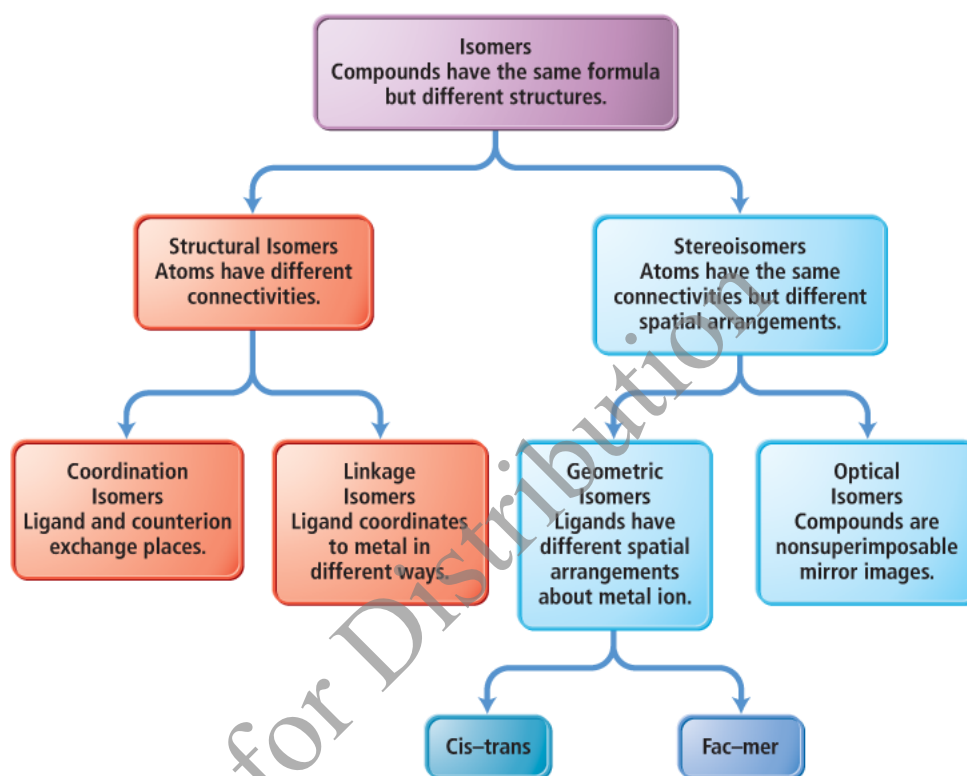


22.4: Structure and Isomerization

Isomerism is common in coordination compounds. We broadly divide the isomerism observed in coordination compounds into two categories, each with subcategories, as shown in Figure 22.6. In **structural isomers**, atoms are connected to one another in different ways, whereas in **stereoisomers**, atoms are connected in the same way but the ligands have a different spatial arrangement about the metal atom.

