Réf : Experimental organic chemistry
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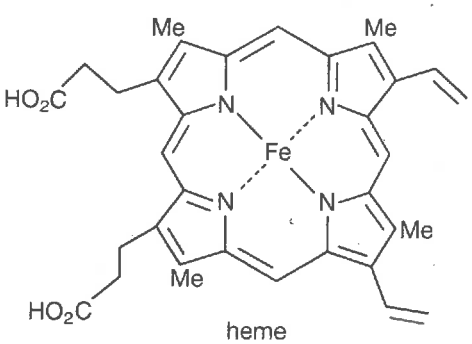
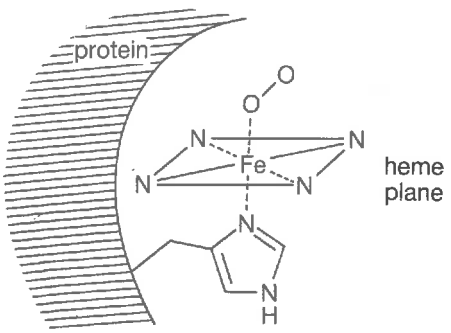
Experiment 90: Synthesis of tetraphenylporphin and its copper complex

In vertebrates, two proteins, myoglobin and hemoglobin, function as oxygen carriers. Myoglobin is located in muscles where it stores oxygen and releases it as necessary. Hemoglobin is present in red blood cells and is responsible for oxygen transport. Although these natural compounds are



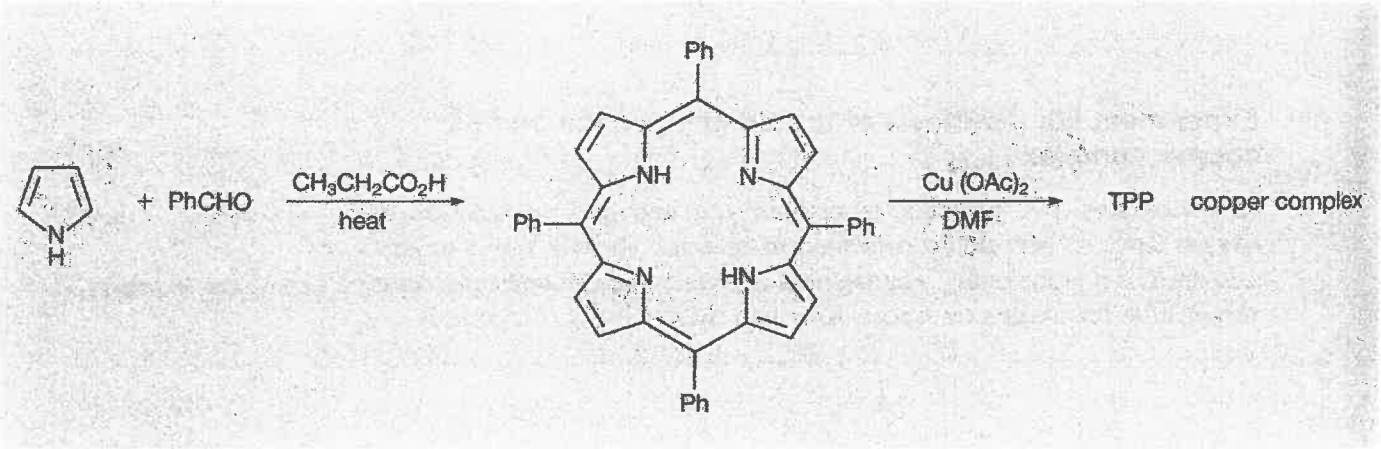
heme



hemoglobin (schematic)

complex proteins, the secret of their oxygen carrying ability lies in the non-protein part of the molecule, the so-called heme unit. Heme is a planar macrocyclic organic molecule made up of four linked pyrrole rings surrounding an iron atom. Although the iron is associated with four nitrogens it can accommodate two additional ligands, one above and one below the plane of the ring. In hemoglobin one of these ligands is the imidazole ring of a histidine residue in the protein chain, and, more importantly, the other ligand is molecular oxygen.

