

Chapter 14 – Inorganic Chemistry

Introduction

Organic chemistry is based on the chemistry of carbon, so that leaves the chemistry of over 100 other elements to be characterized as inorganic chemistry. The chemistry of many of these elements is very rich. In this final chapter, we focus on only one segment of these elements, the transition elements, and introduce only some of their fascinating chemistry.

14.1 Ligands and Coordination

Introduction

The molecules and ions that are bound to metals are called ligands. The ligands are said to coordinate to the metal, and the compounds are called coordination compounds.

Prerequisites

- 5.6 Determining Lewis Structures
- 6.1 Molecular Shapes
- 12.1 Lewis Acids and Bases
- 2.1 The Nature of Light

Objectives

- Describe the common coordination geometries adopted by transition metals.
- Explain what a ligand is and give some examples.

14.1-1. Coordination

The number of donor atoms bound to the metal is called the **coordination number** of the metal, and the spatial arrangement of the ligands is called the metal's **coordination geometry**. The most common coordination numbers are 4, 5, and 6, and their common coordination geometries are described below. Octahedral coordination (coordination number = 6) is the most common coordination geometry in this chapter.

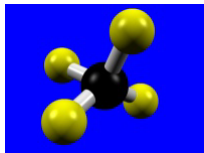
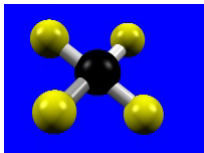
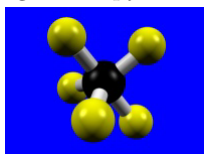
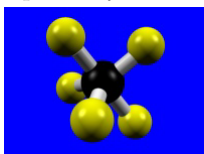
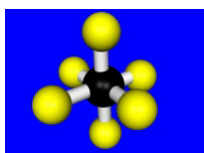
Coordination Number = 4	Tetrahedral 	Square Planar 
Coordination Number = 5	Trigonal Bipyramidal 	Square Pyramidal 
Coordination Number = 6	Octahedral 	

Table 14.1: Common Coordination Numbers

14.1-2. Ligands

Transition metals are frequently found in *complexes*, substances in which the metal is bound to several molecules and/or ions. The molecules or ions that bind to a metal are called **ligands**. Ligands have lone pairs and function as Lewis bases, while metal ions have empty orbitals that can be used to share the lone pair; i.e., metals are Lewis acids.

Although most ligands use only one lone pair to bond to a metal, some ligands can use more than one. If such ligands bond to two different metals, they are called **bridging ligands**, because they form a bridge between the two metals. If more than one lone pair from a ligand binds to the same metal, the ligand is said to be a **chelating ligand**.

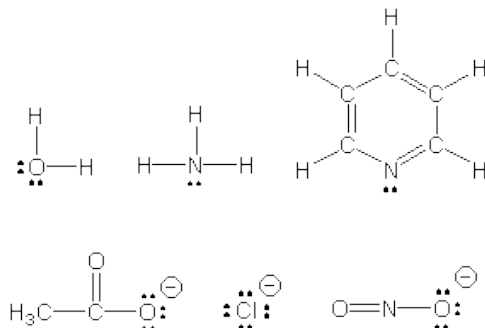


Figure 14.1a: Some Common Ligands Ligands contain lone pairs that are used to bond to the metal. Ligands can be molecules (top row) or ions (bottom row).

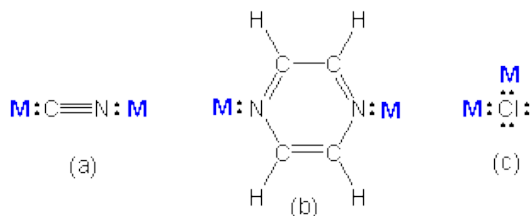


Figure 14.1b: Some Common Bridging Ligands Ligands that contain two lone pairs that can bond to two different metals are called **bridging ligands** because they can bridge two metals. Ligands (a) (cyanide ion) and (b) bridge with 180° bond angles, while ligand (c) (chloride ion) can bridge with ~109° bond angles. Note that these ligands can bridge, but they do not have to. For example, chloride forms bridges in only a small fraction of its compounds with transition elements.