Figure 22.6 Types of Isomers



Structural Isomerism

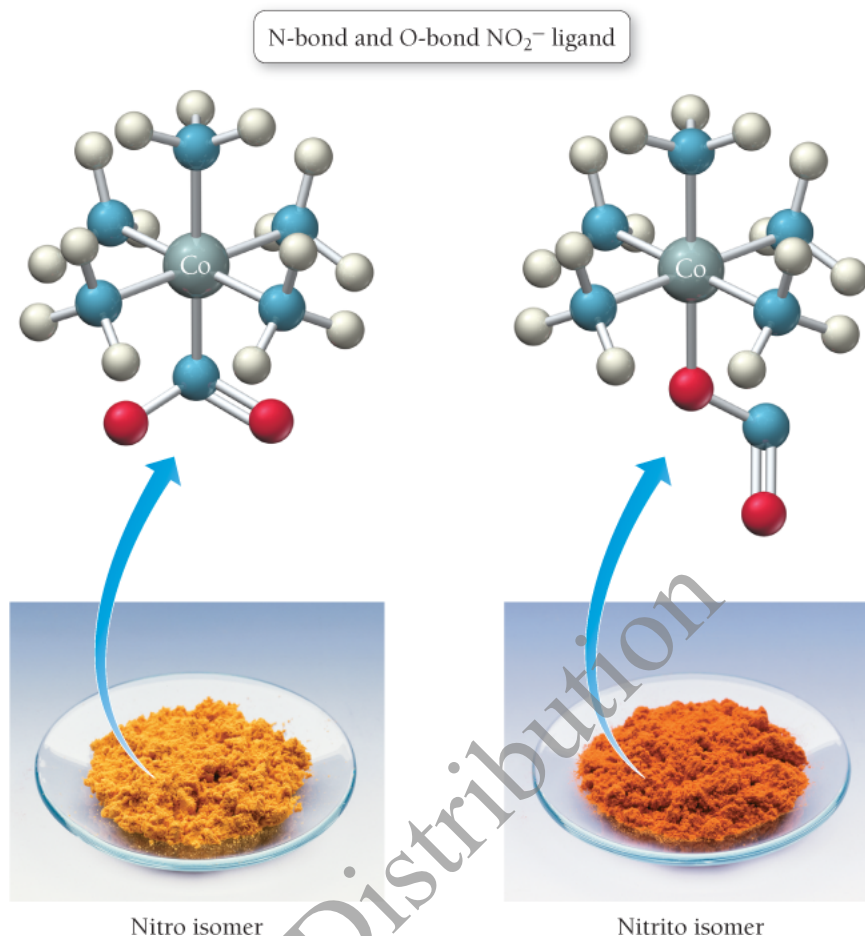
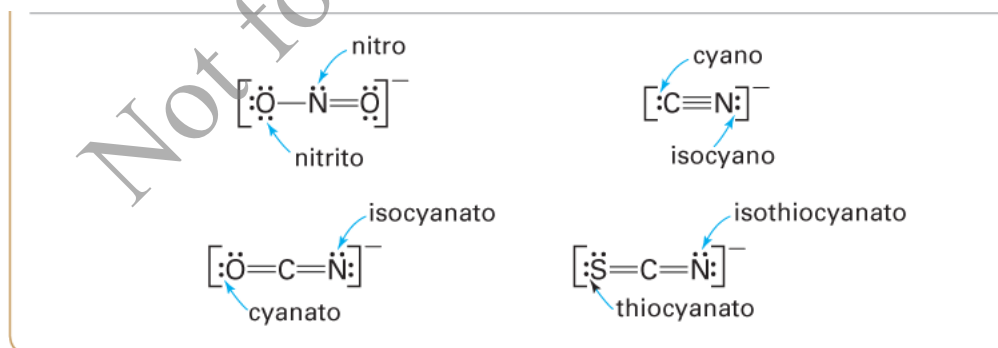
We subdivide the broad category of structural isomers into two types: coordination isomers and linkage isomers.

Coordination isomers occur when a coordinated ligand exchanges places with the uncoordinated counterion. For example, two different compounds have the general formula $\text{Co}(\text{NH}_3)_5\text{BrCl}$. In one of them, the bromine coordinates to the metal and chloride is a counterion, pentaamminebromocobalt(II) chloride, $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}$; in the other one, the chlorine coordinates to the metal and bromide is the counterion, pentaamminechlorocobalt(II) bromide, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}$.

Linkage isomers have ligands that coordinate to the metal in different orientations. For example, the nitrite ion (NO_2^-) has a lone pair on the N atom as well as lone pairs on the O atoms—either of the two atoms can form coordinate covalent bonds with the metal. When the nitrite ion coordinates through the N atom, it is a *nitro* ligand and is represented as NO_2^- , but when it coordinates through the O atom, it is a *nitrito* ligand and is usually represented as ONO^- . We can see an example of linkage isomerization in the yellow-orange complex ion pentaamminenitrocobalt(III), $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$, which contrasts with the red-orange complex ion pentaamminenitritocobalt(III), $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$, as shown in Figure 22.7. Table 22.6 lists other ligands capable of linkage isomerization.

Figure 22.7 Linkage Isomers

In $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$, the NO_2 ligand bonds to the central metal atom through the nitrogen atom. In $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$, the NO_2 ligand bonds through an oxygen atom. The different isomers have different colors.

