

## 19.4: Isomerism

### Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride,  $(\text{NH}_3)_2\text{PtCl}_2$ . This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

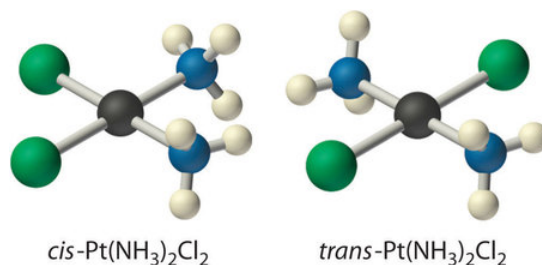


Figure 19.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of [coordination compounds](#) bond together is discussed in the chapter of [Lewis acids and bases](#). For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

### CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

### CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two amines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

### ? Exercise 19.4.1

Draw the cis and trans isomers of the following compounds:

- $(\text{NH}_3)_2\text{IrCl}(\text{CO})$
- $(\text{H}_3\text{P})_2\text{PtHBr}$
- $(\text{AsH}_3)_2\text{PtH}(\text{CO})$

### ? Exercise 19.4.2

Only one isomer of  $(\text{tmeda})\text{PtCl}_2$  is possible [ $\text{tmeda} = (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ ; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

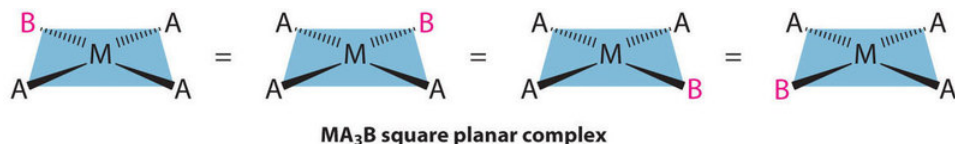
## Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

### Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called **geometrical isomers**. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar  $\text{MA}_3\text{B}$  complex; hence only a single geometrical isomer is possible in this case (and in the analogous  $\text{MAB}_3$  case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



For an  $\text{MA}_2\text{B}_2$  complex, there are two possible isomers: either the A ligands can be adjacent to one another (**cis**), in which case the B ligands must also be cis, or the A ligands can be across from one another (**trans**), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

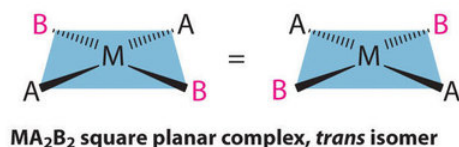
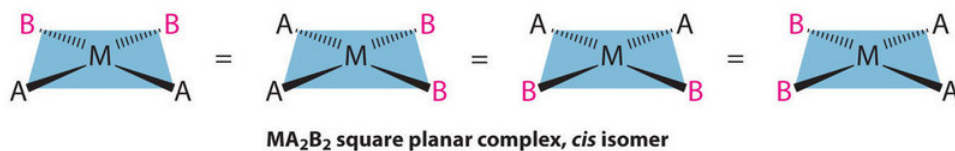
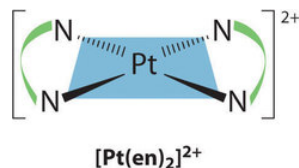


Figure 19.4.1).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed

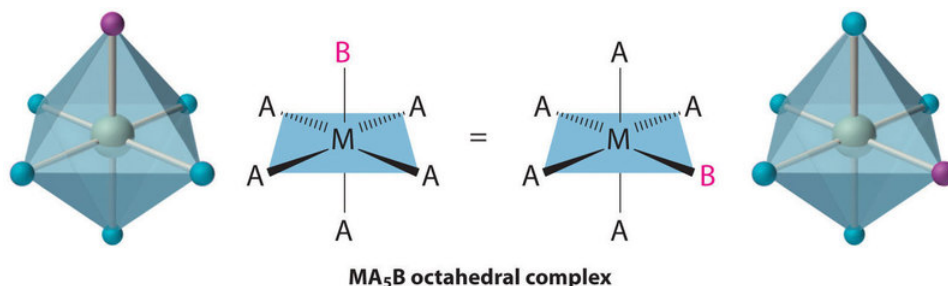
with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

