioned previously, in stereoisomerism the bonds are between the same atoms, but the positions at which the ligands bind, the coordination sites, are different. There are two basic types of stereoisomerism: diastereomerism and enantiomerism (Figure 2.5.6).

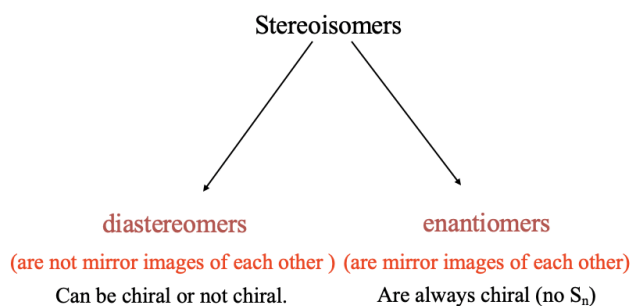


Figure 2.5.6. Types of stereoisomerism

In diastereomerism, the diastereomers are not mirror images to each other.

Definition: Diastereomers

Diastereomers are stereoisomers that are not mirror images of each other. They can be chiral or not chiral.

In enantiomerism, the enantiomers are mirror images to each others. Enantiomers are always chiral molecules.

Definition: Enantiomers

Stereoisomers that are mirror images of each other. They are always chiral.

Diastereomers can be chiral, but do not have to be chiral. Remember, a molecule is chiral when it does not contain an internal plane of symmetry.

Cis-Trans Isomerism

Let us now discuss some common forms of stereoisomerism. The cis-trans isomerism is one very common stereoisomerism. It occurs when two, same ligands are in adjacent or opposite positions. For example, in a square planar complex two ligands can be adjacent or in opposite positions. When in adjacent position, the bond angle is 90° and we have a cis-isomer, when in opposite position, the bond angle is 180° and we have a trans-isomer.

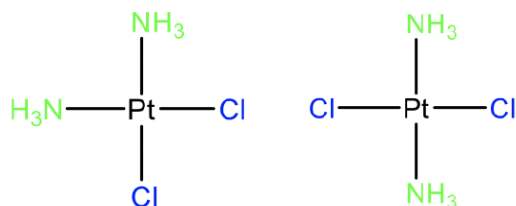


Figure 2.5.7 Cis-platinum and trans-platinum, respectively

The probably most well known example of a cis-isomer in coordination chemistry is cis-platinum which is an anti-cancer drug (Figure 2.5.7). Its trans-isomers does not have these pharmaceutical properties showing that cis-trans isomerism can have a profound impact on the properties of a molecule. Overall cis-trans isomerism in Pt(II) complexes have been most intensely studied, but cis-trans isomerism is also known for other d^8 metal ions in square planar complexes. We can also ask if cis- and trans isomers are diastereomers or enantiomers. Let us look at the example of cis- and trans-platinum to answer this question. Clearly, these two isomers are not mirror images to each other, so they must be diastereomers. Generally, cis- and trans- isomers are diastereomers.

Cis-trans isomerism extends beyond square planar complexes, and is also known for other shapes, for example, the octahedral shape. In the cis-isomer of an octahedral complex two ligands occupy positions on the same face of the octahedron, whereas in the trans-isomer they occupy opposite position of the octahedron.

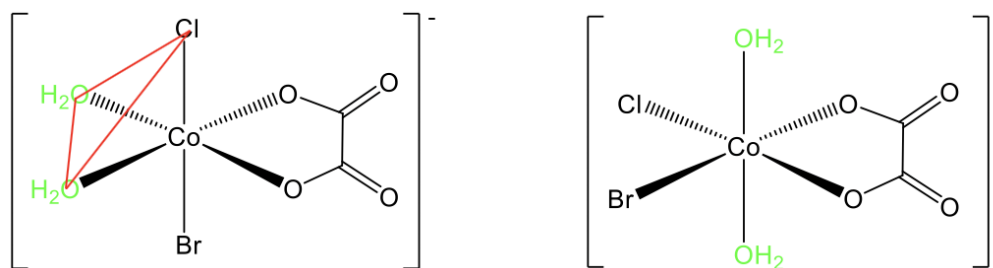


Figure 2.5.8. Cis and trans isomers of the diaquabromochlorooxalato cobalt(1-) complex, respectively