**Table 22.6 Ligands Capable of Linkage Isomerization**

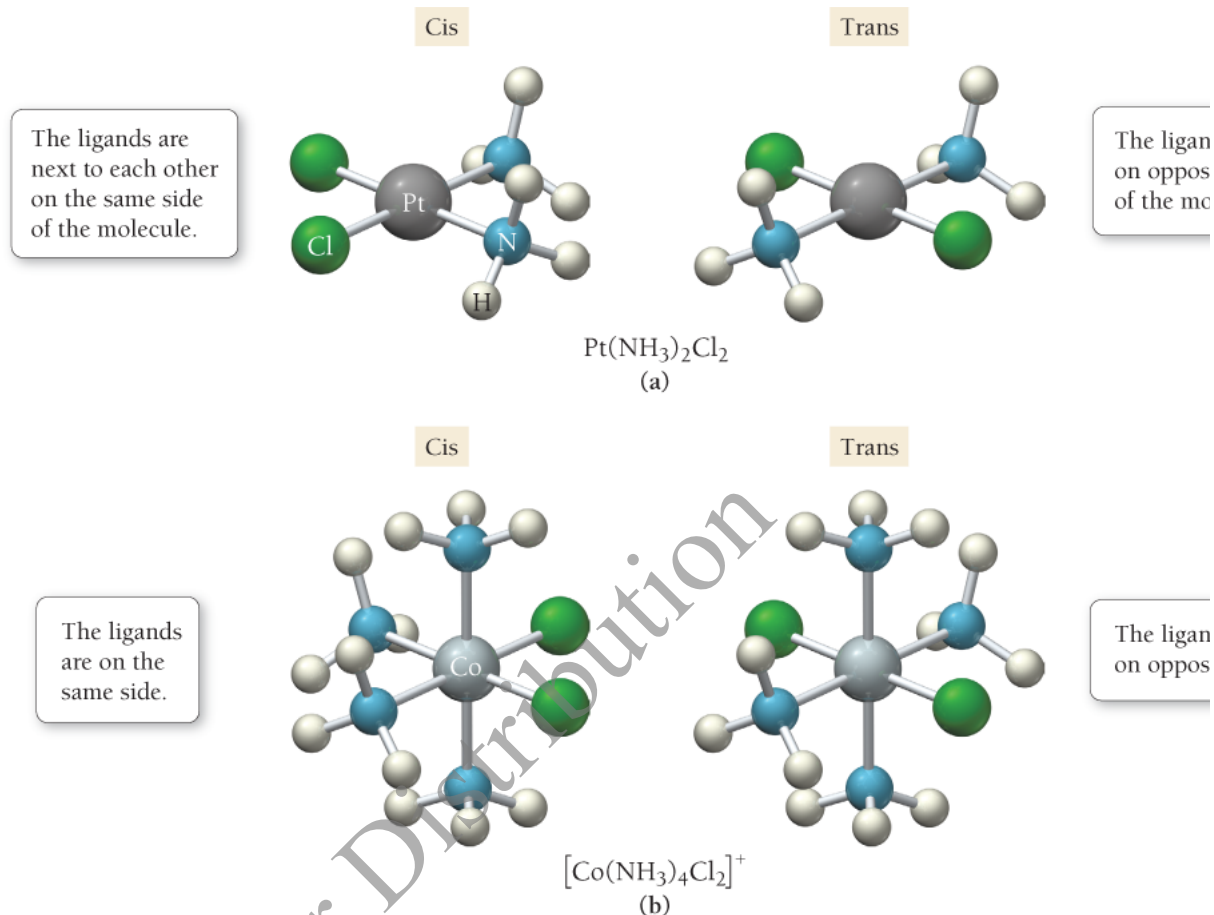
Stereoisomerism

We can also subdivide the broad category of stereoisomers into two types: geometric isomers and optical isomers. **Geometric isomers** result when the ligands bonding to the metal have a different spatial arrangement. One type of geometric isomerism, as we saw in Sections 21.3 and 21.5, is cis-trans isomerism, which in complex ions occurs in square planar complexes of the general formula MA_2B_2 or octahedral complexes of the general formula MA_4B_2 .

For example, cis–trans isomerism occurs in the square planar complex $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. **Figure 22.8a** shows the two distinct ways that ligands can be oriented around the metal. In one complex, the Cl^- ligands are next to each other on one side of the molecule—this is the cis isomer. In the other complex, the Cl^- ligands are on opposite sides of the molecule—this is the trans isomer.

Figure 22.8 Cis–trans Isomerism

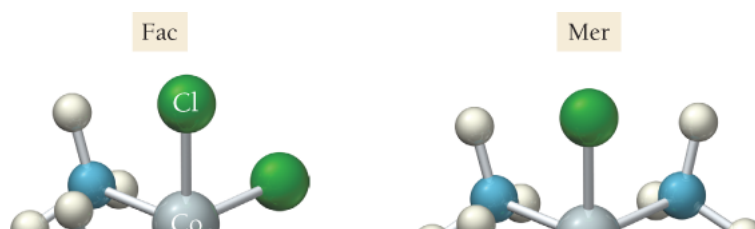
(a) Cis–trans isomerism in square planar (b) Cis–trans isomerism in octahedral $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

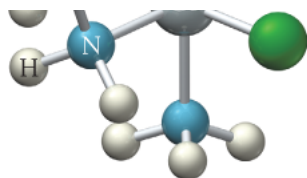


Geometric isomerism also exists in the octahedral complex ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. As shown in **Figure 22.8b**, the ligands in this complex ion arrange themselves around the metal in two ways, one with the Cl^- ligands on the same side (the cis isomer) and another with the Cl^- ligands on opposite sides of the metal (the trans isomer). Note that cis–trans isomerism does not occur in tetrahedral complexes because all bond angles around the metal are 109.5° , and each corner of a tetrahedron is considered to be adjacent to all three other corners.

