EXPERIMENT 43

A Study of Transition Metal Ions

OBJECTIVES

To observe the various colors associated with transition metal ions

To account for a color change in a complex ion due to ligand substitution

To account for and compare the stablity of complex ions

To determine the relative strength of a ligand

INTRODUCTION

One of the most intriguing features of the transition metal ions is their vast array of colors. The blues, greens, and reds that we often associate with chemicals are oftentimes due to the presence of transition metal ions. We observed a variety of these colors in Experiment 13 where it was noted that some colors are characteristic of certain hydrated transition metal ions, e.g., Cu^{2+}—blue, Ni^{2+}—green, and Fe^{3+}—rust.

A second interesting feature of the transition metal ions is that subtle and, on occasion, very significant color changes occur when a molecule or ion other than water bonds to the metal ion to form a *complex ion*. These molecules or ions, called *ligands*, are also Lewis bases which bond directly to the metal ion, producing a change in the electronic energy levels of the metal ion. As a result, the energy (and also the wavelength) of light absorbed by the electrons in the transition metal ion changes; this also changes the energy (and wavelength) of light transmitted resulting in a different-colored solution.

More than the intrigue of the color and color changes are the uses that these complex ions (transition metal ion and ligands) have in chemistry. A few examples of the applicability of complex ion formation are:

- for photographic film development, sodium thiosulfate, called "hypo", is used to remove the unsensitized silver ion from film:

$$AgBr(s) + 2S_2O_3^{2-}(aq) \longrightarrow Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$$

- for removal of calcium hardness from water, soluble polyphosphates, such as $Na_5P_3O_{10}$, are added to detergents to form a soluble calcium complex ion:

$$Ca^{2+}(aq) + P_3O_{10}^{5-}(aq) \longrightarrow CaP_3O_{10}^{3-}(aq)$$

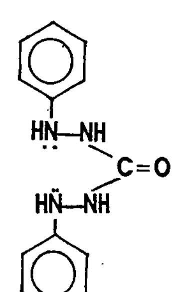
- for mercury or lead poisoning by ingestion, British anti-lewsite, $C_3H_8OS_2$, is swallowed for purposes of forming the complex ion and rendering the free ion ineffective:

$$Hg^{2+}(aq) + 2\ \underset{\displaystyle SH}{\underset{|}{CH_2}} - \underset{\displaystyle SH}{\underset{|}{CH_2}} - \underset{\displaystyle OH}{\underset{|}{CH_2}}(aq) \longrightarrow Hg(C_3H_8OS_2)_2{}^{2+}(aq)$$

- for qualitative identification of transition metal ions. In the previous qualitative analysis experiments, the transition metal ions confirmed present as a result of complex ion formation were Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}. Many quantitative determinations of transition metal ions are also based upon the formation of the complex ion.

The bond strength between the metal ion and ligand varies, depending upon the electron-pair donor (Lewis base) strength of the ligand and the electron-pair acceptor (Lewis acid) strength of the transition metal ion. Ligands may be either anionic (e.g., CN^-, SCN^-, Cl^-) or neutral (e.g., H_2O, NH_3, $O=C(NH_2)_2$); ligands may bond once to the metal ion—these are called monodentate ligands, twice to the metal ion—these are called bidentate ligands, three times to the metal ion—called tridentates, and so on. Ligands that bond two or more times to the transition metal ion are also called *chelating agents*. In Table 43.1 notice that all ligands have one or more electron pairs available for donating and bonding to a metal ion.

TABLE 43.1 Common Ligands in Complex Ions

Monodentate Ligands		
H_2O:	$:S_2O_3^{2-}$	$:I^-$
$:NH_3$	$:F^-$	$:OH^-$
$:CN^-$	$:Cl^-$	
$:SCN^-$	$:Br^-$	
Bidentate Ligands*		
Ethylenediamine (en)	$H_2\ddot{N}—CH_2—CH_2—\ddot{N}H_2$	S-diphenylcarbazide
Oxalate ion, $C_2O_4^{2-}$	$^-:O—\overset{O}{\overset{\Vert}{C}}—\overset{O}{\overset{\Vert}{C}}—O:^-$	
Tartrate ion (tar^{2-})	$^-:O—\overset{O}{\overset{\Vert}{C}}—\overset{OH}{\overset{\vert}{CH}}—\overset{OH}{\overset{\vert}{CH}}—\overset{O}{\overset{\Vert}{C}}—O:^-$	
Tridentate Ligands*		
Diethylenetriamine	$H_2\ddot{N}—CH_2—CH_2—\ddot{N}H—CH_2—CH_2—\ddot{N}H_2$	
*Chelating Agents		

