

2.2: Coordination Chemistry of Transition Metals

Learning Objectives

- List the defining traits of coordination compounds
- Determine the coordination number and oxidation state of the central metal ion in a coordination complex
- Distinguish between monodentate and polydentate ligands
- Identify several natural and technological occurrences of coordination compounds

The hemoglobin in your blood, the chlorophyll in green plants, vitamin B_{12} , and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored (Figure 2.2.1). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.



Figure 2.2.1: Metal ions that contain partially filled d subshell usually form colored complex ions; ions with empty d subshell (d^0) or with filled d subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with $M = Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$, $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$, and $Zn^{2+}(d^{10})$. (credit: Sahar Atwa)

Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4 . The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit $NaCl$ (Figure 2.2.2). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a central metal ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form coordination compounds. The Lewis base donors, called ligands, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a donor atom with a lone pair of electrons that can form a coordinate bond to the metal.

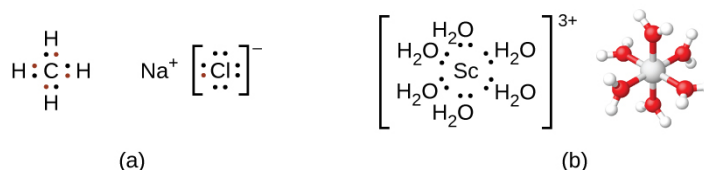


Figure 2.2.2: (a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)

2.2.1: Coordination Number

The coordination sphere consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The **coordination number** of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two (Figure 2.2.3). For the copper(II) ion in $[CuCl_4]^{2-}$, the coordination number is four, whereas for the cobalt(II) ion in $[Co(H_2O)_6]^{2+}$ the coordination number is six. Each of these ligands is monodentate, from the Greek for “one toothed,” meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.

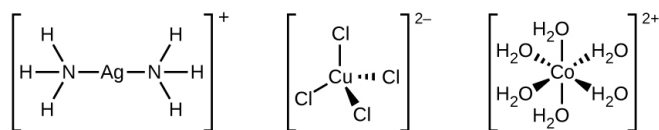


Figure 2.2.3: The complexes (a) $[\text{Ag}(\text{NH}_3)_2]^+$, (b) $[\text{Cu}(\text{Cl})_4]^{2-}$, and (c) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.

Many other ligands coordinate to the metal in more complex fashions. Bidentate ligands are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base (Figure 2.2.4). Both of the atoms can coordinate to a single metal center. In the complex $[\text{Co}(\text{en})_3]^{3+}$, there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.

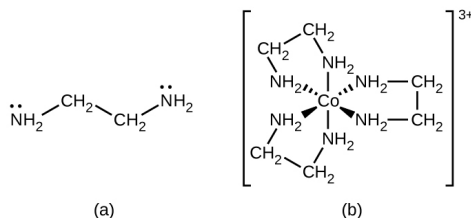


Figure 2.2.4: (a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex $[\text{Co}(\text{en})_3]^{3+}$ contains three of these ligands, each forming two bonds to the cobalt ion.

Any ligand that bonds to a central metal ion by more than one donor atom is a polydentate ligand (or “many teeth”) because it can “bite” into the metal center with more than one bond. The term chelate (pronounced “KEY-late”) from the Greek for “claw” is also used to describe this type of interaction. Many polydentate ligands are chelating ligands, and a complex consisting of one or more of these ligands and a central metal is a chelate. A chelating ligand is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab’s claw would hold a marble. Figure 2.2.4 showed one example of a chelate and the heme complex in hemoglobin is another important example (Figure 2.2.5). It contains a polydentate ligand with four donor atoms that coordinate to iron.

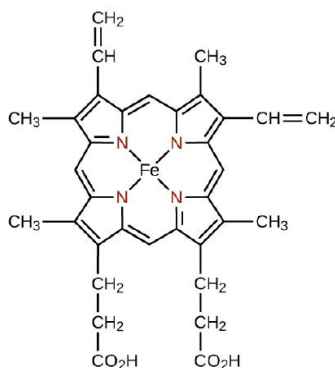


Figure 2.2.5: The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.

Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3 , Cl^- , and H_2O , are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, and the anion of the acid glycine, $\text{NH}_2\text{CH}_2\text{CO}_2^-$ (Figure 2.2.6) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The heme ligand (Figure 2.2.5) is a tetradentate ligand.

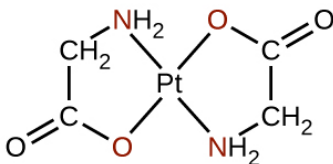


Figure 2.2.6: Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.

2.2.2: Oxidation State

The oxidation state of the metal is determined based on the charges of each ligand and the overall charge of the coordination compound. For example, in $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Br}$, the coordination sphere (in brackets) has a charge of 1+ to balance the bromide ion. The water ligands are neutral, and the chloride ligands are anionic with a charge of 1− each. To determine the oxidation state of the metal, we set the overall charge equal to the sum of the ligands and the metal: $+1 = -2 + x$, so the oxidation state (x) is equal to 3+.

✓ Example 2.2.1: Coordination Numbers and Oxidation States

Determine the name of the following complexes and give the coordination number of the central metal atom.

- $\text{Na}_2[\text{PtCl}_6]$
- $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Solution

- There are two Na^+ ions, so the coordination sphere has a negative two charge: $[\text{PtCl}_6]^{2-}$. There are six anionic chloride ligands, so $-2 = -6 + x$, and the oxidation state of the platinum is 4+. The name of the complex is sodium hexachloroplatinate(IV), and the coordination number is six.
- The coordination sphere has a charge of 3− (based on the potassium) and the oxalate ligands each have a charge of 2−, so the metal oxidation state is given by $-3 = -6 + x$, and this is an iron(III) complex. The name is potassium trisoxalatoferrate(III) (note that tris is used instead of tri because the ligand name starts with a vowel). Because oxalate is a bidentate ligand, this complex has a coordination number of six.
- In this example, the coordination sphere has a cationic charge of 2+. The NH_3 ligand is neutral, but the chloro ligand has a charge of 1−. The oxidation state is found by $+2 = -1 + x$ and is 3+, so the complex is pentaamminechlorocobalt(III) chloride and the coordination number is six.

? Exercise 2.2.1

The $\text{K}[\text{Ag}(\text{CN})_2]$ complex is used to make antiseptic compounds. Give the coordination number and the oxidation state of the metal.

Answer

coordination number two, oxidation state +1

2.2.3: Coordination Complexes in Nature and Technology

Chlorophyll, the green pigment in plants, is a complex that contains magnesium (Figure 2.2.7). 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.

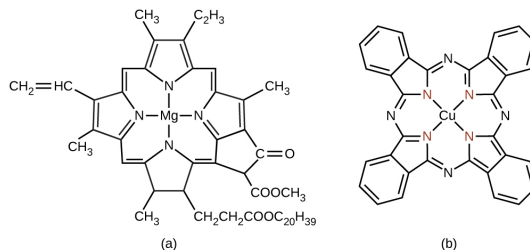


Figure 2.2.7: (a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center. (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.

One of the most important applications of transition metals is as industrial catalysts. As you will learn in 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 (Figure 2.2.8). 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.

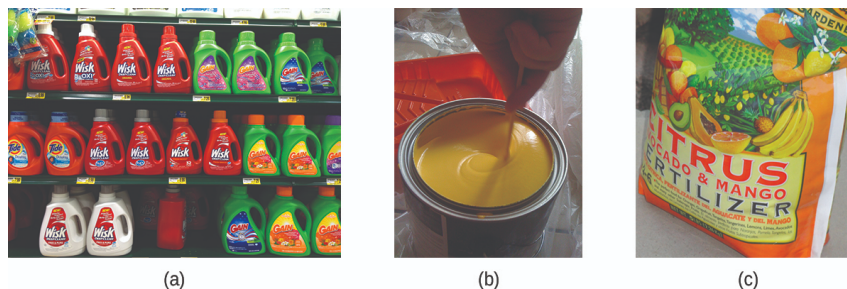


Figure 2.2.8: (a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by “Mr. Brian”/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by “osseous”/Flickr)

Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from Figure 2.2.7) 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 2.2.8), 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.

