

# INTRODUCTION TO COORDINATION CHEMISTRY

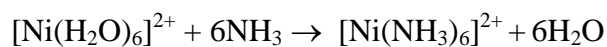
## Introduction

Transition metals differ from main group metals in several key properties. One of the more interesting aspects of transition metals is their ability to form **coordination compounds**. Coordination compounds are formed between a metal atom or ion and a molecule with one or more unshared electron pairs, called a **ligand**. Ligands may be classified according to the number of donor atoms they contain. A **monodentate** ligand donates a single electron pair to the metal or metal ion. Common examples of monodentate ligands include  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2^-$ , and  $\text{CN}^-$ . A **bidentate** ligand, as the name suggests, donates two electron pairs to the metal or metal ion. A good example is ethylenediamine,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ .

Anions as well as neutral molecules may act as ligands. If one or more neutral molecules coordinate to metal ion, the resulting species retains the charge of the transition metal ion and is called a **complex ion**. For example, most transition metal ions form complex ions with water molecules when in aqueous solution. Examples include  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ . If one or more anions coordinate to a metal ion, a complex ion with an overall negative charge may result. Examples include  $[\text{Co}(\text{NO}_2)_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ .

In writing formulas for complex ions and coordination compounds, the molecules inside the brackets represent ligands physically coordinated to the metal ion. Anything outside of the brackets is present for charge balance. Therefore the formulas  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$  and  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_3$  represent neutral compounds in which the chloride ions are present for charge balance. The formulas  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  represent molecules containing negatively charged complex ions with potassium ions present for charge balance.

Most transition metal ions form complex ions with water molecules when in aqueous solution. Such compounds readily form because water is present in excess. However, water is not a particularly strong ligand. Such complexes are prone to **substitution reactions** in which the water molecules are successively replaced with other ligands. Such reactions are often accompanied by a change in the color of the solution. For example, the green  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ion is formed when many nickel (II) salts are dissolved in water. Upon the addition of concentrated  $\text{NH}_3$ , however, the color changes to blue as  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  ion is formed.



Complexes may be classified as **inert** or **labile**, depending upon the speed at which substitution reactions occur. Labile complexes undergo substitution reactions rapidly,

whereas inert complexes undergo substitution reactions slowly. Octahedral  $\text{Co}^{3+}$  and  $\text{Cr}^{3+}$  complexes are inert, making it possible to isolate a large number of complexes containing these metal ions.

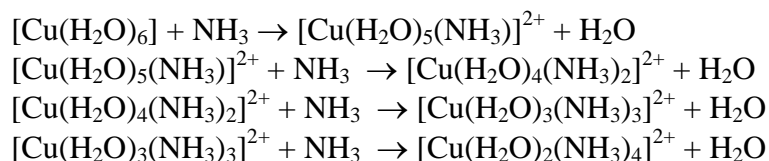
In this laboratory, you will explore some of the coordination chemistry of copper, iron, cobalt, and nickel. The chemistry of these transition metals is discussed in the sections that follow.

## The Chemistry of Copper

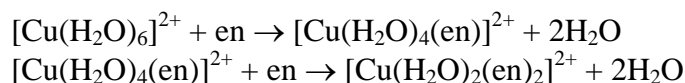
The two most important oxidation states of copper are the +1 (cuprous) and +2 (cupric). The +2 ion is more stable and by far the most common. Commonly encountered copper salts include copper sulfate pentahydrate and copper chloride dihydrate, which have the formulas  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . The former is pale blue in color, and the latter is blue-green in color.

Copper sulfate pentahydrate contains copper(II) in a geometry best described as distorted octahedral. The copper(II) is bound to four water molecules in a square-planar geometry and two oxygen atoms from two sulfate ions. This salt dissolves in water to produce the pale-blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion, in which two of the water molecules are less tightly held and have longer bond distances. The blue-green color of copper chloride dihydrate is due to the presence of some  $\text{CuCl}_4^{2-}$ , which is yellow in color and has a square planar geometry. Concentrated solutions of copper chloride may appear blue-green in color, but dilution results in the formation of the pale-blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion.

