Experiment 4

Thermochromic Tetrachlorocuprate(lI)

INTRODUCTION

A thermochromic substance undergoes a color change upon heating or cooling. One such thermochromic solid is bis(diethylammonium)tetrachlorocuprate(II), $[(CH_3CH_2)_2NH_2]_2CuCl_4$. The tetrachlorocuprate(I1) anion displays discontinuous thermochromism, which is a rapid color change over a narrow temperature range. The color change of bright green to yellow corresponds to a coordination geometry change from distorted square-planar to distorted tetrahedral. There are a number of thermochromic tetrachlorocuprate complexes as well as other inorganic thermochromic compounds.

Thermochromism is a fascinating subject that is based on some fundamental principles taught in advanced undergraduate courses: entropy-driven reactions, crystal field theory, d-d transitions, hydrogen bonding, and prediction of molecular geometry. The delicate balance between the distorted square-planar and distorted tetrahedral geometry in $CuCl_4^{2-}$ is influenced by several factors. Ligand-ligand repulsion favors the tetrahedral geometry; the square-planar geometry is stabilized in the solid by stronger (shorter) hydrogen bonds between the chlorides and the ethylammonium hydrogens, and crystal field stabilization energy favors the square-planar geometry. It is generally accepted that the dominant factor in the thermochromic phase transition of the diethvlammonium cation. This entropy increase is consistent with the weakening of the hvdrogen bonds between the cation hvdrogens and the chlorides at the high-temperature phase. We have developed a multi-technique experiment based on the study of $[(CH_3CH_2)_2NH_2]_2CuCl_2$ for our advanced integrated laboratory course.

The complex is easily prepared in high purity, the thermochromic transition (in the solid phase at 45°C) is studied by differential scanning calorimetry (DSC); a UV/vis absorption spectrum of a solid pellet of the complex above and below the thermochromic transition is obtained to show the effect on the transitions; and the infrared spectrum of the same pellet in the NH stretching region above and below the thermochromic transition shows the change in the hydrogen bonding. The energy of the thermochromic phase transition can be determined from the DSC data. Using the UV/vis data and values from the literature, the transitions can be assigned for the low-temperature square-planar and high-temperature tetrahedral forms of $CuCl_42$-. While this experiment uses a variety of methods and demonstrates several concepts, the instrumentation required is widely available. Any scanning UV/vis spectrometer with a range of 400-800 nm can be used, any medium-resolution dispersive or Fourier transform infrared spectrometer can be used, and any DSC can be used. If a DSC is not available, the temperature range of the thermochromic transition can be obtained using a conventional melting point apparatus.

Experimental

Bis(diethylammonium)tetrachlorocuprate(II) was prepared according to published procedure. Diethylammonium chloride (0.02 mol, 2.2 g) was dissolved in 15 mL is a propyl alcohol with gentle heating; copper(II) chloride (0.01 mol, 1.7 g) was dissolved in 3 mL absolute ethanol with gentle heating. The two hot solutions were mixed and then cooled in an ice bath. Green needle crystals were isolated by filtration and rinsed with isopropyl alcohol. The hygroscopic solid was stored in a desiccator.

Visible absorption spectra were recorded from 800 to 450 nm on a Spectrophotometer equipped with a variable temperature sample compartment. The sample was prepared as a KC1 pellet (as opposed to KBr pellet. to avoid any possible halide exchange).