The complex ion formed between a chelating agent (a polydentate ligand) and the metal ion is generally more stable than that formed with monodentate ligands and a metal ion. This a because it is more difficult to rupture several ligand-metal bonds, as in the case between a polydentate ligand and a metal ion, than single ligand-metal bonds. The stability of complex ions having polydentate ligands will be compared to those having only monodentate ligands.

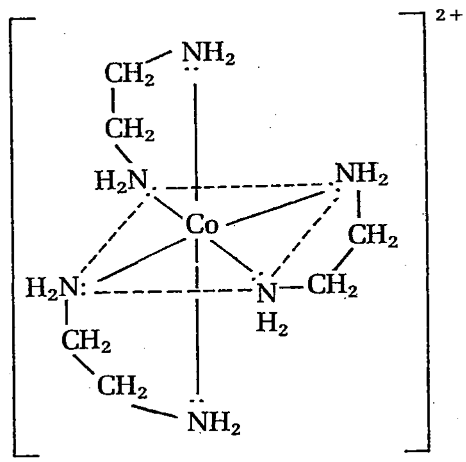
The *number* of bonds between a metal ion and its ligands is called the *coordination number* of the complex ion. If four monodentate ligands or if two bidentate ligands bond to a metal ion, the coordination number in the complex ion is four. Six water molecules, or six cyanide ions, or three ethylenediamine molecules, or two diethylenetriamine molecules bonded to a given metal ion all form a complex ion with a coordination number of six. Coordination numbers of two, four, and six are most common among the transition metal ions.

The formations of typical complex ions are:

$Pt^{2+} + 4\ {:}NH_3 \longrightarrow Pt(NH_3)_4{}^{2+}$

$Ag^{+} + 2\ {:}CN^{-} \longrightarrow Ag(CN)_2{}^{-}$

$Co^{2+} + 3\ en \longrightarrow$



or $Co(en)_3{}^{2+}$

In this experiment we will observe the formation of complex ions between Cu^{2+}, Ni^{2+}, Co^{2+}, and Co^{3+} with the ligands H_2O, NH_3, ethylenediamine (en), the tartrate ion (tar^{2-}), CN^-, and SCN^-. In specified examples, we will determine the stability of the complex ion by adding OH^- and/or S^{2-}. The hydroxides and sulfides of these cations are "insoluble". Thus if a precipitate forms when OH^- and/or S^{2-} is added to a solution containing the complex ion, the complex ion is destroyed and the metal ion combines with the OH^- and/or S^{2-}. On the other hand, if no precipitate forms, the complex ion remains intact indicating its stability.

To write the formulas of the complex ions in this experiment, we will *assume* that the coordination number of Cu^{2+} is always four, and that all of the other transition metal ions have a coordination number of six.

EXPERIMENTAL PROCEDURE

In this experiment several complex ions of Cu^{2+}, Ni^{2+}, Co^{2+}, and Co^{3+} are formed and studied. Some of the colors may be difficult to distinguish; if a precipitate initally forms, add more of the ligand-containing solution. Always compare the solution containing the complex ion with the original solution. On occasion