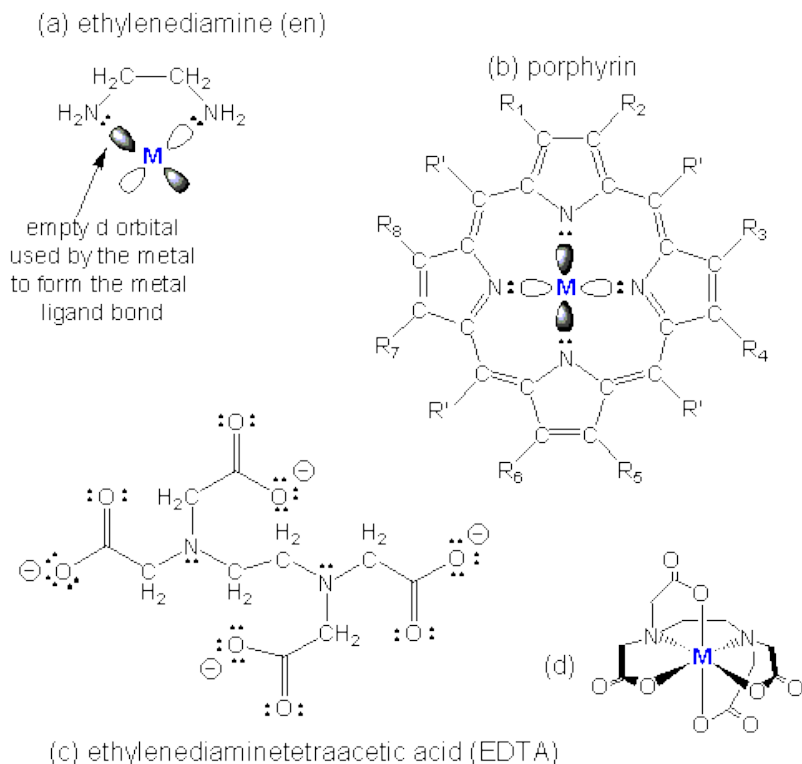


Figure 14.1c: Some Common Chelating Ligands

Chelating ligands appear to “bite” the metal, and the term **dentate** is used to specify the number of places that a ligand “bites.” For example, consider the chelating ligands shown in Figure 14.1c. Ethylenediamine “bites” the metal in two locations, so it is said to be *bidentate*, porphyrin “bites” four locations and is a *tetradentate* ligand, and EDTA bites in six locations and is a *hexadentate* ligand.

14.2 Ligand Fields

Introduction

The chemistry of the transition metals can be understood in terms of the interaction between the ligands and the metal’s d-orbitals. The ligands generate an electric field around the metal that alters the energy of the orbitals and strongly influences the properties of the metal.

Prerequisites

- 2.6 Orbital Shapes and Sizes
- 1.8 Electromagnetism and Coulomb’s Law
- 2.3 Bohr Model

Objectives

- Explain how the d-orbital energies are affected by their orientation to the ligands.
- Determine the total spin from the number of unpaired electrons.

14.2-1. d-orbitals

The five d-orbitals have the following electron distributions:

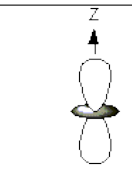
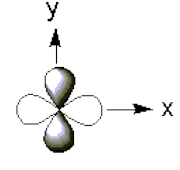
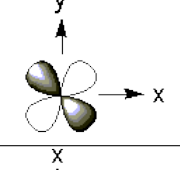
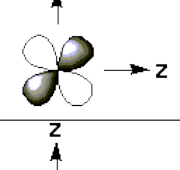
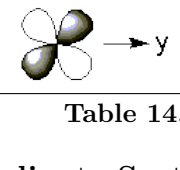
Name	Shape	Electron Distribution
z^2		along the z -axis and in a donut-shaped cloud in the xy plane
x^2-y^2		along the x and y axes
xy		in the xy plane but directed between the axes
xz		in the xz plane but directed between the axes
yz		in the yz plane but directed between the axes

Table 14.2: Electron Distributions in the d-Orbitals

14.2-2. The Coordinate System

As shown in Figure 14.2, the metal-ligand bonds in an octahedral coordination form the coordinate system for the d-orbitals. Thus, the z^2 and x^2-y^2 orbitals are directed along the axis of the metal-ligand bonds as they are directed along the z and the x and y axes, respectively.

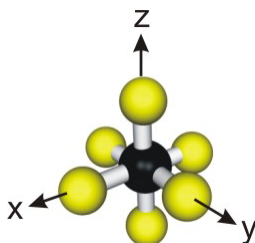


Figure 14.2: Coordinate System in Octahedral Coordination

14.2-3. d-Orbital Energies in Octahedral Fields

The energies of the d-orbitals change in the electric field produced by the ligands. The electric field is called a ligand field.

We saw in Section 2.7 that the orbitals in a d sublevel had the same energy, but that is only in a free atom. When the metal is bound to ligands, the relative energies of the d-orbitals change. The lone pairs on the ligands generate an electric field, known as the **ligand field**, and the energies of the d-orbitals rise in the presence of a ligand field. How much they rise depends upon the strength of the field (electron density on the ligand), the distance between the

metal and the ligand, and the orientation of the d-orbital relative to the ligand. When the six ligands (octahedral field) all lie on the axes, the energies of those orbitals directed along the axes are higher than the energy of those directed between the axes.

Figure 14.3 compares the effect of ligands (grey spheres) lying along the x , y , and z axes on the five d-orbitals. The lobes of the z^2 and x^2-y^2 orbitals are directed along the bonding axes, so the ligands interact with them strongly and raise their energy. However, the ligands are directed at the nodes of the xy , xz , and yz orbitals. Consequently, the ligands do not interact as strongly with these orbitals, so their energy does not rise nearly as much.

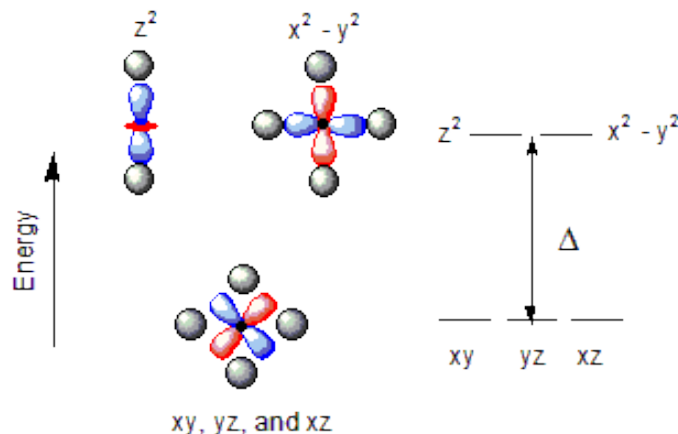


Figure 14.3: d-Orbital Energies in an Octahedral Ligand Field

The energy separation between the two groups of d-orbitals in an octahedral field is given the symbol Δ . A strong field ligand produces a large Δ , while a weak field ligand produces a small one.

