

Isomerism, Equilibria and Biological Systems

Cis and trans configurations are possible in some octahedral and square planar complexes. In addition to these geometrical isomers, optical isomers (molecules or ions that are mirror images but not superimposable) are possible in certain octahedral complexes. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use.

34.1 Isomerism in Complexes

Learning Objectives

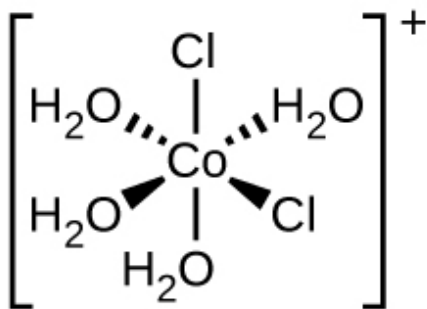
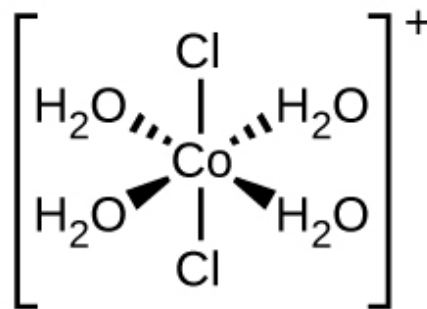
By the end of this section, you will be able to:

- Explain and provide examples of geometric and optical isomerism
- Identify several natural and technological occurrences of coordination compounds

Isomers are different chemical species that have the same chemical formula. Transition metal complexes often exist as **geometric isomers**, in which the same atoms are connected through the same types of bonds but with differences in their orientation in space. Coordination complexes with two different ligands in the *cis* and *trans* positions from a ligand of interest form isomers. For example, the octahedral $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ ion has two isomers. In the *cis* configuration, the two chloride ligands are adjacent to each other ([Figure 34.1](#)). The other isomer, the *trans* configuration, has the two chloride ligands directly across from one another.

Figure 34.1

The *cis* and *trans* isomers of $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ contain the same ligands attached to the same metal ion, but the spatial arrangement causes these two compounds to have very different properties.

Violet, *cis* formGreen, *trans* form

Different geometric isomers of a substance are different chemical compounds. They exhibit different properties, even though they have the same formula. For example, the two isomers of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$ differ in color; the *cis* form is violet, and the *trans* form is green. Furthermore, these isomers have different dipole moments, solubilities, and reactivities. As an example of how the arrangement in space can influence the molecular properties, consider the polarity of the two $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_3$ isomers. Remember that the polarity of a molecule or ion is determined by the bond dipoles (which are due to the difference in electronegativity of the bonding atoms) and their arrangement in space. In one isomer, *cis* chloride ligands cause more electron density on one side of the molecule than on the other, making it polar. For the *trans* isomer, each ligand is directly across from an identical ligand, so the bond dipoles cancel out, and the molecule is nonpolar.

EXAMPLE 34.1.1

Geometric Isomers

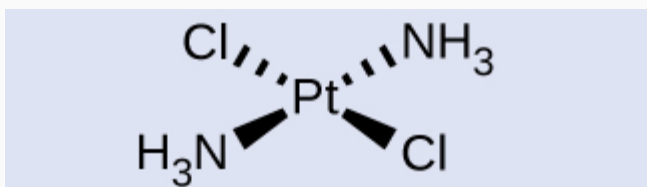
Identify which geometric isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is shown in [Figure 34.3](#). Draw the other geometric isomer and give its full name.

Solution

In the [Figure 34.3](#), the two chlorine ligands occupy *cis* positions. The other form is shown in [Figure 34.2](#). When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diamminedichloroplatinum(II).

