

# Unusual Properties of Tetraphenylporphyrin Copper Complex

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**Abstract**—5,10,15,20-Tetraphenylporphyrin reacted with copper powder in boiling xylene on exposure to air (but not in an inert atmosphere) to give bright red copper complex which differed in properties from the initial porphyrin and its complexes with other metals. The copper complex was stable to oxidation with  $\text{Cu}^{2+}$  ions (during chromatography), and it readily underwent demetalation by the action of  $\text{LiAlH}_4$  in tetrahydrofuran.

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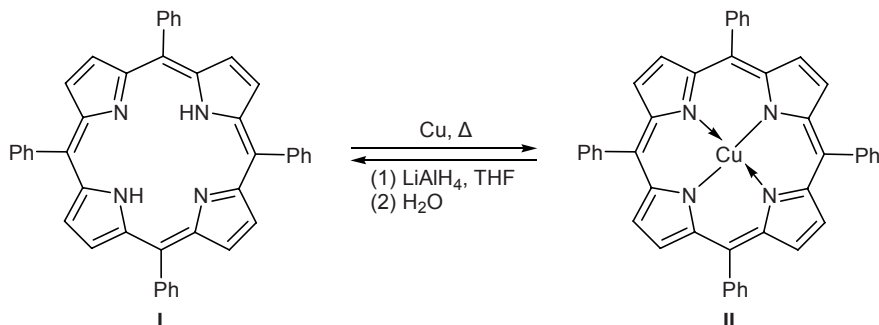
Syntheses of various *meso*-substituted porphyrins [1] generally involve two problems. One of these is related to the fact that the formation of porphyrins from pyrrole and aldehydes under acidic conditions is almost uncontrollable, and the second problem is difficult isolation procedure. Chromatographic isolation of porphyrins is often accompanied by their oxidation. Therefore, synthesis of compounds that are stable to oxidation and chromatographically mobile, attracts researchers' attention. There are no published data indicating that porphyrin copper complexes could be promising in this respect. Although porphyrins are readily identified on thin-layer chromatograms by their color, by-products are often colorless or weakly colored, so that special reagents are necessary to detect and remove such impurities.

We have found that porphyrin copper complexes possess a number of properties that differentiate them fairly strongly from both metal-free porphyrins and porphyrin complexes with other metals. Tetraphenylporphyrin (I) readily reacts with various copper salts,

such as acetate, phthalimide, and phenylacetylde. These are common reactions intrinsic to other metal salts. Tetraphenylporphyrin copper complex turned out to be also formed in the reaction with copper powder provided that it was performed on exposure to atmospheric oxygen rather than in an inert atmosphere. Addition of 1–2 ml of acetonitrile to a xylene solution completes the formation of the copper complex in a few minutes. Partly hydrogenated derivatives, such as chlorin and bacteriochlorin, react in a similar way. No copper complex is formed under argon. The reaction involves oxidation of tetraphenylporphyrin rather than copper, for copper oxide does not react under analogous conditions. Other metals, e.g., zinc powder, failed to react with tetraphenylporphyrin.

Tetraphenylporphyrin copper complex **II** is a crystalline substance which gives rise to bright red solutions in common solvents. Its electronic spectrum consists of the only long-wave absorption band with its maximum at  $\lambda$  540 nm; by contrast, the free ligand and complexes with other metals are characterized by up to

Scheme 1.



four absorption bands in the region  $\lambda$  500–650 nm. Likewise, tetraazaporphyrin copper complex [1] displays only one absorption band in the long-wave region ( $\lambda_{\text{max}}$  600 nm). The presence of only one absorption band suggests that its molecule contains either a single chromophore or several similar chromophores, whereas molecules of other porphyrins comprise chromophores involving both coordination and ionic, as well as covalent, bonds between the metal and pyrrole nitrogen atom.