CN^{1-} is a strong field ligand with a large Δ , while H_2O and Cl^{1-} are both weak field ligands with small Δ s.

14.2-4. Color Complement

The color perceived for a substance is the complement of the one that is absorbed.

Substances are colored because they absorb visible light. However, the color perceived for a substance is that of the reflected light, not the absorbed light. The light that is reflected is the **complement** of the absorbed light. The sum of a color and its complement is black; i.e., the sum absorbs all colors. Thus, when white light (presence of all colors) strikes a substance, it absorbs a portion and reflects the remainder, which is the complement of the color that was absorbed. Two colors that are opposite one another on the **color wheel** (Figure 14.4) are complementary. For example, a substance appears violet when it absorbs photons in the yellow region because yellow is the complementary color of violet. Similarly, yellow compounds absorb violet photons. Similar conclusions can be drawn from the table.

Observed Color	Absorbed Color
green	red
blue	orange
violet	yellow
red	green
orange	blue
yellow	violet

Table 14.3: Complementary Colors



Figure 14.4: Color Wheel

14.2-5. Color and Energy

Recall from Section 2.2 that the energy of a photon (bundle of light energy) is proportional to its frequency:

$$E = h\nu$$

where h is Planck's constant (6.63×10^{-34} J/s) and ν is the frequency of the photon in s^{-1} . Thus, the energy of visible photons increases in the order red < orange < yellow < green < blue < violet.

Substances that are colored absorb photons in the visible region of the electromagnetic spectrum to promote an electron from one orbital to another that is higher in energy. The energy difference between the two orbitals (ΔE) can be determined from the frequency of the light that is absorbed by the following relationship:

$$\Delta E = h\nu$$

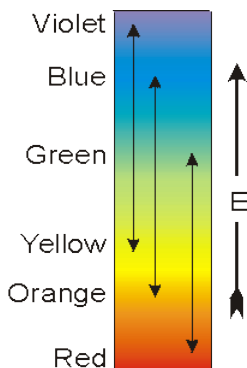


Figure 14.5: Energy and Color The double arrows connect complementary colors. Thus, if a substance appears the color at one end of the double arrow, then it absorbs light at the other end of the arrow.

Using the color wheel, we see that green grass actually absorbs red light, while an orange flower absorbs blue light, and using Figure 14.5, we conclude that the energy separation of the orbitals involved in the color is greater for the orange flower because the blue photons it absorbs have more energy than do the red photons absorbed by the grass.

14.2-6. Color in Transition Metal Ions

Many transition metal ions are colored because the energy separation between the d-orbitals lies in the visible region. The light that is absorbed in these transitions must obey the following relationship:

$$\Delta = h\nu$$

where Δ is the energy separation between the d-orbitals and ν is the frequency of the absorbed light. Thus, the relative field strengths of ligands can sometimes be determined from the color of the compounds they form with a metal.

EXERCISE 14.1:

Use the color wheel and relative energy figures and the fact that CoBr_2 is green while CoCl_2 is blue to determine the relative field strengths of the bromide and chloride ions.

CoBr_2 is green. What color does it absorb?

violet
blue
green
yellow
orange
red

CoCl_2 is blue. What color does it absorb?

violet
blue
green
yellow
orange
red

Which is the stronger field ligand?

chloride
bromide

14.2-7. Electron Spin

We now consider the effect of Δ on the spin of transition metal ions. The **spin** on an ion is the sum of the individual electron spins. Recall from Section 2.5 that the spin quantum number for an electron is either $+1/2$ or $-1/2$. The spin of two paired electrons is $+1/2 + (-1/2) = 0$. Therefore, only unpaired electrons contribute to the spin on a metal ion. In Chapter 2, we used Hund's Rule to determine the number of unpaired electrons in a d sublevel. Hund's Rule is based upon the fact that energy is required to pair two electrons in an orbital. This energy is called the **pairing energy (PE)**.

In the presence of an octahedral ligand field, the d-orbitals are in two groups separated by an energy Δ , so there are two ways in which four to seven electrons can occupy the five orbitals. Which way they actually fill the d-orbitals depends upon the relative sizes of Δ and the pairing energy. Remember that the electrons fill in such a way to minimize their energy.

- **high spin:** If $\Delta < \text{PE}$, the electrons enter the higher energy set of orbitals before pairing. This is most likely in the presence of weak field ligands.
- **low spin:** If $\Delta > \text{PE}$, the electrons pair before entering the higher energy set. This is most common when strong field ligands are present.

In the absence of any field, all of the d-orbitals have the same energy, so five electrons half-fill the d sublevel in accordance to Hund's Rule. This is the case in a free atom such as Mn as shown in Figure 14.6a.

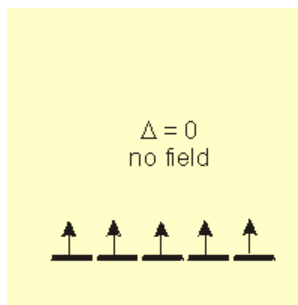


Figure 14.6a: Spin and Field Strength: No Field

In a weak field, the separation between the d-orbitals is less than the pairing energy, so the electrons occupy the higher energy orbitals before pairing. Since the electrons do not pair, this is called the high spin form of the ion.