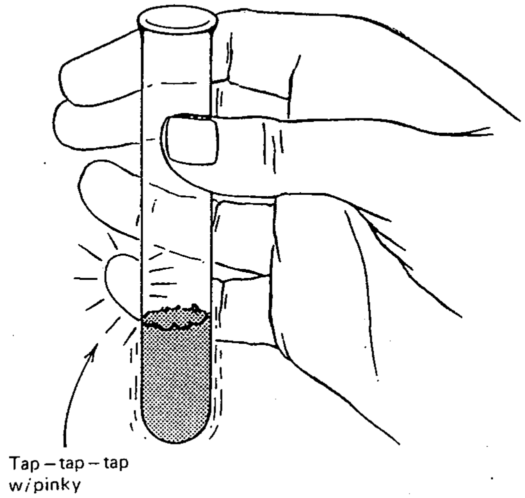


FIGURE 43.1 Tap the side of the test tube to stir the solution

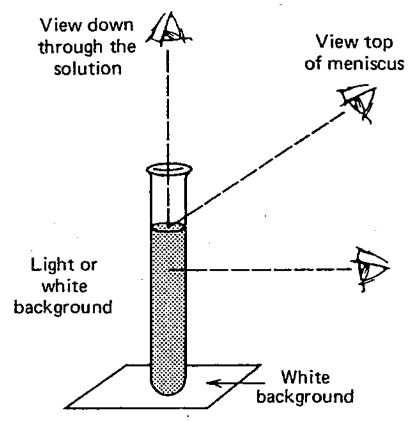
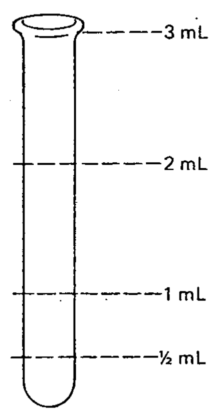


FIGURE 43.2 View solution at all angles

you may need to discard some of the test solution if too much of the original solution was used for testing at the outset. If a color change occurs (*not* a change in color intensity) then a new complex ion has formed. Also after each addition of ligand, tap the test tube to stir the mixture (Figure 43.1) and view the solution at various angles to note the color (Figure 43.2).

Most complex ion formations are completed in 75-mm test tubes. While volumes of solutions need *not* be exact, a volume close to the suggested amount should be used. A 75-mm test tube has a 3-mL volume—proportional fractions should be used in estimating the volume suggested in the procedure.



Several of the ligand-containing solutions should be handled with care. Conc NH_3 and ethylenediamine produce characteristic odors that are strong irritants of the respiratory system; CN^- is very poisonous. You may want to ask your instructor to dispense the KCN solution for you. Be sure to thoroughly wash your hands before leaving the laboratory, and, remember—no eating, drinking, or use of tobacco at any time in the laboratory.

From 6 to 12 75-mm test tubes are used for each part of today's experiment. Plan to keep them clean, rinsing thoroughly after each use. However, do *not* discard any test solutions until the entire subsection of each part of the Experimental Procedure has been completed.

A. Chloro Complexes of Cu^{2+}, Ni^{2+}, and Co^{2+}

1. Place ½ mL of 0.1 *M* $CuSO_4$, 0.1 *M* $Ni(NO_3)_2$, and 0.1 *M* $CoCl_2$ in each of three 75-mm test tubes. Add 1 mL conc HCl (CAUTION: *Handle carefully, do not allow conc HCl to contact skin or clothing. Flush immediately with water*) to each. Tap the test tube to stir. Record your observations on the Report Sheet. If in doubt that a color change has occurred, transfer an equivalent volume of the original solution to a 75-mm test tube and compare.

2. Slowly add 1-2 mL of water to each test tube. Compare the solutions' colors to 2½ mL of the original solutions. Does the original color return, or nearly so?

B. Cu^{2+} Complex Ions

1. Place ½ mL of 0.1 *M* $CuSO_4$ in each of six 75-mm test tubes. Place 5 drops of conc NH_3 (CAUTION: *Avoid breathing its vapors.*) in the first test tube, 5 drops of ethylenediamine (CAUTION: *Avoid breathing its vapors.*) in the second, 0.2 *M* ammonium tartrate, $(NH_4)_2$ tar, in the third, 0.1 *M* KSCN in the fourth test tube, and 1 *M* KCN in the fifth (Figure 43.3). (CAUTION: *KCN is poisonous. Wash the skin thoroughly and immediately after contact.*) If a precipitate forms in any of the solutions, add an excess of the ligand-containing solution; this is especially true for the CN^- ligand. Compare the appearance of the test solutions with that in test tube No. 6

