Experiment 3*

Thermochromism in the Ionic Conductor, Cu_2HgI_4

*This lab taken from "Teaching General Chemistry; A Materials Science Companion," Eds. Ellis, A.B.; Geselbracht, M.J.; Johnson, B.J.; Lisensky, G.C.; Robinson, W.R.R.; American Chemical Society, **1993**

Prelab Reading

Unlike most electrical conductors, which conduct electricity by electronic motion, the salt Cu_2HgI_4 (and the related solid, Ag_2HgI_4) is a good ionic conductor of electricity at temperatures a little above room temperature, where it undergoes an order-disorder phase change. The compound is easily prepared, and its phase change is observable both by increased conductivity and a color change.

Structure and Phase Change

The low temperature ordered structure of Cu_2HgI_4 is shown in Figure 9.20C. Although the overall unit cell is tetragonal, with square bases and rectangular sides, it can be viewed as two fcc cells of iodide ions, with one cube atop the other. The iodide ions are in the fcc unit cells in the same positions as the sulfur atoms in ZnS (sphalerite form, *check your text!*). All of the Cu^+ and Hg^{2+} cations are in tetrahedral holes of the structure that are formed by the iodide ions (there are two such holes for each iodide), hence three-eighths of these holes will be occupied by the cations) but with a particular ordering (*see* Figure 9.20). In this low-temperature phase, the solid is brick red.

At a temperature of about 67°C, disorder sets in, and the cations are randomly distributed about all of the tetrahedral holes in the structure. The phase change is accompanied by a color change to red-brown and a marked increase in electrical conductivity. The color change is due to a small decrease in the band gap (2.1 to 1.9 eV) with the change in structure. In this high-temperature phase, the unit cell is a cube, because X-ray diffraction measures the average occupation of the tetrahedral sites, and the disorder makes it appear that, on average, each tetrahedral site contains one-forth of a copper ion and one-eighth of a mercury ion.

Conductivity Mechanism

Above the transition temperature, Cu_2HgI_4 exhibits ionic conductivity (with some electronic conductivity also). Five-eighths of the tetrahedral holes and all of the octahedral holes formed by the iodide ions are vacant, and these open sites provide possible pathways for the small copper cations to move through the crystal, carrying charge. It is easiest for a copper cation to jump between tetrahedral holes by moving to an octahedral hole and then to the new tetrahedral hole, rather than jumping directly between tetrahedral holes.

