Metallation of Tetraphenylporphyrin

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Chemical Concepts
Coordination chemistry; visible spectroscopy

Green Chemistry Topics
More benign reaction solvent; room-temperature reactions

Introduction
Organic compounds that bind to metals are called ligands. When the metal and ligand bind together they form a coordination complex. The chemical structure of the ligand usually has a significant impact on the solubility and the reactivity of the complex. As you will observe in this laboratory experiment, Zn(II) that is colorless in solution forms a blood-red complex with the tetraphenylporphyrin (TPP) ligand. Whereas the Zn(II) ion is more soluble in water than in organic solvents, the complex is insoluble in water and freely soluble in organic solvents. Thus, ligands such as the porphyrin can be used to impart new properties to a metal through the formation of a complex.

Coordination complexes are important throughout chemistry and biology. They act as catalysts, drugs, oxygen carriers, and electron transfer agents. Metal complexes of the porphyrin ring system are found in two essential biological systems, the heme, an iron-porphyrin structure, and chlorophyll, a magnesium-porphyrin complex. The iron-containing hemes are ubiquitous in biological systems, acting as essential components in the electron transport chain (oxidative phosphorylation). In addition, the iron center of the hemoglobin binds O₂ as the oxygen storage protein myoglobin and the oxygen-transporting protein hemoglobin.

In addition to the metalloporphyrins found in biological systems, many synthetic metal complexes of porphyrins have been prepared by chemists for use as models of the more complex biological systems and as catalysts, sensors, and other functional materials. Usually, the metal-free porphyrin ligand is synthesized and purified before incorporation of the metal into the four-fold (tetradentate) binding site (metallation). Metallation of the porphyrin ring generates 2 equiv of protons, as shown in Scheme 1. As suggested by the scheme, it is possible in some cases to remove the metal from the porphyrin by heating

Scheme 1: Metallation of porphyrins.
will acid. In this experiment, you will metatllate TPP with zinc using zinc acetate. You will monitor the metallation using visible spectroscopy (the 3rd and 4th Q bands disappear during the reaction).

Typically, halogenated solvents or dimethylformamide are used to metallate porphyrins. In this experiment, two more benign solvents, 1-methyl-2-pyrrolidinone (also called N-methylpyrrolidinone, or NMP) and dimethyl sulfoxide (DMSO), will be used to dissolve both of the reagents and ensure facile reaction.

**Prelab Questions**
1. Read the sections in your laboratory manual regarding techniques for visible spectroscopy.
2. In your notebook, write down the balanced reactions for the synthesis.
3. Read over the preparations and write down your plan of attack in your notebook. You may choose a narrative description that paraphrases the procedure given below or perhaps a flowchart illustrating the procedures you will use.

**Chemicals and Equipment**
- Tetrapyrrole porphyrin solution from previous experiment
- Zinc acetate
- Dimethyl sulfoxide (DMSO)
- N-methylpyrrolidinone (NMP)
- Glass cuvette

**Experimental Procedure**

**SAFETY PRECAUTIONS**
Avoid contact with dimethyl sulfoxide (DMSO). Although this solvent has relatively low toxicity, it can readily penetrate the skin and take with it any contaminants that might be on your skin. You should wear gloves, and be careful to avoid getting DMSO solutions on your skin.

**Note:** The zinc acetate solution should be sufficient for about eight students. Before you make the solution, check with others to see if they have any to share.

Prepare a saturated solution of zinc acetate (0.400 g, 2.2 mmol) using approximately 2 mL of DMSO.

The metallation is performed in a cleaned and dried glass cuvette. If this experiment is performed in combination with the microwave preparation of TPP (see page 27), three drops of the i.d. fraction from the column chromatography experiment should be collected, evaporated to dryness, and diluted to 4 mL using N-methylpyrrolidinone (NMP). Collect an initial visible spectrum of the porphyrin solution. The absorption spectrum of TPP shows a strong absorbance at 428 nm along with four weaker absorbances (Q bands) at 510, 550, 590, and 645 nm. Make sure the concentration of your porphyrin solution allows you to observe the weaker Q bands.

Add 5 drops of the zinc acetate solution, thoroughly mix the solution, and collect spectra every 25 min to monitor the progress of the metallation reaction. The metallation is typically complete in approximately 4 h at room temperature.

**Postlab Questions**
1. Label the UV-visible spectra you recorded during the metallation reaction. Be sure to include the wavelength and absorbance of each peak as well as your name and sample identification for each. Attach the spectra to your report.
2. Report any color changes that you noticed during the course of the reaction. Explain how these color changes correlate with the spectral changes that you observed.
Cleanup
Dispose of the reaction mixture in the cuvette in the nonhalogenated waste container.

Green Assessment and Opportunities for Improvement
The solvents used in this metalation offer fewer health and environmental hazards than the traditionally used solvents, chlorinated hydrocarbons and N,N-dimethylformamide. Furthermore, the reaction is conducted at room temperature instead of the elevated temperatures typically used. In the future, it may be possible to find other solvents that could be used in place of DMSO; however, the challenge will be to find a solvent or solvent mixture that will solubilize both the TPP and the zinc salt.

REFERENCE

EXPERIMENT DEVELOPMENT NOTE
This experiment was adapted from the original report by Petit et al. (1) for use in the University of Oregon's organic chemistry teaching labs.