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β-Bromo-Substituted Palladium(II) Tetraphenylporphyrins. Synthesis and Spectral Properties

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Abstract—Bromination of (5,10,15,20-tetraphenylporphyrinato)palladium(II) and [5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato]palladium(II) with *N*-bromosuccinimide in chloroform–dimethylformamide and chloroform afforded mono-, tetra-, and octabromo derivatives substituted at the pyrrole rings. The products were identified by electronic absorption, ^{1}H NMR, and mass spectra and elemental analyses.

Keywords: Palladium(II) tetraphenylporphyrins, β-bromo-substituted palladium(II) tetraphenylporphyrins, metal exchange reactions, bromination, complex formation

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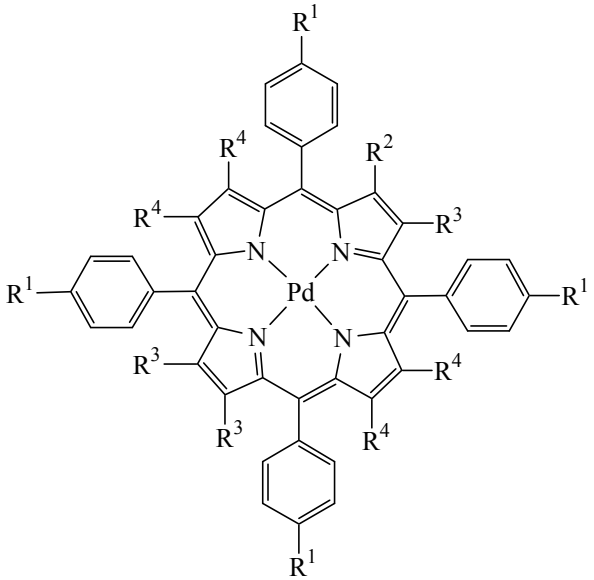
Introduction of bromine atoms into porphyrin molecules gives rise to compounds possessing new practically useful properties, in particular good solubility in organic solvents and high stability of their metal complexes in proton-donor medium. Bromo-substituted porphyrins attract interest as substrates for further chemical transformations. It is known that porphyrins exhibit biological activity and that their metal complexes show catalytic activity. Of particular interest are palladium porphyrin complexes that are used as optical materials, sensors, and molecular switches [1–4].

Bhyrappa and Krishnan [5] previously synthesized (2,3,7,8,12,13,17,18-octabromotetraphenylporphyrinato)copper(II) by reaction of (5,10,15,20-tetraphenylporphyrinato)copper(II) (**1**) with molecular bromine in a mixture of chloroform with carbon tetrachloride. The complexation of the corresponding porphyrin ligand with palladium chloride in acetic acid gave octabromo-substituted palladium(II) complex [5] (Scheme 1).

With the goal of obtaining palladium(II) porphyrins substituted at the pyrrole rings, in this work we studied bromination of (5,10,15,20-tetraphenylporphyrinato) palladium(II) (**1**) and [5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato)palladium(II) (**2**) with *N*-bromosuccinimide (NBS) in chloroform and in a mixture of chloroform and dimethylformamide.

Complex **1** reacted with NBS at a molar ratio of 1:2 in chloroform–DMF (10:1) at room temperature (2.5 h) to give (2-bromo-5,10,15,20-tetraphenylporphyrinato)palladium(II) (**3**). The electronic absorption

Scheme 1.