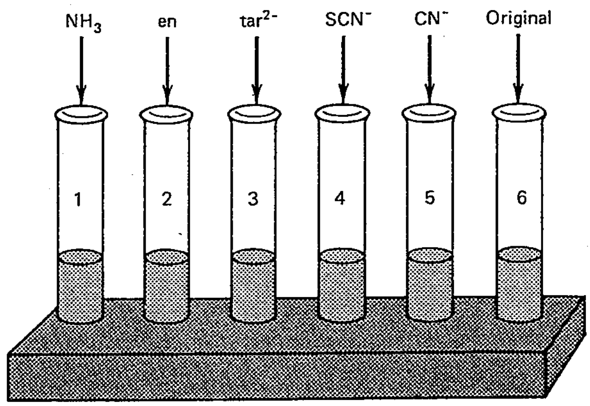


FIGURE 43.3 Addition of ligand-containing solutions

2. Add 3 drops of 1 *M* NaOH to each test solution. Explain your results.
3. Repeat Part B.1. Add several drops of 0.1 *M* Na_2S to each test solution. Does a precipitate form?

C. Ni^{2+} Complex Ions

1. Repeat Part B.1, substituting 0.1 *M* $NiCl_2$ for 0.1 *M* $CuSO_4$. Record your observations.
2. Add 5 drops of 1 *M* NaOH to each test solution. Does a precipitate form?
3. Again repeat Part B.1, substituting 0.1 *M* $NiCl_2$ for 0.1 *M* $CuSO_4$. Add 10 drops of 0.1 *M* Na_2S. Record your observations. What can you conclude?

D. Co^{2+} Complex Ions

1. Repeat Part B.1, substituting 0.1 *M* $Co(NO_3)_2$ for 0.1 *M* $CuSO_4$. Record your observations.
2. Add 3 drops of 1 *M* NaOH to each test solution. Does a precipitate form?
3. Repeat B.1, but again substitute 0.1 *M* $Co(NO_3)_2$ for 0.1 *M* $CuSO_4$. Add several drops of 0.1 *M* Na_2S to each test solution. Record your observations.

E. Co^{3+} Complex Ions

1. Repeat the preparation of the six test tubes in Part B.1, substituting 0.1 *M* $Co(NO_3)_2$ for 0.1 *M* $CuSO_4$. *Before* adding the solutions containing the respective ligands add several drops of 3% H_2O_2 to each test tube. Add the ligand-containing solutions as described. Again if any precipitate forms, add an excess of the solution.

2. Add several drops of 1 *M* NaOH to each test solution. What is observed? Record your observations on the Report Sheet.

3. Repeat Part E.1. Add several of 0.1 *M* Na_2S to each test solution. Does a precipitate form? Record your observations.

PRELABORATORY ASSIGNMENT—EXPERIMENT 43

A Study of Transition Metal Ions

DATE ______________ LAB SEC. ________ NAME ____ DESK NO. ________

1. What is a complex ion?

2. a. What is a ligand?

   b. Distinguish between a monodentate and bidentate ligand?

3. Explain how ligands affect the color of transition metal ions.

4. What is meant by the statement, "the coordination number of Cr^{3+} is usually six"?

5. Write the formula of the complex ion formed between water, the ligand, and

   a. Cu^{2+}, assuming a coordination number of four

b. Co^{2+}, assuming a coordination number of six

c. Ni^{2+}, assuming a coordination number of six

6. Write the formula of the complex ion formed between the tartrate ion, tar^{2-}, a bidentate ligand, and Cr^{3+}, assuming Cr^{3+} has a coordination number of six.

7. Refer to Experiments 39 and 40 and write the formulas for the complex ions that confirmed the presence of each ion in the "qual" scheme.

Cu^{2+} ______________________ Fe^{3+} ______________________

Ni^{2+} ______________________ Zn^{2+} ______________________

8. Write the complex ion that appears in the following equations, identify its ligand(s), its coordination number (C.N.), and the oxidation number of the metal ion.