Addition of  $\text{NH}_3$  to solutions containing the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion results in successive replacement of the first four  $\text{H}_2\text{O}$  molecules. Replacement of the fifth and six water molecules does not occur to an appreciable extent in aqueous solution, and replacement of the sixth only occurs in liquid ammonia.



A similar series of reactions occur when ethylenediamine is added to a solution containing the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion. Addition of the first two ethylenediamine molecules occurs readily, but addition of a third only occurs when the concentration is very high.



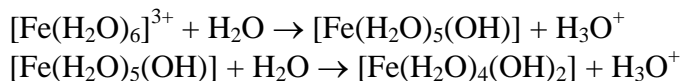
Addition of  $\text{HCl}$  to a solution containing the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion results in the formation of  $[\text{CuCl}_4]^{2-}$  which, as previously mentioned, is yellow in color and has square planar geometry. Salts containing this ion may be isolated with bulky cations, as in  $(\text{NH}_4)_2[\text{CuCl}_4]$ . Addition of  $\text{OH}^-$  to  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  results in the initial formation of solid

$\text{Cu}(\text{OH})_2$ , but with further additions the solid dissolves to form the complex ion  $[\text{Cu}(\text{OH})_4]^{2-}$ . Addition of  $\text{NO}_2^-$  to a solution containing the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion results in the formation of a solution which probably contains the  $[\text{Cu}(\text{NO}_2)_4]^{2-}$  ion.

### The Chemistry of Iron

The two most stable oxidation states of iron are the +2 (ferrous) and +3 (ferric). One of the most commonly encountered ferrous salts is ferrous sulfate hexahydrate. The solid salt is pale-green in color and dissolves in water to give pale green solutions. However, the ferrous ion is readily oxidized to the ferric ion by atmospheric oxygen, and solutions slowly turn yellow due to this oxidation. The ferrous ion has an affinity for amine ligands. Addition of 1,10-phenanthroline and 2,2-bipyridine results in the formation of the complex ions  $[\text{Fe}(\text{bipy})_3]^{2+}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$ . This serves as a test for the presence of the ferrous ion. The ferrous ion is extremely important in biological systems and is found in hemoglobin.

Salts containing the  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion are colorless or pale violet in color. However, in aqueous solution the ferric ion quickly hydrolyzes in water to give yellow-brown color more usually associated with iron.



As a result, such solutions are quite acidic. Strongly acidic solutions are necessary to prevent this hydrolysis. The ferric ion does not have the same affinity for amine ligands as the ferrous ion, but complexes with chelate ligands are formed. The ferric ion forms a well-known blood-red complex ion  $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$  when  $\text{SCN}^-$  is added. The color change is quite striking, even in dilute solutions, and serves as a chemical test for ferric ion.

Two interesting complex ions are the ferrocyanide ion,  $[\text{Fe}(\text{CN})_6]^{4-}$  and the ferricyanide ion,  $[\text{Fe}(\text{CN})_6]^{3-}$ . The ferrocyanide ion is quite stable and can be safely used in the laboratory. The ferricyanide, in contrast, is labile and therefore poisonous. Addition of a solution containing  $\text{Fe}^{3+}$  to a solution of  $[\text{Fe}(\text{CN})_6]^{4-}$  results in the formation of a compound known as Prussian blue, which has the formula  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

### The Chemistry of Cobalt

The two most stable oxidation states of cobalt are the +2 (cobaltous) and +3 (cobaltic). The cobaltous ion is labile and may have either a tetrahedral or octahedral geometry. Common salts include cobalt chloride hexahydrate and cobalt nitrate hexahydrate, which have the formulas  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$  and  $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ . In solution, cobalt(II) forms the octahedral  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ion, which is pale pink in color. Addition of concentrated HCl results in the formation of the complex ion  $[\text{CoCl}_4]^{2-}$ , which has a tetrahedral geometry. Addition of the  $\text{SCN}^-$  ion results in the formation of  $[\text{Co}(\text{SCN})_4]^{2-}$ , which is also tetrahedral.

