## Synthesis of Palladium and Nickel Complexes with Octaphenyltetraazaporphyrins

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**Abstract**—Palladium(II) and nickel(II) complexes with octaphenyltetraazaporphyrin, octakis(4-bromophenyl)tetraazaporphyrin, and octakis(4-nitrophenyl)tetraazaporphyrin were obtained by reactions of octaphenyltetraazaporphyrin, Mg octaphenyltetraazaporphyrin, octakis(4-bromophenyl)tetraazaporphyrin, and octakis(4-nitrophenyl)tetraazaporphyrin with palladium(II) and nickel(II) chlorides in DMF.

At present palladium(II) complexes with porphyrins and phthalocyanines have found use as catalysts and highly effective sensors [1].

There are no published data on palladium(II) complexes with octaphenyltetraazaporphyrins. A nickel(II) complex with octaphenyltetraazaporphyrin was obtained earlier [2] from the ligand and nickel(II) acetate in pyridine. Nickel(II) complexes with octakis(4bromophenyl)tetraazaporphyrin and octakis(4-nitrophenyl)tetraazaporphyrin have not been described.

The aim of the present work was to develop convenient methods of synthesis of palladium and nickel complexes of phenyl-substituted tetraazaporphyrins. We studied the coordination reactions of octaphenyl-tetraazaporphyrin (I) and its magnesium complex (II), octakis(4-bromophenyl)tetraazaporphyrin (III), and octakis(4-nitrophenyl)tetraazaporphyrin (IV) with palladium(II) and nickel(II) chlorides in DMF, following reaction progress by spectrophotometry.

Our studies showed that palladium(II) chloride reacts with octakis(4-nitrophenyl)tetraazaporphyrin (**IV**) in DMF for 2 days at room temperature, and the reaction time with octakis(4-bromophenyl)tetraazaporphyrin (**III**) increases to 80 days. For faster complex formation of octaphenyltetraazaporphyrins with PdCl<sub>2</sub>, the reactions were performed in boiling DMF.

Complex V of palladium with octaphenyltetraazaporphyrin is formed in boiling DMF within 1 h (porphyrazine: metal salt molar ratio 1:20). Introduction of bromine atoms and electron-acceptor nitro groups into benzene rings accelerates coordination with  $PdCl_2$ in DMF. Thus, compound VI is formed in boiling DMF within 10 min (reagent molar ratio 1:20), and compound **VII**, within 20 s (reagent molar ratio 1:10).



Electronic absorption spectra of palladium(II), nickel(II), and magnesium complexes of phenyl-substituted tetraazaporphyrins in chloroform,  $\lambda$ , nm (log  $\epsilon$ )

Complex	Band I	Band II	Soret band
$\begin{array}{c} \mathbf{I} - \mathbf{Pd}^{2+} \\ \mathbf{III} - \mathbf{Pd}^{2+} \\ \mathbf{IV} - \mathbf{Pd}^{2+} \\ \mathbf{I} - \mathbf{Ni}^{2+a} \\ \mathbf{I} - \mathbf{Ni}^{2+} \\ \mathbf{III} - \mathbf{Ni}^{2+} \\ \mathbf{IV} - \mathbf{Ni}^{2+} \\ \mathbf{IV} - \mathbf{Ni}^{2+} \\ \mathbf{I} - \mathbf{Mg}^{2+a} \end{array}$	616 (4.28)	560 (3.83)	350 (4.26)
	619 (4.92)	565 (4.35)	350 (4.87)
	620 (4.92)	565 (4.40)	354 (4.86)
	633 (4.32)	583 (3.75)	377 (4.25)
	630 (4.38)	580 (3.80)	370 (4.37)
	633 (4.95)	580 (4.28)	375 (4.90)
	634 (4.96)	585 (4.30)	375 (4.92)
	639 (4.91)	595 (4.30)	379 (4.86)

<sup>a</sup> Data of [2].

The effect of electron-acceptor substituents on the rate of tetraazaporphyrin coordination with metal salts in strongly coordinating basic solvents was studied earlier [3–5]. The rate of complex formation of bromo and nitro derivatives of porphyrazines increases as the result of enhanced polarization of N–H bonds in the reaction center [4, 5].

Nickel(II) chloride, having a smaller molecular radius compared to  $PdCl_2$ , readily coordinates with nitro- and bromo-substituted octaphenyltetraazaporphyrins in DMF at room temperature. Thus, nitro derivative **X** is formed at 20°C within 20 min (reagent molar ratio 1:10) and compound **IX**, within 20 h (reagent molar ratio 1:20). Nickel(II) chloride reacts with octaphenyltetraazaporphyrin (**I**) in DMF at room temperature for 5 days, and the reaction time decreases to 1 min on boiling (reagent molar ratio 1:10).