1, $R^1 = R^2 = R^3 = R^4 = H$; **2**, $R^1 = MeO$, $R^2 = R^3 = R^4 = H$; **3**, $R^1 = R^3 = R^4 = H$, $R^2 = Br$; **4**, $R^1 = R^4 = H$, $R^2 = R^3 = Br$; **5**, $R^1 = H$, $R^2 = R^3 = R^4 = Br$; **6**, $R^1 = MeO$, $R^2 = Br$, $R^3 = R^4 = H$; **7**, $R^1 = MeO$, $R^2 = R^3 = Br$, $R^4 = H$.

spectrum of **3** in chloroform displayed bands with their maxima at λ 559, 526, and 419 nm, whereas absorption bands at λ_{max} 555, 523, and 416 nm typical of initial complex **1** disappeared. The mass spectrum of **3** contained the molecular ion peak with *m*/*z* 797 (calculated for $C_{44}H_{27}N_4BrPd$: 798). Figure 1 shows the electronic absorption spectrum of **3** in DMF (λ_{max} 560, 525, 418 nm).

The reaction of **1** with 6 equiv of NBS in 3 h (other conditions being the same as above) afforded a mixture of brominated palladium(II) tetraphenylporphyrins containing four to five bromine atoms in the pyrrole rings. Bhyrappa et al. [6] described bromination of tetraphenylporphyrin with NBS at a molar ratio of 1:6 in boiling chloroform. The bromination of **1** with NBS (1:20) under analogous conditions in 2 h afforded (2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrinato)palladium(II) (**4**) (Fig. 1) which showed in the ^{1}H NMR spectrum one signal at δ 8.51 ppm from protons in the pyrrole rings and signals in the region δ 8.04–7.72 ppm due to protons of the phenyl rings. Compound **4** was also formed when a solution of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin and $PdCl_2$ at a molar ratio of 1:3 in dimethylformamide was heated to the boiling point.

The reaction of **1** with 20 equiv of NBS in chloroform–DMF (10:1) at room temperature (5 h) afforded (2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrinato)palladium(II) (**5**). The electronic absorption spectrum of **5** in DMF contained bands at λ_{max} 594, 558, and 451 nm (Fig. 1). Its ^{1}H NMR spectrum lacked signals assignable to protons of the pyrrole rings, and signals of protons of the phenyl rings appeared in a stronger field relative to those of unsubstituted compound **1** and in a weaker field relative to those of tetrabromo derivative **4**. The electronic absorption and ^{1}H NMR spectra of complex **5** fully coincided with the corresponding spectral parameters of the same compound described in [5] (see table).

Introduction of electron-donating methoxy groups into the *para* positions of the *meso*-phenyl groups facilitated bromination of the macrocycle with *N*-bromosuccinimide. The reaction of methoxy-substituted complex **2** with 2 equiv of NBS gave [2-bromo-5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato]-palladium(II) (**6**) in 20 min. When the ratio **2** : NBS was reduced to 1:1.2, compound **6** was formed in 30 min. [2,3,12,13-Tetrabromo-5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato]palladium(II) (**7**) was

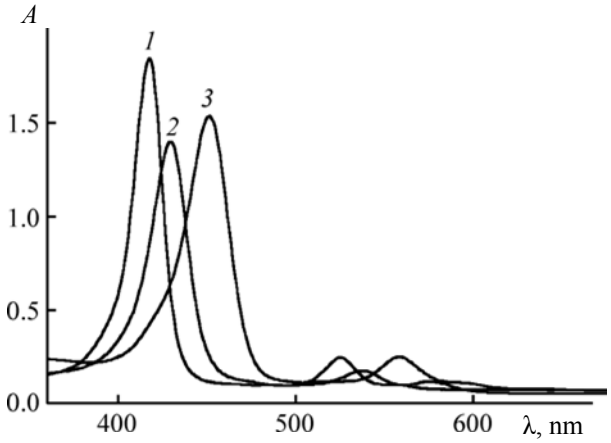


Fig. 1. Electronic absorption spectra of palladium(II) porphyrins (*1*) **3**, (*2*) **4**, and (*3*) **5** in DMF.

obtained by reaction of **2** with 5 equiv of NBS in chloroform–DMF at room temperature in 1 h or in boiling chloroform in 20 min. The electronic absorption spectra of **6** and **7** are shown in Fig. 2.