As shown in Figure 14.6b, Mn^{2+} is high spin when surrounded by weak field ligands such as water molecules and chloride ions.

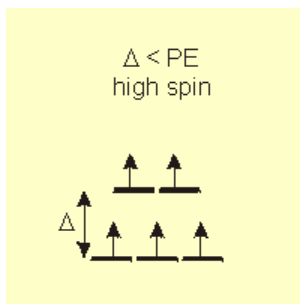


Figure 14.6b: Spin and Field Strength: Weak Field

In a strong field, the separation between the d-orbitals is greater than the pairing energy, so the electrons pair before occupying the higher energy orbitals. Since some of the electrons pair, this is called the low spin form of the ion. As shown in Figure 14.6c, Mn^{2+} is low spin when surrounded by strong field ligands, such as cyanide ion.

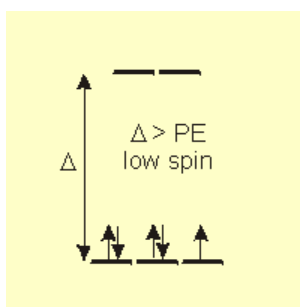


Figure 14.6c: Spin and Field Strength: Strong Field

14.3 Isomers

Introduction

Inorganic compounds can form geometrical isomers when the ligands can situate in different ways relative to one another. In this section, we consider the possible isomers of ML_2X_4 and ML_3X_3 in an octahedral coordination geometry.

Objectives

- Identify cis and trans isomers of ML_2X_4 and meridial and facial isomers of ML_3X_3 .

14.3-1. Isomers

Two ligands in an octahedral geometry can be cis or trans, while three ligands can be meridial or facial.

Two ligands in an octahedral geometry can be situated in two different ways to produce two isomers. Ligands that are situated opposite to one another are said to be **trans**, while two ligands that are adjacent to one another are said to be **cis** to one another.

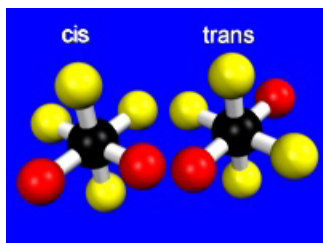


Figure 14.7: Cis and Trans Isomers Two cis ligands (red spheres) are adjacent to one another, while two trans ligands are opposite one another.

Three ligands in an octahedral geometry can also be situated in two different ways to produce two isomers. In *mer or meridial* isomers, the three ligands lie on a meridian of the octahedron, while the three ligands in a *fac or facial* isomer share a face of the octahedron.

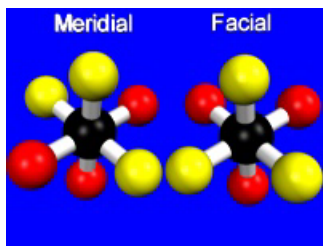


Figure 14.8: Ligand Placement in Facial and Meridial Isomers Three ligands in a meridial isomer lie on a meridian of the octahedron, while three ligands in a facial isomer share a face of the octahedron.

14.4 Metals in Biology

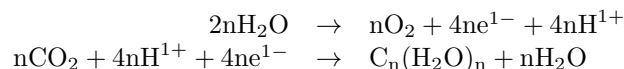
Introduction

Plants extract energy from the sun to synthesize carbohydrates ($C_n(H_2O)_n$) in a process called photosynthesis, and animals extract the energy from the carbohydrates in a process called respiration. Metals are key to both processes.

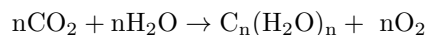
14.4-1. Photosynthesis

Photosynthesis involves a four-electron transfer reaction that is catalyzed by metals.

Plants produce carbohydrates from carbon dioxide and water. The process, which is called *photosynthesis*, involves a four-electron transfer reaction. The two half-reactions are:



Summing the two half-reaction yields the overall reaction:



The reaction is uphill in free energy, and plants use solar energy to carry it out. Photosynthesis is a source of carbohydrates and the only source of oxygen in the atmosphere. However, such reactions have very high activation energies, so nature uses a cluster of four Mn ions coordinated to proteins within the cells break the reaction down into four separate one-electron processes.

The light that drives the reaction is absorbed by chlorophyll (Figure 14.9) in the plants. Chlorophyll contains a Mg^{2+} ion in the center of a porphyrin derivative, which has an extended π system and the characteristic low energy separation between the highest filled π molecular orbital (HOMO) and lowest energy unfilled π^* orbital (LUMO). The extended π system absorbs red light. Plants appear green because green is the complement of red. The Mg^{2+} ion in the center of porphyrin alters the electronic states of the porphyrin slightly so that the excited electron moves

away from the porphyrin rather than returning directly to the ground state. This high-energy electron is used to initiate photosynthesis.

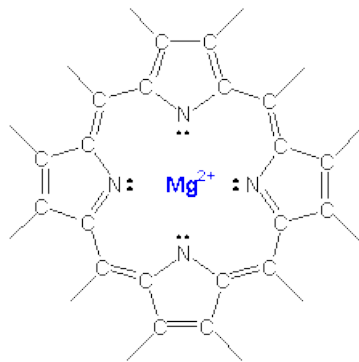
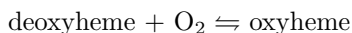


Figure 14.9: Chlorophyll

14.4-2. Heme

Oxygen transport is carried out by binding O₂ to iron in a heme group.