Covalent character of the copper–nitrogen bond is confirmed by high chromatographic mobility of the copper complex which is readily eluted even with benzene–heptane mixtures, and its  $R_f$  values strongly exceed those of tetraphenylporphyrin itself and its complexes with other metals. Tetraphenylporphyrin is very sensitive to acids adsorbed by silica gel from laboratory atmosphere: a sample of tetraphenylporphyrin applied to silica gel from solution turns green almost immediately. By contrast, tetraphenylporphyrin copper complex gives a stable red spot. The ability of tetraphenylporphyrin to undergo oxidation with copper(II) ions directly on a chromatographic plate was reported by us previously [2]. We found that only copper complex **II** is capable of passing through a  $\text{Cu}(\text{BF}_4)_2$  band applied onto the plate, whereas tetraphenylporphyrin **I** and its zinc complex were instantly adsorbed to form, respectively, bright green and almost black zones. Porphyrins can be regenerated from these zones by treatment with diethylamine or pyridine vapor, and just the initial porphyrins are formed in such a way, though tetraphenylporphyrin gives rise to traces of the copper complex. Analogous elution of tetraphenylporphyrin zinc complex through a  $\text{Cu}(\text{BF}_4)_2$  band also gave almost black chromatographically immobile complex, and treatment of the latter with diethylamine recovered initial red–violet zinc complex.

Nevertheless, we can speak about the stability of the copper complex to oxidation only under the above conditions. We previously noticed that perylene, which is known to be readily oxidized with  $\text{Cu}^{2+}$  ions, sometimes passed through the oxidative zone without formation of purple radical cation. The latter was formed only when the superimposed spots were slightly heated. Analogous superposition of spots of the copper complex and copper salt gives rise to a grayish–brown color after slight heating. The subsequent elution with toluene gradually extracts red copper complex from the spot. The fact that the copper complex remains unchanged during chromatography through a zone containing an oxidant indicates the absence of contact

between nonpolar substrate and polar oxidant rather than high stability toward oxidation.

Ionic copper(II) salts are reagents that make it possible to detect by chromatography not only porphyrins but also concomitant products in their synthesis. Compounds containing pyrrole fragments immediately turn black upon contact with  $\text{Cu}(\text{BF}_4)_2$  and, judging by insolubility of the products in organic solvents, undergo polymerization. The chromatograms were treated by drawing cross bands with a solution of copper salt [usually  $\text{Cu}(\text{BF}_4)_2$ ] in acetonitrile: black color appeared in places where contact with pyrrole compounds occurred. Pyrrole itself (even in the vapor phase) undergoes instantaneous polymerization to give deep black insoluble polymers in the presence of even traces of copper salts applied, e.g., to paper or fabric (vapor dyeing).

Porphyrin metal complexes are characterized by higher chromatographic mobility and stability as compared their complexes with other metals, which is important for the isolation of porphyrins. Demetalation of porphyrin metal complexes, including tetraphenylporphyrin complex **II**, is usually accomplished by the action of strong acids (e.g.,  $\text{H}_2\text{SO}_4$ ), which is not always convenient. We found that demetalation of copper complex **II** can be performed under considerably milder conditions, by treatment with  $\text{LiAlH}_4$  in THF. During the process the mixture turned blue, presumably due to intermediate formation of tetraphenylporphyrin radical anion. The subsequent treatment with water gave metal-free tetraphenylporphyrin. Demetalation of tetraphenylporphyrin zinc complex under analogous conditions occurred to an insignificant extent. Presumably, increase in the oxidative stability of the copper complex is accompanied by increase in its ability to undergo reduction.

Copper complexes of tetraphenylporphyrins having substituents in the benzene rings, e.g., 3-methoxy derivatives, are also stable to oxidation and are characterized by enhanced chromatographic mobility as compared to metal-free porphyrins. This may be interesting from the preparative viewpoint. Unlike tetraphenylporphyrin and its *para*-substituted derivatives which separate from reaction mixtures as crystalline materials, *meta*-substituted analogs having hydroxy, methoxy, or acetoxy groups remain in solution. Transformation of such porphyrins into the corresponding copper complexes facilitates their isolation by chromatography due to enhanced mobility and stability to oxidation.

Like porphyrins, dissolution of zinc phthalocyanine in acetonitrile in the presence of  $\text{Cu}(\text{BF}_4)_2$  leads to the

formation of dark red radical cation. The latter is thermally unstable, and heating of the solution to 60–70°C results in its complete decoloration. It is better to use a mixture of acetonitrile with nitromethane as solvent in analogous oxidation of metal-free phthalocyanine. However, copper phthalocyanine does not change under the same conditions, i.e., it is as resistant to oxidation with  $\text{Cu}^{2+}$  ions as tetraphenylporphyrin copper complex.

