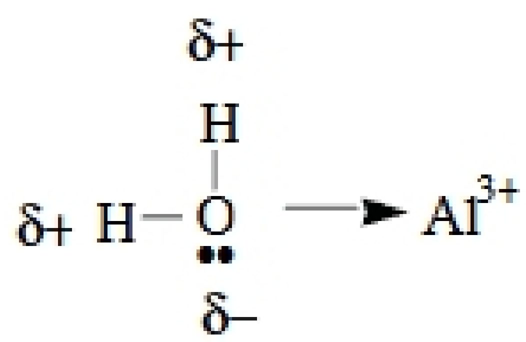
COMPLEX IONS AND AMPHOTERISM

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

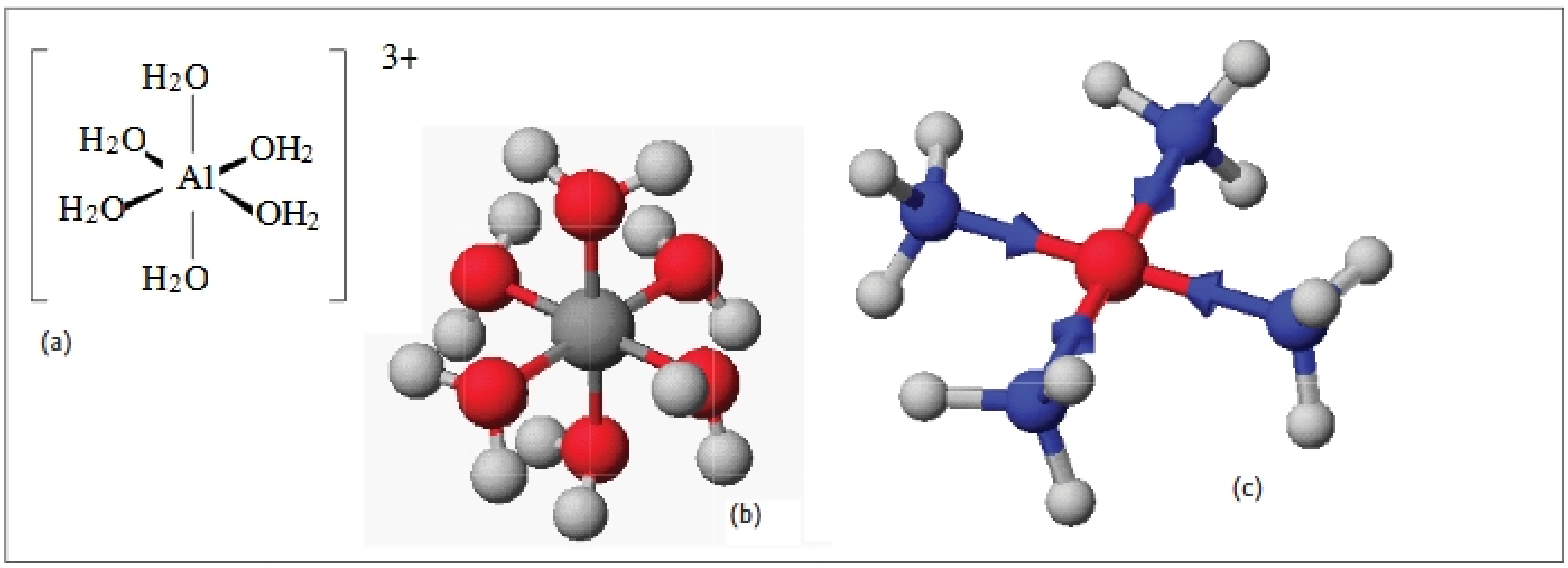
Although we usually write cation formulas in solution as if they were simple ions, such as Al^{3+}, these ions are actually bound to a number of water molecules arranged around the central ion (*see figure below*).

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 $L: \rightarrow M^{n+}$, 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 H_2O and NH_3, but they can also be anions such as Cl^-, OH^-, and S^{2-}.