Square planar complexes that contain symmetrical bidentate ligands, such as  $[\text{Pt}(\text{en})_2]^{2+}$ , have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:

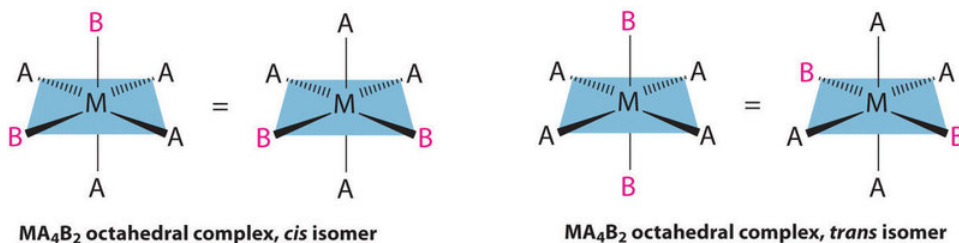


## Octahedral Isomers

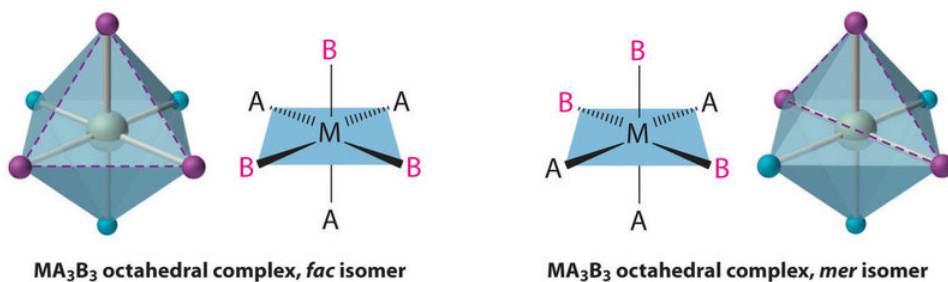
Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five ( $\text{MA}_5\text{B}$ ). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an  $\text{MA}_5\text{B}$  structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an  $\text{MA}_5\text{B}$  structure are as follows:



If two ligands in an octahedral complex are different from the other four, giving an  $\text{MA}_4\text{B}_2$  complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  are examples of this type of system:



Replacing another A ligand by B gives an  $\text{MA}_3\text{B}_3$  complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



### ✓ Example 19.4.1

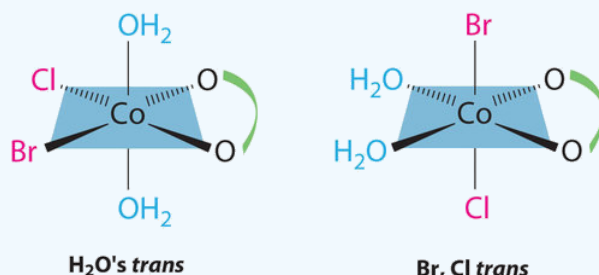
Draw all the possible geometrical isomers for the complex  $[\text{Co}(\text{H}_2\text{O})_2(\text{ox})\text{BrCl}]^-$ , where ox is  $^-\text{O}_2\text{CCO}_2^-$ , which stands for oxalate.

**Given:** formula of complex

**Asked for:** structures of geometrical isomers

#### Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical ( $\text{H}_2\text{O}$ ). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:



In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



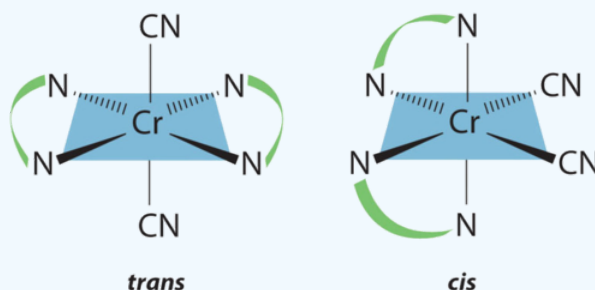
This complex can therefore exist as four different geometrical isomers.

### ? Exercise 19.4.1

Draw all the possible geometrical isomers for the complex  $[\text{Cr}(\text{en})_2(\text{CN})_2]^+$ .

#### Answer

Two geometrical isomers are possible: trans and cis.



## Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

## Contributors and Attributions

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