

PHYSICAL METHODS OF INVESTIGATION

Effect of the Chemical Modification of the Tetrapyrrole Macrocycle on the Reactivity of Porphyrins in Complexation with Pt^{4+} and Pd^{2+} Cations

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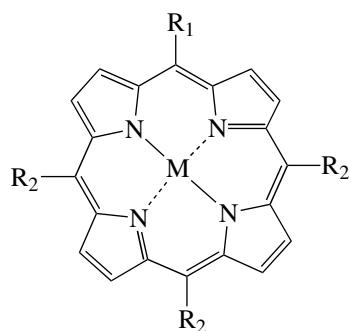
Abstract—The reactions of 5,10,15,20-tetraphenylporphine, 5,10,15-triphenyl-20-(4-hexadecanoxyphe-nyl)porphine, 5,10,15,20-tetra-(4-butoxyphenyl)porphine, and 2,3,7,8,12,13,17,18-octaethylporphine with H_2PtCl_6 in boiling phenol and with PdCl_2 in boiling dimethylformamide are studied by spectrophotometry. Due to a strong electronic effect of the substituents, the reactivity of the tetrapyrrole macrocycle during porphyrinate formation changes by more than two orders of magnitude. Platinum(II) 5,10,15-triphenyl-20-(4-hexadecanoxyphe-nyl)porphinate and palladium(II) 5,10,15,20-tetra-(4-butoxyphenyl)porphinate have been synthesized and identified for the first time.

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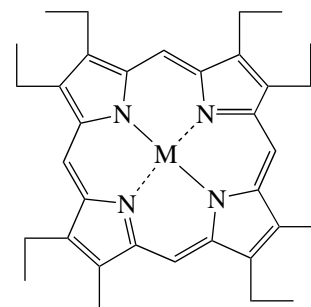
Porphyrins and related tetrapyrrole macrocycles are known to manifest their photochromic and catalytic properties being complexed with metals. Complexes of porphyrins with platinum and palladium, which are widely used in various areas of science and technology for the creation of controlled functional materials [1, 2], are of special interest.

Several methods for the synthesis of platinum(II) and palladium(II) porphyrinates with 5,10,15,20-tetraphenylporphine (**I**) and 2,3,7,8,12,13,17,18-octaethylporphine (**II**) are described in works [3–5]. According to [3], platinum(II) 5,10,15,20-tetraphenylporphyrinate (**III**) and platinum(II) 2,3,7,8,12,13,17,18-octaethylporphyrinate (**IV**) were synthesized in ~20% yield by

the reactions of **I** and **II** with K_2PtCl_2 in boiling benzene. Buchler and colleagues [4] wrote that the yields of platinum(II) and palladium(II) tetraphenylporphyrinates can be increased to 80% by carrying out the reaction in boiling benzonitrile and using PtCl_2 and PdCl_2 as reactants. Platinum(II) and palladium(II) 5,10,15,20-tetra(benzo-15-crown-5)porphyrinates were synthesized in 84 and 87% yields, respectively, under similar conditions. It should be mentioned that Rothmund and Menotti [6] found that the reaction of PdCl_2 with **II** in boiling dimethylformamide resulted in a partial hydrogenation of the tetrapyrrole macrocycle and yielded the corresponding dihydroporphyrin as an admixture.



$\text{M} = \text{H}_2$, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$ (**I**);
 $\text{M} = \text{Pt}^{2+}$, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$ (**III**);
 $\text{M} = \text{H}_2$, $\text{R}_1 = \text{C}_6\text{H}_4\text{-4-OC}_{16}\text{H}_{33}$, $\text{R}_2 = \text{C}_6\text{H}_5$ (**V**);
 $\text{M} = \text{H}_2$, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_4\text{-4-OC}_4\text{H}_9$ (**VI**);
 $\text{M} = \text{Pt}^{2+}$, $\text{R}_1 = \text{C}_6\text{H}_4\text{-4-OC}_{16}\text{H}_{33}$, $\text{R}_2 = \text{C}_6\text{H}_5$ (**VII**);
 $\text{M} = \text{Pt}^{2+}$, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_4\text{-4-OC}_4\text{H}_9$ (**VIII**);
 $\text{M} = \text{Pd}^{2+}$, $\text{R}_1 = \text{C}_6\text{H}_4\text{-4-OC}_{16}\text{H}_{33}$, $\text{R}_2 = \text{C}_6\text{H}_5$ (**IX**);
 $\text{M} = \text{Pd}^{2+}$, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_4\text{-4-OC}_4\text{H}_9$ (**X**);
 $\text{M} = \text{Pd}^{2+}$, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$ (**XI**);
 $\text{M} = \text{Zn}^{2+}$, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$ (**XIII**).



