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Relative Stability of Precipitates and Complex Ions of Cu^{2+}

Introduction

In this experiment, you will prepare solid compounds and aqueous complex ions that contain Cu^{2+} ions combined with NH_3, Cl^-, OH^-, CO_3^{2-}, $C_2O_4^{2-}$, S^{2-}, NO_2^-, or PO_4^{3-} ions. The goal is to rank these copper species in order of stability.

Complex ions. In aqueous solution, metal cations do not exist as free ions. Instead, they form complex ions with surrounding water molecules. In most hydrated cations, either two, four, or six water molecules are loosely bonded to a central metal cation. Copper ion has a coordination number of 4, so it exists in solution as $Cu(H_2O)_4^{2+}$, with four water molecules arranged in a square around the copper ion at the center.

If a hydrated cation such as $Cu(H_2O)_4^{2+}$ is mixed with other species that can bond to Cu^{2+}, those other species (ligands) may displace one or more H_2O molecules. For instance, NH_3 may replace H_2O from the hydrated copper ion, $Cu(H_2O)_4^{2+}$, to form $Cu(H_2O)_3NH_3^{2+}$, $Cu(H_2O)_2(NH_3)_2^{2+}$, $Cu(H_2O)(NH_3)_3^{2+}$, or $Cu(NH_3)_4^{2+}$. At moderate concentrations of NH_3, essentially all of the H_2O molecules are displaced by NH_3 molecules.

$$Cu(H_2O)_4^{2+}\ (aq)\ +\ 4\ NH_3\ (aq) \longrightarrow Cu(NH_3)_4^{2+}\ (aq)\ +\ 4\ H_2O\ (l)$$

All metal cations are Lewis acids. All ligands are Lewis bases, with lone pairs of electrons to donate; some ligands are molecules including H_2O and NH_3, others are anions such as Cl^- and CN^-.

$$Cu(H_2O)_4^{2+}\ (aq)\ +\ 4\ CN^-\ (aq) \longrightarrow Cu(CN)_4^{2-}\ (aq)\ +\ 4\ H_2O\ (l)$$

A ligand that displaces two water molecules and connects to copper at two corners of the square is called bidentate; an example is ethylenediamine, $NH_2CH_2CH_2NH_2$ (en).

$$Cu(H_2O)_4^{2+}\ (aq)\ +\ 2\ en\ (aq) \longrightarrow Cu(en)_2^{2+}\ (aq)\ +\ 4\ H_2O\ (l)$$

All complex ions are species that are dissolved in solution. While solutions containing complex ions may be colored, they are always transparent. Because complex ions are charged, they repel each other in solution and cannot precipitate by themselves.

Precipitates. Metal cations also form precipitates with various anions. This can occur when the combined negative charge of the coordinated anions balances the positive charge of the cations, to form a neutral compound. For example, OH^- ions may displace water from the hydrated copper ion, $Cu(H_2O)_4{}^{2+}$, to form $Cu(H_2O)_3OH^+$ (a complex ion), $Cu(H_2O)_2(OH)_2$ (a precipitate), $Cu(H_2O)(OH)_3{}^-$ (a complex ion), and $Cu(OH)_4{}^{2-}$ (a complex ion). At most concentrations of OH^-, the neutral precipitate is most stable.

$$Cu(H_2O)_4{}^{2+}\,(aq) + 2\,OH^-\,(aq) \longrightarrow Cu(H_2O)_2(OH)_2\,(s) + 2\,H_2O\,(l)$$

Another, familiar way of writing $Cu(H_2O)_2(OH)_2$ (*s*), a hydrated solid, is $Cu(OH)_2$•$2H_2O$. When the waters of hydration are ignored, it is most simply written as $Cu(OH)_2$.

Other ligands form both stable precipitates and complex ions. For example, as CN^- ions are added to a solution containing hydrated copper ions, $Cu(H_2O)_4{}^{2+}$, a precipitate forms. Upon addition of more CN^- ions, the precipitate disappears into solution as a complex ion forms.

$$Cu(H_2O)_4{}^{2+}\,(aq) + 2\,CN^-\,(aq) \longrightarrow Cu(H_2O)_2(CN)_2\,(s) + 2\,H_2O\,(l)$$

$$Cu(H_2O)_2(CN)_2\,(s) + 2\,CN^-\,(aq) \longrightarrow Cu(CN)_4{}^{2-}\,(aq) + 2\,H_2O\,(l)$$

Even before a precipitate settles out of a solution, it can still be distinguished from a complex ion by its opacity. It is not possible to see through a solution that contains an appreciable amount of suspended solid.