Animals utilize other metal-containing proteins to reverse photosynthesis and extract energy from carbohydrates in a process called respiration. **Respiration** is the oxidative process that extracts chemical energy from organic molecules within living cells. These processes involve the consumption of O₂, which is transported to the cells by hemoglobin. The oxygen molecule attaches to a heme group, an iron(II) porphyrin, in a large protein. Thus, the heme group is the “active site” in hemoglobin. The oxygen is added or removed in the following equilibrium:



Whether the heme is in the oxy or deoxy form depends upon the pressure of O₂. Thus, the heme is oxygenated in the lungs where the O₂ pressure is high and comes off in oxygen-poor tissue.

O₂ is not a very strong Lewis base, so it binds weakly to the iron, which is essential for its delivery to the tissue. CO is a much stronger base and binds to the iron much more strongly and does not come off once it binds. When carbon monoxide is inhaled, it binds to the iron and ties up binding sites that would be used for O₂ transport. Asphyxiation results when so many of the heme sites are tied up with CO that O₂ can no longer be delivered to the cells.

Refer to Figure 14.10 in this discussion of the action of heme. Fe²⁺ has six coordination sites, but the porphyrin ligand coordinates to only four and one of the sites is used to bind to the protein. The occupation of the other site depends upon whether O₂ is bound to the iron. Figure 14.10a shows deoxyhemoglobin (no bound O₂). The sixth site is vacant, so the iron is five coordinate and adopts a square pyramidal geometry with the iron pulled out of the plane of the porphyrin. Figure 14.10b shows oxyhemoglobin (bound O₂). The iron is six coordinate and lies in the plane of the porphyrin molecule. The oxygen also hydrogen bonds to the protein.

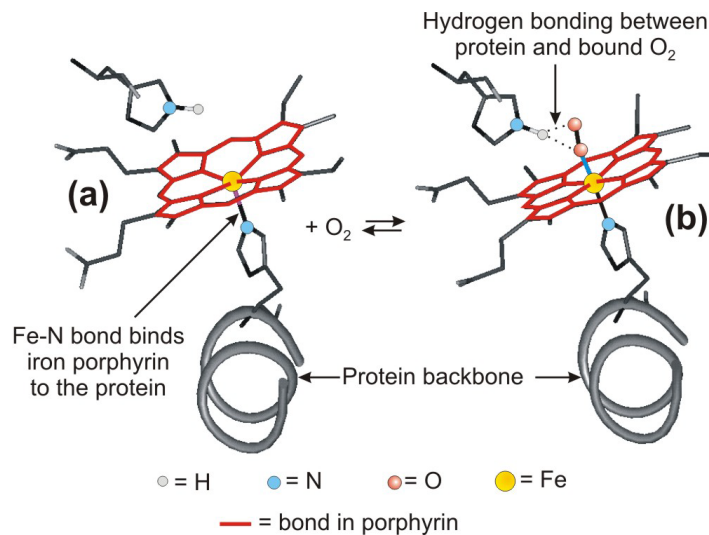


Figure 14.10: Action of Heme

14.4-3. Hemoglobin

Hemoglobin is comprised of 600 amino acids and consists of four similar units (Figure 14.11a). Each unit contains an active site. Although each active site (Figure 14.11b) is the center of the oxygen transport process, the polypeptide chains play critical roles in stabilizing the binding and release of four oxygen molecules.

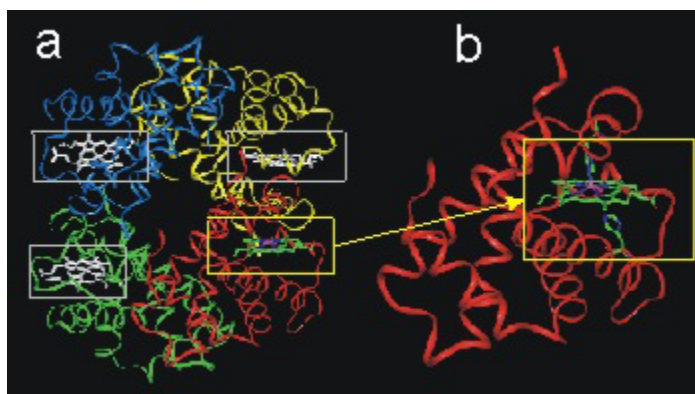


Figure 14.11: Hemoglobin

Only slight changes in that structure can have dramatic effects. For example, in people with sickle-cell anemia, two negatively-charged amino acids are replaced with two neutral amino acids. This small change causes the cell to adopt the sickle shape and greatly reduces the ability of the blood to transport oxygen.

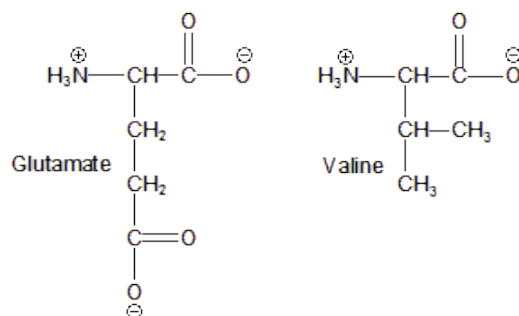


Figure 14.12: Amino Acids Involved in Sickle-Cell Anemia

14.4-4. Cisplatin — Drug Action

Cisplatin binds to DNA, which causes a shape modification in the DNA that hinders its function.

cis-Pt(NH₃)₂Cl₂ (cisplatin) is a square planar complex that is used as an antitumor drug to treat ovarian, testicular, and brain cancers. It functions by binding to DNA, which changes the shape of the DNA double helix and alters its function. Its action is described in the following.

