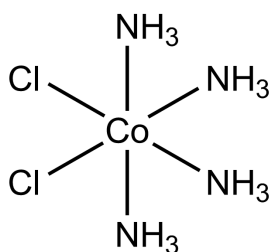


# Isomerism in Coordination Chemistry

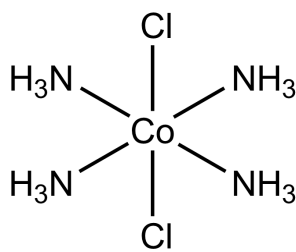
## Introduction

The purpose of this laboratory is to familiarize you with the various forms of isomerism in coordination chemistry. Our focus will be on geometric isomerism, which arises from the three-dimensional arrangement of atoms in space, and optical isomerism, which results from complexes that are mirror images of one another. Although coordination compounds may be tetrahedral, square planar, or octahedral, depending on the metal center, by far the most common geometry is octahedral. Therefore our focus will be on octahedral complexes.

The two primary types of geometric isomerism that arise in octahedral complexes are cis-trans isomerism and facial-meridional isomerism. The first type arises in complexes such as  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  which have two of one type of donor and four of another. The two like ligands, which are in this case the chloride ions, may be located 180 degrees from each other, giving the *trans* isomer, or 90 degrees from each other, giving the *cis* isomer.



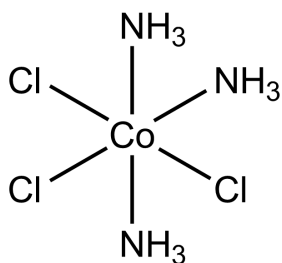
*Cis*



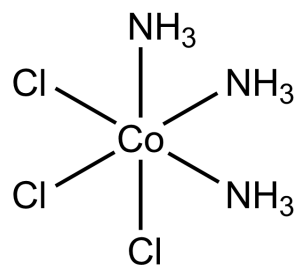
*Trans*

Two geometric isomers, designated *cis* and *trans*, are possible for  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

The second type arises in complexes such as  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  that have three of one type of donor atom and three of another. If any three like ligands are each located 90 degrees from the other two, the result is the facial isomer. This name arises from the fact that the three atoms define one face of the octahedron. If two of the three like ligands are located 180 degrees from each other, then the result is the meridional isomer.



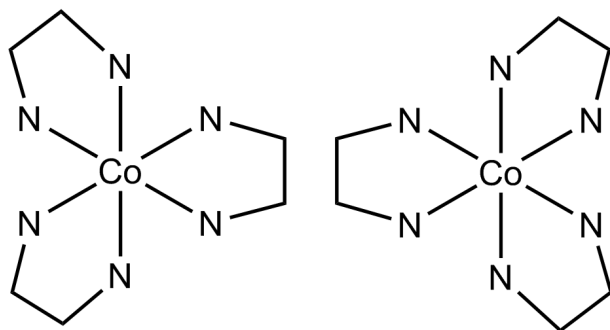
*Mer*



*Fac*

Two geometric isomers, designated *facial (fac)* and *meridional (mer)*, are possible for  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

Optical isomerism arises in complexes that are mirror images of one another. Such molecules are often described as “left-handed” or “right-handed.” Optically active molecules are also referred to as *enantiomers*. In the case of octahedral complexes, any complex ion containing three bidentate ligands will be optically active. Therefore, the compounds  $[\text{Co}(\text{CO}_3)_3]^{3-}$ ,  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ , and  $[\text{Co}(\text{en})_3]^{3+}$  are all optically active. Show below are two enantiomers of the  $[\text{Co}(\text{CO}_3)_3]^{3-}$  ion. Try to rotate and superimpose these in your mind and you will see that they are indeed different molecules.



*Two optical isomers of the  $[\text{Co}(\text{en})_3]^{3+}$  ion.*

Keep in mind that a compound can exhibit geometric as well as optical isomerism. For example, consider the complex ion  $[\text{Co}(\text{CO}_3)(\text{CN})_2(\text{NH}_3)_2]^-$ . Three geometric isomers are possible for this compound; one in which the  $\text{CN}^-$  ligands are *trans*, one in which the  $\text{NH}_3$  ligands are *trans*, and one in which each  $\text{CN}^-$  ligand is *trans* to an  $\text{NH}_3$  ligand. Only the last is optically active and has a nonsuperimposable mirror image.

