## COORDINATION COMPOUNDS

# Palladium(II) Octaalkylporphyrinates: Synthesis and Spectral Properties

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Received May 21, 2007

**Abstract**—Palladium 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrinate (**I**) and its 5,15-diaza (**II**), diphenyl (**III**), and di(4-bromophenyl) (**IV**) derivatives were synthesized by the complex formation reaction of palladium(**II**) chloride with corresponding tetrapyrrole ligands in dimethylformamide, and their spectral properties were studied.

**DOI:** 10.1134/S003602360809009X

Porphyrins are widely used in design of new materials, sensors, and molecular measuring devices of various nature. Interest in this class of tetrapyrrole compounds is mainly caused by the following factors: (1) they are chromophores, which can be used as probes for monitoring the processes in the systems to be studied; (2) they are macrocycles with unique complexation properties; (3) they are convenient building blocks, which can be selectively modified to produce compounds in which required reaction centers are arranged in certain spatial orientation with respect to one another [1, 2].

The introduction of metals into porphyrins significantly changes their spectral characteristics. In particular, as distinct from initial compounds, Pd(II) complexes with porphyrins begin to phosphoresce even at room temperature [3]. This makes it possible to use palladium porphyrinates in molecular electronics (as elementary cells for storage, transformation, transmission, and mapping of information [4]) and analytical biochemistry (as labels for luminescent immunoassay in determination of different biologically active compounds) [5].

In this work, with the aim of designing porphyrincontaining photochromic systems capable of responding to the external impact, we synthesized palladium 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrinate (I) and its 5,15-diaza (II), diphenyl (III), and di(4bromophenyl) (IV) derivatives by the complex formation reaction of Pd<sup>2+</sup> with corresponding tetrapyrrole ligands in dimethylformamide (DMF) and studied their spectral properties.



### **EXPERIMENTAL**

Porphyrin ligands **V–VIII** were synthesized as described in [6]. The course of the reaction of the metal cation with the porphyrin ligand was monitored by spectrophotometry and thin-layer chromatography (**TLC**). The electronic absorption spectra were recorded in chloroform on a Cary-100 spectrophotometer at 298 K. The electron impact mass spectra were recorded on an MX-1310 mass spectrometer at an ionizing electron energy of 70 eV and an ionization chamber temperature of 150–200°C. Analysis by the TLC method was carried out on Silufol (G/UV<sub>254</sub>) plates, a hexane–chloroform (1 : 1) mixture was used as the eluent. The IR spectra were recorded as KBr discs on a Specord M-80 spectro-photometer in the range 4500–400 cm<sup>-1</sup>. Solvents were purified as described in [7].

## Synthesis of Pd<sup>2+</sup> Porphyrinates

**Palladium(II)** 3,7,13,17-Tetramethyl-2,8,12,18tetrabutylporphyrinate (I). A mixture of 0.05 g (0.085 mmol) of porphyrin V and 0.15 g of PdCl<sub>2</sub> (0.85 mmol) was dissolved in 30 mL of DMF and heated under reflux for 1 min. The reaction mixture was cooled and diluted with 50 mL of water. The resulting precipitate was filtered off, washed with water, dried, and chromatographed on neutral alumina (elution with hexane–chloroform (1 : 1)). The yield was 0.031 g (0.045 mmol), 53%.  $R_f = 0.70$ .

For  $PdC_{40}N_4$ , anal. calcd. (wt %): C, 69.10; N, 8.06; H, 7.54.

Found (wt %): C, 69.06; N, 8.02; H, 7.51.

MS: m/z = 693.1 (694.3 (calcd.)),  $I_{rel} = 71\%$ , [M<sup>+</sup>].

IR, cm<sup>-1</sup>: 3057 w, 2923 m, 2851 w, 1809 w, 1634 m, 1565 w, 1543 w, 1472 m, 1429 m, 1352 s, 1314 m, 1237 w, 1210 w, 1159 w, 1073 s, 1036 m, 1014 s, 946 w, 866 w, 833 w, 795 s, 752 s, 724 m, 715 m, 648 m, 459 m, 412 w.

**Palladium(II)** 3,7,13,17-Tetramethyl-2,8,12,18tetrabutyl-5,15-diazaporphyrinate (II). A mixture of 0.05 g of porphyrin VI and 0.15 g of PdCl<sub>2</sub> (molar ratio 1 : 10) was heated under reflux in 50 mL of DMF for 3 min. The reaction mixture was cooled and chromatographed on neutral alumina (elution with hexane–chloroform 1 : 1). The yield was 0.014 g (0.019 mmol), 24%.  $R_f = 0.75$ .