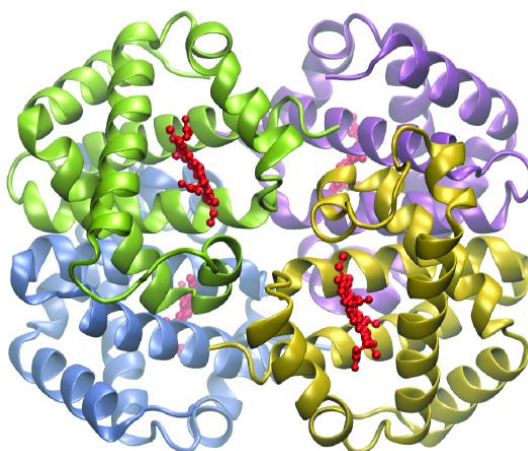


Figure 2.2.8: Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.

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 2.2.9). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

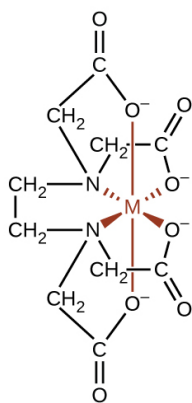


Figure 2.2.9: The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.

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 2.2.10). 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.

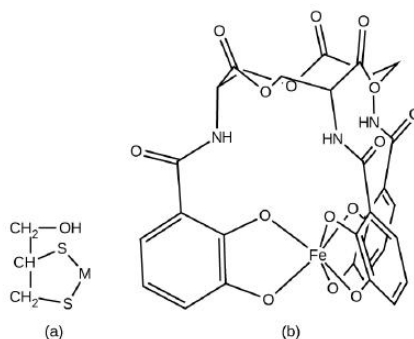


Figure 2.2.10: Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.

✓ Example 2.2.3: 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 2.2.11. Identify which atoms in this molecule could act as donor atoms.

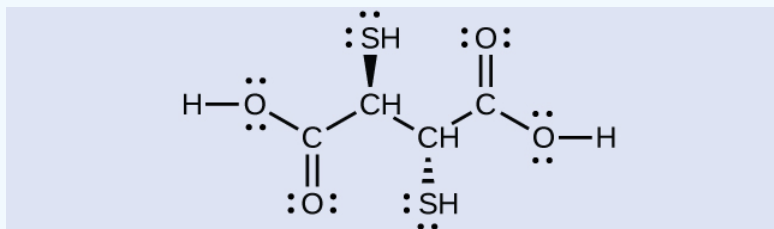


Figure 2.2.11: Dimercaptosuccinic acid is used to treat heavy metal poisoning.

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.

? Exercise 2.2.3

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*-diaminedichloroplatinum(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 diamine $(\text{NH}_3)_2$ portion is retained with other groups, replacing the dichloro $[(\text{Cl})_2]$ portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

Contributors and Attributions

Summary

The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by coordinate covalent bonds. Ligands with more than one donor atom are called polydentate ligands and form chelates. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use.

2.2.4: Footnotes

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

Glossary

bidentate ligand

ligand that coordinates to one central metal through coordinate bonds from two different atoms

central metal

ion or atom to which one or more ligands is attached through coordinate covalent bonds

chelate

complex formed from a polydentate ligand attached to a central metal

chelating ligand

ligand that attaches to a central metal ion by bonds from two or more donor atoms

cis configuration

configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

coordination compound

substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

coordination number

number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

coordination sphere

central metal atom or ion plus the attached ligands of a complex

donor atom

atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

ionization isomer

(or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

ligand

ion or neutral molecule attached to the central metal ion in a coordination compound

linkage isomer

coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

monodentate

ligand that attaches to a central metal through just one coordinate covalent bond

optical isomer

(also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

polydentate ligand

ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

trans configuration

configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

Contributors and Attributions

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