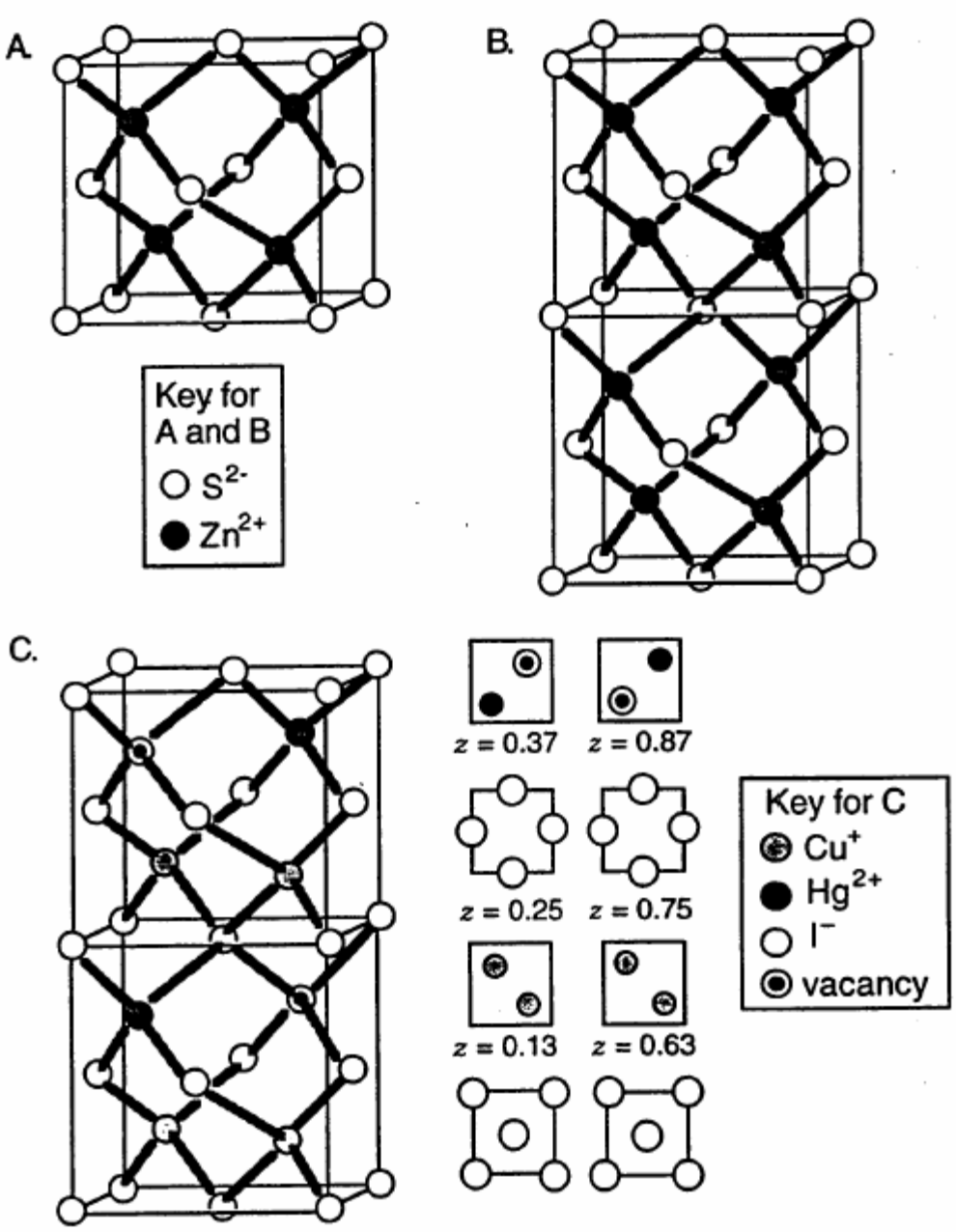

Figure 9.20A–C. The structure of Cu_2HgI_4 is related to the structures of ZnS (sphalerite) and of CaF_2 (fluorite). A: A sphalerite unit cell. B: Two stacked sphalerite unit cells. C: The ordered (low-temperature) structure of Cu_2HgI_4, with the z layer sequence. Three-eighths of the tetrahedral holes are occupied (2 of the 10 vacancies are shown; *see* the fluorite-like structure in D).

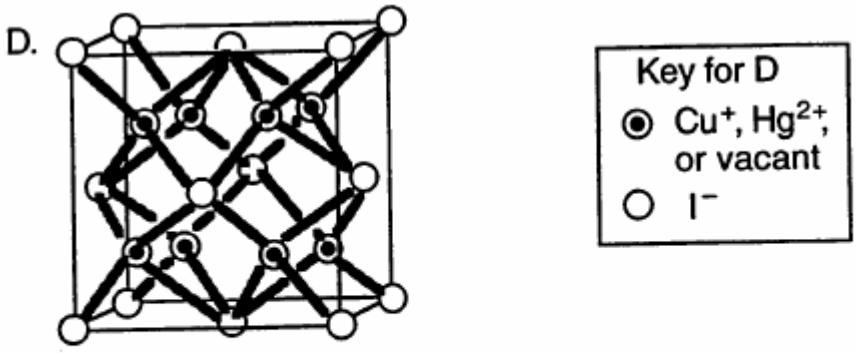

Figure 9.20D. The disordered (high-temperature) structure of Cu_2HgI_4. The cations are randomly distributed throughout all of the tetrahedral holes.

Purpose

To synthesize copper(I) tetraiodomercurate(II), Cu_2HgI_4, and study its changes in color and conductivity as the compound undergoes a phase transition upon heating.

Introduction

Cu_2HgI_4 is thermochromatic; it reversibly changes color with temperature. At low temperatures this compound is bright red, and at high temperatures it is dark brown. In the low-temperature form, the Cu^+ and Hg^+ ions are arranged in separate alternating layers, packed between layers of I^- ions (Figure 1). In the high-temperature form, the I^- ions occupy the same positions as before, but the metal ions now randomly occupy all the tetrahedral holes in the iodide array. The transition from one crystal form to the other takes place fairly sharply at a distinct temperature.

