Experiment 9

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**

Introduction

A great variety of structure types are derived from filling cations into the voids of a face-centered cubic (FCC) anion lattice. One simple example is the zinc blende structure of ZnS where one half of the tetrahedral FCC voids are filled (Fig. 1, far left). The ordered tetragonal low-temperature structure of Cu_2HgI_4 (Fig. 1, far right) involves a more complex arrangement of cations in the tetrahedral voids, and closely resembles a doubled zinc blende unit cell. Cu^+ and Hg^{2+} ions are arranged in separate layers, both sandwiched between close-packed layers of I^- ions. The stability of this complex order is tenuous – when heated above room temperature, the cations begin to move freely and a degree of randomness will be incorporated into the manner in which the Cu^+ and Hg^{2+} ions fill tetrahedral voids. As a result, Cu_2HgI_4 will undergo a structural phase transition to a disordered cubic structure of one-half the volume of the tetragonal phase.

At high temperatures, the Cu^+ and Hg^{2+} tetrahedral sites are indistinguishable to x-rays (because X-ray diffraction measures the cell contents averaged over all unit cells within a crystal, and on average, each of the four available sites has a 50% chance of being occupied by a Cu^+ ion, a 25% chance of being occupied by a Hg^+ ion, and a 25% chance of being vacant), giving the high temperature phase the same high symmetry cubic unit cell as ZnS. The phase change is accompanied by a color change (from red to brown) and a marked decrease in resistance. The thermochromic color change of Cu_2HgI_4 is due to a small decrease in the semiconducting band gap (2.1 to 1.9 eV) with the temperature-induced change in structure.

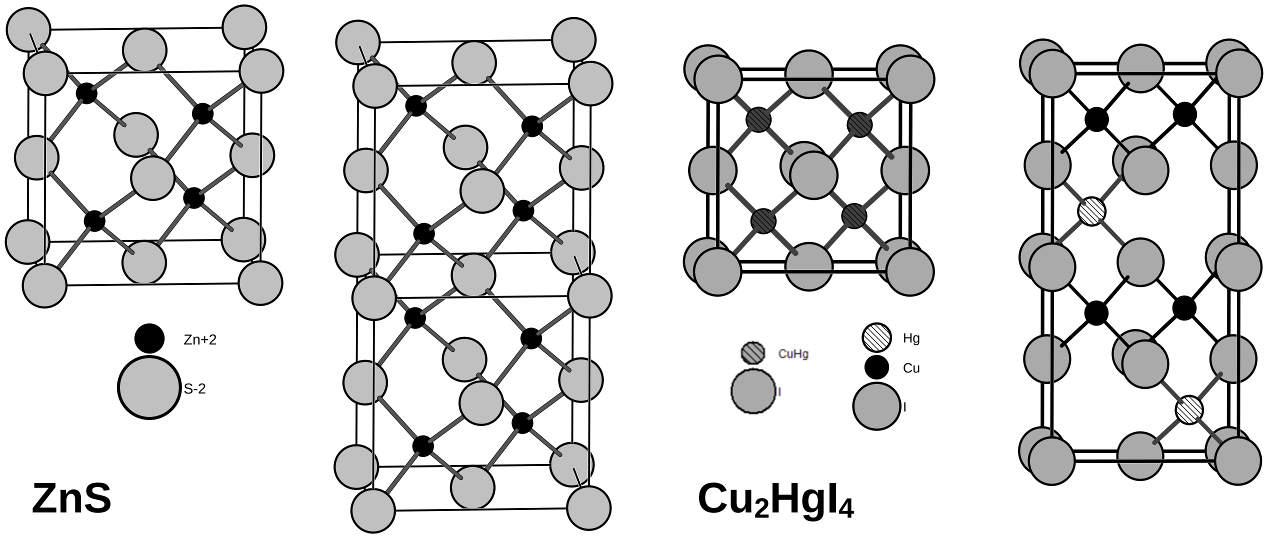

Figure 1. Left: A single and doubled unit cell of zinc blende structure of ZnS. **Right**: The closely related disordered cubic high-temperature (HT) and ordered tetragonal low-temperature (LT) structures of Cu_2HgI_4. Despite the fact that four different tetrahedral voids in the cubic HT cell can host Cu^+ and Hg^{2+} ions, only three of these sites actually contain an atom in a typical cell.

Ionic conduction

Unlike most electrical conductors where electrons move in response to an applied voltage, *ionic* conductors such as Cu_2HgI_4 (and the related solid, Ag_2HgI_4) can transport a current due to the ability of their constituent ions to move in response to an applied voltage. Ionic conductors are the solid analogues of electrolyte solutions, which also conduct electricity via the motion of ions. Ionic conductors are generally broken into two classes – those which conduct cations, and those which conduct anions. The latter class is of crucial importance to fuel cell applications, which demand a material capable of conducting oxygen in the form of O^{2-} ions through a solid barrier.

