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Coordination Dimer Based on Zinc Octaethylporphyrin and *meso*-Pyridyl-Substituted Porphyrin

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Abstract—New dimeric porphyrin was synthesized as a result of coordination interaction between 2,3,7,8,12,13,17,18-octaethylporphyrinatozinc(II) and 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(pyridin-4-yl)porphyrin. The new compound was characterized by spectral and TLC data, and equilibrium constant for the formation of molecular ensemble was determined.

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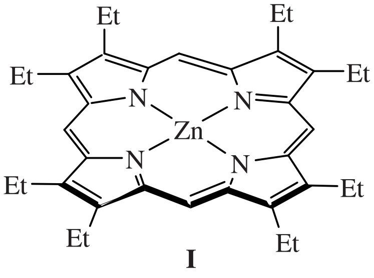
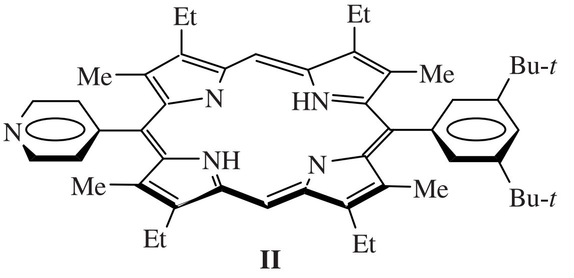
In the recent years, many publications were concerned with the design of self-organized supramolecular systems via coordination interactions between porphyrin metal complexes and porphyrins containing peripheral electron-donating groups [1, 2]. The results of studies performed in some laboratories in USA, Japan, Germany, and France showed that porphyrins and related compounds are quite promising for the design of supramolecular assemblies for highly effective directional transformation of light energy and creation of new materials for nonlinear optics, sensor systems, and membrane technology [2–5]. The main approach to such systems is based on studies on axial coordination to metal porphyrin complexes. It is known that the ability to take up extra ligands is very inherent to porphyrin complexes with triply charged metal cations (Al^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, etc.) and complexes with metals in the oxidation state 2^+ which have either considerable effective positive charge (Zn, Mg, etc.) or unpaired electrons (Fe, Co, Re, etc.). The charge on the metal ion and the nature of extra ligand are crucial factors for the formation of stable axial complexes by metal porphyrins [6].

We have synthesized dimeric porphyrin **III** as a result of coordination interaction between 2,3,7,8,12,13,17,18-octaethylporphyrinatozinc(II) (**I**) and 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(pyridin-4-yl)porphyrin **II**.

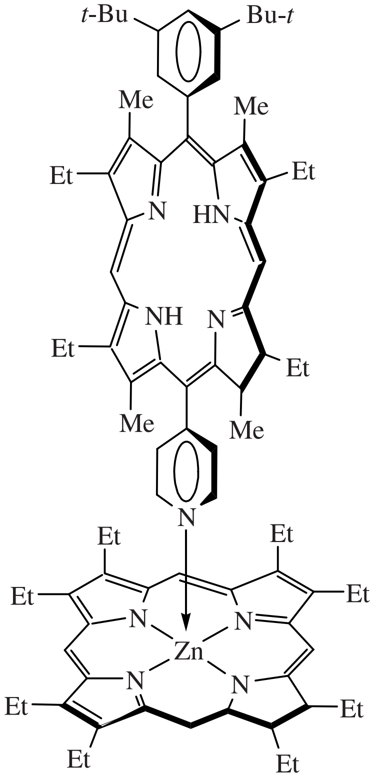


I



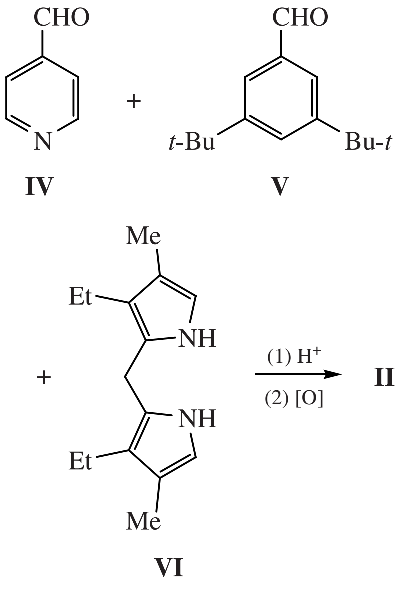
II

Compound **II** was obtained following a specially developed procedure by mixed condensation of bis(3-ethyl-4-methyl-1*H*-pyrrol-2-yl)methane (**VI**) with pyridine-4-carbaldehyde (**IV**) and 3,5-di-*tert*-butylbenzaldehyde (**V**) in methylene chloride in the presence of chloroacetic acid, followed by oxidation (without

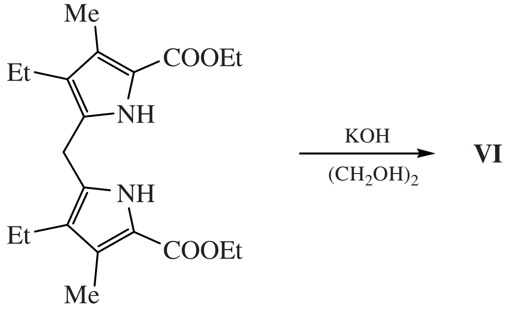


III

isolation) of the resulting porphyrinogen mixture with *p*-chloranil. The porphyrin mixture was separated by column chromatography.