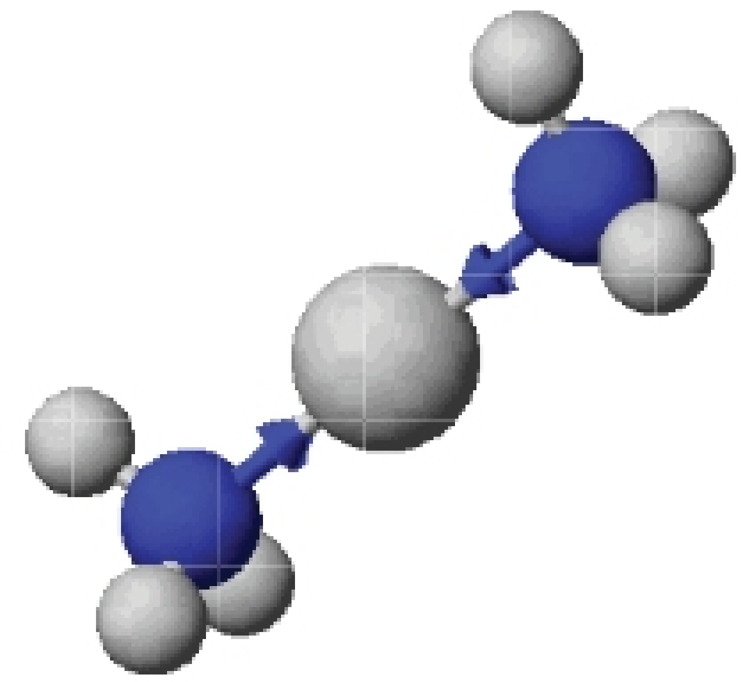
As noted in the experiment on the silver group ions, a ligand is a Lewis base (a donor of one or more pairs of electrons), and the metal ion in the complex ion is a Lewis acid (an electron pair acceptor).

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 $[H_3N{:}\rightarrow Ag \leftarrow{:}NH_3]^+$, the complex ion formed by silver ion and ammonia that allows you to dissolve AgCl.



Complex Ions. (a) Six water molecules, located at the corners of an octahedron, cluster about an 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, $Cu(NH_3)_4^{2+}$.

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 $[Ag(NH_3)_2]^+$ complex ion.

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 $Cu(OH)_2$, for example, so adding excess ammonia to a solution of copper ion leads preferentially to the $[Cu(NH_3)_4]^{2+}$ 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 Ag^+ from Hg_2^{2+}. Recall that AgCl dissolved when NH_3 was added because the soluble complex ion $[H_3N\text{-}Ag\text{-}NH_3]^+$ was formed.

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 $[Al(OH)_3]$ and zinc hydroxide $[Zn(OH)_2]$. Insoluble aluminum hydroxide can be formed by the addition of hydroxide ion, OH^-, to a soluble salt of Al^{3+}.

$$[Al(H_2O)_6]^{3+}(aq) + 3\ OH^-(aq) \rightarrow Al(H_2O)_3(OH)_3(s) + 3\ H_2O(\ell)$$

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

Brønsted base

$$Al(H_2O)_3(OH)_3(s) + 3\ H_3O^+(aq) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3\ H_2O(\ell)$$

