Tris(2,2'-bipyridine)ruthenium(II) Dichloride Hexahydrate

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.[1,2] It was first prepared in low yields by pyrolysis of ruthenium(III) chloride with 2,2'-bipyridine and later by reflux of these compounds in ethanol. 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:

$$RuCl_3 + 3\ C_{10}H_8N_2 \xrightarrow{NaH_2PO_2/H_2O} [Ru(C_{10}H_8N_2)_3]Cl_2{\cdot}6H_2O$$

The same method may be used to prepare the orthophenanthroline and related diamine ligand complexes. This method is adapted from the Inorganic Syntheses preparation by Broomhead and Young.[1]

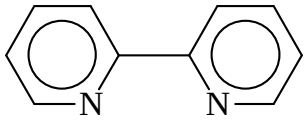
In this synthesis, sodium phosphinate is freshly prepared by neutralization of a phosphinic acid solution with sodium hydroxide:

$$H_3PO_2(aq) + NaOH(aq) \rightarrow NaH_2PO_2(aq) + H_2O$$

Phosphinate ion is a moderately strong reducing agent, which is used to reduce Ru^{3+} to Ru^{2+}:

$$\begin{array}{ll} H_2PO_2^- + 2H_2O & \rightarrow\ H_2PO_4^- + 4H^+ + 4e^- \\ 4(Ru^{3+} + e^- & \rightarrow\ Ru^{2+}) \\ \hline H_2PO_2^- + 2H_2O + 4Ru^{3+} & \rightarrow\ H_2PO_2^- + 2H_2O + 4Ru^{2+} \end{array}$$

The Ru^{2+} thus formed is complexed with 2,2'-bipyradine, commonly called “bipy”, which functions as a bidentate ligand.



The complex is then precipitated by adding excess Cl^- (as KCl), using the common ion effect:

$$Ru^{2+} + 3bipy + 2Cl^- + 6H_2O \rightarrow [Ru(bipy)_3]Cl_2{\cdot}6H_2O$$

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 pre-dried 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 $RuCl_3{\cdot}xH_2O$ may be conveniently stored at this temperature.

Procedure

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.

You will be given $RuCl_3$ that has been dried at 120 °C for at least 3 hours for the following synthesis. Weigh the material into a 10-mL beaker and transfer with small quantities of water to the reaction flask. Do the same for the 2,2'-bipyridine.

"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 3.2 g 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.

Prepare a solution for UV-visible spectroscopy so that the absorbance maximum at 454 nm is close to 1 absorbance unit. You may want to do this quantitatively (3 significant figures using the analytical balance and volumetric flasks), 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 ϵ = 11,700) and 454 nm (ϵ = 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 (λ_{max} 600 nm). The complex may be resolved into its optical enantiomers using the iodide antimonyl(+) tartrate salt.

Phosphorescent Emission of Tris(2,2'-bipyridine)ruthenium(II) Ion[3]

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?

Laboratory Report

1. Is the uv-vis spectrum of your sample consistent with what is predicted for a solution of pure tris(2,2'-bipyridine)ruthenium(II) complex cation? Explain in detail.

2. What is the structure of phosphinic acid? Is the pK_a of this acid consistent with its structure? Explain.

3. What is the purpose of the phosphinic acid in this experiment?

4. What is the purpose of adding such a large amount of potassium chloride?

5. Explain the luminescence reaction (see reference 3)?

5. Describe the difference between fluorescence and phosphorescence?

6. Draw a structure of the tris(2,2'-bipyridine)ruthenium(II) complex cation.

References

1. *Inorg. Synth.* **1992**, *29,* 127.

2. Noble, B.; Peacock, R. D., *Inorg. Chem.*, **1996**, *35*, 1616

3. Bolton, E.; Richter, M., *J. Chem. Educ.*, **2001**, *78*, 47.