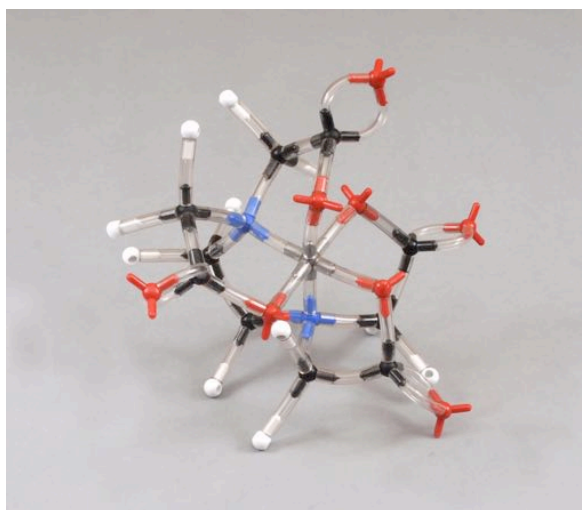


Super Models




Coordination Chemistry Model Kit

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Recommended for ages 10-adult

 **Caution!** Atom centers and vinyl tubing are a choking hazard. Do not eat or chew model parts.

Kit Contents:

5 silver 6-peg metal atom centers

11 blue 4-peg nitrogen atom centers

41 white 1-peg hydrogen atom centers

17 red 4-peg oxygen atom centers

8 green 1-peg halogen atom centers

12 black 4-peg carbon atom centers

70 clear, 1.25" tubes (single bonds)

13 clear, 4 cm tubes (double/triple bonds)

Phone: 806-438-6865

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Address: 5701 1st Street, Lubbock, TX 79416

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COORDINATION CHEMISTRY

The focus of this kit is the study of the coordination chemistry associated with octahedral complexes.

- I. A **coordination compound** is composed of a complex ion and a counter ion.
- A. A **complex ion** is made up of a metal (usually transition or post transition) ion or neutral atom, which acts as a Lewis acid, and two or more **ligands**, which act as Lewis bases.
 - B. The ion is called complex because it is composed of two or more species which could be independent of each other.
 - C. The ligands, which may be ions or neutral molecules, donate one or more lone pairs of electrons to the metal ion or atom to form coordinate covalent bonds.
 - D. The counter ion will be either a cation or anion, as needed, to balance the charge on the complex ion and produce a neutral compound. The counter ion may also be another complex.
 - E. In $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ the complex ions are in brackets, [], and the ligands are in parentheses () if made of more than one atom. The counter ions are outside the brackets. Some coordination compounds have no brackets because the metal charge equals the charge on the anion, or the metal is atomic rather than ionic, and the molecule is neutral. Two examples are $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$ and $\text{Fe}(\text{CO})_5$.
 - F. The **coordination number** (C.N.) of the metal tells us the number of bonded ligands. The most common number is six, then four. The range of C.N. for *d*-block elements is 2 to 9, and the range of C.N. for *f*-block elements is 8 to 12.

II. Naming of coordination compounds.

- A. Name the entire cationic species first, followed by the name of the entire anion. This is the same convention you are accustomed to using for ionic compounds.
- B. Within the complex ion, name the ligand(s) first, in alphabetical order (ignoring prefixes such as di, tri, etc., but not bis, tris, etc.), then name the metal followed by its oxidation state in parentheses (this can be omitted for atoms with only one oxidation state).
- C. An anionic ligand with a name ending in -ide changes -ide to -o. As of 2005, IUPAC changed the naming convention to dropping the -e is from -ide, resulting in the suffix, -ido. However, the older system persists, so it is a good idea to learn both methods of naming. A few examples are given below.

<u>Anion</u>	<u>Formula</u>	<u>Name as ligand</u>	<u>New IUPAC name</u>
chloride	Cl^{1-}	chloro	chlorido
bromide	Br^{1-}	bromo	bromido
cyanide	CN^{1-}	cyano	cyanido
hydroxide	OH^{1-}	hydroxo	hydroxido
oxide	O^{2-}	oxo	oxido

Ligands that have names ending in -ite or -ate change suffixes to -ito and -ato respectively. Some examples follow.

<u>Anion</u>	<u>Formula</u>	<u>Name as ligand</u>
carbonate	CO_3^{2-}	carbonato
thiocyanate	SCN^{1-}	thiocyanato (when bonded to S)
	NCS^{1-}	isothiocyanato (when bonded to N)
oxalate	$\text{C}_2\text{O}_4^{2-}$	oxalato
nitrite	ONO^{1-}	nitrito (when bonded to O)
	NO_2^{1-}	nitro (when bonded to N)

A neutral ligand keeps its same name, with some exceptions such as H_2O , aquo, CO, carbonyl, and NH_3 , ammine (notice the two m's, not one). When a ligand has two donor atoms e.g. SCN^{1-} and NO_2^{1-} the ligand is called **ambidentate**.