Heme is an example of a general class of biologically important macrocyclic nitrogen containing pigments known as *porphyrins*. All porphyrins have the ability to complex metal ions (*cf.* crown ethers, Experiment 91), and the simplest, unsubstituted porphyrin is known as porphin. The ring system is planar, contains 18 delocalizable π- electrons, and on the basis of the Hückel $[4n+2]$-rule, can be considered as an aromatic compound. This project illustrates a simple laboratory preparation of a porphyrin derivative, 5,10,15,20-tetraphenylporphin (*meso*-tetraphenylporphyrin or TPP, for short), and its copper (II) complex. The preparation involves the condensation of benzaldehyde with pyrrole in boiling propanoic acid. Both TPP and its copper complex are deeply colored solids with interesting UV/visible spectra.



Level 2

Time 2 × 3 h

Equipment hotplate; apparatus for: reflux, suction filtration

Instruments UV

Materials

1. meso-Tetraphenylporphin		
pyrrole (FW 67.1)	1.4 mL, 1.35 g (20 mmol)	**flammable**
benzaldehyde (FW 106.1)	2.0 mL, 2.1 g (20 mmol)	**irritant, toxic**
propanoic acid	75 mL	**corrosive, toxic**
methanol	*ca.* 50 mL	**flammable, toxic**
2. Copper complex		
dimethylformamide	10 mL	**irritant, toxic**
copper (II) acetate monohydrate (FW 199.7)	40 mg (0.2 mmol)	**irritant**

Procedure

1. Preparation of meso-tetraphenylporphin ***HOOD***

Place the propanoic acid in a 250 mL round bottomed flask, fit a reflux condenser,[1] add some boiling stones, and bring the acid to reflux. Simultaneously, add the pyrrole[2] and the benzaldehyde to the refluxing propanoic acid down through the condenser using two Pasteur pipets. Continue to heat the mixture under reflux for 30 min. Cool the mixture to room temperature,[3] and collect the deeply colored product by suction filtration.[4] Wash the product thoroughly with methanol until the methanol washings are colorless. Dry the product by suction for a few minutes. Record the yield and the UV spectrum ($CHCl_3$) of your product.

[1] *Figure 3.20*
[2] *Best if freshly distilled*
[3] *May be left at this stage*
[4] *Figure 3.7*

2. Preparation of TPP copper complex [5,10,15,20-tetraphenylporphyrinatocopper (II)]

Place the dimethylformamide in a 25 mL Erlenmeyer flask, add a few boiling stones, and heat the flask on a hotplate until the solvent begins to boil gently. Add 100 mg (0.16 mmol) TPP to the hot dimethylformamide, and allow it to dissolve. Add the copper (II) acetate, and continue to heat the solvent at its boiling point for 5 min. Cool the flask in an ice bath for about 15 min, and then dilute the mixture with 10 mL distilled water. Collect the solid product by suction filtration,[4] wash it well with water, and dry by suction. Record the yield and the UV spectrum ($CHCl_3$) of your product. If required, the product can be purified by column chromatography on alumina,[5] eluting with chloroform.[6]

HOOD

[5] *See Chapter 3*
[6] ***Toxic!***

Problems

1 Suggest a reaction mechanism for the reaction of pyrrole with benzaldehyde.
2 Compare and contrast the UV spectra of TPP and its copper complex.
3 Which other metals might form complexes with TPP?

Further reading

Morrison & Boyd p. 1367; Streitwieser & Heathcock p. 1006; McMurry p. 1000; Fessenden & Fessenden p. 790; Vollhardt p. 1257.

References

For the procedures on which this experiment is based, see: A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
A.D. Adler, F.R. Longo, and V. Varadi, *Inorg. Synth.*, 1975, **16**, 213.