Experiment 6: The Preparation of Tetrphenylporphyrins and Their Zinc Complexes

A porphyrin (Figure 1) is a heterocyclic macrocycle derived from four pyrrole-like subunits interconnected via α-carbon methane bridges (=CH-). This macrocycle is a highly-conjugated system having 22-π electrons, and is consequently deeply colored. In fact, the name “porphyrin” comes from a Greek word for purple. Porphyrins can bind to a wide variety of metals to form complexes in which the metal sits in the middle of the macrocycle bound to the four nitrogen atoms. These tetradentate metal complexes are employed extensively in biological systems and serve as the active sites of many enzymes. For example, some iron-containing porphyrins are called “hemes,” which function as the O₂-binding proteins in hemoglobin and myoglobin.

In this experiment, each group will prepare one of three different tetrphenylporphyrins, as well as the corresponding ZnⅡ porphyrin derivative. Both the porphyrin ligand and the corresponding metal complex will be characterized by ¹H NMR spectroscopy. The NMR spectra for the different derivatives will be shared between groups for comparative purposes.

Procedure

1. Preparation of tetrphenylporphyrins

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\begin{align*}
4 \text{H} & \quad + \quad 4 \text{X} \quad \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \\
\text{O}_2, \Delta & \quad \rightarrow \\
\text{X} & = \text{H} \\
\text{CH}_3 & \\
\text{OCH}_3 & \\
\end{align*}
\]

The appropriate benzaldehyde (0.0012 mol) is refluxed for 30 minutes with 0.083 mL (0.0012 mol) of pyrrole in 12 mL of propanoic acid in a 25-mL round-bottom flask fitted with a water-cooled condenser. The mixture is cooled to room temperature and 10 mL of cold methanol is added. The flask is then chilled in an ice bath while stirring. The deep-purple
crystals that form are collected by vacuum filtration in a Hirsch funnel. The flask and crystals are washed with three 0.5-mL portions of cold methanol followed by three 0.5-mL portions of boiling distilled water. The crystals are air-dried in the Hirsch funnel for 15 minutes. The material is weighed and an $^1$H NMR sample is prepared. (expected yield 40 mg)

2. Preparation of Zn$^{II}$ (tetraphenylporphyrin) derivatives$^{ii}$

To a 25-mL round-bottom flask is added the tetraphenylporphyrin (0.025 g), zinc acetate (0.1 g), and dichloromethane (10 mL). The flask is fitted with a water-cooled condenser and the mixture is warmed to reflux. The progress of the reaction is followed by TLC (eluent dichloromethane/hexane 1/1). When TLC indicates that the starting material is consumed, pour the solution into a separatory funnel and wash with water (2 x 10 mL). Dry the organic layer over sodium sulfate and filter. Dilute the mixture with an equal volume of hexane and boiling off the more volatile dichloromethane on a hotplate until crystals start to form. Cool the solution, and collect the crystals by filtration.

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$^{ii}$ Adapted from http://courses.chem.psu.edu/chem431/500Expts/EX501.pdf.