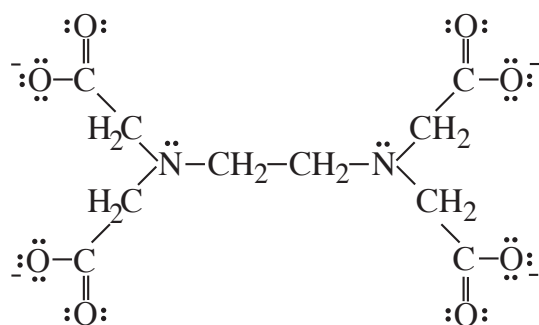
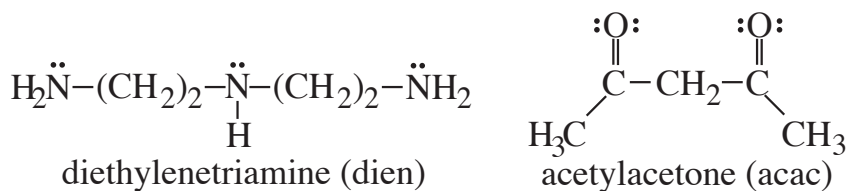
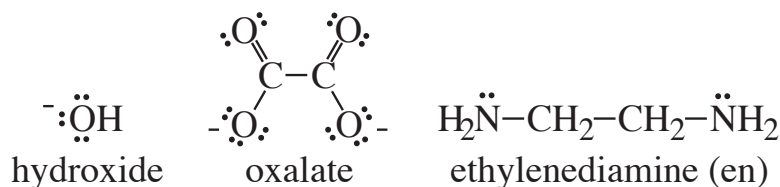
The kappa (Greek letter κ) convention is an alternate way of naming ambidentate ligands as follows. $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$, according to the table above, should be called pentaamminenitrocobalt (III) chloride, but with the κ notation we can also call the compound, pentaamminenitroso- κN -cobalt(III) chloride.

We can call $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$ either pentaamminenitrocobalt(III) chloride or pentaamminenitroso- κO -cobalt(III) chloride.

A ligand may bond one of its atoms to a metal and be **monodentate**, bond two atoms and be **bidentate**, or bond several atoms and be **polydentate**. Ligands that bind with two or more of their atoms are **chelating agents** (from *chela* meaning claw). The resulting structure is called a **chelate** (metal plus the chelating agent). The table below shows the classes of some common ligands, followed by their structures.

<u>LIGAND</u>	<u>CLASS</u>	<u>NAME</u>
ammonia	monodentate	ammine
water	monodentate	aquo
chloride	monodentate	chloro (chlorido)
carbon monoxide	monodentate	carbonyl
hydroxide	monodentate	hydroxo (hydroxido)
oxalate	bidentate	oxalato
ethylenediamine	bidentate	(en)
acetylacetone	bidentate	(acac)
diethylenetriamine	tridentate	(dien)
ethylenediaminetetraaceto	polydentate	(EDTA)





- D. When more than one of a bi- or poly-dentate ligand already using a Greek prefix (di, tri, etc.) in its name might be confusing, alternative prefixes are used. **bis-** is used for two when di might be confusing. For example, we use **bis** in the complex ion dichloridobis(ethylenediamine)platinum(IV), which has the formula $[\text{PtCl}_2(\text{en})_2]^{2+}$. For the same reason **tris-** is used for three, and **tetrakis-** for four, and so on. Follow these prefixes with parentheses as in the preceding example.
- E. The oxidation number of the metal is written as a Roman numeral in parentheses after the metal name, which is the last part of the name of the cation. For a neutral metal atom, use (0). For example; $[\text{Fe}(\text{NH}_3)_6](\text{NO}_3)_3$, hexaamineiron(III) nitrate, and $\text{Fe}(\text{CO})_5$, pentacarbonyliron(0).
- F. Negative complexes have names that end in -ate, the latter suffix being added to the name of the metal atom. Use Latin names where possible, but not for mercury. For example; $[\text{Fe}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ is called hexaammineiron(III) hexacyanidochromate(III), and $(\text{NH}_4)_2[\text{CuCl}_4]$, ammonium tetrachloridocuprate(II).

<u>Metal</u>	<u>Metal name in anionic complex</u>
Aluminum	aluminate
copper	cuprate
iron	ferrate
lead	plumbate

G. Some coordination compounds are named with common names.

Formula	Systematic name	Common name
$K_4[Fe(CN)_6]$	potassium hexacyanidoferrate(II)	potassium ferrocyanide
$K_3[Fe(CN)_6]$	potassium hexacyanidoferrate(III)	potassium ferricyanide
$Fe(CO)_5$	pentacarbonyliron(0)	iron carbonyl

III. Writing formulas for coordination compounds.

- A. Put the complex ion in brackets [] if there is a charge, positive or negative, on the ion. Write the symbol for the metal first, followed by symbols for ligands. According to the IUPAC 2005 RULES, anionic ligands in alphabetical order should follow the symbol for the metal. Neutral ligands, in alphabetical order, then follow the anions.