Chlorides are displaced in the nucleus: The chloride ion concentration in the blood is quite high (~0.1 M), so the chloride ions remain bound to the platinum, but, in the nucleus the chloride ion concentration is very low (~0.003 M) and the chloride ions on cisplatin are replaced by water molecules. Water is a weak Lewis base and is easily displaced by a stronger base.

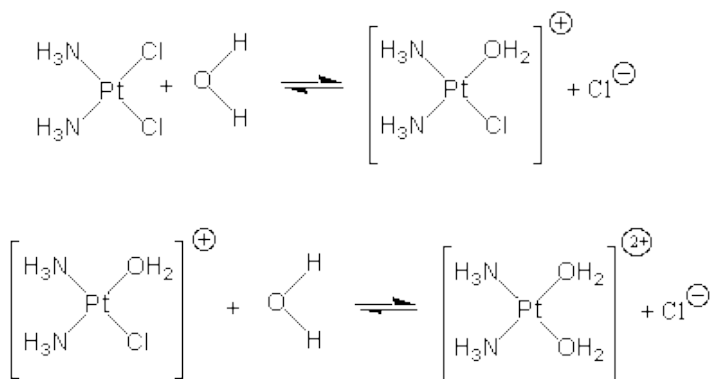


Figure 14.13: Replacement of Chloride with Water

Interaction of Cisplatin and DNA: The lone pairs on the nitrogen atoms make these DNA sites strong Lewis bases, so they displace the water molecules from the drug and bind to the platinum. However, in order for both basic sites to bind, the DNA must bend. The angle by which it bends (α) is 30–40°.

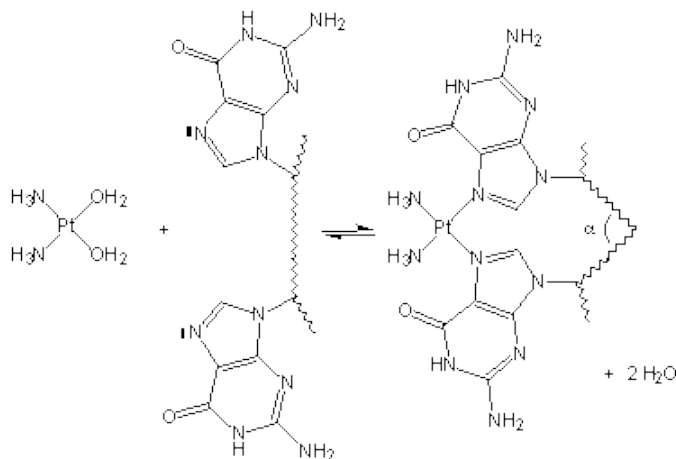


Figure 14.14: Cisplatin Bound to Two Sites of a DNA Strand

Drug Action: Many cellular events are initiated by interactions in which a protein “reads” a specific sequence on the DNA strand. The process is based almost entirely on the ability of the protein to conform its shape to that of the double helix. When the shape of the double helix is altered by the cisplatin, the interactions are modified and the protein can no longer function, which causes the cell to die.

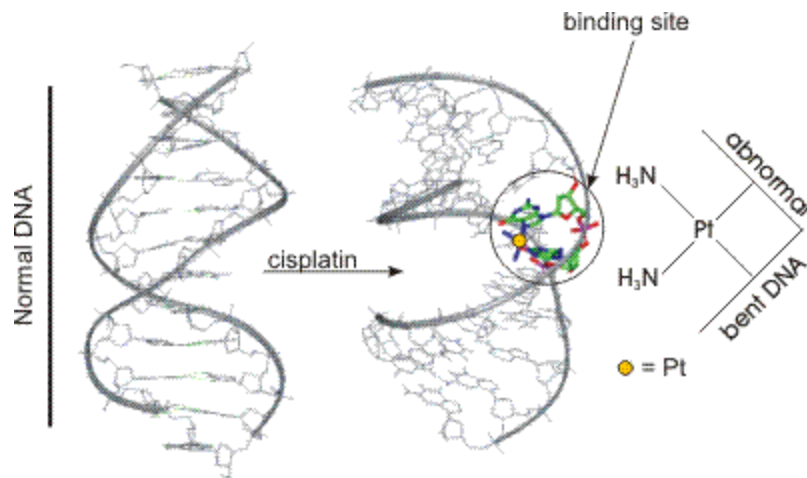


Figure 14.15: Changes in DNA Double Helix Due to Cisplatin Binding

14.5 Metals as Catalysts

Introduction

The interaction between a ligand and a metal can be used to provide new pathways for chemical reactions; i.e., metals catalyze some reactions. A catalyst is classified as either homogeneous (the catalyst is in the same phase as the reactants) or heterogeneous (the catalyst is in a different phase than the reactants).

Prerequisites

- 9.10 Rates of Reaction and the Rate Law

14.5-1. Heterogeneous Catalysts

Heterogeneous catalysts are solids that catalyze solution or gas phase reactions on their surfaces.

When a reactant adsorbs onto a solid surface, the reactant's bonds are weakened, which makes it more reactive.

Hydrogenation is an important reaction, but it has a high activation energy because it involves breaking H–H and C=C bonds. Thus, the reaction is very slow at normal conditions. However, in the presence of Ni, Pt, or Pd and a high pressure of hydrogen, the reaction proceeds rapidly by the mechanism shown for a platinum surface in Figure 14.16. The mechanism consists of the following steps:

- 1 H₂ adsorbs on the surface as H atoms.
- 2 H atoms migrate across the surface.
- 3 An ethylene molecule adsorbs on the surface by using its pi electrons.
- 4 H atoms and ethylene molecules migrate into one another.
- 5 C–H bonds form to produce an ethane molecule that desorbs from the surface.