## The Chemistry of Chromium

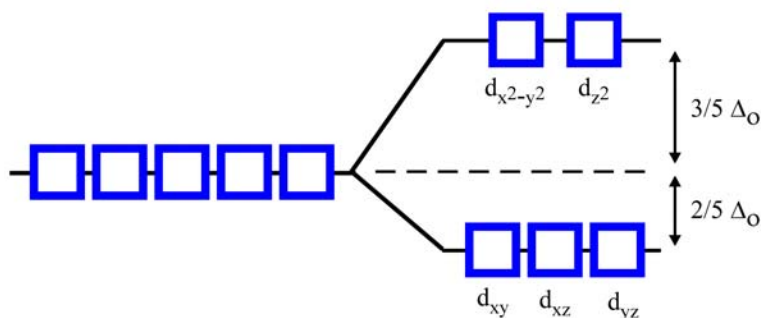
Chromium exists in a wide variety of oxidation states. Common oxidation states include +2, +3, and +6. The +2 ion is labile, and in aqueous solution forms the blue  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  ion. The +3 ion is kinetically inert, and therefore it has been widely studied with many different compounds isolated. Examples of the +6 oxidation state can be found in the chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) ions.

Two common chromium salts include chromium potassium sulfate and chromium chloride. Both are hydrates, with the formulas  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . The sulfate salt dissolves in water to give the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion, which is violet in color. However, the chloride salt does not dissolve to give the same violet  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion. Due to the inertness of the +3 ion, one or more chlorides remain coordinated in aqueous solution and complex ions such as  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$  or  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$  persist in solution. If allowed to stand for several days, the solutions eventually do form the violet  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion.

### A Brief Introduction to Crystal Field Theory

One of the most striking aspects of transition metal chemistry is formation of highly colored solutions. The colors of such complexes can be explained by a simple model known as **crystal field theory**.

In an isolated transition metal atom or ion, the d orbitals are **degenerate**, meaning they all have the same energy. In the presence of a ligand field, the energies of the d orbitals become split. In an octahedral environment, the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals are lowered in energy, and the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are raised in energy. The  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  are collectively referred to as the  $t_{2g}$  orbitals, and the  $d_{x^2-y^2}$  and  $d_{z^2}$  are collectively referred to as the  $e_g$  orbitals.

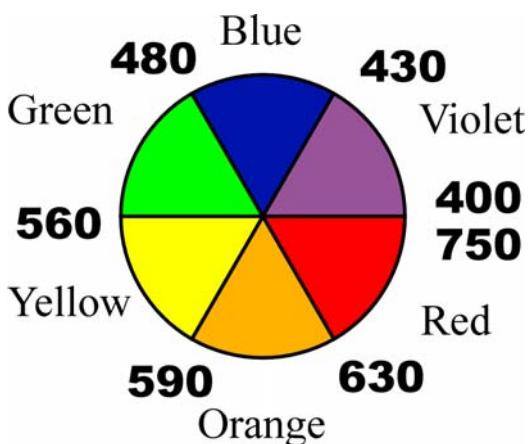


The reason transition metal complexes appear colored is that the magnitude of the orbital splitting often matches the energy of photons of visible light. When this occurs, the light is absorbed by the sample and electrons are promoted from a lower energy state (one of the  $t_{2g}$  orbitals) to a higher energy state (one of the  $e_g$  orbitals). The magnitude of the orbital splitting is dependent upon the nature of the ligands attached to the metal center.

The **spectrochemical series** ranks ligands from those producing the smallest ligand field splitting to those producing the largest ligand field splitting.



It is important to note that the absorption of light is a **subtractive color process**. A solution that appears blue is not absorbing blue light, but rather light that is the **complimentary color** to blue. A rough idea of complimentary colors can be obtained from a color wheel; those colors that are opposite one another are complimentary. Red and green are complimentary colors, as are blue and orange.