If the complex has a positive charge, write the complex formula followed by the counter ion or negative complex. If the complex is negative, write the counter ion or the positive complex first, then follow with the negative complex.

- B. Examples.

pentaamminechloridocobalt(III) chloride	$[CoCl(NH_3)_5]Cl_2$
tris(ethylenediamine)cobalt(III) sulfate	$[Co(en)_3]_2(SO_4)_3$
triamminetriaquachromium(III) chloride	$[Cr(NH_3)_3(OH_2)_3]Cl_3$
sodium tetrachloridonickelate(II)	$Na_2[NiCl_4]$
ammonium diaquabis(oxalato)nickelate(II)	$(NH_4)_2[Ni(O_4C_2)_2(OH_2)_2]$
diamminesilver(I) dicyanidoargentate(I)	$[Ag(NH_3)_2][Ag(CN)_2]$
tribromidotrichloridocobalt(II) ion	$[CoBr_3Cl_3]^{4-}$ or $[Co^{II}Br_3Cl_3]^{4-}$
diamminebis(ethylenediamine)nickel(II) ion	$[Ni(en)_2(NH_3)_2]^{2+}$ or $[Ni^{II}(en)_2(NH_3)_2]^{2+}$
hexafluoridocobaltate(III) ion	$[CoF_6]^{3-}$ or $[Co^{IV}F_6]^{3-}$

IV. Names and formulas of isomers.

The naming and writing formulas for isomers will be treated in more detail below.

V. Isomerism.

Isomers are compounds that have the same chemical formula, but have different arrangements of atoms. There are several kinds of isomerism, but here we look at two of the major categories, i.e. structural (constitutional) isomers and stereoisomers.

A. Structural isomers.

There are four types of structural isomers, ionization, coordination, hydration, and linkage.

1. Ionization isomers arise when one of the ions included in the complex exchanges positions with one of the counter ions. $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ are examples.
2. Coordination isomers occur when one ligand of a complex ion is exchanged for a ligand in an oppositely charged complex, e.g. $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{C}_2\text{O}_4)_3]$ and its isomer $[\text{Co}(\text{C}_2\text{O}_4)_3] [\text{Cr}(\text{NH}_3)_6]$
3. A hydration isomer is similar to an ionization isomer. In this type of isomerism, the solvent (here it is water) changes places with a counter ion. Three examples follow; in the second and third isomer, H_2O becomes water of hydration.

$[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$: violet (three ionic chlorines)

$[\text{CrCl}(\text{OH}_2)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$: green (two ionic chlorines)

$[\text{CrCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$: bright green (one ionic chlorine)

4. In order to have linkage isomers, the complex must have an ambidentate ligand, e.g. the nitrite ion NO_2^{1-} and the thiocyanate ion SCN^{1-} both of which were listed in II. C above. An explanation of an alternate method of naming the first two isomers was given in II. C. above.

$[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}$ the nitrito isomer –O attached

$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}$ the nitro isomer –N attached

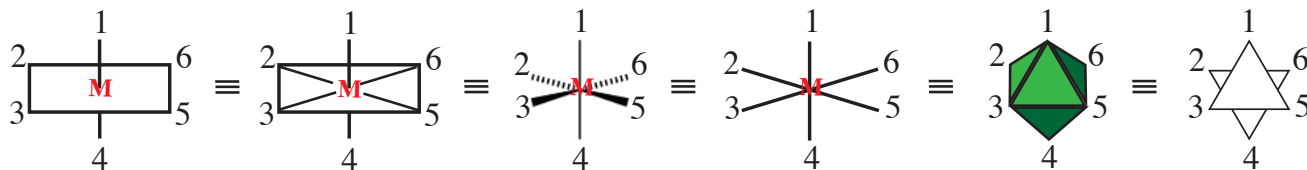
$[\text{Co}(\text{NCS})(\text{NH}_3)_5]\text{Cl}_2$ the isothiocyanato isomer –N attached

$[\text{Co}(\text{SCN})(\text{NH}_3)_5]\text{Cl}_2$ the thiocyanato isomer –S attached

B. Stereoisomers.

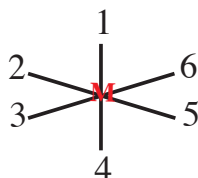
Stereoisomerism arises when the atoms of a compound are arranged in more than one pattern in space but the attachments of atoms is not altered. The only way to make one of these isomers into the other is to break chemical bonds. The two types of stereoisomerism are geometric and optical.