It was found that palladium(II) and nickel(II) complexes with octaphenyltetraazaporphyrins can be obtained from magnesium(II) complex and metal chlorides in boiling DMF by metal exchange. In this case, the procedures of synthesis of compounds V and VIII are simplified (complex II obtained by Linstead's procedure is used, the amount of the solvent is dereased).

The electronic absorption spectra of the synthesized palladium(II) and nickel(II) complexes with octaphenyltetraazaporphyrins **I**, **III**, and **IV** in chloroform are given in the table, together with the spectra of the nickel(II) and magnesium complexes obtained earlier.

When passing from magnesium to nickel(II) and palladium(II) octaphenyltetraazaporphyrins, a hypsochromic shift of bands is observed in the electronic absorption spectra (spectral criterion of bond strength) [6]. This shift is indicative of strengthening of  $M \leftarrow N$   $\sigma$  bonds (for all the porphyrazines presented) and also of the M $\rightarrow$ N back dative  $\pi$  bond [for nickel(II) and palladium(II) complexes]. The electronic absorption spectra of nickel(II) and palladium(II) complexes with bromo- and nitro-substituted porphyrazines are batochromically shifted by as little as 1–4 nm with respect to the spectra of nickel(II) and palladium(II) octaphenyltetraazaporphyrins, and bands are stronger.

Solutions of palladium complexes with bromo and nitro derivatives of octaphenyltetraazaporphyrin in benzene and chloroform fluoresce in light (the color changes from bluish green to dark red).

Nitro substitution in porphyrin molecules is known [7] to increase their resistance to oxidation, whereas bromine substitution in tetraazaporphyrin molecules increases their photochemical stability [8].

Complex **VII** of palladium(II) with octakis(4-nitrophenyl)tetraazaporphyrin appeared to be highly resistant to sulfuric acid. A solution of complex **VII** in 100% H<sub>2</sub>SO<sub>4</sub> did not decompose within 1 year at room temperature (the electronic absorption spectrum remained unchanged). The half-life of nickel complex **X** in 100% H<sub>2</sub>SO<sub>4</sub> was 3 months at room temperature.

## EXPERIMENTAL

The electronic absorption spectra were recorded on a Specord M-40 instrument. Thin-layer chromatography was carried out on Silufol plates.

Magnesium octaphenyltetraazaporphyrin complex (II) was synthesized by the procedure in [9].

**Octaphenyltetraazaporphyrin** (I). A solution of 0.1 g of complex II in 50 ml of trifluoroacetic acid, was allowed to stand at room temperature for 2 h. Dimethylformamide, 40 ml, was then added, and the mixture was poured into cold distilled water, the precipitate was filtered off and washed with a solution of NaHCO<sub>3</sub> (to neutral reaction), water, and ethanol, and dried. Yield 0.07 g (70%).

Octakis(4-bromophenyl)tetraazaporphyrin (**III**) and octakis(4-nitrophenyl)tetraazaporphyrin (**IV**) were synthesized by the procedures in [10, 11].

**Palladium(II) octaphenyltetraazaporphyrin** (V). *a*. A solution of 0.1 g of compound I and 0.19 g of  $PdCl_2$  (molar ratio 1:10) in 40 ml of DMF was heated under reflux for 30 min, 0.19 g of  $PdCl_2$  was then added and refluxing was continued for an additional 30 min. After cooling, the mixture was poured into water, the precipitate was filtered off, washed with water, dried in air, and subjected to chromatography on alumina (eluent pyridine–diethyl ether, 1:4). Yield 0.073 g (66%),  $R_f$  0.67 (CHCl<sub>3</sub>-CCl<sub>4</sub>, 1:1).

b. A solution of 0.1 g of compound **II** and 0.19 g of PdCl<sub>2</sub> (molar ratio 1:10) in 20 ml of DMF was refluxed for 30 min, 0.19 g of PdCl<sub>2</sub> was then added and refluxing was continued for an additional 30 min. After cooling, the mixture was poured into water, the precipitate was filtered off, washed with water, dried in air, and subjected to chromatography on alumina (eluent pyridine–diethyl ether, 1:4). Yield 0.087 g (80%),  $R_f$  0.67 (CHCl<sub>3</sub>–CCl<sub>4</sub>, 1:1). Found, %: C 75.38; H 3.08; N 10.87; Pd 10.36. C<sub>64</sub>H<sub>40</sub>N<sub>8</sub>Pd. Calculated, %: C 75.44; H 3.14; N 10.87; Pd 10.44.

