

Isomerism in Octahedral Transition Metal Complexes

As you have seen in the chemistry of carbon-containing compounds, often there are several isomers possible for the same compound formula. Even when atoms are connected in the same order it is possible that we have not uniquely described the structure of the molecule. For example, because there is no free rotation about a double bond, the cis and trans isomers are separate entities with different properties. This type of isomerism is referred to as diastereomerism (or geometric isomerism or cis-trans isomerism). Alternatively, if the four groups surrounding a tetrahedral atom are not the same, the molecule is not superimposable on its mirror image. Molecules not superimposable on their mirror images are called enantiomers (or optical isomers).

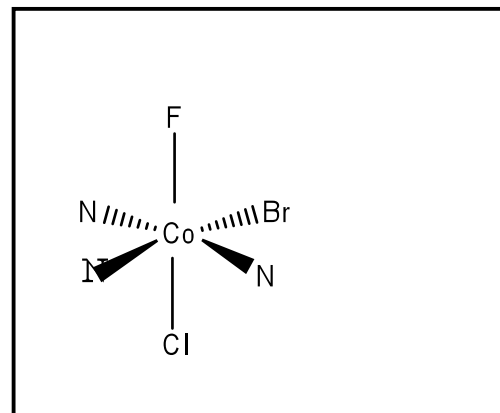
Because carbon obeys the octet rule, there are at most four different groups and two enantiomers possible per tetrahedral carbon. But what happens when there are more than four groups around a central atom? This commonly happens in transition metal chemistry where there are often six groups (called ligands) around a central metal atom. [In fact, if there are six different groups in an octahedral arrangement around a metal atom, there are 15 different geometric isomers, and each one exists as a pair of enantiomers, for a total of thirty stereoisomers!] This activity will introduce you to a systematic way to determine the number of geometric and optical isomers in an octahedral transition metal complex.

Before you begin, you should be familiar with the common ligands that can connect to a transition metal. There is such a list on page 825 of your textbook. Note that many donate one pair of electrons (monodentate ligands) while others donate two pairs of electrons (from different atoms in the ligand). The latter are called bidentate ligands. In an octahedral complex there are a total of six pairs of electrons around the metal ion. These pairs can come from six monodentate ligands, three bidentate ligands, a bidentate ligand and four monodentate ligands, or any other combination that you can think of. By knowing the names and abbreviations of the ligands you can determine number of electron pairs around the metal ion.

Let's do an example. Determine the number of geometric and optical isomers of $[\text{Co}(\text{NH}_3)_3\text{BrClF}]$.

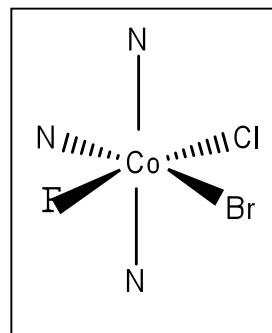
Quick check—we have six monodentate ligands attached to the cobalt, so this should be an octahedral complex.

1. Draw one isomer. (It doesn't matter which one.) In this case we can abbreviate the ligand names further, as long as doing so doesn't create confusion—for example $\text{NH}_3 = \text{N}$.
2. Ligands that are 180° to each other are said to be trans. Describe the isomer by writing trans pairs in parentheses. Thus, the structure drawn here is (Br, N), (Cl, F), (N, N). Each



geometric isomer will have a unique combination of trans ligands. You can avoid confusion by alphabetizing ligands both within the parentheses and among the set of three trans pairs. If you do this, it allows you to easily recognize whether another structure is just another picture of what you have already drawn or a unique isomer.

Example- Does the following represent a new geometric isomer of the complex?:



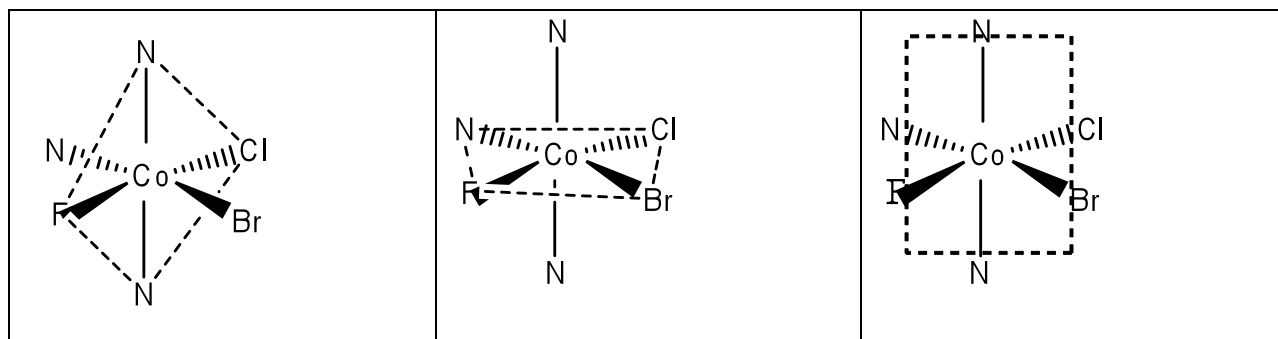
- Ligands that are 90° to each other are said to be cis. Now try switching a pair of cis ligands and drawing the picture. (You can avoid drawing repeat structures if you switch just two ligands at a time rather than randomly drawing a new structure.) Use the method for describing the complex's ligands as given in #2. Is it the same isomer as one you already have? Continue this process until you can't generate any new structures.

Example—draw all of the remaining geometric isomers for $[\text{Co}(\text{NH}_3)_3\text{BrClF}]$. Under each one that you draw, list the ligands in trans pairs as described above. (Hint—there are a total of four, including the first one already shown.)

- If the complex contains a bidentate ligand, the ends of that ligand must occupy cis sites around the octahedron. (For all common ligands, the chain of atoms connecting the atoms attached to the metal ion is not long enough for the atoms in the same bidentate ligand to be across from each other.) Connect the atoms in a bidentate ligand with a line.

Thus, en= N — N .

5. For each geometric isomer, there is the possibility that its mirror image is non-superimposable. If so, that isomer exists as a pair of enantiomers. There are two ways of determining this. First, you could build a model of the isomer, build its mirror image, and then attempt to lay the two models on top of each other. If you can get all of the atoms to align, the mirror image is superimposable and you just have two copies of the same thing. If you can't get them to align, then the two structures are enantiomers and represent different ways of arranging the atoms. The second method is really just a variation on the first but does not involve building models. In this case, look for a mirror plane within the molecule. If there is a plane within the molecule such that one half of the molecule is identical to the other half, then the mirror image WILL be superimposable on the original. If there are no such planes then the structure will exist as a pair of enantiomers. There are several "trial" planes that we might look at. Three are shown below.



In the first one, the plane contains two trans N's, the Cl and the F. (All planes must also contain the central atom.) Any atom that is in the selected plane reflects into itself. Note that the Br and one of the N's are outside of the plane. If this represented a plane of symmetry within the molecule, the reflection of the Br would have to be another Br. Since there is an N on the opposite side of the mirror from the Br, this site does not represent a mirror plane of symmetry within the structure. So, let's look at the second picture. In this case a mirror plane containing N, F, Br and Cl is shown (perpendicular to the plane of the paper). This reflects an N into another, so there is a mirror plane of symmetry in this location. In the third picture, a mirror plane is showing passing between the Br and Cl, an N and an F and containing the other two N's (this is the plane containing the paper). This plane would reflect the Br into the Cl (and the F into the N) so it cannot be a symmetry plane. Because we have found one symmetry plane within the molecule, this isomer will be superimposable on its mirror image and thus will not exist as optical isomers.

Note—when looking for symmetry planes in molecules containing bidentate ligands, you must take into account the part of the molecule that connects the two ends of the bidentate ligand.

Example: Examine the geometric isomers you have drawn for $[\text{Co}(\text{NH}_3)_3\text{BrClF}]$. For those that have one, draw a symmetry plane within the molecule. (Hint—there is one isomer that doesn't have a symmetry plane.)

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Takehome points: (These points are more completely explained earlier.) Carefully read it for complete explanation.) To determine the number of possible isomers (geometric and optical) for an octahedral transition metal complex,

1. Draw one isomer with the ligands arranged in any convenient way.
2. Write each of the three pairs of trans ligands enclosed in a set of parentheses
3. Switch a pair of cis ligands and describe the new complex using the method in #2. If two structures do not have the same sets of trans pairs of ligands, they are geometric isomers.
4. The different ends of bidentate ligands must occupy cis sites around the octahedron.
5. Examine each geometric isomer for internal mirror planes. If there are no such mirror planes, that geometric isomer will exist as a pair of enantiomers.

Practice: for each of the following complexes, draw all geometric isomers and label them using the "trans pair" naming system. Indicate which exist as a pair of enantiomers.