Before we investigate stereoisomers, we will look at six different methods of illustrating octahedral complexes and their ligands. See diagram below. The numbers refer to the ligand sites of attachment. The metal is in the center of each diagram.

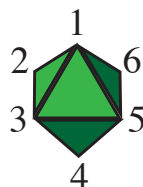


Six methods of drawing octahedral complex ligand positions.

1. There are two types of geometric isomerism; *cis*-, *trans*-, and *fac*-, *mer*-. Ligands which are *cis* are at 90° to each other: ligands which are *trans* are at 180° to each other. In the diagram below, there are 12 *cis* combinations of numbers, e.g. (1-2), (1-3), (1-5), (1-6), (2-3), (3-5), (5-6), (6-2), (4-2), (4-3), (4-5), and (4-6). How many *trans* combinations are there? What are they?

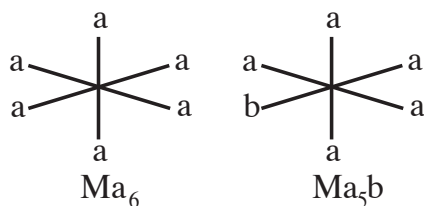


2. Octahedral complexes have eight faces (sides). Observe the diagram below and you will see that four of the faces are visible triangles with vertices at (1,2,3), (1,3,5), (1,5,6), and (4,3,5). There are four faces that are not visible. One of them is (1, 2,6). What are the other three faces?

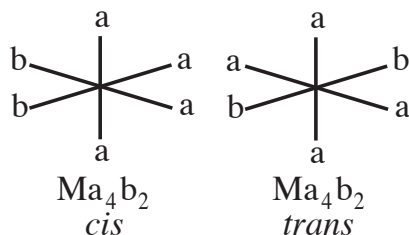


3. Just as a globe has meridians that run from north-pole to south-pole and east to west at the equator, an octahedron also has these meridians. Using three numbers at a time, we can describe the meridians (there are twelve of them). Using the digit 1 in the middle, we see two combinations of ligand positions: (2,1,5), and (3,1,6). Now we put 2 in the middle of the triad and obtain the meridians (3,2,6) and (1,2,4). For the next two combinations, 3 is placed in the center, and so on. There are twelve different meridional possibilities: write the remaining eight.
4. Depending upon the number of different types of ligands that are bonded to the central metal atom, the number of *cis*- and *trans*-, and *fac*- and *mer*-isomers found in octahedral complexes can vary. The table on the next page shows the general formulas of octahedral complexes and the numbers of possible isomers. The M, stands for any metal atom or ion, the lower case letters symbolize monodentate ligands, and the subscripts indicate the numbers of those ligands.

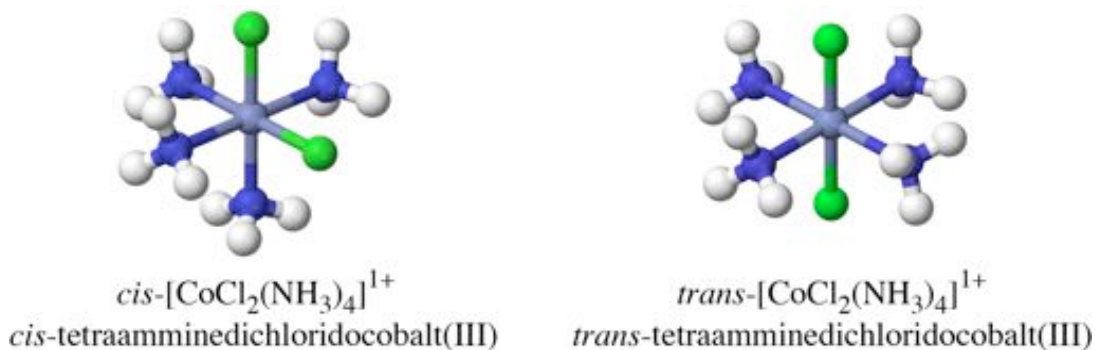
- a. Both Ma_6 and Ma_5b complexes have no isomeric forms, as you can see in the following diagram. If any changes are made to the positions of the ligands, the relationships among them stay the same.



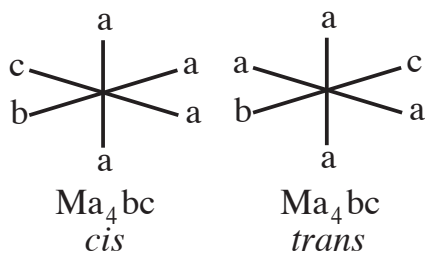
- b. Ma_4b_2 and Ma_4bc have two isomers each; both have cis and trans isomers. For Ma_4b_2 , use the two b ligands as a starting point putting them in the cis position and then in the trans position, as illustrated below. No other arrangements can be made.