Figure 34.2

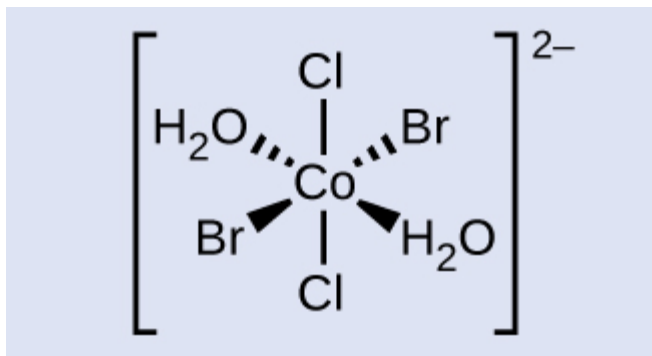
The *trans* isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has each ligand directly across from an adjacent ligand.



Check Your Learning

Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).

✓ Answer

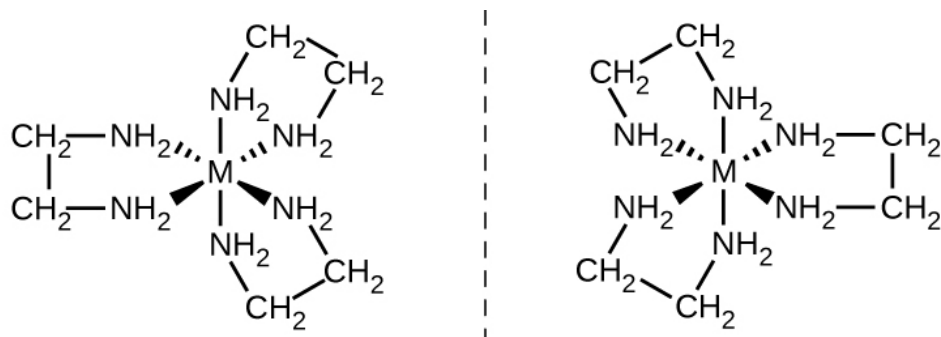


Another important type of isomers are optical isomers, or enantiomers, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as $[\text{M}(\text{en})_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in [Figure 34.3](#). These two isomers will react differently with other optical isomers. For example, DNA helices are

optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.

Figure 34.3

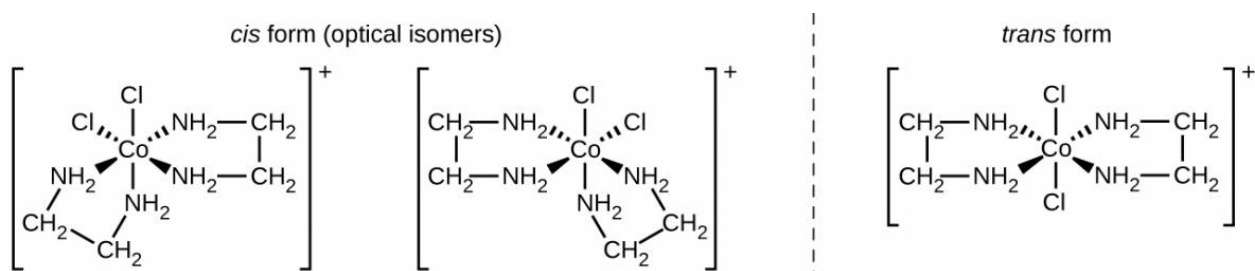
The complex $[M(en)_3]^{n+}$ (M^{n+} = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.



The $[Co(en)_2Cl_2]^+$ ion exhibits geometric isomerism (*cis/trans*), and its *cis* isomer exists as a pair of optical isomers ([Figure 34.4](#)).

Figure 34.4

Three isomeric forms of $[Co(en)_2Cl_2]^+$ exist. The *trans* isomer, formed when the chlorines are positioned at a 180° angle, has very different properties from the *cis* isomers. The mirror images of the *cis* isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.



Linkage isomers occur when the coordination compound contains a ligand that can bind to the transition metal center through two different atoms. For example, the CN ligand can bind through the carbon atom (cyano) or through the nitrogen atom (isocyano). Similarly, SCN^- can be bound through the sulfur or nitrogen atom, affording two distinct compounds ($[Co(NH_3)_5SCN]^{2+}$ or $[Co(NH_3)_5NCS]^{2+}$).