For  $PdC_{38}H_{50}N_6$  anal. calcd. (wt %): C, 65.52; N, 12.07; H, 7.18.

Found (wt %): C, 65.47; N, 12.01; H, 7.13.

MS: m/z = 695.4 (696.3 (calcd.)),  $I_{rel} = 64\%$ , [M<sup>+</sup>].

IR, cm<sup>-1</sup>: 2997 w, 2929 w, 2833 w, 1632 w, 1606 s, 1574 w, 1541 w, 1505 s, 1462 m, 1440 m, 1410 w, 1353 s, 1311 w, 1288 m, 1247 s, 1175 s, 1106 w, 1075 w, 1016 s, 1009 s, 849 w, 811 m, 799 m, 714 m, 640 w, 608 m, 541 m, 438 w, 408 w.

In addition to the major product (porphyrinate II), the 3 : 2 complex of porphyrinate II with  $PdCl_2(\mathbf{X})$  was isolated from the reaction mixture by column chromatography on neutral alumina (elution with hexane-chloroform 1 : 2). The yield was 0.005 g (0.002 mmol), 2.4(%.  $R_f = 0.15$ .

For  $Pd_5C_{114}H_{150}N_{18}Cl_4$  anal. calcd. (wt %): C, 56.02; N, 10.32; H, 6.14.

Found (wt %): C, 55.91; N, 10.21; H, 6.03.

**Palladium(II)** 3,7,13,17-Tetramethyl-2,8,12,18tetrabutyl-5,15-diphenylporphyrinate (III). A mixture of 0.05 g of porphyrin VII and 0.12 g of PdCl<sub>2</sub> (molar ratio 1 : 10) was boiled in 60 mL of DMF for 15 s. The reaction mixture was cooled and chromatographed on neutral alumina (elution with hexane–chloroform 1 : 1). The yield was 0.043 g (0.051 mmol), 85%.  $R_f = 0.77$ .

For  $PdC_{52}H_{60}N_4$  anal. calcd. (wt %): C, 73.30; N, 6.61; H, 7.14.

Found (wt %): C, 73.65; N, 6.57; H, 7.11.

MS: m/z = 844.9 (846.3 (calcd.)),  $I_{rel} = 82\%$ , [M<sup>+</sup>].

IR, cm<sup>-1</sup>: 3186 w, 3051 w, 2959 s, 2927 s, 2867 m, 1734 w, 1670 w, 1634 w, 1553 w, 1452 s, 1388 s, 1372 s, 1309 w, 1264 s, 1235 s, 1153 s, 1106 m, 1058 s, 1015 s, 990 s, 938 w, 832 s, 754 w, 732 m, 716 m, 611 w, 468 w, 451 w, 425 w.

**Palladium(II)** 3,7,13,17-Tetramethyl-2,8,12,18tetrabutyl-5,15-4-dibromophenylporphyrinate (IV). A mixture of 0.05 g of porphyrin VIII and 0.1 g of PdCl<sub>2</sub> (molar ratio 1 : 10) was heated in 40 mL of DMF to boiling. The reaction was instantaneous. The reaction mixture was cooled and chromatographed on neutral alumina (elution with hexane–chloroform 1 : 1). The yield was 0.042 g (0.042 mmol), 76%.  $R_f$  = 0.78.

For  $PdC_{52}H_{58}N_4Br_2$  anal. calcd. (wt %): C, 62.13; N, 5.57; H, 5.82.

Found (wt %): C, 62.09; N, 5.54; H, 5.78.

MS: m/z = 1003.1 (1004.2 (calcd.)),  $I_{rel} = 67\%$ , [M<sup>+</sup>].

IR, cm<sup>-1</sup>: 2922 w, 2851 w, 1732 w, 1645 w, 1603 w, 1570 m, 1485 s, 1450 w, 1408 s, 1352 s, 1314 m, 1287 w, 1244 m, 1208 w, 1181 m, 1140 w, 1068 s, 945 m, 883 m, 821 s, 795 s, 715 m, 695 m, 569 w, 528 w.

### **RESULTS AND DISCUSSION**

According to the mechanism of coordination of porphyrins by metal cations in solutions, metalloporphyrins are formed upon the bimolecular collision of the porphyrin ligand and solvated salt (IX) [9]. The complex formation rate depends on two factors: (1) the strength of the N–H bond of the porphyrin reaction center and (2) donor–acceptor interaction of the nitrogen atoms of porphyrin with the metal cation of the salt. The effect of these factors can vary as a function of specific conditions of the process.