Determining Relative Stabilities. Different ligands can form stronger or weaker bonds to copper ions. In a solution containing copper ions and several possible ligands, an equilibrium will develop in which most of the copper ions are coordinated to the ligands that form the strongest (most stable) bonds to copper ions. For example, when OH^- ions and NH_3 molecules are added in equal concentrations to a solution containing $Cu(H_2O)_4{}^{2+}$, the $Cu(OH)_2$ precipitate is observed. This indicates that $Cu(OH)_2$ is more stable than the complex ion $Cu(NH_3)_4{}^{2+}$.

However, changes in ligand concentrations can shift this equilibrium. When you add a small amount of 1 M NH_3 solution to a solution of 0.1 M copper nitrate, a light blue precipitate forms. The precipitate is copper hydroxide, formed by the reaction of the hydrated copper ion with the small amount of hydroxide ion present in the NH_3 solution. The fact that this reaction occurs means that even at very low OH^- ion concentration $Cu(OH)_2$ is a more stable species than $Cu(H_2O)_4{}^{2+}$ ion.

If you add more NH_3, the solid redissolves into a dark purple-blue solution. The new copper species is $Cu(NH_3)_4{}^{2+}$. This implies that the $Cu(NH_3)_4{}^{2+}$ ion is also more stable in NH_3 solution than is the hydrated copper ion. However, it would be incorrect to conclude that $Cu(NH_3)_4{}^{2+}$ is always more stable than $Cu(OH)_2$. In this example, the NH_3 concentration is much larger than the OH^- concentration. Given a higher concentration of hydroxide ion, perhaps $Cu(OH)_2$ might precipitate even in the presence of substantial concentrations of NH_3.

To resolve this question, you could add a little 1 M NaOH solution to the solution containing the $Cu(NH_3)_4^{2+}$ ion. $Cu(OH)_2$ actually does precipitate. These observations show that $Cu(OH)_2$ is more stable than $Cu(NH_3)_4^{2+}$ in solutions in which the ligand concentrations (OH^- and NH_3) are roughly equal. The stability of a copper species in a solution always depends on what ligands are present, and what their concentrations are.

In this experiment, you will prepare nine solid compounds and aqueous complex ions that contain Cu^{2+} ions, by mixing equal volumes of a copper nitrate solution and 1 M solutions of NH_3, Cl^-, OH^-, CO_3^{2-}, $C_2O_4^{2-}$, S^{2-}, NO_2^-, or PO_4^{3-} ions.

To determine the relative stabilities of the precipitates and complex ions that form, you will prepare one copper-containing species, and then you will add a second solution that contains ions which can also react with copper. If you observe a reaction, you will know that the new copper-containing species is more stable (when in the presence of roughly equal ligand concentrations). If you do not observe a reaction, you will know that the original copper-containing species is more stable.

After you have ranked the known species in order of stability, you will test an unknown copper-containing precipitate or complex ion. You should be able to determine the relative stability of the unknown as compared to the nine other known species in this experiment.

Experimental Procedure

SAFETY PRECAUTIONS: Wear your SAFETY GOGGLES. The $(NH_4)_2S$ solution smells strongly of rotten eggs. USE $(NH_4)_2S$ IN THE FUME HOOD! DO NOT bring any $(NH_4)_2S$ solution to your desk. DO NOT bring test tubes containing $(NH_4)_2S$ to your desk. If any of the copper-containing solutions used in this experiment splash on your skin or clothes, wash them off immediately with copious amounts of running water.

WASTE DISPOSAL: Pour all waste from this experiment into the INORGANIC WASTE containers in the fume hood. If you have trouble getting solid compounds out of the tiny test tubes, you can dissolve them in small amounts of hydrochloric acid.

Part 1. Preparation of the solid compounds and complex ions.

Goal: To prepare the different copper-containing precipitates and complex ions.

Add 5 drops of copper nitrate solution to a tiny test tube. This solution contains the complex ion, $Cu(H_2O)_4^{2+}$. Then add 5 drops of another solution that contains one of the following: NH_3, Cl^-, OH^-, CO_3^{2-}, $C_2O_4^{2-}$, S^{2-}, NO_2^-, or PO_4^{3-} ions. Describe the appearance of the product and figure out its chemical formula. Repeat this procedure (with fresh copper nitrate in clean test tubes) until you have observed all eight copper-containing species. Since most of these complex ions and solid compounds are blue, you will need to describe the various shades of blue, as well as the texture of solids that form.