Ionization isomers (or coordination isomers) occur when one anionic ligand in the inner coordination sphere is replaced with the counter ion from the outer coordination sphere. A simple example of two ionization isomers are $[CoCl_6][Br]$ and $[CoCl_5Br][Cl]$.

34.1.2 Isomers of Coordination Compounds



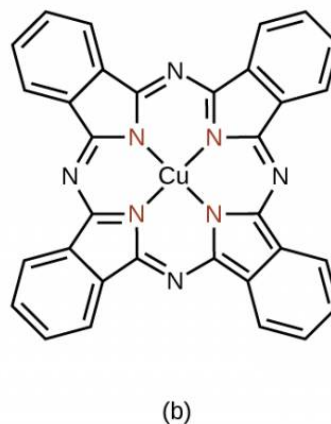
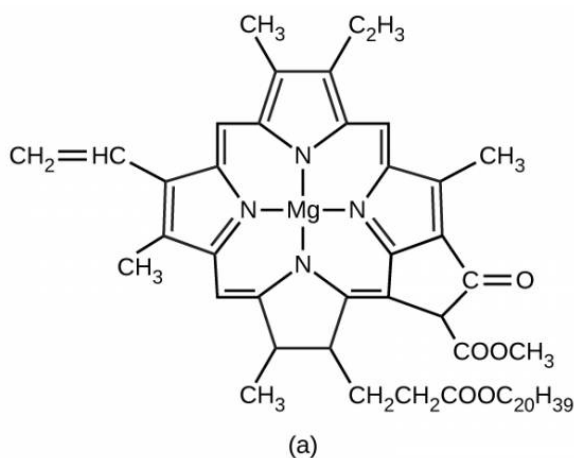
[Watch on YouTube](#)

34.1.3 Coordination Complexes in Nature and Technology

Chlorophyll, the green pigment in plants, is a complex that contains magnesium ([Figure 34.5](#)). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

Figure 34.5

- (a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center.
(b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.



34.1.4 CHEMISTRY IN EVERYDAY LIFE

Transition Metal Catalysts

One of the most important applications of transition metals is as industrial catalysts. As you recall from the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (see [Figure 34.6](#)). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.

Figure 34.6

(a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by "Mr. Brian"/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by "osseous"/Flickr)



(a)



(b)



(c)