### Types of Atom Centers

In this laboratory you will be called upon to construct models of some various coordination compounds. The kits you will be given have several types of atom centers. Many of the ligands you are to build have one or more double bonds. While there is no way to represent the double bonds with the models, you must nevertheless use atom centers of the correct geometry.

1. Tetrahedral centers – have four prongs and are used to represent  $\text{sp}^3$ -hybridized atoms. Use these for any atom that is bonded to four others, such as the carbon atoms in ethylenediamine.
2. Trigonal planar centers – have three prongs and are used to represent  $\text{sp}^2$ -hybridized species. Use these for any atom that is bonded to only three others, such as the carbon atoms in oxalate and nitrate.
3. Bent centers – have two prongs and are usually used to represent oxygen.
4. Octahedral centers – have six prongs and are used to represent metal ions with an octahedral geometry.
5. Single prong centers are used to represent atoms such as H or Cl.

In addition to the geometry, you should also pay attention to the atom color. Black is usually used for carbon, blue for nitrogen, white for hydrogen, red for oxygen, and green for chlorine. The metal center may be black or silver.



Tetrahedral  
(C, N)



Trigonal Planar  
(C, N)



Bent  
(O)



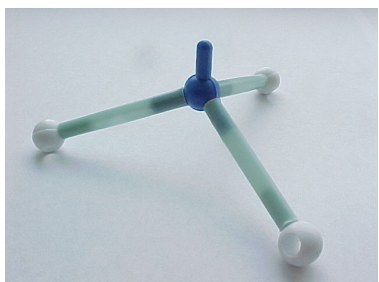
Octahedral  
(Co)



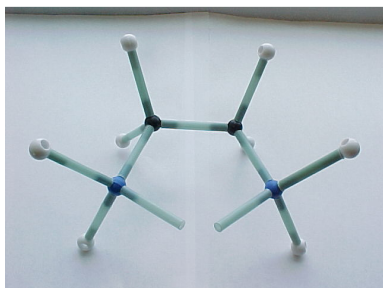
Single-Prong  
(H, Cl)

### Constructing Ligands

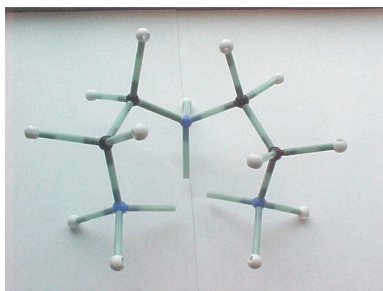
Some notes regarding the ligands to be constructed are discussed below.



Ammonia – use a blue tetrahedral center to represent nitrogen; three connect to hydrogen, and the fourth (which represents the unshared electron pair) connects to the central metal ion.



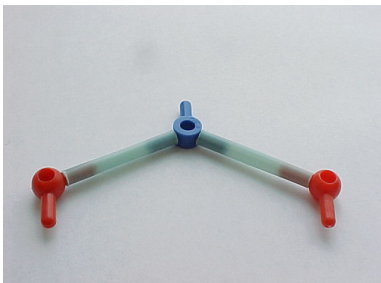
Ethylenediamine (en,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) – use four tetrahedral centers; two black (representing carbon) and two blue (representing nitrogen). The two nitrogen donors connect to the central metal ion. Note that this ligand (and other bidentate ligands) is restricted to a *cis* configuration and cannot bind in a *trans* configuration.



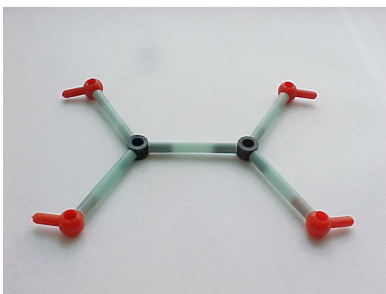
Diethylenetriamine (dien,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ ) use seven tetrahedral centers; four black (representing carbon) and three blue (representing nitrogen). The three nitrogen atoms bind to the central metal ion and may adopt either a facial or meridional configuration. Note that the terminal nitrogen atoms have two attached hydrogen atoms, but the center nitrogen atom has only one.