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

Lewis acid

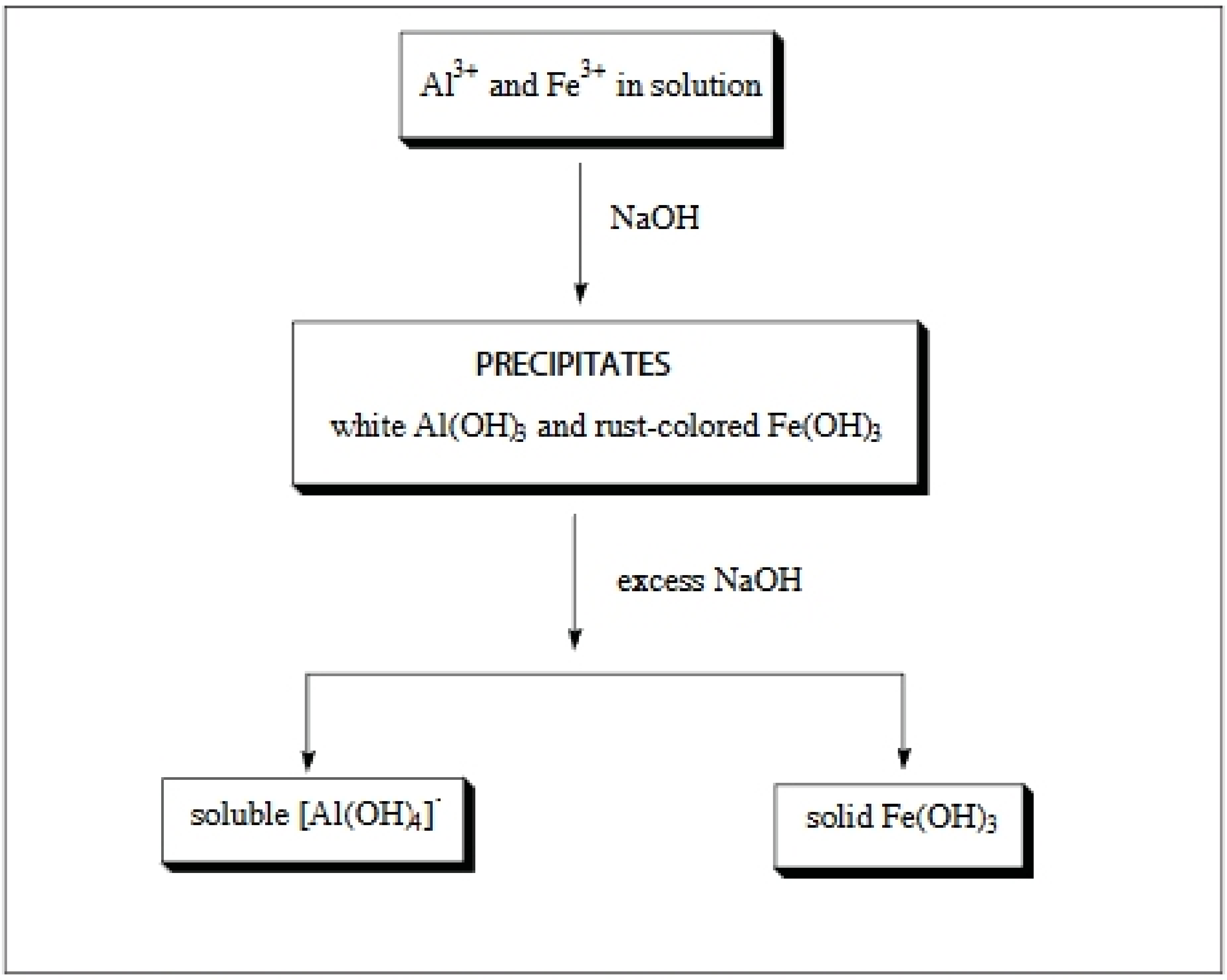
$$Al(H_2O)_3(OH)_3(s) + OH^-(aq) \rightarrow [Al(H_2O)_2(OH)_4]^-(aq) + H_2O(\ell)$$

Thus, $Al(OH)_3$ is said to be **amphoteric**.

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

$$[Fe(H_2O)_6]^{3+}(aq) + 3\ OH^-(aq) \rightarrow Fe(H_2O)_3(OH)_3(s) + 3\ H_2O(\ell)$$

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



from Fe^{3+}. Commonly encountered cations that form amphoteric hydroxides are Al^{3+}, Cr^{3+}, Zn^{2+}, Pb^{2+}, Sn^{4+}, and 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 NaOH, 6 M HCl, and 6 M 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

Cu^{2+} Ni^{2+} Bi^{3+} Sb^{3+} Mn^{2+}

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

1. Preliminary Observations

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