Experiment 1

Synthesis and observation of phosphorescent emission of Tris(2,2´-bipyridine) ruthenium(II) Dichloride Hexahydrate

Introduction

The tris(2,2'-bipyridine) ruthenium(II) complex cation is an important chemical species in the study of electron-transfer, spectroelectrochemistry, solar energy conversion, ESR, and luminescence studies. The method presented here requires about one hour and is of high yield. It involves the reaction of ruthenium(III) chloride with 2,2'-bipyridine in a medium of sodium phosphinate by the following overall reaction: In this synthesis, sodium phosphinate is freshly prepared by neutralization of a phosphinic acid solution with sodium hydroxide: Phosphinate ion is a moderately strong reducing agent, which is used to reduce Ru^{3+} to Ru^{2+}.The Ru^{2+} thus formed is complexed with 2,2'-bipyridine, commonly called "bipy", which functions as a bidentate ligand. 2,2'- bipyridine The complex is then precipitated by adding excess Cl^- (as KCl), using the common ion effect.

Samples of $RuCl_3 \cdot xH_2O$ may contain Ru(IV), various oxo-and hydroxychloro- complexes, and nitrosyl species. In this synthesis the $RuCl_3 \cdot xH_2O$ is dried and stored in an oven at 120°C before use. The drying procedure has already been carried out so that students will obtain predried material. The method used is to dry the $RuCl_3 \cdot xH_2O$ at 120 °C for 3 hours, grind in a mortar and pestle to a fine powder, and then dry for an additional hour at 120 °C. The dry RuCl3·xH2O may be conveniently stored at this temperature.

CHEMICAL REQUIRED

$RuCl_3$, 2,2'-bipyridine, hypophosphorus acid, NaOH, KCl, acetone, $K_2S_2O_8$, acetonitrile, HCl, magnesium pieces.

GLASSWARE REQUIRED

25 mL R.B.flask with condenser, 100 mL beaker (2), dropper, 1 mL measuring pipette, funnel, 50 mL conical flask, 10 mL measuring cylinder, glass rod. (There may be little changes)

PROCEDURE

Preparation of Sodium phosphinate(will be supplied): The sodium phosphinate used in this synthesis is prepared by the careful addition of sodium hydroxide pellets to about 2 mL of 31% phosphinic acid (hypophosphorus acid, H_3PO_2) until a slight cloudy precipitate is obtained. Phosphinic acid is then added dropwise until the precipitate just redissolves.

$RuCl_3$ that has been dried at 120 °C for at least 3 hours for the following synthesis.

Weigh the 0.1 g $RuCl_3$ into a 10-mL beaker and transfer with small quantities of water to the reaction flask. Do the same for the 2,2'-bipyridine. (OR can be weighed in butterpaper)

"Dried" $RuCl_3$ (0.1 g, 0.48 mmol), 2,2'-bipyridine (0.23 g, 1.44 mmol), and water (10 mL) are placed in a 25-mL flask fitted with a water-cooled reflux condenser. Freshly prepared **sodium**

phosphinate (sodium hypophosphite) solution (0.5 mL) is added and the mixture heated to a boil for 30 minutes. During reflux, the initial green solution changes to brown and finally orange. After cooling the solution is filtered through a medium porosity sintered glass filter to remove traces of undissolved material. The solution is then transferred to a 50-mL conical flask, and 3.2g of potassium chloride is added. The solution containing the crude product is now heated to boiling (hot plate under the hood) for a few minutes to give a deep red solution, which on cooling to room temperature yields beautiful, red, platelike crystals. These crystals are filtered on a medium porosity sintered glass filter, washed with ice-cold 10% aqueous acetone (2 x 3 mL) and acetone (10 mL), and air dried. The Inorganic Syntheses yield is reported to be 0.29 g or 80% (adjusted for 25% of the materials used). The product may be recrystallized from boiling water (~2.8 mL/g) and air dried. For this laboratory air drying is sufficient.

Analytical Characterization: ESI-MS and 1H NMR

TA s will help you regarding these measurements

UV-Vis spectra and Phosphorescent Emission of Tris(2,2'-bipyridine)ruthenium(II) Ion

Prepare a solution for UV-visible spectroscopy so that the absorbance maximum at 454 nm is close to 1 absorbance unit, using the ε values given below for your computations. Record the spectrum between 400 and 700 nm.

Aqueous solutions of $[Ru(C_{10}H_8N_2)_3]Cl_2{\cdot}6H_2O$ have two characteristic absorption maxima at 428 nm (shoulder $\varepsilon = 11{,}700$) and 454 nm ($\varepsilon = 14{,}000$) which have been assigned to metal ligand charge transfer (CT transitions). The CT transition has a relatively long life (~600 nsec), and the luminescence spectrum results from a triplet-singlet phosphorescence ($\lambda_{max} = 600$ nm).

Chemiluminescence experiment of Tris(2,2'-bipyridine)ruthenium(II) Ion

Weigh out approximately 0.025 g $[Ru(C_{10}H_8N_2)_3]Cl_2{\cdot}6H_2O$ into a 10 mL beaker. Transfer the $[Ru(C_{10}H_8N_2)_3]Cl_2{\cdot}6H_2O$ with a small amount of water to a 125-mL conical flask. Add 18 mL water and 0.33 g $K_2S_2O_8$ to the flask along with a Teflon stirring bar, and stir the solution on a magnetic stirrer. To this solution add 20 mL of acetonitrile and wait until all the solid dissolves. Adjust the pH to approximately 1 by the addition of 2 M hydrochloric acid. Now add approximately 12 small pieces of magnesium to the stirred solution. Observe in a darkened room. Report your observations.

Cyclic Voltammetric experiment

TA s will help you regarding this experiment