

## COMPLEX IONS AND AMPHOTERISM

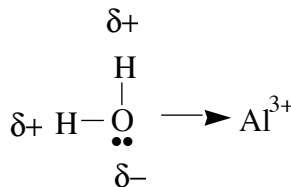
This experiment involves the separation and identification of ions using two important reaction types: (i) the formation of complex ions and (ii) the amphoteric behavior of some metal hydroxides. You have already encountered complex ion formation in the analysis of the silver group ions and in the experiment on metal sulfides, but more needs to be said about this topic as an introduction to this experiment.

### THE FORMATION OF COMPLEX IONS

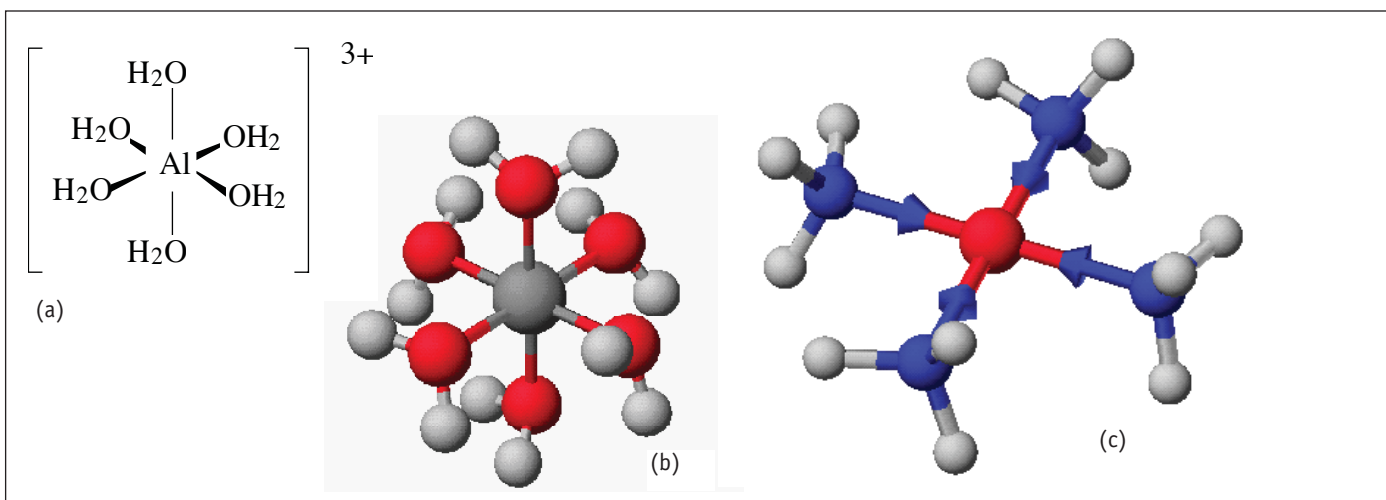
Although we usually write cation formulas in solution as if they were simple ions, such as  $\text{Al}^{3+}$ , these ions are actually bound to a number of water molecules arranged around the central ion (*see figure below*).

The water molecules in this case are examples of a much larger class of molecules and ions called **ligands** that form coordinate covalent bonds with a central metal cation. That is, the bond is of the form  $\text{L}:\rightarrow\text{M}^{n+}$ , where L has donated an otherwise unused lone pair of electrons to the electron accepting metal ion. In the water molecule, there are two lone pairs of electrons on the O atom, and either of these may form a coordinate covalent bond with a metal cation. Ligands are often small, polar molecules such as  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , but they can also be anions such as  $\text{Cl}^-$ ,  $\text{OH}^-$ , and  $\text{S}^{2-}$ .

The combination of a ligand or ligands with a metal cation is often called a **coordination complex**. If the complex is an ion, it is then called a **complex ion**. A complex ion you have already seen is  $[\text{H}_3\text{N}:\rightarrow\text{Ag}\leftarrow:\text{NH}_3]^+$ , the complex ion formed by silver ion and ammonia that allows you to dissolve  $\text{AgCl}$ .



As noted in the experiment on the silver group ions, a ligand is a Lewis base (a donor of one or more pairs of electrons), and the metal ion in the complex ion is a Lewis acid (an electron pair acceptor).