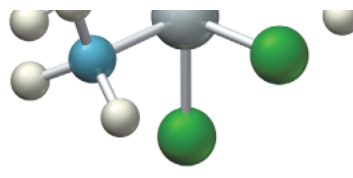
Another type of geometric isomerism is fac–mer isomerism, which occurs in octahedral complexes of the general formula MA_3B_3 . For example, in $\text{Co}(\text{NH}_3)_3\text{Cl}_3$, the ligands arrange themselves around the metal in two ways (**Figure 22.9**). In the fac isomer the three Cl^- ligands are all on one side of the molecule and make up one face of the octahedron (fac is short for facial). In the mer isomer, the three ligands form an arc around the middle of the octahedron (mer is short for meridional).

Figure 22.9 Fac–Mer Isomerism in $\text{Co}(\text{NH}_3)_3\text{Cl}_3$





The three ligands are all on the same side of the molecule and make up one face of the octahedron.



The three ligands inscribe an arc around the middle (or meridian) of the octahedron.

Example 22.5 Identifying and Drawing Geometric Isomers

Draw the structures and label the type of all the isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.

PROCEDURE Identify the coordination number and the geometry around the metal.

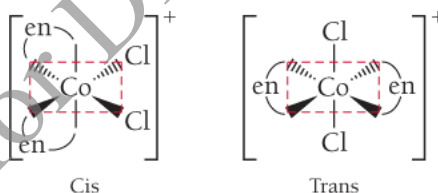
SOLUTION The ethylenediamine (en) ligand is bidentate, so each occupies two coordination sites. Each Cl^- is monodentate, occupying one site. The total coordination number is 6, so this must be an octahedral complex.

PROCEDURE Identify whether this is a cis-trans or fac-mer isomerism.

SOLUTION With ethylenediamine occupying four sites and Cl^- occupying two sites, it fits the general formula MA_4B_2 , leading to cis-trans isomers.

PROCEDURE Draw and label the two isomers.

SOLUTION



FOR PRACTICE 22.5 Draw the structures and label the type of all the isomers of $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]^+$.

Example 22.6 Identifying and Drawing Geometric Isomers

Draw the structures and label the type for all the isomers of $[\text{Ni}(\text{CN})_2\text{Cl}_2]^{2-}$.

PROCEDURE Identify the coordination number and the geometry around the metal.

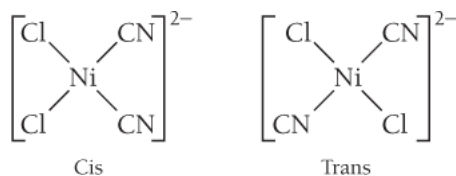
SOLUTION All the ligands are monodentate, so the total coordination number is 4. Ni^{2+} is a d^8 electronic configuration, so we expect a square planar complex.

PROCEDURE Identify whether this is a cis-trans or fac-mer isomerism.

SOLUTION Square planar complexes can only have cis–trans isomers.

PROCEDURE Draw and label the two isomers.

