Isomerism in Coordination Complexes

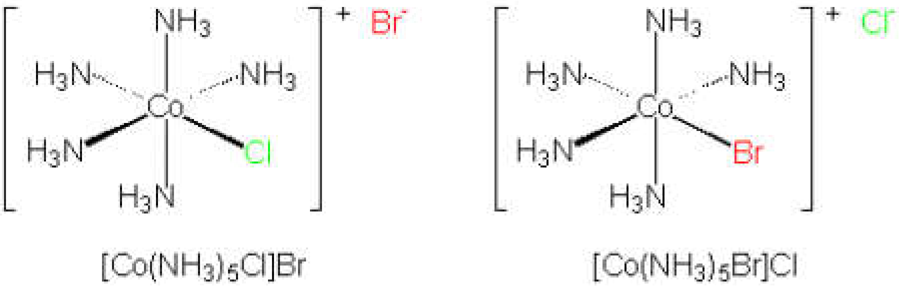
The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. 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. Isomers are compounds with the same molecular formula but different structural formulas and do not necessarily share similar properties. There are many different classes of isomers, like stereoisomers, enantiomers, and geometrical isomers. There are two main forms of isomerism: **structural isomerism** and **stereoisomerism** (spatial isomerism).

ClassI: Structural Isomers

Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural isomers, which differ in structure or bond type. For inorganic complexes, there are three types of structural isomers: *ionization*, *coordination* and *linkage*. Structural isomers, as their name implies, differ in their structure or bonding, which are separate from stereoisomers that differ in the spatial arrangement of the ligands are attached, but still have the bonding properties. The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms. When determining a structural isomer, youlook at (1) the ligands that are bonded to the central metal and (2) which atom of the ligands attach to the central metal.

Ionization Isomerism

Ionization isomers occur when a ligand that is bound to the metal center exchanges places with an anion or neutral molecule that was originally outside the coordination complex. The geometry of the central metal ion and the identity of other ligands are identical. For example, an octahedral isomer will have five ligands that are identical, but the sixth will differ. The nonmatching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers is different. A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.



which are counter ions in the second coordination sphere. (left) The chloride ion is bound to the cobalt as a chloro-ligand with the bromide ion as the counter ion. (right) In the other ionization isomer the bromide is acting as a bromo-ligand to the cobalt with the chloride acting as the counter ion. These two isomers are called pentaammine**chloro**cobalt(II) **bromide** (left) and pentaammine**bromo**cobalt(II) **chloride** (right).

The difference between the ionization isomers can be view within the context of the ions generated when each are dissolved in solution. For example, when pentaamminebromocobalt(II) chloride is dissolved in water, ions are generated:

$$\mathrm{CoBr(NH_3)_5Cl(s)} \rightarrow \mathrm{CoBr(NH_3)_5^+(aq)} + \mathrm{Cl^-(aq)}$$

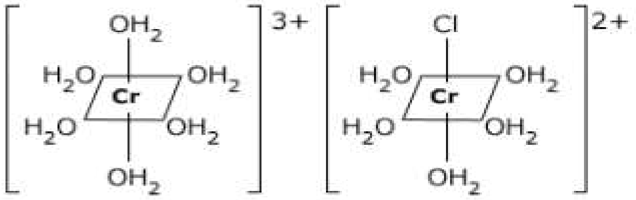
whereas when pentaamminechlorocobalt(II) bromide is dissolved, ions are generated:

$$\mathrm{CoCl(NH_3)_5Br(s)} \rightarrow \mathrm{CoCl(NH_3)_5^+(aq)} + \mathrm{Br^-(aq)}$$

Notice that both anions are necessary to balance the charge of the complex, and that they differ in that one ion is directly attached to the central metal, but the other is not. A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*), which in the case of water is called *Hydrate Isomerism*. The best known example of this occurs for chromium chloride ($\mathbf{CrCl_3 \cdot 6H_2O}$) which may contain 4, 5, or 6 coordinated water molecules (assuming a coordination number of 6). The dot here is used essentially as an expression of ignorance to indicate that, though the parts of the molecule separated by the dot are bonded to one another in some fashion, the exact structural details of that interaction are not fully expressed in the resulting formula. Using Alfred Werner's coordination theory that indicates that several of the water molecules are actually bonded directly (via coordinate covalent bonds) to the central chromium ion. In fact, there are several possible compounds that use the brackets to signify bonding in the complex and the the dots to signify "water molecules that are not bound to the central metal, but are part of the lattice:

$[\mathrm{CrCl_2(H_2O)_4}]\mathrm{Cl} \cdot 2\,\mathrm{H_2O}$: bright-green colored
$[\mathrm{CrCl(H_2O)_5}]\mathrm{Cl_2} \cdot \mathrm{H_2O}$: grey-green colored
$[\mathrm{Cr(H_2O)_6}]\mathrm{Cl_3}$: violet colored

These isomers have very different chemical properties and on reaction with to test for ions, would find 1, 2, and 3 ions in solution, respectively. Upon crystallization from water, many compounds incorporate water molecules in their crystalline frameworks. These "waters of crystallization" refers to water that is found in the crystalline framework of a metal complex or a salt, which is **not directly bonded** to the metal cation. In the first two hydrate isomers, there are water molecules that are artifacts of the crystallization and occur inside crystals. These water of crystallization is the total weight of water in a substance at a given temperature and is mostly present in a definite (stoichiometric) ratio.



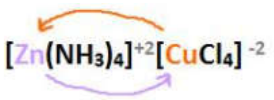
$3\ \mathrm{Cl^-}$ $\quad$ $2\ \mathrm{Cl^-},\ \mathrm{H_2O}$

$[\mathrm{Cr(OH_2)_6}]\mathrm{Cl_3}$ $\quad$ $[\mathrm{Cr(OH_2)_5Cl}]\mathrm{Cl_2} \cdot \mathrm{H_2O}$

The hydrate isomer (left) is violet colored and [CrCl(H2O)5]Cl2 · H2O the hydrate isomer is green-grey colored.

Coordination Isomerism

Coordination isomerism occurs compounds containing complex anionic and cationic parts can be thought of as occurring by interchange of some ligands from the cationic part to the anionic part. Hence, there are two complex compounds bound together, one with a negative charge and the other with a positive charge. In coordination isomers, the anion and cation complexes of a coordination compound exchange one or more ligands. For example, the compounds [Co(NH3)6][Cr(C2O4)3] and [Co(C2O4)3][Cr(NH3)6] compound are coordination isomers.

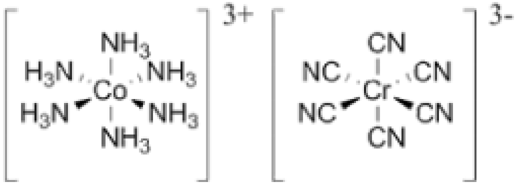


$[Zn(NH_3)_4]^{+2}[CuCl_4]^{-2}$

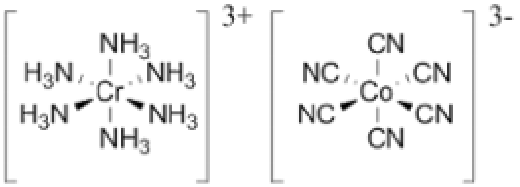
Tetraaminezinc(II)
TetrachloroCuprate(II)

$[Cu(NH_3)_4]^{+2}[ZnCl_4]^{-2}$

TetraamineCopper(II)
TetrachloroZincate(II)



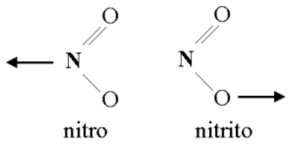
$[Co(NH_3)_6][Cr(CN)_6]$



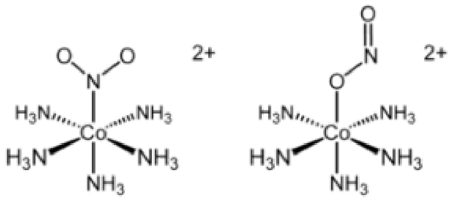
$[Cr(NH_3)_6][Co(CN)_6]$

Linkage Isomerism

Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: SCN^-/NCS^- and NO_2^- /ONO^-. The only difference is what **atoms the molecular ligands bind to the central ion**. The ligand(s) must have more than one donor atom, but bind to ion in only one place. For example, the (NO_2^-) ion is a ligand can bind to the central atom through the nitrogen or the oxygen atom, but cannot bind to the central atom with both oxygen and nitrogen at once, in which case it would be called a *polydentate* rather than an *ambidentate* ligand.