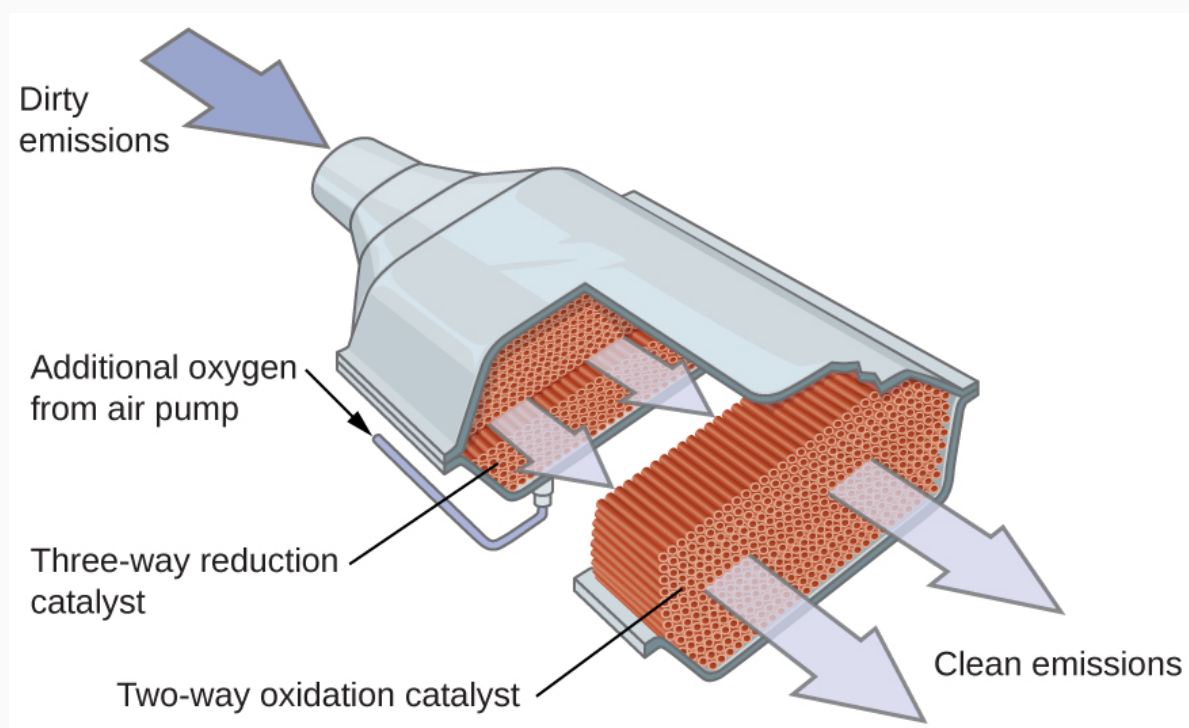
34.1.5 PORTRAIT OF A CHEMIST

Deanna D'Alessandro

Dr. Deanna D'Alessandro develops new metal-containing materials that demonstrate unique electronic, optical, and magnetic properties. Her research combines the fields of fundamental inorganic and physical chemistry with materials engineering. She is working on many different projects that rely on transition metals. For example, one type of compound she is developing captures carbon dioxide waste from power plants and catalytically converts it into useful products (see [Figure 34.7](#)).

Figure 34.7

Catalytic converters change carbon dioxide emissions from power plants into useful products, and, like the one shown here, are also found in cars.



Another project involves the development of porous, sponge-like materials that are “photoactive.” The absorption of light causes the pores of the sponge to change size, allowing gas diffusion to be controlled. This has many potential useful applications, from powering cars with hydrogen fuel cells to making better electronics components. Although not a complex, self-darkening sunglasses are an example of a photoactive substance.

Watch this [video](#) to learn more about this research and listen to Dr. D'Alessandro (shown in [Figure 34.8](#)) describe what it is like being a research chemist.

Figure 34.8

Dr. Deanna D'Alessandro is a functional materials researcher. Her work combines the inorganic and physical chemistry fields with engineering, working with transition metals to create new systems to power cars and convert energy (credit: image courtesy of Deanna D'Alessandro).