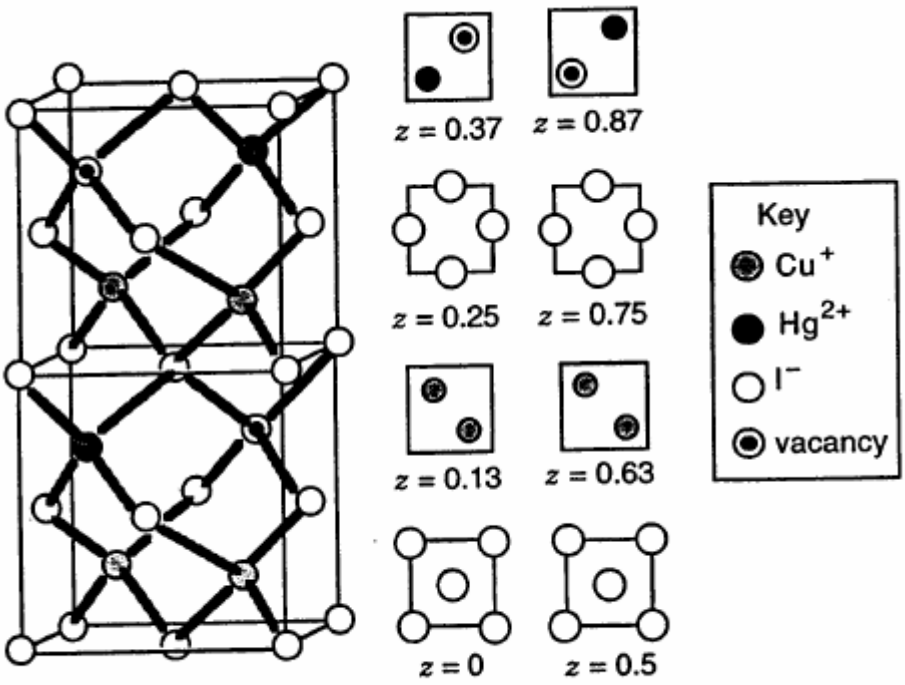

Figure 1. The structure of the low-temperature form of Cu_2HgI_4.

In the high-temperature form, the number of metal ions is smaller than the number of positions among which these ions are distributed. Thus, it is easy for the metal ions to move through the crystal by simply moving into unoccupied positions. In the high temperature form the metal ions diffuse through the crystal much like they would diffuse through an aqueous solution. With suitable equipment we can easily demonstrate that the electrical conductivity of the high-temperature form is much larger than that of the low-temperature form.

Copper(I) tetraiodomercurate(II), Cu_2HgI_4, is prepared by combining cupric iodide with mercury iodide. Cupric iodide is formed by reacting copper(II) sulfate with potassium iodide, in which the iodide ion reduces Cu(II) to Cu(I), thereby forming solid CuI (*see* the Appendix).

$$2Cu^{2+}(aq) + 4I^-(aq) \leftrightarrows 2CuI(s) + I_2(aq) \qquad (1)$$

In the presence of excess iodide ion, the iodine undergoes further reaction to form the triiodide ion (eq. 2)

$$I_2(aq) + I^- \leftrightarrows I_3^-(aq) \quad (2)$$

The net ionic equation for the formation of copper(I) iodide is shown below (eq. 3).

$$2Cu^{2+}(aq) + 5I^-(aq) \leftrightarrows 2CuI(s) + I_3^-(aq) \quad (3)$$

Triiodide can act as an oxidizing agent, by the reversal of equations 2 and 1, so it must be removed from solution. Sodium sulfite is used to reduce the triiodide ion back to iodide, eq. 4.

$$I_3^-(aq) + SO_3^{2-}(aq) + 3H_2O \leftrightarrows 3I^-(aq) + SO_4^{2-}(aq) + 2H_3O^+(aq) \quad (4)$$

The solid copper(I) iodide can be separated from the reaction mixture by carefully pouring off the excess solution of supernatant liquid.

A mercury(II) iodide precipitate is synthesized by an anion metathesis reaction, in which mercuric nitrate is combined with potassium iodide. The insolubility of HgI_2 helps to pull the equilibrium toward the right of eq. 5.

$$Hg^{2+}(aq) + 2I^-(aq) \leftrightarrows HgI_2(s) \quad (5)$$

Finally, Cu_2HgI_4 is prepared by adding the solid copper(I) iodide to the mixture containing the mercury(II) iodide precipitate.