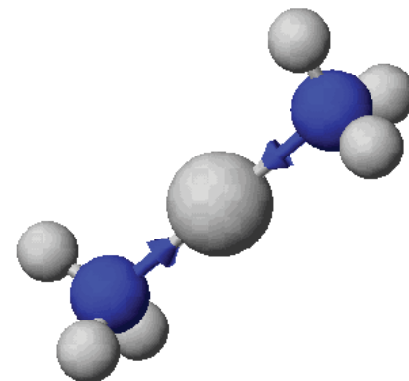
**Complex Ions.** (a) Six water molecules, located at the corners of an octahedron, cluster about an  $\text{Al}^{3+}$  ion. (b) A ball & stick model of a complex ion having a metal cation in the center of an octahedron of water molecules. (c) The copper-ammonia complex ion,  $\text{Cu}(\text{NH}_3)_4^{2+}$ .

Formulas and stabilities of complexes vary greatly. Usually complexes involve four or six ligands arranged at the corners of a tetrahedron (or square plane) or octahedron about a metal cation, and the cation is most often a transition metal ion. However, complexes having other than four or six ligands are possible, such as the silver-ammonia complex mentioned above.

The presence of a transition metal in a complex often leads to highly colored complexes. Recall the deep blue copper(II)-ammonia complex that you synthesized in Chemistry 111. (The complex ion is seen in Figure 17.7 on page 830 of your text, *Chemistry & Chemical Reactivity*. See also the figure on the first page of this experiment.) This complex is much more stable than the insoluble compound  $\text{Cu}(\text{OH})_2$ , for example, so adding excess ammonia to a solution of copper ion leads preferentially to the  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex ion.

You will see many other examples of this behavior in this laboratory and in other experiments, and it is a feature of metal complexes that their colors can sometimes be used to identify the particular metal ion involved. A number of such complexes appear in Figure 22.12 on page 1081 of *Chemistry & Chemical Reactivity*.

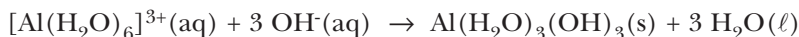
You have already seen in the analysis of the ions of the silver group that complex ion formation can often be used to advantage in ion separation: if two salts precipitate together, they can sometimes be separated by dissolving one through complex ion formation while the other remains uncomplexed. Indeed, this is the way you separated  $\text{Ag}^+$  from  $\text{Hg}_2^{2+}$ . Recall that  $\text{AgCl}$  dissolved when  $\text{NH}_3$  was added because the soluble complex ion  $[\text{H}_3\text{N-Ag-NH}_3]^+$  was formed.



The  $[\text{Ag}(\text{NH}_3)_2]^+$  complex ion.

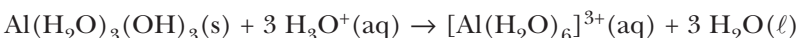
## AMPHOTERIC METAL HYDROXIDES

An amphoteric substance is one that can behave as a Lewis acid and a Brønsted base. The best examples are found with metal hydroxides such as aluminum hydroxide  $[\text{Al}(\text{OH})_3]$  and zinc hydroxide  $[\text{Zn}(\text{OH})_2]$ . Insoluble aluminum hydroxide can be formed by the addition of hydroxide ion,  $\text{OH}^-$ , to a soluble salt of  $\text{Al}^{3+}$ .



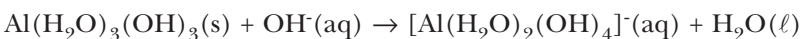
The insoluble metal hydroxide can act as a base, since it can be redissolved by reacting it with an acid.

Brønsted base



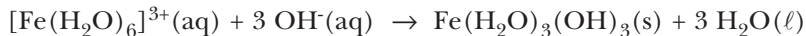
Alternatively, the metal hydroxide can act as an acid, since it can react with a base.