Initial bis(3-ethyl-4-methyl-1*H*-pyrrol-2-yl)-methane (**VI**) was prepared from diethyl 5,5′-methylenebis(4-ethyl-3-methyl-1*H*-pyrrole-2-carb-oxylate) by simultaneous hydrolysis and decarboxyla-tion in ethylene glycol. Compound **VI** was then used in the condensation without additional purification. Apart from porphyrin **II**, the condensation gave symmetric 5,15-bis(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin and 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15-bis(pyridin-4-yl)-porphyrin as by-products.



Systematic studies on the ability of metal porphyrins to coordinate nitrogen-containing extra ligands showed that zinc porphyrins give rise to fairly stable five-coordinate complexes with pyridine, piperidine, and other nitrogen-containing bases. Such complexes are characterized by a considerable red shift of absorption bands in the electronic spectra (Fig. 1). The stability constants (K_s) of extra coordination compounds derived from zinc porphyrins with planar macroring structure range from 4×10^3 to 6×10^3 l mol^{-1}, depending on the substituents [2, 7, 8]. Therefore, we were able to detect molecular complex **III** by spectral methods. Complex **III** is formed via donor–acceptor interaction between octaethylporphyrin zinc complex **I** and 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(pyridin-4-yl)porphyrin (**II**). When solutions of porphyrins **I** and **II** with a

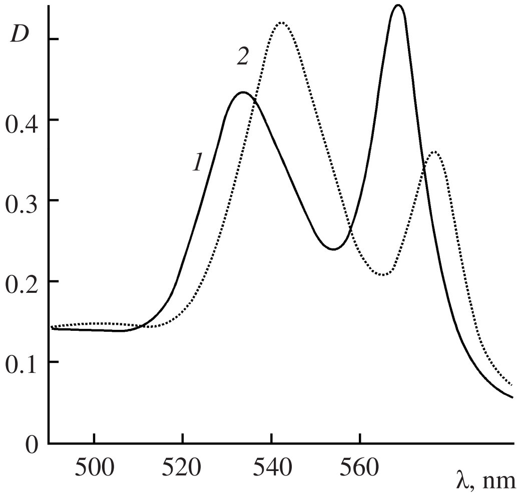


Fig. 1. Electronic absorption spectra of 2,3,7,8,12,13,17,18-octaethylporphyrinatozinc(II) (**I**) in (*1*) benzene and (*2*) in benzene containing 0.2 mol l^{-1} of pyridine.

Electronic absorption spectra of porphyrins **I–III** in benzene at 298 K and their R_f values

Comp. no.	λ_{max}, nm (log ε)					R_f[a]
I	620 (3.74)	568 (3.86)	535 (4.04)	499 (4.15)	400 (5.25)	–
II	625 (3.61)	573 (3.79)	540 (3.96)	507 (4.36)	407 (5.39)	0.21
Zn(I)	–	568 (4.12)	530 (3.93)	–	403 (5.19)	0.85
III		575	539	506	412	0.46

[a] Benzene–chloroform (1 : 1) + 2% of EtOH.

concentration of (1–2.5)×10^{-5} M were mixed at a ratio of 1 : 2 and kept in an inert atmosphere (argon), new bands appeared in the electronic absorption spectra. By analytical thin-layer chromatography we succeeded in separating the mixture into three zones, two of which corresponded to zinc complex **I** and free ligand **II**. The second intermediate zone was isolated and characterized by electronic spectra (Fig. 2). The positions of the absorption maxima and R_f values are given in table. Addition of excess nitrogen-containing reagent, e.g., pyridine, leads to decomposition of the molecular assembly. The spectrum of the mixture thus obtained is superposition of the spectra of porphyrin **II** and pyridine complex of zinc porphyrin **I**. According to the TLC data, the chromatogram contained no third zone. The stability constant of coordination dimer **III** (Zn-**I** + **II** ↔ **III**) was estimated on the basis of the reactant concentrations used in the spectral measurements: $K_s = 9 \times 10^6$ l mol^{-1}.

EXPERIMENTAL

The purity of the synthesized compounds was checked by TLC on aluminum plates with a fixed layer of silica gel (Merck F_{254}, layer thickness 0.5 mm; $CHCl_3$–C_6H_6–C_2H_5OH) and by spectrophotometry. The electronic absorption spectra of porphyrins **I–III** are given in table.