Procedure

CAUTION: The chemicals used in this experiment, particularly mercury-containing compounds, are toxic. Avoid creating or breathing dust. Avoid eye and skin contact. Wash your hands thoroughly after handling.

Synthesis of Cu_2HgI_4

CuI: Add 2.5ml of 0.5 M $CuSO_4$ solution, 3.0ml of 1M KI solution and several drops of 6M acetic acid to 25ml of deionized water in a 100ml beaker. A precipitate of CuI will form. Add to this precipitate, with continuous stirring, a solution of 0.10g Na_2SO_3 dissolved in 5ml of water. Allow the precipitate of CuI to stand for 5 – 10 mins and then pour off as much as possible of the supernatant solution without losing much of the precipitate.

HgI_2 (in situ): Combine 12.5 ml of 0.05 M $Hg(NO_3)_2$, 1.5ml of 1M KI and 50ml of deionized water in a 200ml beaker. Note your observations. "in situ" is Latin for "in its original place." In synthesis, this means that an intermediate compound is not isolated before using it in a further reaction.

Cu_2HgI_4: Transfer the suspension CuI into the suspension of HgI_2, using a stream of deionized water to wash all the CuI from the beaker. Heat the mixed suspension of CuI of and HgI_2 almost to boiling for about 20 minutes on a stirring hot plate. A single dark-brown solid should form – but note your observations, such as initial colors, etc. Suction filter the solution while it is still hot, and then wash the precipitate of Cu_2HgI_4 with small portions of acetone.

CAUTION: Acetone is quite volatile and flammable. No open flames should be present.

Let the solid air-dry for 10 minutes.

Determination of the Transition Temperature

The transition temperature of Cu_2HgI_4 lies between 40 and 90° C, a temperature that can be can be conveniently studied using a mel-temp. You should be able to determine the transition temperature by finding the temperature at which a color change takes place as a sample of Cu_2HgI_4 is heated. Determination of the transition of the transition temperature involves packing a small amount of dry Cu_2HgI_4 precipitiate into a piece of capillary tubing that has one end sealed. The capillary tube is used as a small test tube and immersed in a mel-temp. Record the transition temperature, and be sure to repeat this measurement on the exact same sample. Can the same sample be thermally cycled more than one time, or is the transition irreversible?

Comparison of Electrical Conductivities

Insert a straight piece of 18-gauge copper wire (~8" long) into a glass capillary tube (Figure 2). The fit should be tight. Push the open end of the tube into some Cu_2HgI_4 so that some of the material is stuck in the tube. Flip the tube upside down and tap the copper wire end against a hard surface so that the Cu_2HgI_4 falls to the wire. Repeat this tapping until there is about 1 cm of the material in the tube. Finally, insert another length of copper wire into the open end of the glass capillary, so the Cu_2HgI_4 is packed between the two copper electrodes. In order to ensure a tightly packed tube, carefully bend the copper wire electrodes and place a rubber band around the electrodes:

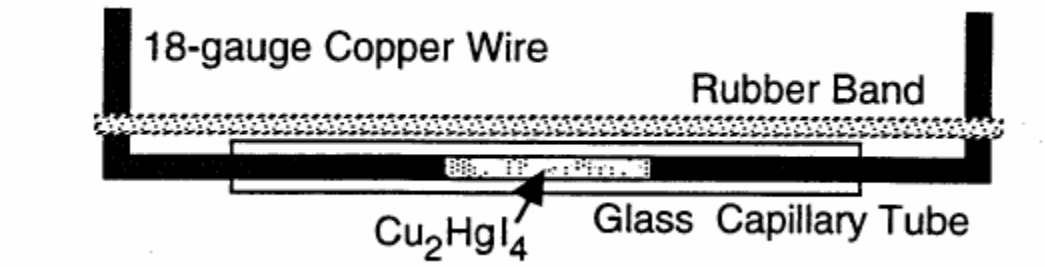

Figure 2. Apparatus for measuring conductivity.

Using an ohmmeter (adjust the meter to read in the 1-10-MΩ range), measure the electrical resistance between the electrodes of the Cu_2HgI_4 sample. Heat the tube by putting it in contact with your hot plate and measure the electrical resistance between the electrodes. How does the conductivity change as the color changes?

CAUTION: the hot plate is hot, thus its name. Take care to not hurt yourself.