Complex **2** reacted with NBS at a molar ratio of 1:12 in chloroform–DMF at room temperature to produce in 3 h a compound which displayed absorption bands at λ_{max} 604, 561, and 460 nm in the electronic spectrum (chloroform solution). The complex isolated from the reaction mixture partially decomposed, and appreciable changes were observed in the electronic absorption spectrum recorded from a solution in chloroform. In particular, the *I* and *II* bands shifted blue by ~3–6 nm, and the Soret band was split

Electronic absorption spectra of palladium(II) tetraphenylporphyrins **1**–**7** in chloroform

Comp. no.	λ_{max}, nm (log ε)		
	I	*II*	Soret
1	555 sh	523 (4.53)	416 (5.63)
2	558 sh	525 (4.44)	419 (5.43)
3	559 sh	526 (4.42)	419 (5.41), 310 (4.31)
4	572 sh	536 (4.33)	428 (5.24), 332 (4.27)
5[a]	589 sh	556 (4.36)	449 (5.30), 355 (4.46)
5	591 sh	556 (4.45)	450 (5.34), 356 (4.52)
6	561 sh	528 (4.48)	422 (5.45), 311 (4.27)
7	573 sh	537 (4.37)	431 (5.30), 334 (4.24)

[a] In methylene chloride [5].

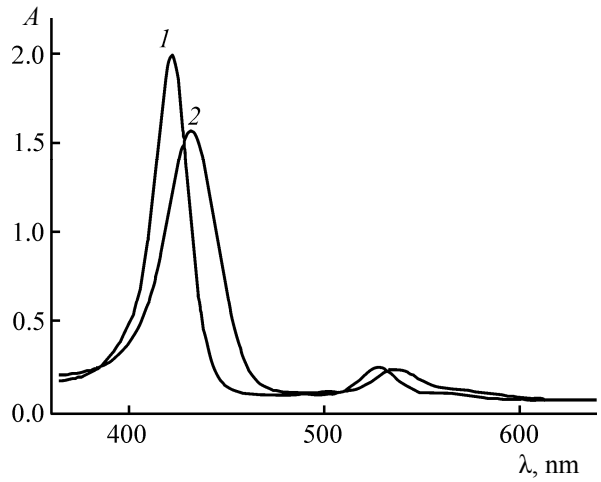


Fig. 2. Electronic absorption spectra of metal porphyrins (*1*) **6** and (*2*) **7** in DMF.

into two bands with their maxima at λ 457 and 440 nm with approximately equal intensities. The electronic spectrum of a sample withdrawn from the reaction mixture and dissolved in DMF did not change over a long time (λ_{max} 606, 564, 463 nm). After isolation from the DMF solution, a mixture of brominated palladium porphyrins was formed, which showed absorption bands at λ_{max} 558, 460, and 438 nm in the electronic spectrum.

The bromination of **2** with excess NBS in boiling chloroform for 1 h gave a product characterized by absorption bands at λ_{max} 596, 557, and 454 nm. The product partially decomposed upon isolation from the reaction mixture to form a mixture of bromo-substituted palladium porphyrins.

In summary, by bromination of palladium(II) tetraphenylporphyrins **1** and **2** with *N*-bromosuccinimide in a mixture of chloroform and DMF under mild conditions we obtained the corresponding mono- and octabromo derivatives. Exhaustive bromination of [5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato]palladium(II) gave a product which is stable in DMF solution, but it was converted into a mixture of bromo-substituted palladium(II) porphyrins during isolation from the reaction mixture. The bromination of **1** and **2** with NBS in boiling chloroform afforded the corresponding tetrabromo derivatives. The isolated compounds were characterized by electronic absorption, ^{1}H NMR, and MALDI TOF mass spectra and elemental analyses.