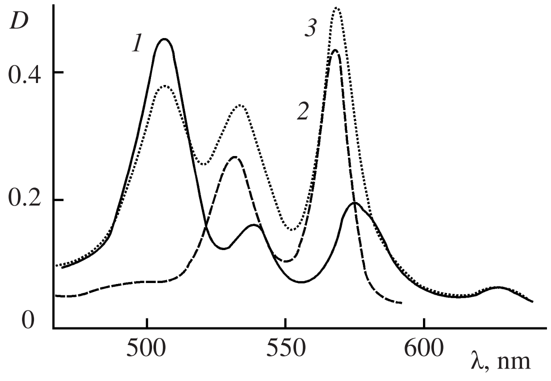


Fig. 2. Electronic absorption spectra in benzene of (*1*) 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(pyridin-4-yl)porphyrin, (*2*) 2,3,7,8,12,13,17,18-octaethylporphyrinatozinc(II) (**I**), and (*3*) coordination dimer **III**.

The extra coordination process was studied at 293.15±0.1 K by spectrophotometry using a Specord M-400 instrument (50-ml cells with a path length of 100 mm). A required volume of extra ligand solution was added with the aid of a microsyringe to a solution of metal porphyrin. The volume of the reaction mixture increased during the process by no more than 0.05%. The ^{1}H NMR spectra were recorded on a Bruker-200 spectrometer in $CDCl_3$; the chemical shifts were measured relative to tetramethylsilane as internal reference. The solvents used (benzene, chloroform, and pyridine) were preliminarily purified according to standard procedures [9, 10].

2,3,7,8,12,13,17,18-Octaethylporphyrin was prepared as described in [11]. It was purified by chromatography on aluminum oxide of activity grades II and III (eluent chloroform). Octaethylorphyrin zinc complex **I** was synthesized by reaction of 2,3,7,8,12,-13,17,18-octaethylporphyrin with excess zinc(II) acetate in boiling dimethylformamide. The complex was purified by chromatography on aluminum oxide of activity grade **III** using chloroform as eluent. ^{1}H NMR spectrum, δ, ppm: 10.07 s (4H, *meso*-H), 3.98 q (16H, CH_2CH_3), 1.70 t (24H, CH_2CH_3).

Bis(3-ethyl-4-methyl-1*H*-pyrrol-2-yl)methane (VI). A mixture of 1 g of diethyl 5,5-methylenebis(4-ethyl-3-methyl-1*H*-pyrrole-2-carboxylate), 0.1 g of hydrazine sulfate, 1 g of potassium hydroxide, and 30 ml of ethylene glycol was heated to the boiling point, maintained boiling for 1 h, poured into 200 ml of water, and kept for 3 h at room temperature. The precipitate was filtered off, washed with water, and dried at room temperature. Yield 0.56 g. Compound **VI** was used in further synthesis without additional purification.

5-(3,5-Di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(pyridin-4-yl)porphyrin (II). A solution of 0.45 g of chloroacetic acid in 20 ml of methylene chloride was added under stirring at room temperature in carbon dioxide atmosphere to a solution of 0.56 g of compound **VI**, 0.13 g of pyridine-4-carbaldehyde, and 0.26 g of 3,5-di-*tert*-butylbenzaldehyde in 150 ml of methylene chloride. The mixture was stirred for 4 h with protection from direct light, a solution of 0.9 g of *p*-chloranil in 20 ml of THF was added, the mixture was stirred for 16 h at room temperature, and the solvent was distilled off to dryness on a rotary evaporator. The residue was treated with a 5% solution of sodium hydroxide, and the precipitate was filtered off, washed with water, and dried at 70°C in air. The product (a mixture of porphyrins) was dissolved in chloroform, and the solution was subjected to chromatography on aluminum oxide of activity grade III using chloroform as eluent. The first fraction contained 5,15-bis(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, the second fraction contained the desired 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(pyridin-4-yl)porphyrin, and from the third fraction we isolated 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15-bis(pyridin-4-yl)porphyrin. The second fraction was concentrated to a small volume and was subjected to repeated chromatography on aluminum oxide of activity grade III using chloroform as eluent, the eluate was evaporated, and the product was precipitated with methanol, filtered off, washed with methanol, and dried at 70°C in air. Yield 0.20 g (22%). Electronic absorption spectrum ($CHCl_3$), λ_{max}, nm (logε): 625 (3.68), 573 (4.06), 540 (3.98), 507 (4.36), 408 (5.39). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 10.20 s (2H, *meso*-H), 8.95 d (2H, α-H), 8.06 d (2H, β-H), 7.84 d (2H, *o*-H), 7.74 t (1H, *p*-H), 3.95 q (8H, CH_2CH_3), 2.46 s (6H, 13,17-CH_3), 2.39 s (6H, 3,7-CH_3), 1.71 t (12H, CH_2CH_3), 1.49 s (18H, *t*-Bu), –2.52 s (2H, NH).

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