Dispose of the Cu_2HgI_4 in the waste container provided. And remember, mercury wastes need to be segregated away from other wastes so that they can be treated properly.

Questions

1. When you made Cu_2HgI_4, you filtered it while the suspension was still hot. What impurity are you trying to avoid by filtering while hot?

2. Cu_2HgI_4 is an ionic conductor, which means than charge is carried by the net movement of ions rather than due to the motion of electrons. Why do you think the cations move, rather than the anions, to lead to ionic conduction?

3. At room temperature, Cu_2HgI_4 crystallizes in a tetragonal unit cell with unit cell lengths $a = b = 6.09$ Å and $c = 12.24$ Å. All of the angles in a tetragonal cell are 90°. Note that the c-axis length is almost double the a and b axis lengths (the unit cell is almost made from two cubes) as shown in Figure 1. What is the coordination and the geometry about the Cu(I) and Hg(II) ions? Even if the iodide ions did form a perfect face-centered cubic array, the cell would not be cubic. Why not?

4. When Cu_2HgI_4 is heated above the transition temperature, the iodide ions move into the exact positions of a face-centered cubic array, and the Cu^+ and Hg^{2+} ions diffuse through the solid by hopping from tetrahedral site to tetrahedral site. On average throughout the crystal, each tetrahedral site contains one-fourth of a Cu^+ ion and one-eighth of an Hg^{2+} ion. An X-ray measurement of a crystal measures the average of a great many unit cells, so the crystal appears cubic with $a = b = c = 6.10$ Å. Why is the height of the unit cell only half as large as for the low-temperature form?

5. You recently learned that x-ray diffraction is useful in determining lattice spacing and unit cell sizes, since the Bragg diffraction equation relates lattice spacing (d) to the diffraction angle (θ) and a multiple of the x-ray wavelength (nλ):

   $$n\lambda = 2d \sin\theta$$

   Will the diffraction angle θ increase or decrease when Cu_2HgI_4 is heated above its transition temperature? You might find the program "X-rays and Diffraction", by R.P. Grosso, J.T. Fermann, and W.J. Vining to be helpful.

Appendix. The Stability of Cu(I) Compounds

The synthesis of Cu_2HgI_4 contains some interesting chemistry. Beginning with an aqueous copper(II) sulfate solution that is treated with potassium iodide, a precipitate is formed, but not the one that might first be expected. Rather than obtaining a precipitate of copper(II) iodide, CuI_2, the precipitate analyzes as copper(II) iodide, CuI. Copper(II) is reduced to Cu(I), and some of the iodide(I^-) is oxidized to I_2.

When an element can exist in more than one oxidation state in aqueous solution, each oxidation state will have a different termodynamic stability. The relative stability of two oxidation states in aqueous solution is most conveniently expressed in terms of the electrochemical potential for the reaction.

$$Cu^{2+}(aq) + e^- \leftrightarrows Cu^{+}(aq)$$

The potential for a solution containing the ions Cu^+ and Cu^{2+} is given by the Nernst equation,

$$E = E^0 - \frac{RT}{nF} \ln \frac{[Cu^+]}{[Cu^{2+}]}$$

where n is the number of electrons per ion transferred at the electrode; F is the Faraday constant, 96,480 c/mol; E is the potential of the solution; $E°$ is the standard potential; $[Cu^+]$ is the concentration of Cu^+ ions in the solution; R is the gas constant; and T is the absolute temperature.

Therefore, any species added to the solution that decreases the concentration of Cu^+ or Cu^{2+} and alters the ratio $[Cu^+]/[Cu^{2+}]$ will cause an observable change in the potential and in the relative stability of Cu^+ and Cu^{2+}. If $[Cu^{2+}]$ is decreased, then the observable potential will become less positive, that is, the higher oxidation state will become more stable. Alternatively, if $[Cu^+]$ is decreased, the observed potential will become more positive and the lower oxidation state will become more stable.

Copper(I) iodide is a very insoluble salt ($K_{sp} = 5.1 \times 10^{-12}$). Thus, the addition of iodide ion to a solution of copper(I) will decrease the Cu^+ concentration, favoring the further reduction of Cu^{2+} to Cu^+. The concentration of free Cu^+ in a solution containing iodide ions is so low that it is very easy to reduce Cu^{2+}: even the weakly reducing iodide ion is strong enough to reduce Cu^{2+} to Cu^+ under these conditions.