## EXPERIMENTAL

### 5,10,15,20-Tetraphenylporphyrinatocopper(II)

**(II).** *a. Reaction with copper powder.* Copper powder, 0.6 g, was added to a solution of 0.3 g of tetraphenylporphyrin **I** in 10 ml of *o*-xylene. The mixture was heated for 1 h under reflux. During that time, the initial crimson–red fluorescing porphyrin was converted into bright red nonfluorescing copper complex (TLC, silica gel, toluene) which was eluted with toluene almost at the front. The xylene solution was separated by decanting, the solvent was removed, and the residue was subjected to chromatography using toluene as eluent. The solvent was removed from the red eluate, and the residue was washed with hexane. Yield 0.31 g (91%). Electronic absorption spectrum (heptane):  $\lambda_{\text{max}}$  540 nm. Found, %: C 77.88; H 4.47; Cu 9.30; N 8.28.  $\text{C}_{44}\text{H}_{30}\text{N}_4$ . Calculated, %: C 77.91; H 4.46; Cu 9.37; N 8.26.

*b. Reaction with copper salts.* As described in *a*, heating of 0.3 g of tetraphenylporphyrin and copper(II) acetate, phthalimide, or phenylacetylde in DMF, followed by chromatographic isolation, gave tetraphenylporphyrin copper complex **II** in 90–95% yield. No complex **II** was formed by heating tetraphenylporphyrin **I** with powdered copper(II) oxide.

**Oxidation of tetraphenylporphyrin with copper(II) ions on a chromatogram.** Tetraphenylporphyrin was applied to a chromatographic plate to obtain a crimson band, and a band containing  $\text{Cu}(\text{BF}_4)_2$  was applied from a solution in acetonitrile to the same plate in front of the tetraphenylporphyrin band. Elution with toluene gave a bright green band which was treated with a drop of pyridine or with pyridine or diethylamine vapor. The plate was dried, and the bright red complex was washed off from the violet band (complex of pyridine with copper tetrafluoroborate) with toluene–hexane. The initial tetraphenylporphyrin was then eluted with toluene.

Copper complex **II** passed through the  $\text{Cu}(\text{BF}_4)_2$  without change. When a plate with superimposed spots

of  $\text{Cu}(\text{BF}_4)_2$  and copper complex **II** was heated to 30–40°C, weak gray color appeared. The subsequent elution with toluene gradually removed the initial red complex from the spot.

**Demetalation of tetraphenylporphyrin copper complex II with  $\text{LiAlH}_4$ .** Copper complex **II**, 0.34 g (0.05 mmol), was dissolved in 20 ml of THF, and 0.2 g of  $\text{LiAlH}_4$  was added under stirring. The original crimson–red solution turned blue. After 10 min, 5 ml of isopropyl alcohol was added, the mixture was diluted with 20 ml of toluene, acidified with aqueous acetic acid, and diluted with water, the organic phase was separated, and the solvent was removed. According to the TLC data, complex **II** almost completely disappeared, and tetraphenylporphyrin was formed. By chromatography (toluene–ethyl acetate, 4:1) we isolated 0.29 g (94%) of tetraphenylporphyrin **I**. Under analogous conditions, demetalation of tetraphenylporphyrin zinc complex occurred by 3–5%.

**Isolation of tetraphenylporphyrin.** A chromatographic column containing a layer with copper(II) tetrafluoroborate on the top was prepared by applying a solution of  $\text{Cu}(\text{BF}_4)_2$  in 2–3 ml of ethyl acetate and subsequent eluting with toluene. A light blue zone was thus formed at the top. A reaction mixture containing tetraphenylporphyrin and by-products was applied to the column from toluene solution. Tetraphenylporphyrin underwent oxidation (green zone), while by-products were transformed into black insoluble compounds. The column was then eluted with toluene containing several drops of pyridine, and bright-red nonfluorescing copper complex and then crimson tetraphenylporphyrin (exhibiting strong red fluorescence) were washed off. The eluate was washed with water and subjected to repeated chromatography. Copper complex **II** thus isolated was dissolved in THF and treated with  $\text{LiAlH}_4$ , and the blue solution was diluted with isopropyl alcohol and water, extracted with toluene, and passed through a thin layer of  $\text{Al}_2\text{O}_3$ . We isolated tetraphenylporphyrin **I** which was identified by comparing with an authentic sample. Electronic absorption spectrum (toluene),  $\lambda_{\text{max}}$ , nm: 510, 545, 595, 650.

## REFERENCES

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