Our spectrophotometric study of complex formation of the Pd(II) cation with porphyrin ligands **V–VIII** in DMF by the sampling method [10] showed that Pd(II) porphyrinates are formed faster from porphyrins **VII** and **VIII** than from porphyrin **V**. It is likely that electron-donating aryl (aryl =  $C_6H_5$ , 4-Br $C_6H_4$ ) substituents in the 5- and 15-positions of the porphyrin macrocycle increase the electron density on the tertiary nitrogen atoms of the macrocycle and, hence, enhance the coordination interaction of the cation of the solvate complex with porphyrin in the transition state. As a result, the reactivity of porphyrins **VII** and **VIII** during complex formation with PdCl<sub>2</sub> increases as compared to mesounsubstituted porphyrin **V**.

A decrease in the reactivity of VI with respect to  $PdCl_2$  is presumably explained by the electronic effect of the meso-substituent: the electron-accepting nitrogen atoms decrease the electron density on the tertiary nitrogen atoms of the porphyrin reaction center and, thus, suppress the coordination interaction of the cation

of the solvate complex with the porphyrin in the transition state.

A change in the reaction rate in going from V to VI, VII, and VIII is evidence that the decisive contribution to the energy of the transition state of the complexforming process is made by the coordination interaction between the metal cation and the porphyrin nitrogen atoms.

Elemental analysis data, mass spectra, and electronic absorption and IR spectra are consistent with the structures of the synthesized compounds. The hypsochromic shift of absorption bands in the electronic spectra of palladium porphyrinate **II** as compared with Cu<sup>2+</sup> 3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-diaza-porphyrinate (**XI**) is explained by the enhancement of the  $\pi$ -dative interaction between the metal ion and the porphyrin macrocycle of the  $d_{\pi}$ - $e_{e}(\pi^{*})$  type (table).

Formation of metalloporphyrin from the porphyrin ligand is accompanied by an increase in the symmetry of a molecule. This is due to the substitution of a metal atom for the two hydrogen atoms of the coordinating center of the tetrapyrrole macrocycle and to equalization of the geometric parameters of the pyrrole moieties of porphyrin. A change in the molecular geometry upon complexation clearly manifests itself in the IR spectra: the number of bands decreases due to degeneracy of odd in-plane vibrations. The spectra of porphyrinates I-IV show the following characteristic changes as compared with porphyrin ligand V studied in [11]: (1) the bands due to N-H vibrations (stretching vibrations at 3320 cm<sup>-1</sup> and bending vibrations at 965 and 685 cm<sup>-1</sup>) disappear; (12) new strong "metal-sensitive" bands appear at  $\approx 1015$  cm<sup>-1</sup>, which, according to [12] are due to Pd-N vibrations. In addition, formation of metalloporphyrin gives rise to considerable changes in the intensity of skeletal vibrations of the pyrrole rings of porphyrin at 625 (I) and 715 (II) cm<sup>-1</sup>. A sharp decrease in the band I intensity is accompanied by the buildup of band II. The frequencies typical of vibrations of periph-

Electronic absorption spectra of  $Pd^{2+}$  porphyrinates in chloroform

Compound	Band I $\lambda$ , nm (log $\epsilon$ )	Band II $\lambda$ , nm (log $\epsilon$ )	Soret band $\lambda$ , nm (log $\epsilon$ )
Ι	558 (3.79)	527 (4.11)	412 (5.21)
II	559 (3.48)	525 (4.10)	420 (5.10)
III	553 (4.38)	519 (4.06)	412 (5.19)
IV	553 (3.60)	528 (4.31)	414 (5.41)
X	560 (3.41)	527 (4.03)	423 (4.98)
XI*		587 (4.96)	384 (4.99)

\* Taken from [8].

eral substituents of the macrocycle remain almost unaltered.

We found that palladium chloride reacts with diazaporphyrin **VI** to form, in addition to compound **II** (the complex in which the metal ion is located in the plane of the macrocycle), complex **X**, in which  $Pd^{2+}$  ions are bound to the mesoatoms of the macrocycle. Elemental analysis supports the formation of the 3 : 2 complex of porphyrinate **II** with  $PdCl_2$  (**X**). Analogous palladium chloride complexes with tetrapyridylporphyrin were described in [13]. Good outlook for compounds of this type is determined by the selectivity and high sensitivity of porphyrins to low-energy impacts, which create conditions for controlling their photophysical and electrochemical properties.



## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 05-03-32055 and 06-03-81001-Bel) and program no. 7 "Chemistry and Physical Chemistry of Supramolecular Systems and Clusters" of the Division of Chemistry and Materials Science of the RAS.

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