Lewis acid

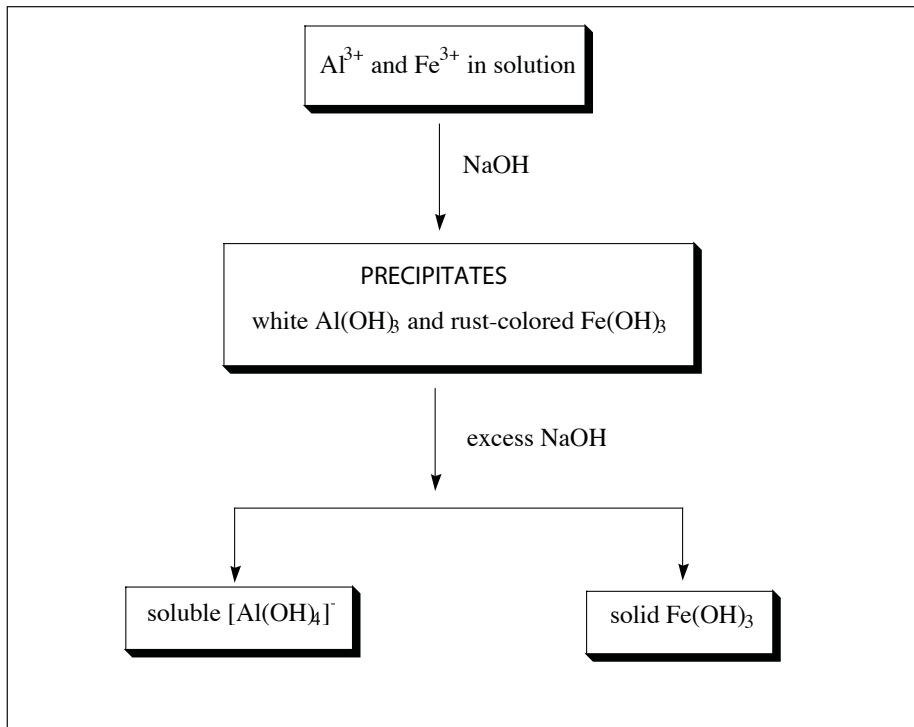


Thus,  $\text{Al}(\text{OH})_3$  is said to be **amphoteric**.

Only certain cations show amphoteric behavior, so this can be exploited in separating cations. If, for example,  $\text{NaOH}$  is added in small amounts to solutions of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , both will initially form precipitates: rust colored iron(III) hydroxide



and white aluminum hydroxide,  $\text{Al}(\text{OH})_3$  (see above). Because  $\text{Al}(\text{OH})_3$  is an amphoteric hydroxide, while  $\text{Fe}(\text{OH})_3$  is not, further treatment with  $\text{NaOH}$  will redissolve  $\text{Al}(\text{OH})_3$  and leave  $\text{Fe}(\text{OH})_3$  as an insoluble solid. If you then centrifuge the mixture, and decant off the solution, you will have separated  $\text{Al}^{3+}$



from  $\text{Fe}^{3+}$ . Commonly encountered cations that form amphoteric hydroxides are  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Sb}^{3+}$ . Most of the other cations you see in Chemistry 112 laboratory do not form amphoteric hydroxides.

## EXPERIMENTAL PROCEDURE

Before beginning this experiment, place the following solutions in the small dropping bottles in your desk: 6 M  $\text{NaOH}$ , 6 M  $\text{HCl}$ , and 6 M  $\text{NH}_3$ . Labels are available in the laboratory so that you can label the bottles.

The observations you make on the known solutions can be entered on the table provided with the experiment. When you have completed the table, tape or staple the table in your laboratory notebook.

### A. Tests of Ions

The ions to be studied in this experiment are

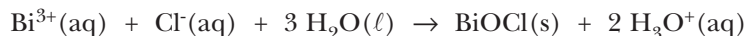


Place a few drops of each known solution in separate, small test tubes.

#### 1. Preliminary Observations

- First, note the color of each solution. Solutions of transition metal ions in particular are often colored.

- (b) Add distilled water to about half-fill each test tube. In the case of  $\text{Bi}^{3+}$  or  $\text{Sb}^{3+}$  a white precipitate may form. Such precipitates are oxychlorides and form by such reactions as



The white oxychlorides of bismuth(III) or antimony(III) can be redissolved by acidifying the solution with HCl. Do this by adding 3 drops of 6 M HCl and stirring vigorously. If 3 drops is not enough acid to redissolve the oxychloride, continue adding acid until the precipitate does dissolve.