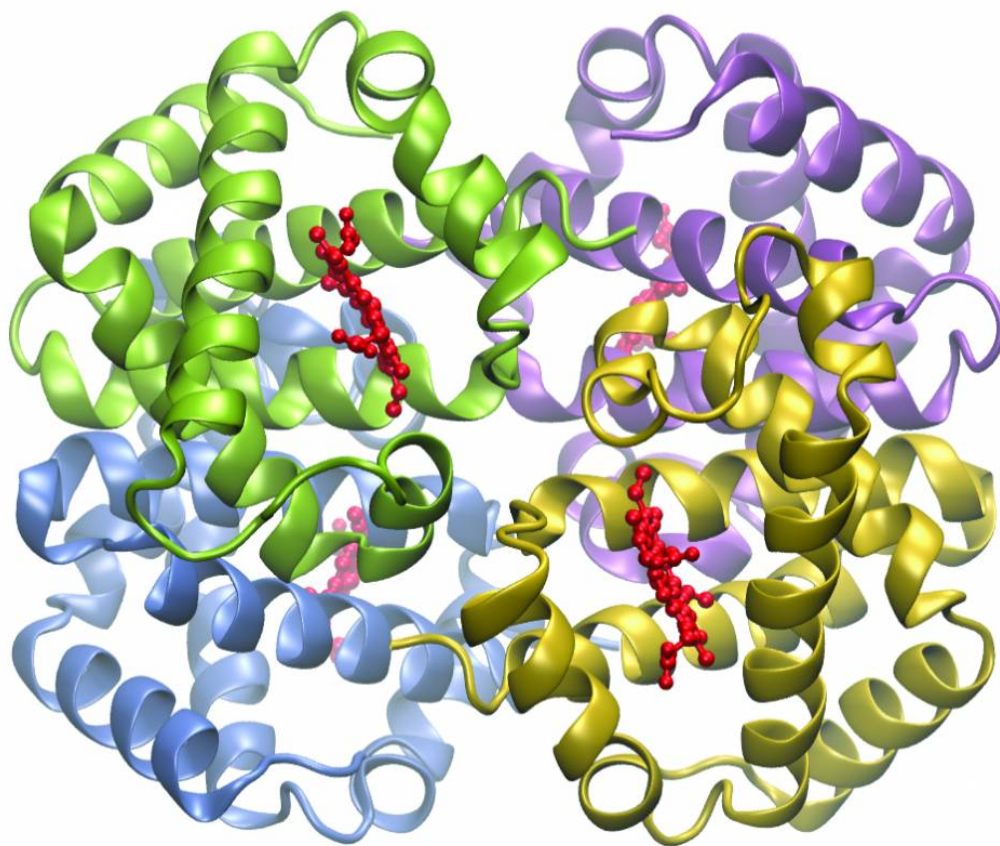


Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from [Figure 34.5](#)) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme ([Figure 34.9](#)), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is Fe^{2+} ; oxidation of the iron to Fe^{3+} prevents oxygen transport.

Figure 34.9

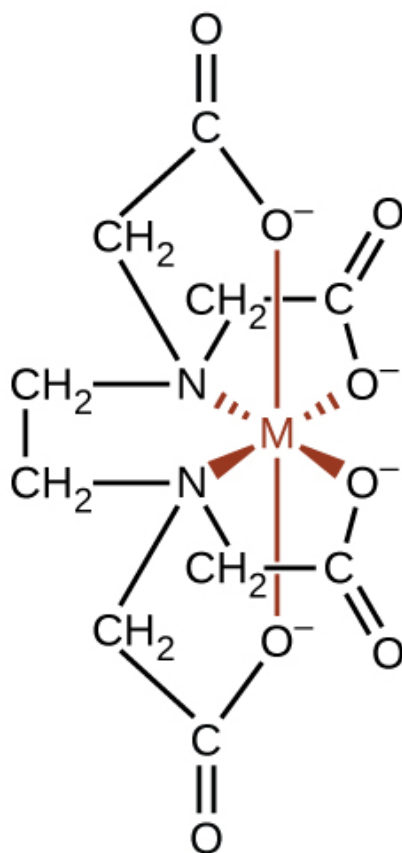
Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.



Complexing agents often are used for water softening because they tie up such ions as Ca^{2+} , Mg^{2+} , and Fe^{2+} , which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA, $(\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$, coordinates to metal ions through six donor atoms and prevents the metals from reacting ([Figure 34.10](#)). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

Figure 34.10

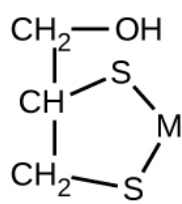
The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.