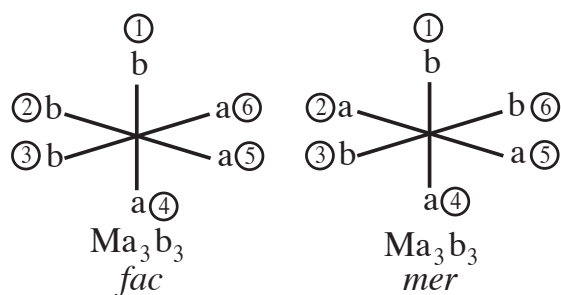
In order to show how to write the names and formulas of these isomers, we will use the complex ion tetraamminedichloridocobalt(III). One isomer has the name *cis*-tetraamminedichloridocobalt(III) and the formula is $\text{cis}[\text{CoCl}_2(\text{NH}_3)_4]^{1+}$. Its isomer is *trans*-tetraamminedichloridocobalt(III), with the formula $\text{trans}[\text{CoCl}_2(\text{NH}_3)_4]^{1+}$. Both isomers are shown below.



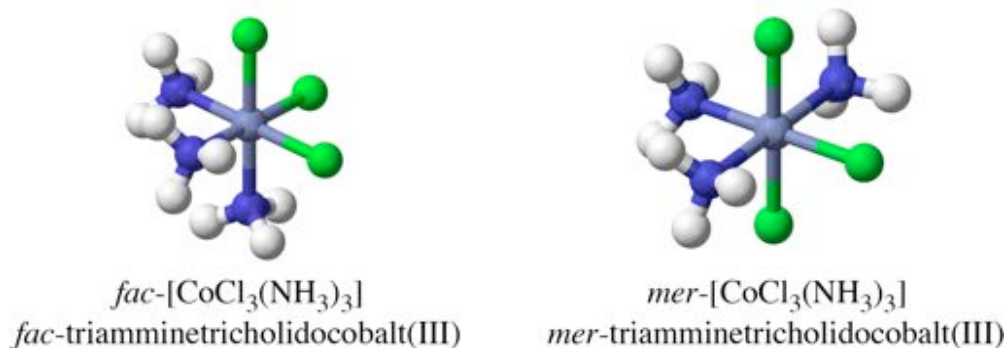
- c. For Ma_4bc , use the b and c ligands as a starting point putting them in the cis position and then in the trans position, as illustrated below. No other arrangements can be made.



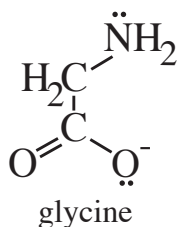
- d. For Ma_3b_3 , use the three **b** ligands as a starting point putting them in any positions you like and then add the three **a** ligands in the spots left open. As illustrated on the next page, you can only make two arrangements, either fac- or mer-. Fac stands for facial, meaning the **b** ligands are located at the vertices of the triangle (1,2,3) which is one face of the octahedron. The **a** ligands make up another face. The mer (meridional) isomer has the **b** ligands on a meridian (3,1,6) and the **a** ligands on (2,4,5). No other arrangements can be made.



$[\text{CoCl}_3(\text{NH}_3)_3]$, triamminetrichloridocobalt(III), is a neutral complex with two isomers, fac- and mer-. Their structures are presented below.



- e. Complexes may also be formed when polydentate ligands bond with the central metal atom. Capital letters are used to indicate these ligands. For instance, in the general formula $\text{M}(\text{AA})_2\text{b}_2$. The (AA) refers to the same two types of atoms of the ligand. An example of this type of ligand is the oxalate anion (see structure on the top of page 3). If the ligand has two or more different kinds of atoms that can bind to the metal, the general formula might look like $\text{M}(\text{AB})_2\text{cd}$. Glycine is an example of a bidentate ligand that can use two different kinds of atoms; its nitrogen and its oxygen as donor atoms. See structure below.