$\text{M} = \text{H}_2$ (**II**),
 $\text{M} = \text{Pt}^{2+}$ (**IV**),
 $\text{M} = \text{Pd}^{2+}$ (**XII**).

For the purpose of creating porphyrin-containing photochromic systems able to respond to external action, in the present work we developed new methods

for the synthesis of platinum(II) and palladium(II) *ms*- and β -substituted porphyrinates and studied the effect of chemical modification of the tetrapyrrole macrocy-

cle on the reactivity of **I**, **II**, 5,10,15-triphenyl-20-(4-hexadecanoxyphenyl)porphine (**V**), and 5,10,15,20-tetra-(4-butoxyphenyl)porphine (**VI**) in complexing H_2PtCl_6 in boiling phenol and PdCl_2 in boiling dimethylformamide. Platinum(II) 5,10,15-triphenyl-20-(4-hexadecanoxyphenyl)porphyrinate (**VII**), platinum(II) 5,10,15,20-tetra-(4-butoxyphenyl)porphyrinate (**VIII**), palladium(II) 5,10,15-triphenyl-20-(4-hexadecanoxyphenyl)porphyrinate (**IX**), and palladium(II) 5,10,15,20-tetra-(4-butoxyphenyl)porphyrinate (**X**) have been synthesized for the first time.

EXPERIMENTAL

Porphyrin ligands **V** and **VI** were synthesized according a known procedure [7]. The complex formation of the metal cation with the porphyrin ligand was monitored by spectrophotometry and thin-layer chromatography (TLC). The spectrophotometric procedure was as follows: aliquot volumes were taken from the reaction mixture at certain time intervals and dissolved in a certain amount of dimethylformamide, and the solution was placed in a cell. Electronic absorption spectra were recorded on a Specord M40 spectrophotometer at 298 K. Electron-impact mass spectra were measured on an MX-1310 mass spectrometer at an ionizing electron energy of 70 eV and an ionization chamber temperature of 150–200°C. Thin-layer chromatography was carried out on Silufol plates (G/UV₂₅₄) using hexane–chloroform (1 : 2) as the eluent. IR spectra were recorded on a Specord M80 spectrometer as KBr pellets. The solvents were purified according to [8].

Synthesis of platinum(II) 5,10,15,20-tetraphenylporphyrinate (III). A mixture of porphyrin **I** (0.05 g, 0.0813 mmol), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.244 mmol), and phenol (6 g) was refluxed for 2 h; the melt was cooled, dissolved in dimethylformamide (20 ml), and poured into water. A precipitate that formed was filtered off, washed with water, and dried. The residue was chromatographed on silica gel 40/100 (CHCl_3 : C_6H_{12} (1 : 2) as eluent). The yield was 0.05 g (0.0619 mmol, 76%). $R_f = 0.76$.

For $\text{C}_{44}\text{N}_4\text{H}_{28}$ anal. calcd. (%): C, 65.41; N, 6.94; H, 3.50.

Found (%): C, 65.38; N, 6.92; H, 3.47.

Mass spectrum (m/z): 807.2 ($I_{\text{rel}} = 76\%$) [M^+].

IR (cm^{-1}): 3060 w, 3028 w, 2824 m, 2852 w, 1809 w, 1733 w, 1633 m, 1591 m, 1441 m, 1360 m, 1317 m, 1176 w, 1077 m, 1019 s, 796 m, 754 m, 713 m, 668 m, 434 w.

Porphyrinates **IV**, **VII**, and **VIII** were synthesized similarly.

Platinum(II) 2,3,7,8,12,13,17,18-octaethylporphyrinate (IV). Porphyrin **II** (0.05 g) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.145 g) were taken in a molar ratio of 1 : 3. The reaction time was 9 h. The yield was 0.05 g (0.0687 mmol, 76%), $R_f = 0.69$.

Electronic absorption spectra of the Pt^{2+} and Pd^{2+} porphyrinates in chloroform

Compound	Band I λ , nm ($\log \epsilon$)	Band II λ , nm ($\log \epsilon$)	Soret band λ , λ_{nm} ($\log \epsilon$)
III	540 (4.10)	510 (4.40)	402 (5.48)
III*	541 (3.92)	511 (4.11)	402 (4.84)
IV	536 (4.53)	502 (4.12)	381 (5.31)
VII	539 (4.18)	510 (4.41)	402 (5.46)
VIII	540 sh	512 (4.58)	407 (5.56)
IX	531 sh	523 (4.54)	417 (5.61)
X	535 sh	526 (4.58)	421 (5.67)
XI	531 sh	523 (4.53)	417 (5.63)
XII	545 (4.76)	512 (4.32)	400 (5.24)
XIII*	597 (4.99)	558 (4.36)	420 (5.19)

* The data are borrowed from [9, 7], respectively.