SOLUTION

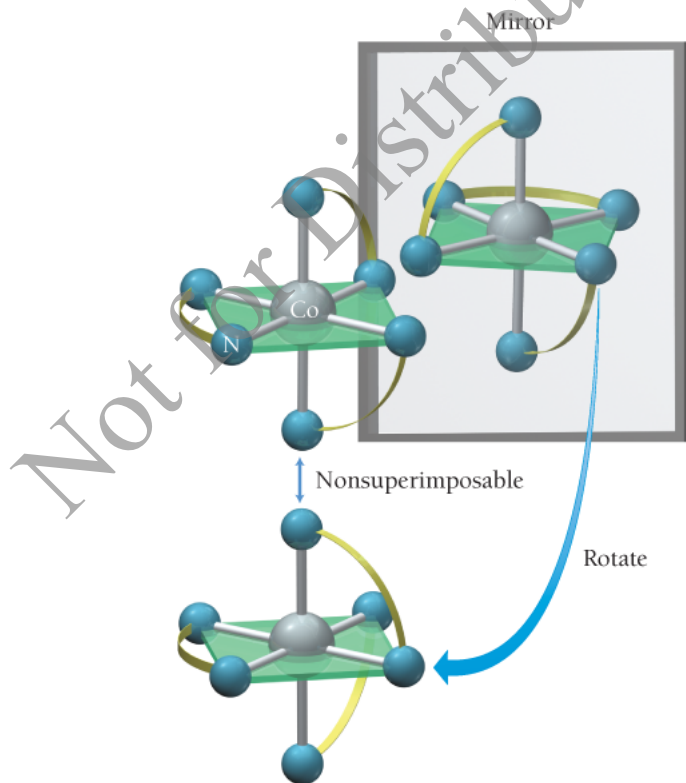


FOR PRACTICE 22.6 Draw the structures and label the type of all the isomers of $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{ox})]^-$.

The second category of stereoisomerism is optical isomerism. Recall from [Section 21.3](#) that **optical isomers** are nonsuperimposable mirror images of one another. If you hold your right hand up to a mirror, the image in the mirror looks like your left hand. No matter how you rotate or flip your left hand, you cannot superimpose it on your right hand. Molecules or ions that exhibit this quality are *chiral*. The isomers are *enantiomers*, and they exhibit the property of optical activity (the rotation of polarized light). The complex ion $[\text{Co}(\text{en})_3]^{3+}$ is nonsuperimposable on its mirror image, so it is a chiral complex ([Figure 22.10](#)).

Figure 22.10 Optical Isomerism in $[\text{Co}(\text{en})_3]^{3+}$

The mirror images of $[\text{Co}(\text{en})_3]^{3+}$ are not superimposable. (The connected nitrogen atoms represent the ethylenediamine ligand.)

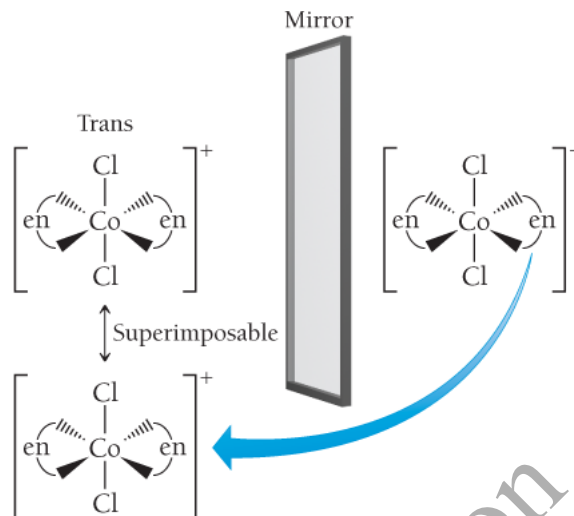


The compounds in [Example 22.7](#) demonstrate optical isomerism in octahedral complexes. Tetrahedral complexes can also exhibit optical isomerism, but only if all four coordination sites are occupied by different ligands. Square planar complexes do not normally exhibit optical isomerism, as they are superimposable on their mirror images.

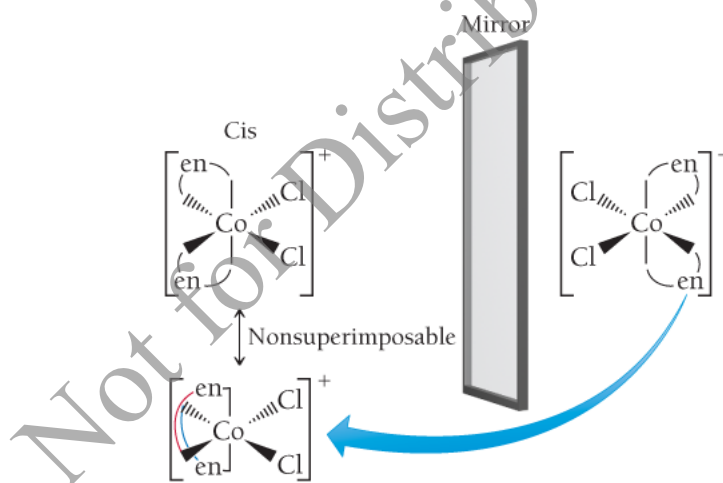
Example 22.7 Recognizing and Drawing Optical Isomers

Determine whether the cis or trans isomers in [Example 22.5](#) are optically active (demonstrate optical isomerism).

SOLUTION Draw the trans isomer of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ and its mirror image. Check to see if they are superimposable by rotating one isomer 180° .



Draw the cis isomer and its mirror image. Check to see if they are superimposable by rotating one isomer 180° .



FOR PRACTICE 22.7 Determine whether the fac or mer isomers of $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]^+$ are optically active.

Not for Distribution