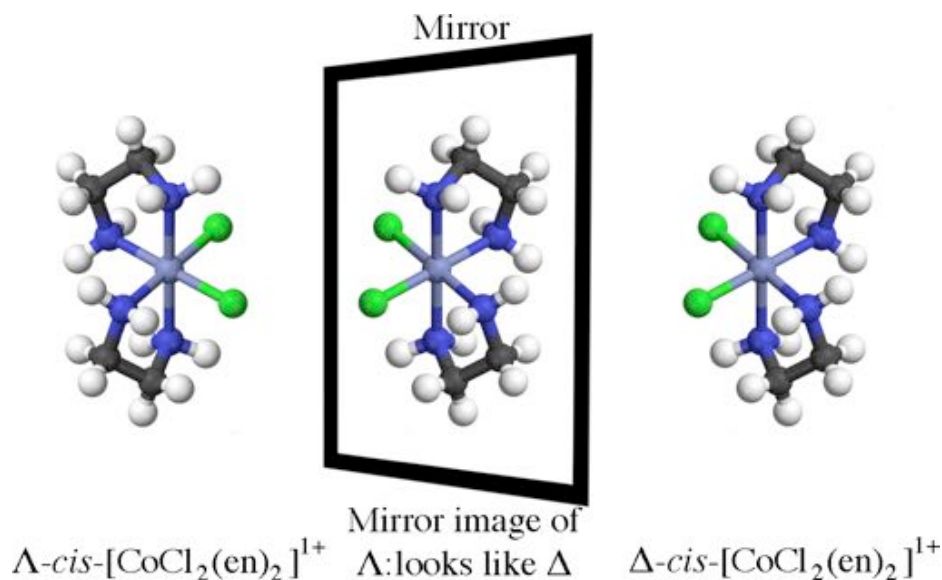


5. We will now turn our attention to optical isomers (enantiomers) of $M(AA)_2$ and $M(AA)_3$. Enantiomers are compounds that are mirror images of each other and are not able to be superimposed, one on the other, with their atoms in perfect register. In addition to the mirror image test to qualify molecules as enantiomers, a molecule will not have an enantiomer if it has a plane of symmetry.

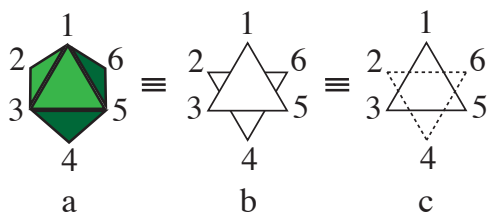
The best way to begin a study of optical isomerism is to use molecular models, and this kit serves that purpose well.

One system of naming enantiomers uses the Greek letters lambda, Λ (left-handed) and delta, Δ (right-handed).

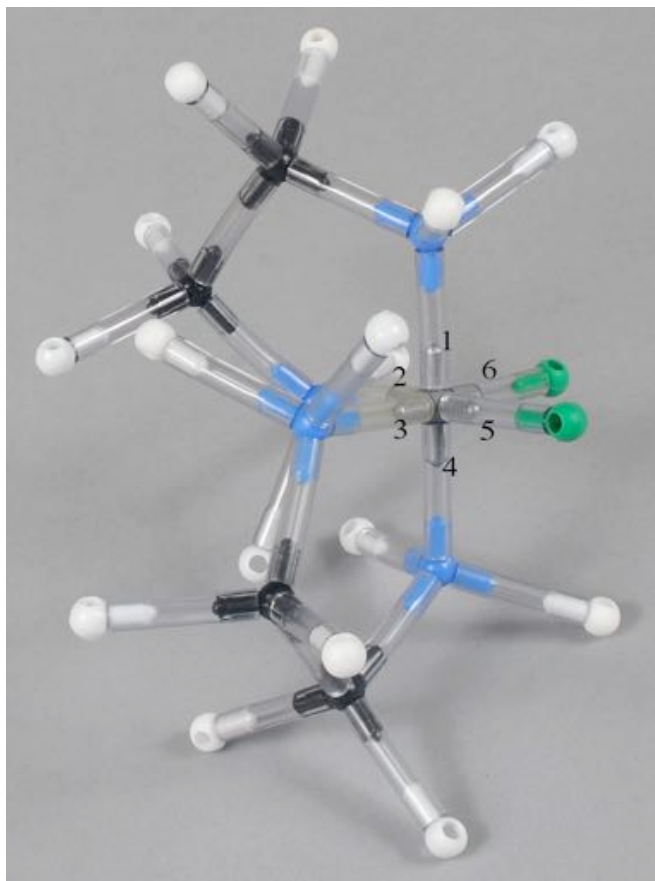
cis-dichloridobis(ethylenediamine)cobalt(III) has two enantiomers. The following diagram shows how each is the mirror image of the other.