EXPERIMENTAL

The electronic absorption spectra were recorded on a Varian Cary-100 spectrophotometer. The mass spectra (MALDI TOF) were recorded on a Shimadzu Biotech Axima Confidence mass spectrometer using 2,5-dihydroxybenzoic acid as matrix. The ^{1}H NMR spectra were measured on a Bruker AV III-500 instrument at 500 MHz using $CDCl_3$ as solvent and tetramethylsilane as internal standard. The elemental analyses were obtained on a Thermo Scientific Flash EA 1112 analyzer.

5,10,15,20-Tetraphenylporphyrin, 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin (Porphychem), *N*-bromosuccinimide, $PdCl_2$ (Acros), and aluminum oxide (Merck) were commercial products; chloroform, DMF, hexane, and pyridine were of chemically pure grade. 2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrin was synthesized as described in [6]. (5,10,15,20-Tetraphenylporphyrinato)cadmium(II) was synthesized according to Adler [7]. (5,10,15,20-Tetraphenylporphyrinato)palladium(II) was synthesized according to the procedure described for transmetalation of labile porphyrin complexes [8].

(5,10,15,20-Tetraphenylporphyrinato)palladium(II) (1). A mixture of 0.05 g of (5,10,15,20-tetraphenylporphyrinato)cadmium(II) and 0.037 g of palladium(II) chloride at a molar ratio of 1:3 was dissolved in 20 mL of DMF, and the solution was refluxed for 2 min. The mixture was cooled and poured into water, and the precipitate was filtered off, washed with water, dried, and purified by alumina chromatography using chloroform as eluent. Yield 0.04 g (0.0556 mmol, 81%). ^{1}H NMR spectrum, δ, ppm: 8.84 s (8H, β-pyrrole), 8.20 d (8H, *o*-H, J = 7.70 Hz), 7.81–7.76 m (12H, *m*-H, *p*-H). Mass spectrum: m/z 718 (I_{rel} 87%) $[M - H]^+$; calculated for $C_{44}H_{28}N_4Pd$: 719.

[5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrinato]palladium(II) (2). A mixture of 0.05 g of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin and 0.036 g of palladium(II) chloride at a molar ratio of 1:3 was dissolved in 30 mL of DMF. The solution was refluxed for 20 s and was then treated as described above for complex **1**. Yield 0.041 g (0.049 mmol, 72%). ^{1}H NMR spectrum, δ, ppm: 8.86 s (8H, β-pyrrole), 8.10 d (8H, *o*-H, J = 7.70 Hz), 7.30 d (8H, *m*-H, J = 7.60 Hz), 4.11 s (12H, OCH_3). Found, %: C 68.84; H 4.27; N 6.63. $C_{48}H_{36}N_4O_4Pd$. Calculated, %: C 68.87; H 4.32; N 6.68.

(2-Bromo-5,10,15,20-tetraphenylporphyrinato)-palladium(II) (3). *N*-Bromosuccinimide, 0.01 g (0.0557 mmol), was added with stirring to a solution of 0.02 g (0.0278 mmol) of complex **1** in a mixture of

10 mL of chloroform and 1 mL of DMF. The mixture was stirred for 2.5 h at room temperature, 0.1 mL of pyridine and water were added, and the organic phase was separated, washed with water, dried over Na_2SO_4, and evaporated to a minimum volume. The residue was purified by alumina chromatography (eluent chloroform), followed by reprecipitation from ethanol. Yield 0.017 g (0.0215 mmol, 78%). ^{1}H NMR spectrum, δ, ppm: 8.97–8.95 m (2H), 8.81 s (1H), 8.80–8.77 m (2H), and 8.74–8.72 m (2H) (β-pyrrole); 8.18–8.15 m (6H) and 8.03–7.99 m (2H) (*o*-H), 7.76–7.68 m (12H, *m*-H, *p*-H). Mass spectrum: *m*/*z* 797 (I_{rel} 69%) $[M - H]^+$; calculated for $C_{44}H_{27}N_4BrPd$: 798.