Carbonate ( $\text{CO}_3^{2-}$ ) – use a trigonal planar atom center to represent the carbon atom (the carbon is  $\text{sp}^2$ -hybridized) and three red two-prong atom centers to represent oxygen. The carbonate ion can be monodentate or bidentate - one or two of the oxygen atoms bind to the central metal ion.



Nitrite ( $\text{NO}_2^-$ ) – use a trigonal planar atom to represent the nitrogen atom (the nitrogen is  $\text{sp}^2$ -hybridized) and two red two-prong atom centers to represent oxygen. The third site on the nitrogen is occupied by a lone electron pair. Either the nitrogen atom or one oxygen atom may coordinate, but both oxygen atoms cannot coordinate (the nitrite ion cannot be bidentate).



Oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) – use two trigonal planar atom centers to represent the carbon atoms and the red two-prong atom centers to represent the oxygen atoms. The oxalate ion is usually bidentate, binding through two oxygen atoms on two different carbon atoms. It does *not* bind through two oxygen atoms on the same carbon. To understand why this is, construct a dot structure of the oxalate molecule. The negative charges lie on the singly bonded oxygen atoms, and only these atoms coordinate.

### Drawing Sketches

In addition to construction of physical models, you will also be called upon to provide a sketch of the complex ions. In drawing such sketches it customary to disregard the hydrogen atoms. For example, you may represent ammonia with a simple “ $\text{-NH}_3$ ” rather than trying to represent the orientations of the hydrogen atoms. Furthermore, for molecules such as ethylenediamine, you may represent the ethylene ( $\text{-CH}_2\text{CH}_2\text{-}$ ) linkages with simple curved lines joining two nitrogen atoms. Similarly, you may represent oxalate ions as simple curved line joining two oxygen atoms.

<b>Isomerism in Coordination Chemistry</b> <b>Pre-Laboratory Exercise</b>	<b>Name:</b>
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Draw all possible resonance structures for each of the following ligands. Indicate the formal charge on each atom in each structure.

1. Carbonate,  $\text{CO}_3^{2-}$

2. Nitrite,  $\text{NO}_2^-$

3. Oxalate,  $\text{C}_2\text{O}_4^{2-}$

<b>Isomerism in Coordination Chemistry</b> <b>Report Page 1</b>	<b>Name:</b>
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Construct a model of and sketch each of the following complex ions. You must obtain your instructor initials before going on to the next model.

<b>Formula</b>	<b>Sketch</b>	<b>Instructor Initials</b>
cis – $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$		
trans – $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$		
fac – $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$		
mer – $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$		

<b>Isomerism in Coordination Chemistry Report Page 2</b>	<b>Name:</b>
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Construct a model of and sketch each of the following complex ions. You must obtain your instructor initials before going on to the next model.

<b>Formula</b>	<b>Sketch</b>	<b>Instructor Initials</b>
cis – $[\text{Co}(\text{en})_2\text{Cl}_2]^+$		
trans – $[\text{Co}(\text{en})_2\text{Cl}_2]^+$		
fac – $[\text{Co}(\text{dien})\text{Cl}_3]$		
mer – $[\text{Co}(\text{dien})\text{Cl}_3]$		

<b>Isomerism in Coordination Chemistry</b> <b>Report Page 3</b>	<b>Name:</b>
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Construct and sketch models of the left-handed and right-handed forms of the  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  ion. Sketch these as mirror images.

<b>Sketches</b>		<b>Instructor Initials</b>

A total of four isomers are possible for the compound  $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_2\text{Cl}_2]^-$  (three geometric isomers, one of which is optically active.) Construct models and make sketches of these four isomers. For the two that are optical isomers, draw them as mirror images.

<b>Sketches</b>		<b>Instructor Initials</b>

<b>Isomerism in Coordination Chemistry</b> <b>Post-Laboratory Questions</b>	<b>Name:</b>
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1. Explain why both *cis* and *trans* isomers are possible for  $[\text{Co}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2]^-$  but only the *cis* isomer is possible for  $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^+$ . You may want to try constructing a *trans* isomer of the second complex before answering this question.

2. Is more than one geometric isomer possible for the complex  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  ion? Why or why not? If your answer is yes, provide a sketch of both isomers.

3. How many total isomers are possible for the compound  $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)\text{Cl}]^{2-}$ ? Make sketches of these isomers. Indicate optical isomers and draw them as mirror images.