Catalytic converters in automobiles are also heterogeneous catalysts that use Pt, Pd, and Rh to catalyze the complete combustion of CO and unspent hydrocarbons to CO₂ and H₂O.

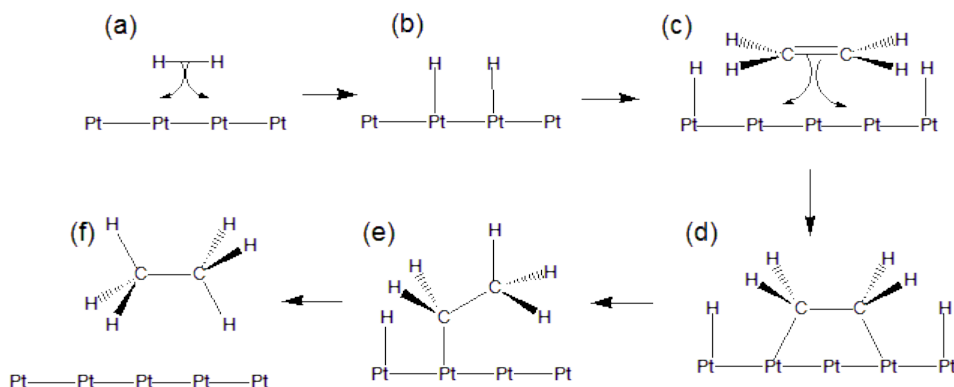


Figure 14.16: Mechanism for Metal Catalyzed Hydrogenation of Ethene Hydrogenation of ethene to ethane on a platinum surface.

14.5-2. Homogeneous Catalysts

Homogeneous catalysts function in the same phase as the reactants.

Consider the metal catalyzed polymerization of ethene into polyethylene. Titanocene, which is a catalyst for this reaction, is a four coordinate complex with one chloride ion, two ligands that do not directly affect the reaction, and an ethyl (C_2H_5) group that is the base upon which the polymer grows. The titanium is in a high oxidation state (+4) and its coordination number can readily be increased from four to five, so titanocene is a good Lewis acid, which is why it is a good catalyst for alkenes, which are weak Lewis bases. The steps of the mechanism, which is illustrated in Figure 14.17, are:

- 1 The pi bond is weakened by coordination to Ti and the Ti adopts a five coordinate geometry.
- 2 The pi electrons of the $C=C$ bond are used to form a $Ti-C$ bond
- 3 The electrons in the original $Ti-C_2H_5$ bond are used to form a $C-C$ bond to the ethene.
- 4 The ethene is inserted between Ti and C_2H_5 .
- 5 The process is repeated with each ethene being inserted between the Ti and the growing polymer chain.

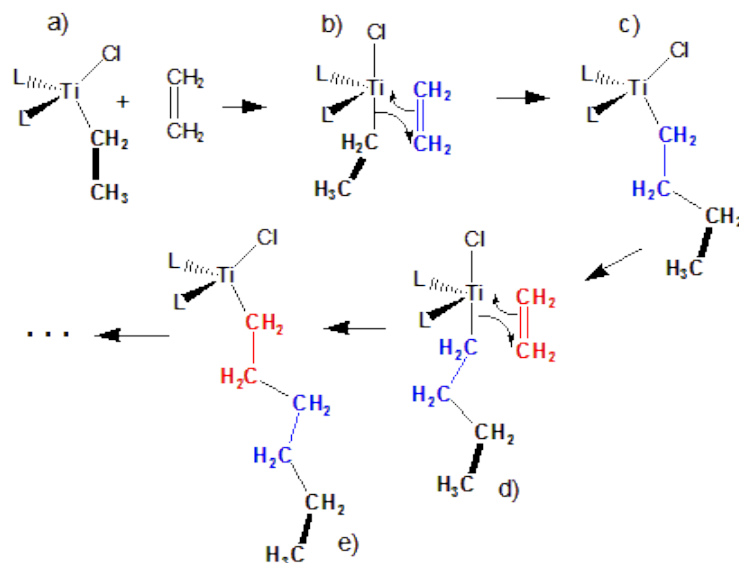


Figure 14.17: Mechanism for Titanocene Catalyzed Polymerization of Ethene

14.6 Transition Metals as Electronic and Magnetic Materials

Introduction

Thus far, we have focused on reactive complexes in solution, but transition metal complexes that are used in materials applications must be stable (ligands bound tightly) and they must be in their crystalline state.

Prerequisites

- 8.6-3 The Definition of a Band

14.6-1. Electronic Conductivity

Electrical conductivity in solids results from partially filled bands. Such bands can be produced by partially oxidizing or reducing a compound.

In order to make a transition metal complex that conducts electricity in the solid state, we must make one whose structure results in band formation and then find a way to make the band partially filled. One of the first conducting transition metal complexes was based on $[\text{Pt}(\text{CN})_4]^{2+}$ ions.

$[\text{Pt}(\text{CN})_4]^{2+}$ ions stack face-to-face to form one-dimensional chains in $\text{K}_2\text{Pt}(\text{CN})_4$. Interaction of the z^2 orbitals produces a band.