**Palladium(II) octakis(4-bromophenyl)tetraazaporphyrin (VI).** A solution of 0.1 g of compound **III** and 0.23 g of PdCl<sub>2</sub> (molar ratio 1:20) in 20 ml of DMF was refluxed for 10 min, cooled, poured into water, the precipitate was filtered off, washed with water, dried in air, subjected to chromatography on silica gel (chloroform), and reprecipitated from m ethanol. Yield 0.1 g (90%),  $R_f$  0.41 (CCl<sub>4</sub>), 0.77 (CHCl<sub>3</sub>-CCl<sub>4</sub>, 1:4). Found, %: C 46.38; H 1.88; Br 38.44; N 6.69; Pd 6.36. C<sub>64</sub>H<sub>32</sub>Br<sub>8</sub>N<sub>8</sub>Pd. Calculated, %: C 46.35; H 1.93; Br 38.54; N 6.76; Pd 6.42.

**Palladium(II) octakis(4-nitrophenyl)tetraazaporphyrin (VII).** A solution of 0.1 g of compound **IV** and 0.14 g of PdCl<sub>2</sub> (molar ratio 1:10) in 15 ml of DMF was refluxed for 20 s, cooled, poured into water, the precipitate was filtered off, washed with water, dried in air, subjected to chromatography on silica gel (acetone), and reprecipitated from methanol. Yield 0.1 g (93%),  $R_f$  0.73, (CHCl<sub>3</sub>). Found, %: C 55.44; H 2.28; N 16.08; Pd 7.59. C<sub>64</sub>H<sub>32</sub> · N<sub>16</sub>O<sub>16</sub>Pd. Calculated, %: C 55.42; H 2.31; N 16.15; O 18.45; Pd 7.67.

Nickel(II) octaphenyltetraazaporphyrin (VIII). a. A solution of 0.1 g of compound I and 0.15 g of NiCl<sub>2</sub> (molar ratio 1:10) in 35 ml of DMF was refluxed for 1 min, cooled, poured into water, the precipitate was filtered off, washed with water, dried in air, and subjected to chromatography on alumina (eluent pyridine–diethyl ether 1:4). Yield 0.83 g (80%),  $R_f$  0.69 (CHCl<sub>3</sub>–CCl<sub>4</sub>, 1:1).

b. A solution of 0.1 g of compound **II** and 0.14 g of NiCl<sub>2</sub> (molar ratio 1:10) in 20 ml of DMF was refluxed for 1 min, cooled, poured into water, the precipitate was filtered off, washed with water, dried in air, and subjected to chromatography on alumina (eluent pyridine–diethyl ether 1:1). Yield 0.094 g (90%),  $R_f$  0.69 (CHCl<sub>3</sub>–CCl<sub>4</sub>, 1:1). Found, %: C 79.08; H 3.24; N 11.45; Ni 5.98. C<sub>64</sub>H<sub>40</sub>N<sub>8</sub>Ni. Calculated, %: C 79.11; H 3.32; N 11.53; Ni 6.04.

Nickel(II) octakis(4-bromophenyl)tetraazaporphyrin (IX). A solution of 0.1 g of compound III and 0.17 g of NiCl<sub>2</sub> (molar ratio 1:20) in 20 ml of DMF was allowed to stand at 20°C for 20 h, after which it was poured into water, the precipitate was filtered off, washed with water, dried in air, subjected to chromatography on silica gel (chloroform), and reprecipitated from methanol. Yield 0.096 g (92%),  $R_f$  0.78 (CHCl<sub>3</sub>-CCL<sub>4</sub>, 1:4). Found, %: C 47.68; H 1.92; Br 39.70; N 6.88; Ni 3.58. C<sub>64</sub>H<sub>32</sub>Br<sub>8</sub>N<sub>8</sub>Ni. Calculated, %: C 47.72; H 2.00; Br 39.68; N 6.96; Ni 3.64.

Nickel(II) octakis(4-nitrophenyl)tetraazaporphyrin complex (X). A solution of 0.1 g of compound IV and 0.101 g of NiCl<sub>2</sub> (molar ratio 1:10) in 15 ml of DMF was allowed to stand at 20°C for 20 min, after which it was poured into water, the precipitate was filtered off, washed with water, dried in air, subjected to chromatography on silica gel (acetone), and reprecipitated from methanol. Yield 0.098 g (93%),  $R_f$  0.75 (CHCl<sub>3</sub>). Found, %: C 57.26; H 2.35; N 16.66; Ni 4.33. C<sub>64</sub>H<sub>32</sub>N<sub>16</sub>NiO<sub>16</sub>. Calculated, %: C 57.38; H 2.41; N 16.73; Ni 4.38.

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