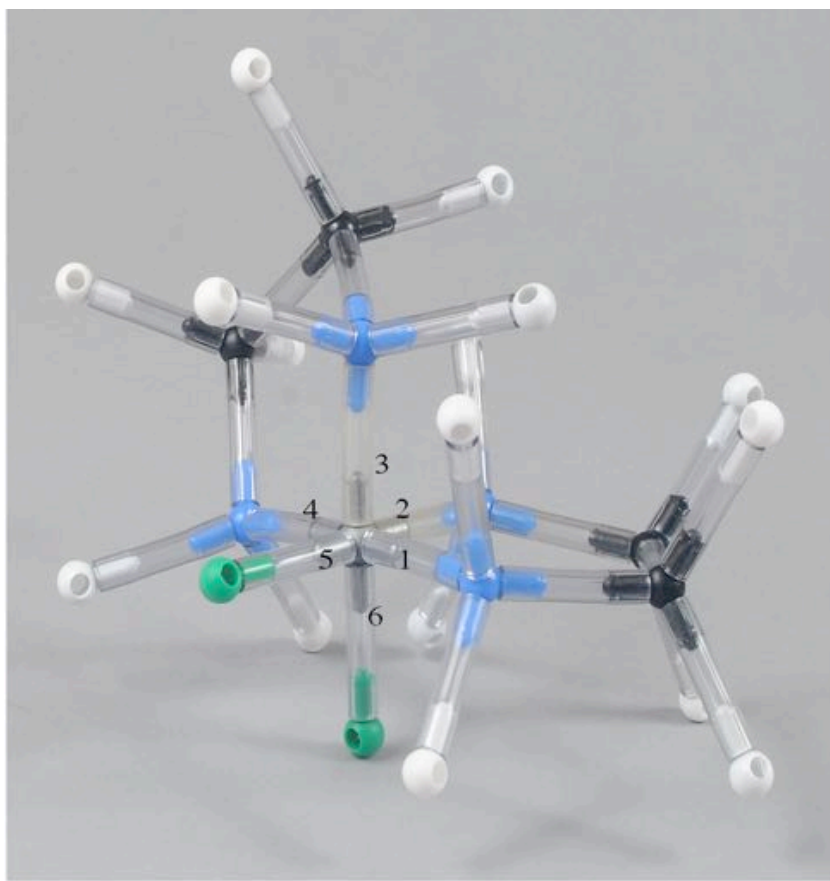
How can you determine the handedness of an enantiomer when it is not given? On the top of page 6, equivalent diagrams of octahedral shapes were illustrated, two of which are in the diagram below. When attempting to assign handedness to a molecule, it can be helpful to draw it in a simple form. If you select “c” from the diagram below, it should be the easiest to draw.



Using “c,” let’s see how we decided that Λ -*cis*-[CoCl₂(en)₂]¹⁺ was in fact in the Λ form. First make a model of the molecule that will look like the picture on the next page.



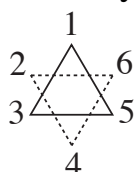
Before turning model.



After turning model.

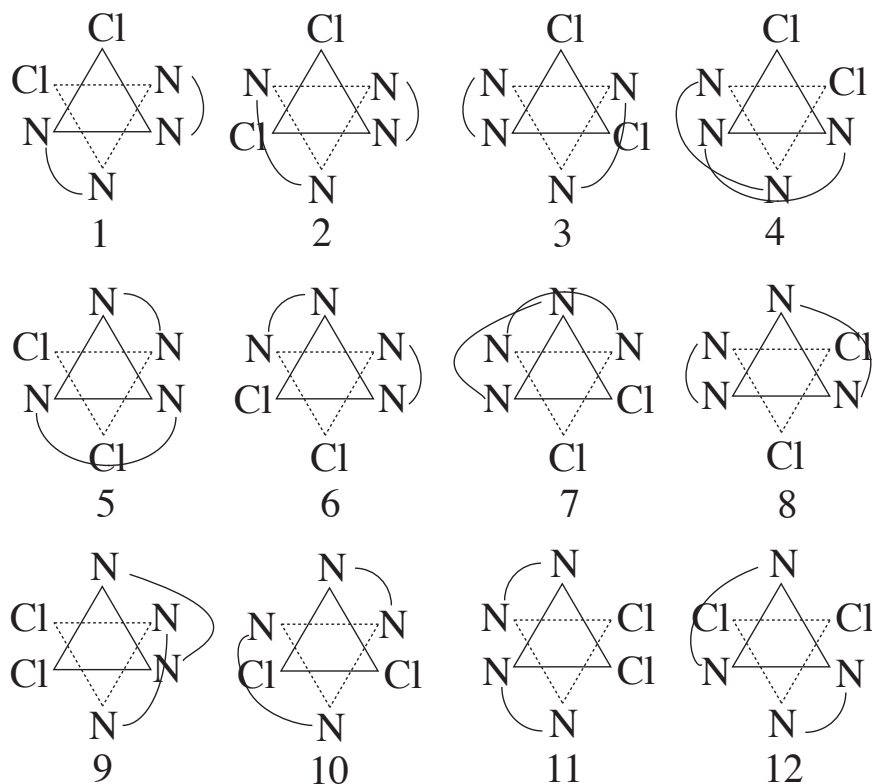
Two views of Λ -*cis*-[CoCl₂(en)₂]¹⁺.

Next analyze the placements of the ligands using diagram “c” from page 9. Simplify the ethylenediamine by using two N’s and an arc.