Equation	Complex Ion	Ligand(s)	C.N.	Oxidation No. of Metal Ion
37.11	$Cu(NH_3)_4^{+2}$			
37.21	$Fe(CN)_6^{-2}$			
38.4	$Ni(NH_3)_6^{+2}$			
38.5	$Fe(NCS)_6^{3-}$			
39.7	$Zn(NH_3)_4^{+2}$			
39.11	$PbCl_4^{2-}$			
39.12	$Ag(NH_3)_2^{+}$			
39.15	$AgCl_2^{-}$			
39.18	AgF_4^{-}			
39.19	$TiCl_5^{-3}$			
40.17	$Fe(H_2O)_6^{+2}$			
40.18	$Cr(OH)_4^{-}$			
40.21	$Cr(H_2O)_4Cl_2^{-}$			
40.22	$Co(en)^{+2}$			
40.27				
40.30				

REPORT SHEET—EXPERIMENT 43

A Study of Transition Metal Ions

DATE ________ **LAB SEC.** ________ **NAME** ________________________ **DESK NO.** ________

A. Chloro Complexes of Cu^{2+}, Ni^{2+}, and Co^{2+}

1.

Solution	Color/H_2O	Color/HCl	Formula of Complex Ion	Effect of H_2O
0.1 *M* $CuSO_4$				
0.1 *M* $Ni(NO_3)_2$				
0.1 *M* $CoCl_2$				

2. In each case state whether the aquo complex or the chloro complex ion is more stable.
Cu^{2+} ________; Ni^{2+} ________; Co^{2+} ________________

B. Cu^{2+} Complex Ions

Ligand	Color	Formula	Effect of OH^-	Effect of S^{2-}
NH_3				
en				
tar^{2-}				
SCN^-				
CN^-				
H_2O				

C. Ni^{2+} Complex Ions

Ligand	Color	Formula	Effect of OH^-	Effect of S^{2-}
NH_3				
en				
tar^{2-}				
SCN^-				
CN^-				
H_2O				

D. Co^{2+} Complex Ions

Ligand	Color	Formula	Effect of OH^-	Effect of S^{2-}
NH_3				
en				
tar^{2-}				
SCN^-				
CN^-				
H_2O				

E. Co^{3+} Complex Ions

Ligand	Color	Formula	Effect of OH^-	Effect of S^{2-}
NH_3				
en				
tar^{2-}				
SCN^-				
CN^-				
H_2O				

Summary of Data

1. Identify (✓) the complex ions that showed a precipitate with the addition of 1 *M* NaOH.

Ligand/Metal	Cu^{2+}	Ni^{2+}	Co^{2+}	Co^{3+}
NH_3				
en				
tar^{2-}				
SCN^-				
CN^-				
H_2O				

2. Identify (✔) the complex ions that showed a precipitate with the addition of 0.1 *M* Na_2S.

Ligand/Metal	Cu^{2+}	Ni^{2+}	Co^{2+}	Co^{3+}
NH_3				
en				
tar^{2-}				
SCN^-				
CN^-				
H_2O				

POST-LABORATORY ASSIGNMENT

1. a. Compare the stability of the NH_3 and ethylenediamine complex ions of Ni^{2+}.

   b. Compare the stability of the NH_3 and ethylenediamine complex ions of Co^{2+}.

   c. Compare the stability of the ethylenediamine complex ions of Co^{2+} and Co^{3+}.

   d. What is characteristic of the ethylenediamine ligand that accounts for these observations?

2. In this experiment the ligands Cl^-, NH_3, en, tar $^{2-}$, SCN^-, CN^-, and H_2O were used to form complex ions.

   a. Which ligand appeared to be the strongest?

   b. Which ligand appeared to be the weakest?

   c. List, as best possible from the limited available data, the ligands in order of decreasing strength.

   _____, _____, _____, _____, _____, _____, _____

   strong   weak

3. Select the complex ion that is most stable:

   a. $Cu(NH_3)_4^{2+}$, $Co(NH_3)_6^{2+}$. Explain.

   b. $Cu(tar)_3^{4-}$, $Co(tar)_3^{4-}$. Explain.

4. When 1 *M* NaOH is slowly added to a solution containing the Cr^{3+}, a precipitate forms. With a continued addition of 1 *M* NaOH, the precipitate dissolves forming a complex ion with a coordination number of four.

   a. Write the formula of the precipitate.

   b. Write the formula of the complex ion.

5. When excess 1 *M* KSCN is added to an aqueous solution containing Fe^{3+}, a red-amber solution appears. If solid NaF is added to the Fe^{3+} solution before the KSCN is added, the red-amber solution does *not* appear. Write the formulas of the two complex ions, each having a coordination number of six.