Above its 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 a possible mechanism 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. Substantial ionic conductivity is rare in ionic solids.

Chemical reactivity

Despite having a solid state (and not molecular) structure, Cu_2HgI_4 is readily prepared through a solution synthesis, as are most nanoparticles. Copper(I) tetraiodomercurate(II), Cu_2HgI_4, is prepared by combining copper(I) iodide with mercury(II) iodide. Copper(I) 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 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, forming triiodide ions

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

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

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

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.

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

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.

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

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

$$2\,CuI(s) + HgI_2(s) \rightarrow Cu_2HgI_4(s) \qquad (6)$$

Procedure:

CAUTION: The mercury-containing compounds, are toxic. Avoid creating or breathing dust. Use gloves when working with the mercury compounds, and avoid eye contact. Make extra efforts to ensure that all mercury waste ends up in the proper container. Keep your work surfaces clean at all times so that mercury waste is not inadvertently transferred.

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 and HgI_2 almost to boiling for about 20 min on a stirring hot plate. A single dark-brown solid should form. Record your observations of initial colors, etc. Suction filter the solution while it is still hot, wash the precipitate (Cu_2HgI_4) with small portions of acetone, and air-dry the solid 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 precipitate 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 then 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 (Fig. 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. To ensure a tightly packed tube, place a rubber band around the electrodes:

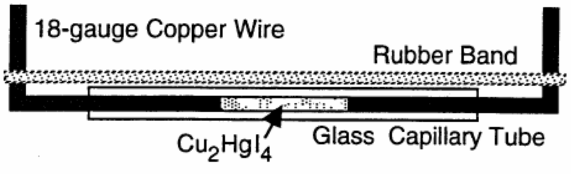

Figure 2. Apparatus for measuring sample resistance.

Using an ohmmeter (adjust the meter to read in the 1-10-MΩ range), measure the electrical resistance (R) 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? Record the dimensions (radius, length) of your cylinder of Cu_2HgI_4, and use them to calculate the dimension-independent resistivity (ρ) and conductivity (σ) of your sample.

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. Mercury wastes must 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 were you trying to avoid by filtering while hot?
2. 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. What are the coordination numbers of and the geometry about the Cu(I) and Hg(II) ions?
3. What are the ionic radii of the Cu and Hg ions in this compound? Refer to the paper by Shannon (provided in the solid state lab) for a table of radii, making sure you use the appropriate coordination number for each element.
4. The ionic radius of iodine in the high temperature form can be determined once the unit cell is known. Calculate the radius of I^- given that the cubic a lattice parameter is 6.10Å.
5. Download the Diamond structure file for the low-temperature (LT-Cu2HgI4.dsf) and high-temperature (HT-Cu2HgI4.dsf) forms of Cu_2HgI_4, and examine these structures in Diamond. List the most important bond distances in this structure (remember that there are no bonds if atoms are not neighbors). Create an informative structural representation of each compound using Diamond showing appropriate coordination polyhedra, and hand in a printed copy with your lab report (ignoring any "Demo version" banners…).
6. Cu_2HgI_4 is an ionic conductor, which means that charge is carried by the net movement of ions rather than by the motion of electrons through a stationary lattice. Give two reasons for why the cations are mobile in this compound but the anions are stationary.
7. Do you expect the Cu or Hg ions to be more mobile? Justify your answer.
8. Download the PowderCell files for the low-temperature (Cu2HgI4-LT.cel) and high temperature (Cu2HgI4-HT.cel) forms of Cu_2HgI_4 from the class website, and view their calculated x-ray diffraction patterns simultaneously using PowderCell. What similarities and/or differences are there? Should it be possible to follow the structural phase transition of Cu_2HgI_4 using an x-ray diffractometer with a heated stage?

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(I) 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 thermodynamic stability. The relative stability of two oxidation states in aqueous solution is most conveniently expressed in terms of the standard reduction 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.

Determination of resistivity and conductivity

An ohmmeter measures the resistance (R) of a material (through the relation V = IR, with the units of resistance are Ω = V / A). The resistance in Ω (Ohms) is not independent of sample geometry, as the resistance will increase linearly with the length of a sample, and will decrease proportionally to the cross-sectional area of the sample. The resistivity (ρ) of a sample is defined to be independent of sample geometry, through the formula below. The preferred units of ρ are Ω cm (obtained if all dimensions are reported in cm). The conductivity (σ) of a sample is the inverse of its resistivity. Its units are typically reported in S / cm, where $S = \Omega^{-1} = A/V$.

$$\rho = R \times \frac{area}{length} \qquad \sigma = \frac{1}{\rho}$$