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 MA3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:

![Planar Isomers Diagram](image)

For an MA2B2 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:

![Planar Isomers Diagram](image)

Because there is no way to convert the cis structure to the trans by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of cis and trans isomers of an MA2B2 square planar complex are cis-Pt(NH3)2Cl2, also known as cisplatin, and trans-Pt(NH3)2Cl2, which is actually toxic rather than therapeutic.
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 \([\text{Pt(en)}_2]^{2+}\), 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 (MA₅B). 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 MA₅B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA₅B structure are as follows:
If two ligands in an octahedral complex are different from the other four, giving an MA₄B₂ complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-[Co(NH₃)₄Cl₂]Cl are examples of this type of system:

Replacing another A ligand by B gives an MA₃B₃ 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 \(\PageIndex{1}\)

Draw all the possible geometrical isomers for the complex [Co(H₂O)₂(ox)BrCl]⁻, where ox is \(^{-}O₂CCO₂^{-}\), 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 (H₂O). 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 \(\PageIndex{1}\))

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

**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.