## 2. Metal Hydroxide Formation

Take each of the solutions from step 1(b) above and add 1-5 drops of 6 M NaOH and mix well. (You should add enough NaOH to insure that you form a metal hydroxide precipitate in each case.) In the case of the bismuth(III) and antimony(III) solutions, add enough 6 M NaOH to neutralize the HCl you added to dissolve the oxychloride and then add at least 1-3 drops more. Use your litmus paper to make sure the solution is basic at this point (red litmus fi blue in base).

Once a metal hydroxide has been formed, centrifuge the mixture and then decant the liquid, saving the metal hydroxide precipitate. Note the color and appearance of each precipitate.

## 3. Amphoteric Metal Hydroxides

In this step you will test each of the hydroxides formed in Step 2 above for amphoteric behavior. Add at least 10 drops of 6 M NaOH to each precipitate. Stir well and heat if necessary in an attempt to dissolve each precipitate. (You will find that  $\text{Sb}(\text{OH})_3$  dissolves only with difficulty.) Centrifuge and record any changes you see.

## 4. Action of Dilute, Aqueous Ammonia

Prepare a new set of known solutions as you did in Step 1 above. To each add a drop of 6 M  $\text{NH}_3$ . (You will have to add more  $\text{NH}_3$  to the  $\text{Sb}^{3+}$  and  $\text{Bi}^{3+}$  solutions to make them basic.) In each case use your litmus paper to make sure the solution is basic after adding ammonia.

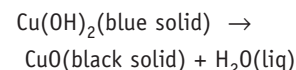
Mix each solution well and then centrifuge but do not decant. Note the appearance and color of each precipitate and any other changes you may see.

## 5. Formation of Complexes with Ammonia

Check each solution from Step 4 above and make sure it is just basic, and then add 10 more drops of  $\text{NH}_3$  to each. Mix well and centrifuge but do not decant.

When doing your unknown, the appearance of a white precipitate at this stage is a good indication of the presence of  $\text{Bi}^{3+}$  or  $\text{Sb}^{3+}$  in the unknown solution.

Copper(II) hydroxide,  $\text{Cu}(\text{OH})_2$ , will undergo the following dehydration reaction if you heat and stir:



Try to get this reaction to occur, since it provides a good test of the presence of  $\text{Cu}^{2+}$  in an unknown solution.

$\text{Mn}(\text{OH})_2$  might turn dark brown-black on heating. The hydroxide loses water to form the brown-black oxide,  $\text{MnO}_2$ .

10 drops of 6 M  $\text{NH}_3$  should be enough to complete the formation of metal complexes if indeed complexes are possible. However, if you believe complexation is not complete, you may add more ammonia. Stir well and centrifuge again. Be sure to note where you added extra  $\text{NH}_3$  (this may be especially true in the case of  $\text{Sb}^{3+}$ ).

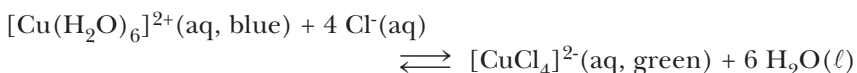


The colors of ammonia complexes of transition metal ions are often highly characteristic of the metal ion and can be used to identify the ion.

### C. The Unknown Solution

After you have completed all of the tests on the known solutions, you will be given an *unknown solution* that *contains TWO cations, one of which is colored in aqueous solution and the other of which is colorless*. Using the chemical reactions you explored above, you should be able to *work out a scheme for separating and then identifying the ions*. The following are notes of advice and caution regarding the unknowns in this experiment.

1. Do some preliminary tests on your unknown to get some notion of the ions that may be present. Then, using your observations on the known solutions, work out a scheme for separating one ion from the other and identifying the ions. For example, suppose your unknown contains  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$ . The color of the solution will be blue, suggesting immediately that it contains  $\text{Cu}^{2+}$ , but you do not know if the colorless ion is  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$ , or  $\text{Mn}^{2+}$ . If you add  $\text{NH}_3$  (and make sure the solution is basic), the  $\text{Cu}^{2+}$  ion will form the deep blue water-soluble ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , and  $\text{Mn}^{2+}$  will precipitate as the hydroxide  $\text{Mn}(\text{OH})_2$ . By centrifuging and decanting, the solution and precipitate can be separated and the ions present in each part can be identified by tests based on your investigation of the chemistries of the known solutions.
2. You can usually identify the colored ion in your unknown quite readily by simply observing the color. However, be very careful here! If your unknown contains  $\text{Sb}^{3+}$  or  $\text{Bi}^{3+}$  along with  $\text{Cu}^{2+}$  you can be misled easily for the following reason: When solutions of  $\text{Sb}^{3+}$  and  $\text{Bi}^{3+}$  salts are made up, we must add a large amount of  $\text{HCl}$  (as you learned in the observations above). However, if the solution also contains  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$ , the colors of these ions can change. Aqueous solutions of copper(II) ions, for example, are blue, but they become green when  $\text{Cl}^-$  ion is present in large concentration.