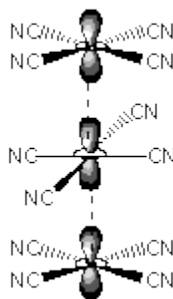


Figure 14.18: Linear Chains Formed from Face-to-Face Stacking of $[\text{Pt}(\text{CN})_4]^{2+}$ Ions

The platinum atom in $\text{K}_2\text{Pt}(\text{CN})_4$ is in the +2 oxidation state and has two electrons in the z^2 . Since the z^2 is filled, the band formed from the interactions of the z^2 orbitals is also filled. Complete oxidation to the +4 state removes both electrons from the z^2 , which would empty the band. However, conductors are characterized by partially filled bands, so neither the +2 nor +4 oxidation states leads to a conducting material. Thus, the material must be partially oxidized to produce the partially filled band required for conduction. A conducting material has been produced by reacting $\text{K}_2\text{Pt}(\text{CN})_4$ with a limited amount of Br_2 (a good oxidizing agent) to produce a material with the stoichiometry of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}$. The oxidation state of the Pt in this compound is 2.3; i.e., it has been partially oxidized. This is equivalent to removing about 15% of the electrons from the band to produce a partially filled band and a conductor.

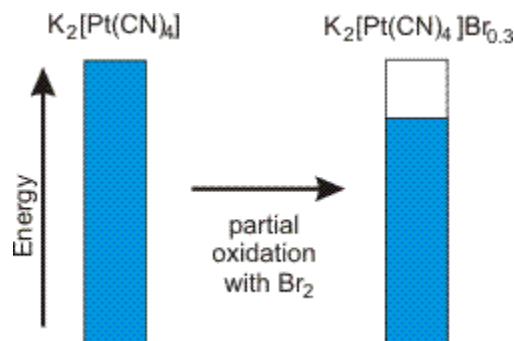


Figure 14.19: Band Occupancy Change due to Partial Oxidation of Platinum

14.6-2. Magnetic Materials

Magnetism is a bulk property that requires unpaired electrons to align in the same direction.

When many atoms that have unpaired electrons in the gas phase combine to form solids, the unpaired electrons pair to form bonds between the atoms. For example, a sodium atom has one unpaired electron, but sodium metal is not magnetic. However, other atoms, such as iron, are magnetic. The three most common magnetic classifications of materials with unpaired electrons are discussed below.

In ferromagnetic materials, the unpaired electrons on adjacent atoms align in the same direction to produce a magnetic field. Iron atoms have four unpaired, and some of them do pair to form the solid. However, not all pair and those that do not align so as to produce a magnetic material. The crystal structure plays a key role in the magnetism as it keeps the spins aligned. Thus, molten iron is not magnetic!

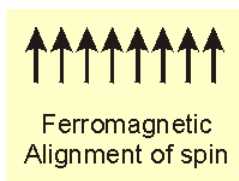


Figure 14.20a: Common Magnetic Classifications: *Ferromagnet*

Materials are not magnetic when the unpaired spins of adjacent atoms align in opposite directions and cancel their magnetic fields. Materials of this type are not magnetic. Sodium is antiferromagnetic.

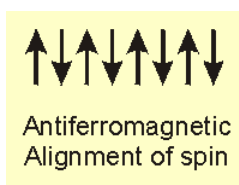


Figure 14.20b: Common Magnetic Classifications: *Antiferromagnet*

Substances that have adjacent atoms with electron spins of unequal magnitude that are aligned in opposite directions are said to be ferrimagnetic. Although there is some cancellation of magnetic fields as a result of the opposite directions of the spins, these substances are magnetic because the opposite spins do not completely cancel one another because they have different magnitudes.

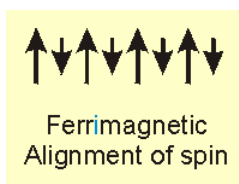


Figure 14.20c: Common Magnetic Classifications: *Ferrimagnet*

14.6-3. Ferrimagnet Example

The structure of $\text{Cs}_2\text{Mn}[\text{V}(\text{CN})_6]$, which is a ferrimagnet in which the spins of the vanadium and manganese atoms are opposed, is shown in Figure 14.21. However, the vanadium atoms (red spheres), which are in the +2 oxidation state, have three unpaired electrons ($S = 3/2$), while the manganese atoms (yellow spheres), which are also in the +2 oxidation state, have five unpaired electrons ($S = 5/2$). Since the spin on Mn is almost twice that on V, a net magnetic field is produced even though the two spins oppose one another.

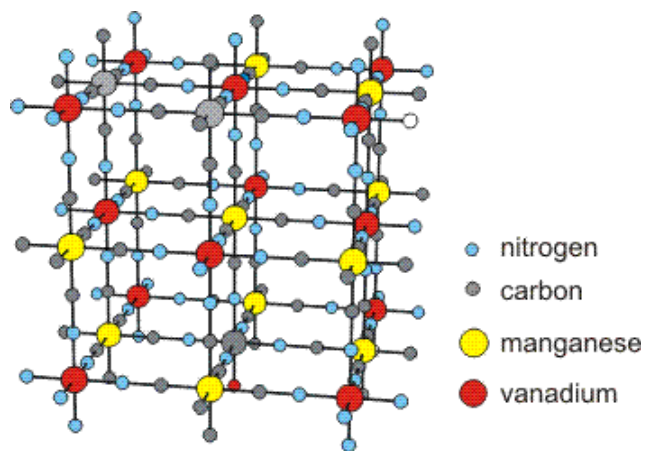


Figure 14.21: Structure of $\text{Cs}_2\text{Mn}[\text{V}(\text{CN})_6]$

14.7 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.