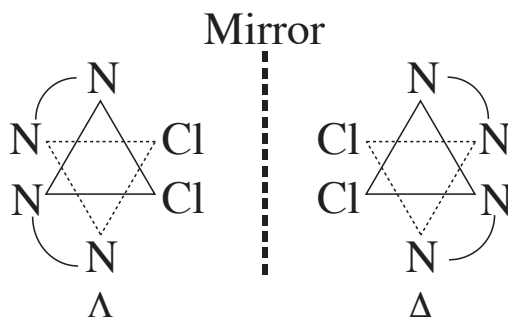
Starting with the first bidentate ligand at the top, we see the arc turning to the left. That means the molecule is left-handed and has the symbol Λ .

If you use the octahedral symbol above to analyze the configuration of a $M(AA)_2b_2$ molecule, you will find the twelve different structures can be drawn. How will you know which one to pick? One of the atoms of a bidentate ligand must be at the top, so 1-4 can be eliminated. If an arc goes over or around an atom, the structure can be eliminated so structures 5, 7-10, and 12 are rejected. Two acceptable configurations remain; 6 and 11. Starting at the top (number 1 position), the arc is on the left side, so this is a left-handed Λ isomer. After just a little bit of practice, it should be possible to find the correct view of any enantiomer in order to identify its configuration without the use of the structural diagrams.

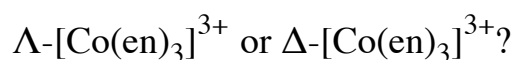
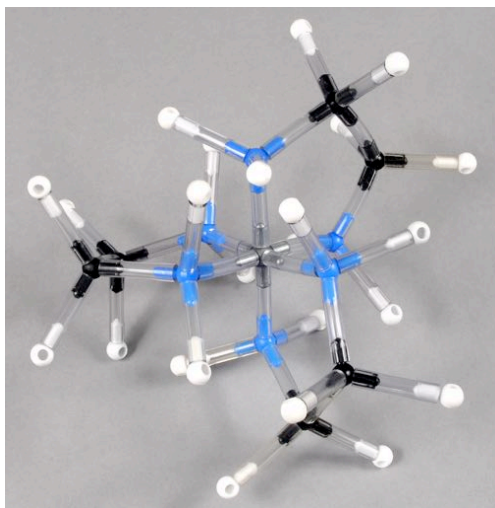


Twelve possible views of Λ -*cis*-[CoCl₂(en)₂]¹⁺.

An optical isomer model can be converted into its enantiomer by breaking and reforming two of its bonds. Now that you have the Λ isomer, use the diagram below to construct the Δ isomer.



Is the model of the tris(ethylenediamine)cobalt(III) ion, [Co(en)₃]³⁺, in the photo on the next page left- or right-handed? If necessary draw a diagram like those above to help with the answer.



LAB PROCEDURE

1. Each team of two or more students will pick up a Ryler Coordination Chemistry kit.
2. Student teams will make models of each complex ion and show it to the teacher who will fill in column 4 with initials or a rubber stamp.
3. Each student will fill in a separate-lab report table, filling in each empty space. The information required for each blank is indicated at the top of each column.
4. In addition to the table, on a separate sheet of paper, each student will complete the instructions given in column 3.
5. At the conclusion of the lab, each student will hand in a lab-report table with an attached sheet of completed items from column 3.

Coordination Chemistry

Names_____

Date_____ Period_____

Name	Chemical Formula	On a separate sheet, complete the following:	Type of Ligand/isomer	Model checked
ethylenediamine		Demonstrate the attachment of ethylenediamine to a silver metal atom.	bidentate	
diethylenetriamine		Demonstrate the attachment of diethylenetriamine to a silver metal atom.		
EDTA		Demonstrate the attachment of EDTA to a silver metal atom.		
oxalate ion		Demonstrate the attachment of the oxalate ion to a silver metal atom.		
	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	How do the ammonia ligands form bonds with the nickel ion?		
	$[\text{Cr}(\text{CN})(\text{OH}_2)_5]^{2+}$	How do water and cyanide ligands bond with the chromium ion?		
	$[\text{MnCl}_4(\text{en})]^{3+}$	How do (en) and chloride bond with the manganese ion?		
	$[\text{CoCl}_2(\text{NH}_3)_4]^{1+}$	Explain why these two structures are geometric isomers and not identical complexes.	<i>cis</i>	
	$[\text{CoCl}_2(\text{NH}_3)_4]^{1+}$		<i>trans</i>	
Λ - <i>cis</i> -bis(ethylenediamine) dihydroxidoiron(III) ion		Explain why these two structures are optical isomers and not identical complexes.	optical	
Δ - <i>cis</i> -bis(ethylenediamine) dihydroxidoiron(III) ion			optical	
	$[\text{CrCl}_2(\text{O}_4\text{C}_2)_2]^{3-}$	Find another lab group and demonstrate the two optical isomers of this complex.		