This means that a solution which appears blue is actually absorbing orange light and a solution which appears orange is actually absorbing blue light. Therefore the complex ion  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , which is green in color, is actually absorbing red light. When concentrated  $\text{NH}_3$  is added, the complex ion  $[\text{Ni}(\text{NH}_3)_6]^{3+}$  is formed, which is blue in color and therefore is absorbing orange light. Since red light has a longer wavelength (and therefore lower energy) than orange light, the  $\text{NH}_3$  is producing a stronger ligand splitting field than  $\text{H}_2\text{O}$ , which is consistent with the established spectrochemical series.

## PROCEDURE

### Copper(II) Complexes

Locate the bottles containing solid  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . Record your observations regarding the appearance of these two compounds. How can you account for the difference in color of these two compounds?

Add 0.50 mL (approximately 10 drops) of 0.10 M copper sulfate to each of six small test tubes. Note the color of the solution. To one test tube, add a few drops of 15 M  $\text{NH}_3$ . To the next test tube, add a few drops of ethylenediamine. To the third test tube, carefully add 12 M HCl dropwise until the color change to a yellow solution is complete. To the fourth, add 6M NaOH. An initial precipitate of  $\text{Cu}(\text{OH})_2$  may form, which redissolves in excess  $\text{OH}^-$  to form  $[\text{Cu}(\text{OH})_4]^{2-}$ . To the fifth test tube, add 5-10 drops of saturated

NaNO<sub>2</sub> solution. To the sixth, add a few drops of 0.10 M K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution. In each case, record your observations and write the formula for the complex ion that is formed.

### **Iron(II) and Iron(III) Complexes**

To a small test tube add 0.50 mL of water (approximately 10 drops) and a small portion of solid ferrous sulfate. What color is solid ferrous sulfate? What color is the resulting solution? Add to the test tube add a small crystal of solid 1,10-phenanthroline. What do you observe? What complex ion is formed?

To two small test tubes add approximately 0.50 mL (approximately 10 drops) of 0.10 M of Fe(NO<sub>3</sub>)<sub>3</sub> solution. What color is the solution? To the first test tube add a drop of KSCN solution. Note any changes in the color of the solution. To the second test tube add a few drops of 0.10 M K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution. What do you observe?

### **Nickel(II) Complexes**

To each of three small test tubes add 0.50 mL (approximately 10 drops) of 0.10 M Ni(NO<sub>3</sub>)<sub>2</sub> solution. To the first, add a few drops of 15 M ammonia. To the second, add a few drops of ethylenediamine. To the third, add a solution of dimethylglyoxime (DMG). Record your observations.

### **Cobalt(II) Complexes**

Locate two containers of **solid** [Co(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>2</sub> and [Co(H<sub>2</sub>O)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>. Record your observations regarding the color of the crystals. How can you account for the difference in color of these two compounds?

Obtain two small test tubes. To the first add approximately 0.50 mL of ethanol, and to the second approximately 0.50 mL of water. To each test tube add a small crystal of solid [Co(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>2</sub>. What color are the resulting solutions? How can you account for the difference in color?

Add 0.50 mL (approximately 10 drops) of 0.10 M CoCl<sub>2</sub> solution to each of two small test tubes. To one test tube, 12M HCl dropwise until the color change appears complete. To the next test tube, add 10-15 drops of saturated KSCN solution. What do you observe? Write the formulas for the complex ions that are formed.

### **Chromium(III) Complexes**

Locate two containers of KCr(SO<sub>4</sub>)<sub>2</sub>•12H<sub>2</sub>O and CrCl<sub>3</sub>•6H<sub>2</sub>O. Obtain two small test tubes and add 0.50 mL of water to each test tube. Add a very small portion of solid KCr(SO<sub>4</sub>)<sub>2</sub>•12H<sub>2</sub>O to one tube and a very small portion of solid CrCl<sub>3</sub>•6H<sub>2</sub>O to the other. What do you observe? What complex ions are responsible for the color in each test tube?