As with all structural isomers, the formula of the complex is unchanged for each isomer, but the properties may differ. The names used to specify the changed ligands are changed as well. For example, the ion is called *nitro* when it binds with the atom and is called *nitrito* when it binds with the atom.



(left) The nitro isomer (Co-NO_2) and (right) the nitrito isomer (Co-ONO)

When donation is from nitrogen to a metal center, the complex is known as a *nitro*-complex and when donation is from one oxygen to a metal center, the complex is known as a *nitrito*- complex. An alternative formula structure to emphasize the different coordinate covalent bond for the two isomers.

Geometric Isomers

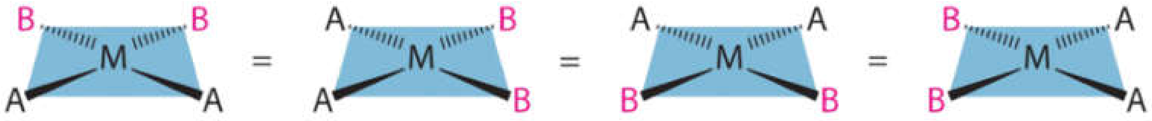
The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different 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.

Geometric Isomers: Planar Isomers

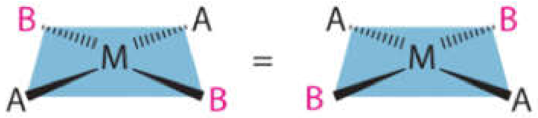
Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes. Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:

MA_3B square planar complex

For an MA_2B_2 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:

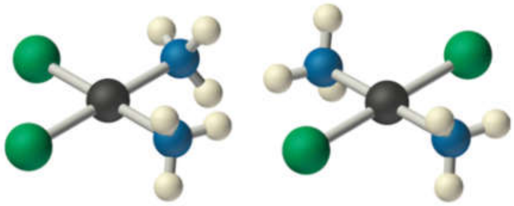


MA_2B_2 square planar complex, *cis* isomer



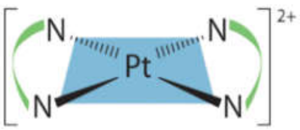
MA_2B_2 square planar complex, *trans* isomer

Because there is no way to convert the cis structure to the trans by rotating or flipping the molecule in space, they arefundamentally different arrangements of atoms in space. Probably the best-known examples of cis and trans isomers of an MA_2B_2 square planar complex are cis-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and trans-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



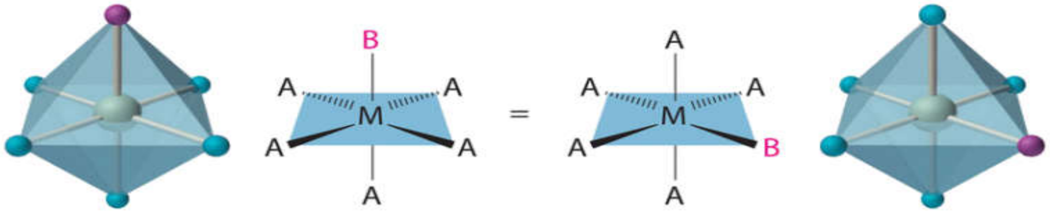
cis-$Pt(NH_3)_2Cl_2$ *trans*-$Pt(NH_3)_2Cl_2$

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 $[Pt(en)_2]^{+2}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



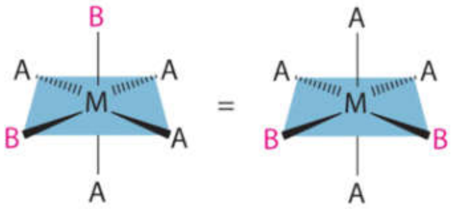
Geometric Isomers: Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible foroctahedral complexes in which only one ligand is different from the other five (MA_5B). 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 sixvertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:

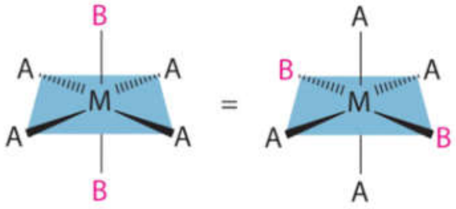


MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving an MA4 B2 complex, two isomers are possible.The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_2Cl_2]Cl$ are examples of this type of system:

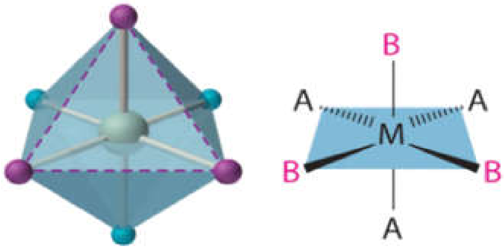


MA_4B_2 octahedral complex, *cis* isomer

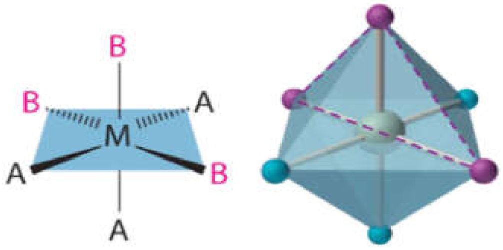


MA_4B_2 octahedral complex, *trans* isomer

Replacing another A ligand by B gives an MA_3B_3 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):



MA_3B_3 octahedral complex, *fac* isomer

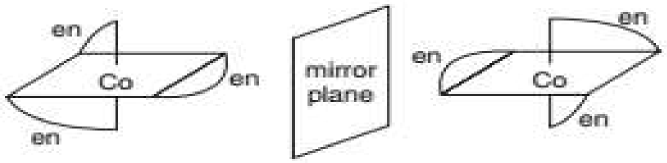


MA_3B_3 octahedral complex, *mer* isomer

Optical Isomers:

For structures that do not possess a plane of symmetry, the mirror images are not superimposable. Known as *chiral* structures, such molecules rotate a beam of polarized

light. If the beam is rotated to the right (when looking along the beam in the direction of propagation), the substance is said to be *dextrorotatory* (or simply *dextro*) and indicated by (+). Those substances that rotate the plane of polarized light to the left are said to be *levorotatory* or *levo* and indicated as (-). A mixture of equal amounts of the two forms is called a racemic mixture, and it produces no net rotation of the polarized light. The dichlorobis(ethylenediamine)cobalt(II) ion can exist in two geometrical isomers. For the *trans* isomer, there is a plane of symmetry that bisects the cobalt ion and the ethylenediamine ligands, leavingone Cl on either side of the plane. However, the *cis* isomer has no plane of symmetry so two optical isomers exist. This is also the case for [Co(en)3]3 as is illustrated in Figure below .
Light behaves as though it consists of waves vibrating in all directions around the direction of wave propagation. For polarized light, the propagation can be regarded as a vector, which can be resolved into two circular vectors. If there is no rotation of the plane, it is expected that motion along each vector is equivalent so that each vector traverses an equal distance around the circle as shown in below Figure

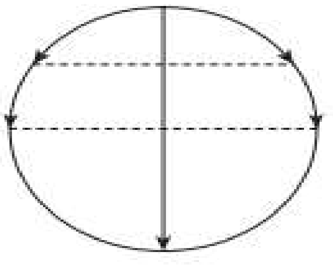


Nonsuperimposable mirror images of $[Co(en)_3]^{3+}$

Λ (lambda) isomer
(left rotation)

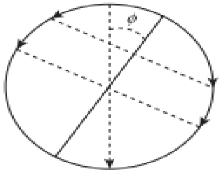
Δ (delta) isomer
(right rotation)

The optically active isomers of $[Co(en)_3]^{3+}$ (top) and their directions of rotation of polarized light.



Polarized light represented as a vector with no rotation.