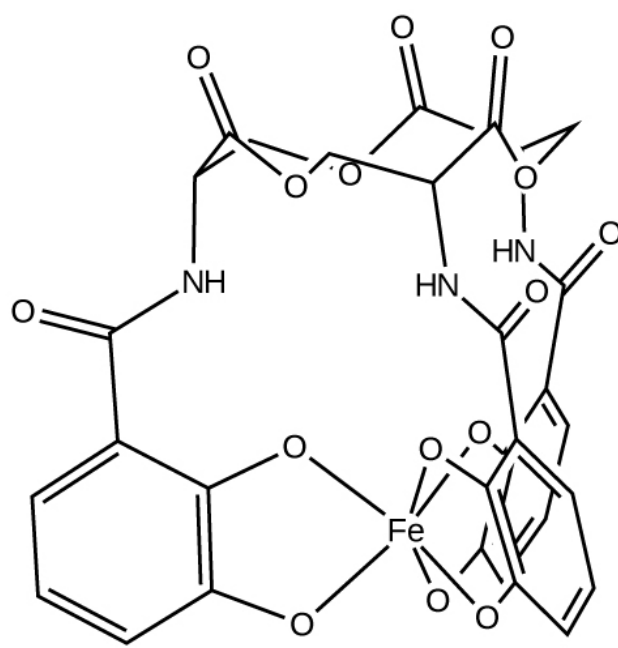
Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL), $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OH}$, is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate ([Figure 34.11](#)). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering from blood diseases such as Cooley's anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.

Figure 34.11

Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.



(a)



(b)

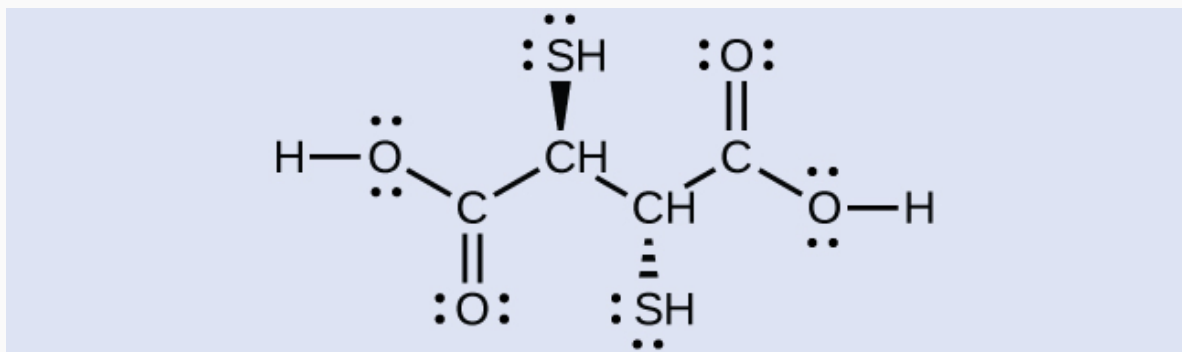
EXAMPLE 34.1.6

Chelation Therapy

Ligands like BAL and enterobactin are important in medical treatments for heavy metal poisoning. However, chelation therapies can disrupt the normal concentration of ions in the body, leading to serious side effects, so researchers are searching for new chelation drugs. One drug that has been developed is dimercaptosuccinic acid (DMSA), shown in [Figure 34.12](#). Identify which atoms in this molecule could act as donor atoms.

Figure 34.12

Dimercaptosuccinic acid is used to treat heavy metal poisoning.



Solution

All of the oxygen and sulfur atoms have lone pairs of electrons that can be used to coordinate to a metal center, so there are six possible donor atoms. Geometrically, only two of these atoms can be coordinated to a metal at once. The most common binding mode involves the coordination of one sulfur atom and one oxygen atom, forming a five-member ring with the metal.

Check Your Learning

Some alternative medicine practitioners recommend chelation treatments for ailments that are not clearly related to heavy metals, such as cancer and autism, although the practice is discouraged by many scientific organizations.¹ Identify at least two biologically important metals that could be disrupted by chelation therapy.

✓ Answer

Ca, Fe, Zn, and Cu

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$ are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diamminedichloroplatinum(II), $[\text{Pt}(\text{NH}_3)_2(\text{Cl})_2]$,

and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diammine (NH₃)₂ portion is retained with other groups, replacing the dichloro [(Cl)₂] portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

Footnotes

- 1National Council against Health Fraud, *NCAHF Policy Statement on Chelation Therapy*, (Peabody, MA, 2002).

Files

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