(2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrinato)palladium(II) (4). *a*. *N*-Bromosuccinimide, 0.025 g (0.139 mmol), was added in four portions with stirring to a solution of 0.02 g (0.0278 mmol) of complex **1** in 10 mL of chloroform. The mixture was refluxed for 30 min and cooled, 0.2 mL of pyridine and water were added, and the organic phase was separated, washed with water, dried over Na_2SO_4, and evaporated. The residue was purified by alumina chromatography using first chloroform–hexane (1:2) and then chloroform as eluent, followed by reprecipitation from ethanol. Yield 0.018 g (0.0174 mmol, 63%). ^{1}H NMR spectrum, δ, ppm: 8.51 s (8H, β-pyrrole), 8.04 d (8H, *o*-H, *J* = 7.70 Hz), 7.77–7.72 m (12H, *m*-H, *p*-H). Mass spectrum: *m*/*z* 1033 (I_{rel} 72%) $[M - H]^+$; calculated for $C_{44}H_{24}N_4Br_4Pd$: 1034.

b. A mixture of 0.02 g (0.0215 mmol) of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin and 0.011 g (0.0644 mmol) of palladium(II) chloride was dissolved in 8 mL of DMF, and the solution was heated to the boiling point over a period of 1 min, cooled, and poured into water. The precipitate was filtered off, washed with water, dried, and purified by alumina chromatography (chloroform). Yield 0.019 g (0.0184 mmol, 86%).

Compounds **5** and **6** were synthesized as described above for complex **3**.

(2,3,7,8,12,13,17,17,18-Octabromo-5,10,15,20-tetraphenylporphyrinato)palladium(II) (5) was synthesized from 0.02 g (0.0278 mmol) of complex **1** and 0.1 g (0.556 mmol) of NBS; reaction time 5 h. Yield 0.027 g (0.02 mmol, 72%). ^{1}H NMR spectrum, δ, ppm: 8.07 d (8H, *o*-H, *J* = 7.70 Hz), 7.79–7.75 m (12H, *m*-H, *p*-H). Mass spectrum, *m*/*z* 1349 (I_{rel} 69%) $[M - H]^+$; calculated for $C_{44}H_{20}N_4Br_8Pd$: 1350.

[2-Bromo-5,10,15,20-tetrakis(4-methoxyphenyl)-porphyrinato]palladium(II) (6) was synthesized from 0.02 g (0.0238 mmol) of complex **2** and 0.0051 g (0.0286 mmol) of NBS; reaction time 30 min. Yield 0.018 g (0.0196 mmol, 82%). ^{1}H NMR spectrum, δ, ppm: 8.97–8.94 m (2H), 8.88 s (1H), 8.82–8.79 m (2H), and 8.77–8.75 m (2H) (β-pyrrole); 8.10–8.05 m (6H) and 8.04–8.01 m (2H) (*o*-H), 7.92–7.88 m (8H, *m*-H), 4.10 s (12H, OCH_3). Mass spectrum: *m*/*z* 917 (I_{rel} 72%) $[M - H]^+$; calculated for $C_{48}H_{35}N_4Br_4O_4Pd$: 918.

[2,3,12,13-Tetrabromo-5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato]palladium(II) (7) was synthesized as described above for complex **4** (method *a*) from 0.02 g (0.0238 mmol) of complex **2** and 0.022 g (0.119 mmol) of NBS; reaction time 20 min. Yield 0.02 g (0.0173 mmol, 73%). ^{1}H NMR spectrum, δ, ppm: 8.84 s (8H, β-pyrrole), 7.95 d (8H, *o*-H, *J* = 7.70 Hz), 7.88 d (8H, *m*-H, *J* = 7.60 Hz), 4.08 s (12H, OCH_3). Mass spectrum: *m*/*z* 1154 (I_{rel} 67%) $[M - H]^+$; calculated for $C_{48}H_{32}N_4Br_4O_4Pd$: 1155.

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