For example, in the complex diaquabromochlorooxalato cobalt(1-) there are cis and trans isomers known (Figure 2.5.8). In the trans-isomer the two aqua-ligands stand in opposite position, and there is a 180° angle between them. In the cis-isomer they are in adjacent position, and the angle is 90° . We can see that the two ligands are on the same triangular face of the octahedron, shown in red.

Fac-mer Isomerism

Another common type of stereoisomerism in coordination chemistry is fac-mer isomerism. Fac stands for facial and mer stands for meridional. In a fac-isomer the same ligands are on a common face of a polyhedral complex, in the mer isomer they are on a plane that bisects the polyhedron. This kind of isomerism is very common for octahedral complexes, but not restricted to those.



Figure 2.5.9. Fac- (left) and mer-isomers (right) of the triammine trichloro cobalt(III) complex.

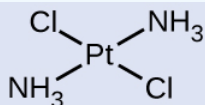
For example the complex triamminetrichlorocobalt(III) has a fac- and a mer-isomer. You can see that in the fac-isomer the identical ligands are on two opposite triangular faces of the octahedron. In the mer-isomers they lie on two planes that bisect the octahedron. We can again ask if they are diastereomers or enantiomers? The answer is: They are not mirror images to each other, so they are not enantiomers, but diastereomers.

✓ Example 2.5.1: Geometric Isomers

Identify which geometric isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is shown in Figure 2.5.9b. Draw the other geometric isomer and give its full name.

Solution

In the Figure 2.5.9b, the two chlorine ligands occupy *cis* positions. The other form is shown in below. When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diaminedichloroplatinum(II).

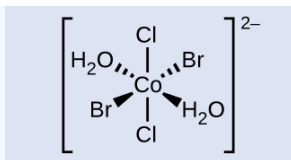


The *trans* isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has each ligand directly across from an adjacent ligand.

? Exercise 2.5.1

Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).

Answer



Optical Isomerism

Another important type of isomers are optical isomers, or enantiomers, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as $[M(en)_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in Figure 2.5.10. These two isomers will react differently with other optical isomers. For example, DNA helices are optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.

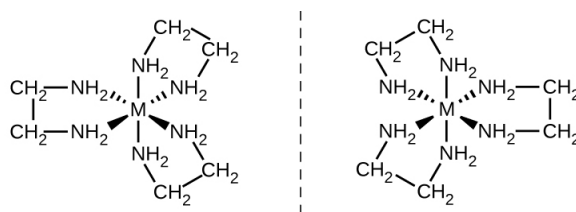


Figure 2.5.10: The complex $[M(en)_3]^{n+}$ (M^{n+} = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.

The $[Co(en)_2Cl_2]^+$ ion exhibits geometric isomerism (*cis/trans*), and its *cis* isomer exists as a pair of optical isomers (Figure 2.5.11).


 For the *cis* isomers, the structural formula shown are mirror images of one another. The two chlorine atoms are adjacent to one another in each *cis* structure. The *trans* form is also shown with the chlorine directly opposite from one another.

Figure 2.5.11: Three isomeric forms of $[Co(en)_2Cl_2]^+$ exist. The *trans* isomer, formed when the chlorines are positioned at a 180° angle, has very different properties from the *cis* isomers. The mirror images of the *cis* isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.

Glossary

cis configuration

configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

ionization isomer

(or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

linkage isomer

coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

optical isomer

(also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

trans configuration

configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

Dr. Kai Landskron ([Lehigh University](#)). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: [Click Here to Donate](#).

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