If polarized light passes through a medium that exhibits optical rotation, the motion along one of the circular vectors is slower than that of the other. The resultant vector is thus displaced from the original vector by some angle, φ. Figure below shows the vector model in which the phase difference is φ and a is defined as one-half of the phase difference.



The index of refraction of a medium, n, is the ratio of the velocity of light in a vacuum, c, to the velocity in the medium, v:

$$n = c/v$$

When a material exhibits different indices of refraction for the right- and left-hand components of the circular vectors, the velocities in these directions are different and the plane of polarized light undergoes rotation. For the left- and right-hand vectors, the indices of refraction are

$$n_l = c/v_l \quad \text{and} \quad n_r = c/v_r$$

Which leads to the relationship

$$v_l/v_r = n_r/n_l$$

If we represent the length of the path of the polarized light in the sample as d and let φ be the phase difference in the two directions, we find that

$$\phi = 2\pi d\nu/v_r - 2\pi d\nu/v_l$$

For light, the velocity and frequency are related by

$$\lambda\nu = c$$

Therefore, after simplification we obtain

$$\phi = 2\pi d(n_r - n_l)/\lambda_o$$

where λo is the wavelength of the light undergoing rotation. When expressed in terms of a, the relationship is

$$\alpha = \phi/2 = \pi d(n_r - n_l)/\lambda_o$$

Solving for the difference in index of refraction, we obtain

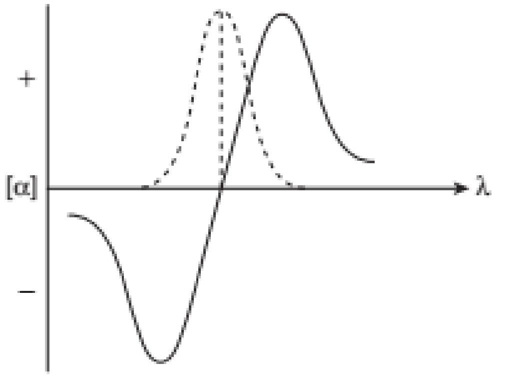
$$(n_r - n_l) = \alpha\lambda_o / \pi d$$

When a solution is studied, the specific rotation of light having a wavelength of λ at a temperature *t* iswritten as $[\alpha]\lambda t$, and it is defined by the relationship

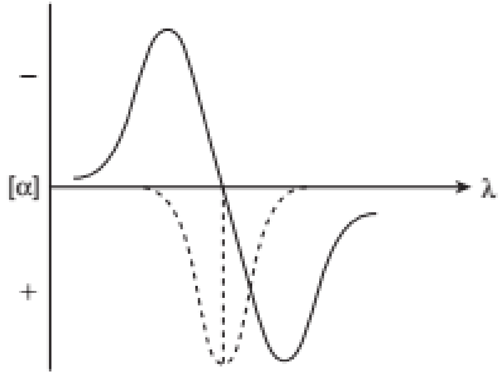
$$[\alpha]_\lambda^t = \alpha/ds = \alpha/d\sigma\rho$$

In this relationship, α is the observed rotation, *d* is the path length, *s* is the concentration of the solution in g solute/mL solution, σ is the concentration in g solute/g of solution, and ρ is the density of the solution. The most commonly used light source is the sodium lamp, which has λ = 589nm. Therefore, designations of a specific rotation are indicated by the use of symbols such as $(+)_{589}$-$[Co(en)_3]_3$. The preceding discussion makes use of the relationship between optical rotation and the index of refraction. However, the optical rotation varies with the wavelength of the light as does the index of refraction. When the variation of optical rotation with wavelength is studied, it is found that the curve undergoes a change in slope in the region of the maximum in an absorption band arising from an electronic transition. The change in rotation as a function of wavelength is known as *optical rotatory dispersion* (ORD).

Figure below shows a schematic diagram that illustrates the change in rotation that occurs in the region of an absorption band. The rapid change in rotation at the wavelength where absorption by the complex occurs is known as the *Cotton effect* because it was discovered in 1895 by A. Cotton.



(a) Initially levorotatory (a positive Cotton effect)



(b) Initially dextrotatory (a negative Cotton effect)