<b>Introduction to Coordination Chemistry</b> <b>Pre-Laboratory</b>	<b>Name:</b>
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1. List the chemical formula, chemical properties, and any special hazards associated with the following reagents.

a. Ammonia

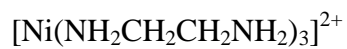
b. Ethylenediamine

c. 1,10-phenanthroline

d. Potassium thiocyanate

h. Potassium ferrocyanide

2. Name each of the following complex ions



<b>Introduction to Coordination Chemistry Report Sheet 1</b>	<b>Name:</b>
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### Copper(II)

What is the color of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ?

What is the color of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ?

Record your observations regarding the addition of reagent to a solution of aqueous copper(II). In each case write a formula for the complex ion formed.

Reagent Added	Complex Ion Formed	Observation
15 M $\text{NH}_3$		
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$		
12 M HCl		
6 M NaOH		
$\text{NaNO}_2$		
0.10 M $\text{K}_4[\text{Fe}(\text{CN})_6]$		

**Nickel(II)** Record your observations regarding the addition of reagent to a solution of aqueous nickel(II). In each case write a formula for the complex ion formed.

Reagent Added	Complex Ion Formed	Observation
15 M $\text{NH}_3$		
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$		
DMG		

<b>Introduction to Coordination Chemistry Report Sheet 2</b>	<b>Name:</b>
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**Iron(II)** Record your observations regarding the addition of reagent to a solution of aqueous iron(II) and write a formula for the complex ion formed

<b>Reagent Added</b>	<b>Complex Ion Formed</b>	<b>Observation</b>
1,10-phenanthroline		

**Iron(III).** Record your observations regarding the addition of reagent to a solution of aqueous iron(III).

<b>Reagent Added</b>	<b>Complex Ion Formed</b>	<b>Observation</b>
KSCN		
K <sub>4</sub> [Fe(CN) <sub>6</sub> ]		

### **Cobalt(II)**

What is the color of **solid** [Co(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>2</sub>?

What is the color of **solid** [Co(H<sub>2</sub>O)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>?

What is the color of [Co(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>2</sub> in ethanol? What is the color of [Co(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>2</sub> in water? Why is the color of these two solutions different?

Record your observations regarding the addition of reagent to a solution of aqueous cobalt(II) and write a formula for the complex ion formed

<b>Reagent Added</b>	<b>Complex Ion Formed</b>	<b>Observation</b>
12 M HCl		
KSCN		

<b>Introduction to Coordination Chemistry Report Sheet 3</b>	<b>Name:</b>
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### Chromium(III)

<b>Reagent Added</b>	<b>Complex Ion Formed</b>	<b>Observation</b>
KCr(SO <sub>4</sub> ) <sub>2</sub> •12H <sub>2</sub> O		
CrCl <sub>3</sub> •6H <sub>2</sub> O		

Explain why [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> does not immediately form when CrCl<sub>3</sub>•3H<sub>2</sub>O is dissolved in water, but [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is formed when CoCl<sub>2</sub>•6H<sub>2</sub>O is dissolved in water.

The complex [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> can exist as two isomers. Name and sketch a structure for each isomer.

<b>Introduction to Coordination Chemistry</b> <b>Post-Laboratory Questions</b>	<b>Name:</b>
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1. Using your laboratory data, complete the following table.

<b>Complex Ion</b>	<b>Color of Solution</b>	<b>Color Absorbed by Solution</b>
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$		
$[\text{Ni}(\text{NH}_3)_6]^{2+}$		
$[\text{Ni}(\text{en})_3]^{2+}$		

Which ligand produces a stronger ligand field,  $\text{H}_2\text{O}$  or  $\text{NH}_3$ ? Explain your answer.

2. Using your laboratory data, complete the following table.

<b>Complex Ion</b>	<b>Color of Solution</b>	<b>Color Absorbed by Solution</b>
$[\text{CoCl}_4]^{2-}$		
$[\text{Co}(\text{SCN})_4]^{2-}$		

Which ligand produces a stronger ligand field,  $\text{Cl}^-$  or  $\text{SCN}^-$ ? Explain your answer.