*Be careful* you do not confuse such solutions for ones containing  $\text{Ni}^{2+}$ .

3. If your unknown contains  $\text{Sb}^{3+}$  or  $\text{Bi}^{3+}$  you will know this quickly, because these ions precipitate  $\text{SbOCl}$  or  $\text{BiOCl}$  when distilled water is added. Thus, you can separate these ions from the colored one in the unknown by adding water to the unknown and then centrifuging to collect the solid oxychloride in the bottom of the test tube. The colored solution and the solid oxychloride can then be separated and the ion in each fraction identified.
4. Be very careful of  $\text{Sb}^{3+}$  and  $\text{Bi}^{3+}$ . Their chemistries are similar. However, in your study of the known solutions you should have found at least one point on which they differ.
5. As noted above, a characteristic reaction of  $\text{Cu}^{2+}$  is that its hydroxide dehydrates to form black  $\text{CuO}$  when heated. This is an excellent way to identify the ion. Additionally,  $\text{Bi}(\text{OH})_3$  forms a yellow hydrated oxide when heated.

NOTE: Before your instructor gives you an unknown he or she will want to see your observations on the known solutions and will ask you about possible schemes for the separation and identification of the unknown ions.

6. As usual, once you have analyzed your unknown and believe you have an answer, you can check yourself if you use the known solutions to make up a solution that contains the suspected ions. If the chemistry of your known and unknown are identical in all respects, then you know you are correct.
7. As you work on your unknown solution, be sure to write down your observations completely. In that way your instructor can help you if you have made any errors in identification.

## WRITING UP THE NOTEBOOK

As usual, you must make complete observations of your work. It is acceptable to write your observations on the known solutions on the table that accompanies this experiment (although it would be better to make a new one in your laboratory notebook). You can then tape or staple this in your laboratory book. Observations on the unknown solution, however, must be entered completely in your notebook. When you have completed the unknown, show your notebook to your instructor, complete with your observations, and list the results as

Ions probably present \_\_\_\_\_

Ions probably absent \_\_\_\_\_

After the laboratory period, complete the write-up in your notebook by answering the following questions:

- (a) Write a balanced equation for the precipitation of nickel(II) hydroxide when  $\text{NaOH}(\text{aq})$  is added to  $\text{Ni}^{2+}(\text{aq})$ .
- (b) Write a balanced equation showing how copper(II) hydroxide,  $\text{Cu}(\text{OH})_2$ , can be precipitated when  $\text{NH}_3(\text{aq})$  is added to  $\text{Cu}^{2+}(\text{aq})$ .
- (c) Write balanced equations showing the amphoteric behavior of  $\text{Sb}(\text{OH})_3$ . That is, start with  $\text{Sb}(\text{OH})_3$  and show that (i) adding  $\text{HCl}$  gives  $\text{Sb}^{3+}$  and  $\text{H}_2\text{O}$  and that (ii) adding  $\text{OH}^-$  gives  $\text{Sb}(\text{OH})_4^-$ .
- (d) Write a balanced equation to show that the complex ion  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is formed when  $\text{NH}_3$  is added to aqueous nickel(II) ion,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ .





| Ion/Color     | Add 1 drop NaOH | Add 10 drops NaOH | Add 1 drop NH <sub>3</sub> | Add 10 drops NH <sub>3</sub> |
|---------------|-----------------|-------------------|----------------------------|------------------------------|
| Copper(II)    |                 |                   |                            |                              |
| Nickel(II)    |                 |                   |                            |                              |
| Bismuth       |                 |                   |                            |                              |
| Antimony      |                 |                   |                            |                              |
| Manganese(II) |                 |                   |                            |                              |