Figure out the chemical formula of each precipitate and complex ion that formed. Oxalate ion ($C_2O_4^{2-}$) is a bidentate ligand, while the others ligands are monodentate.

Part 2. Determining relative stabilities.

Goal: To rank the copper-containing precipitates and complex ions in order of stability.

To determine the relative stability of two copper-containing species, add 5 drops of copper nitrate solution to a tiny test tube and then 5 drops of a solution that contains the anion (or NH_3) needed for the first copper-containing substance. Now add 5 drops of a second solution that contains the anion needed for the second copper-containing substance. Record what happens in your table of observations. Did a chemical reaction occur? Which of the copper-containing species is more stable?

Since many of the copper-containing substances are blue, it is not always obvious whether a chemical reaction has occurred. You will need to make very careful observations. Here are a couple of hints. Hint #1: Sometimes it is easier to see whether the *reverse* reaction occurs. That is, add the two anions (or NH_3) in reverse order. Hint #2: When complex ions are involved, sometimes a solution appears lighter because a new lighter-colored complex ion has been formed in a chemical reaction. But, sometimes a solution appears lighter because you have diluted the color by adding another clear solution that does not react. To help you distinguish between these two situations, you could make a comparison test tube to which you add copper nitrate and the first anion, but 5 drops of water instead of 5 drops of the second anion.

Continue these tests until you are able to list all of the copper-containing species, including $Cu(H_2O)_4^{2+}$, in order of increasing stability. Your ranking must be supported by the observations recorded in your notebook.

Part 3. Relative Stability of an Unknown Copper-Containing Substance.

Goal: To determine the position of an unknown copper-containing substance in your list.

Do this part individually: lab partners should use different unknowns.

Some of the unknowns are copper-containing solids and some are copper-containing complex ions. If the bottle containing your unknown contains a solution with some precipitate, shake it well so that you can dispense the some of the solid and solution together. In this case, the solid will contain the copper ions, and the solution will contain an excess of the precipitating anion.

To determine the relative stability of your unknown and one of the other copper-containing substances, it will not be necessary to add more copper nitrate. You should just add the second anion (or NH_3) to an appropriate amount of the unknown, and record the results. Did a chemical reaction occur? Which is more stable? Continue doing similar tests until you have determined the correct position of the unknown in your list. You will not be able to determine the identity or chemical formula of your unknown.

Pre-lab Questions

1. In testing the relative stabilities of Cu^{2+} species, a student adds 2 mL 1 M NH_3 to 2 mL 0.1 M $Cu(NO_3)_2$. She observes that a light blue precipitate initially forms, but that in excess NH_3 the precipitate dissolves and the solution turns dark purple-blue. Addition of 2 mL 1 M NaOH to the dark purple-blue solution results in the formation of a light blue precipitate.

(a) What is the formula of Cu^{2+} species in the dark purple-blue solution?

(b) What is the formula of the light blue precipitate present after addition of 1 M NaOH?

(c) According to this experiment, which Cu^{2+} species is more stable in equal concentrations of NH_3 and OH^-, the one in Part a or the one in Part b?

2. Another way of looking at stability is by comparing equilibrium constants.

(a) Look up the values of the equilibrium constants for the following two reactions in your textbook.

$Cu(OH)_2\ (s) \rightleftharpoons Cu^{2+}\ (aq) + 2\ OH^-\ (aq)$ $K_{sp} =$

$Cu^{2+}\ (aq) + 4\ NH_3\ (aq) \rightleftharpoons Cu(NH_3)_4^{2+}\ (aq)$ $K_f = 6.8 \times 10^{12}$

(b) Use these values to calculate the value of the equilibrium constant for:

$Cu(OH)_2\ (s) + 4\ NH_3\ (aq) \rightleftharpoons Cu(NH_3)_4^{2+}\ (aq) + 2\ OH^-\ (aq)$ $K =$

(c) According to your calculation, which Cu^{2+} species is more stable in a solution with equal concentrations of OH^- and NH_3, $Cu(OH)_2$ or $Cu(NH_3)_4^{2+}$?

3. By doing a calculation similar to that in Question 2, determine which Cu^{2+} species is more stable in a solution with equal concentrations of CO_3^{2-} and NH_3, $CuCO_3$ or $Cu(NH_3)_4^{2+}$?