For $\text{PtC}_{36}\text{N}_4\text{H}_{44}$ anal. calcd. (%): C, 59.37; N, 7.67; H, 6.07.

Found (%): C, 59.40; N, 7.70; H, 6.10.

Mass spectrum (m/z): 727.6 ($I_{\text{rel}} = 82\%$) [M^+].

IR (cm^{-1}): 3049 w, 2958 s, 2926 m, 2868 w, 1735 s, 1564 w, 1455 m, 1391 w, 1266 m, 1238 m, 1156 s, 1058 w, 993 w, 875 m, 835 m, 734 m, 467 w, 442 w.

Platinum(II) 5,10,15-triphenyl-20-(4-hexadecanoxyphenyl)porphyrinate (VII). Porphyrin **V** (0.05 g) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.091 g) were taken in a molar ratio of 1 : 3. The reaction time was 4 h. The yield was 0.05 g (0.0477 mmol, 80%), $R_f = 0.71$.

For $\text{PtC}_{60}\text{N}_4\text{H}_{59}\text{O}$ anal. calcd. (%): C, 68.80; N, 5.35; H, 5.69.

Found (%): C, 68.77; N, 5.32; H, 5.66.

Mass spectrum (m/z): 1046.3 ($I_{\text{rel}} = 92\%$) [M^+].

IR (cm^{-1}): 3055 w, 3022 w, 2923 s, 2852 m, 1727 w, 1656 w, 1598 m, 1455 m, 1359 (m), 1317 m, 1287 m, 1184 m, 1078 m, 1019 s, 797 m, 754 w, 714 m, 701 m, 1667 w, 430 w.

Platinum(II) 5,10,15,20-tetra(4-butoxyphenyl)porphyrinate (VIII). Porphyrin **VI** (0.05 g) and H_2PtCl_6 (0.086 g) in the molar ratio of 1 : 3. Reaction time: 12 h. Yield: 0.05 g (0.0456 mmol, 78%). $R_f = 0.70$.

For $\text{PtC}_{60}\text{N}_4\text{H}_{60}\text{O}_4$ anal. calcd. (%): C, 65.73; N, 5.08; H, 5.53.

Found (%): C, 65.70; N, 5.11; H, 5.50.

Mass spectrum (m/z): 1095.1 ($I_{\text{rel}} = 79\%$) [M^+].

IR spectrum (cm^{-1}): 2957 m, 2929 m, 2870 w, 1607 s, 1507 s, 1464 m, 1358 m, 1285 m, 1244 s, 1174 s, 1107 w, 1076 w, 1021 m, 1009 m, 967 w, 820 m, 798 m, 714 w, 647 w, 560 w, 437 w.

Palladium(II) 5,10,15-triphenyl-20-(4-hexadecanoxyphenyl)porphyrinate (IX). A mixture of porphyrin **V** (0.1 g) and PdCl₂ (0.21 g) in a molar ratio of 1 : 10 was dissolved in dimethylformamide (60 ml) and refluxed for 5 min. The mixture was cooled, a precipitate was filtered off, and the filtrate was poured into water. The precipitate was filtered off, washed with water, and chromatographed on silica gel 40/100 (CHCl₃ : C₆H₁₂ (1 : 2) as eluent). The yield was 0.09 g (0.0938 mmol, 80%), $R_f = 0.74$.

For PdC₆₀N₄H₅₉O anal. calcd. (%): C, 75.17; N, 5.85; H, 6.22.

Found (%): C, 75.15; N, 5.82; H, 6.19.

Mass spectrum (m/z): 954.4 ($I_{rel} = 97%$) [M⁺].

IR (cm⁻¹): 3049 w, 3022 w, 2922 s, 2851 m, 1803 w, 1598 m, 1568 m, 1441 m, 1353 m, 1312 m, 1287 m, 1194 m, 1076 m, 1014 s, 797 m, 753 m, 713 m, 701 m, 667 w, 461 w.

Palladium(II) 5,10,15,20-tetra-(4-butoxyphenyl)porphyrinate (X), palladium(II) 5,10,15,20-tetraphenylporphyrinate (XI), and palladium(II) 2,3,7,8,12,13,17,18-octaethylporphyrinate (XII) were synthesized in a similar manner.

Palladium(II) 5,10,15,20-tetra-(4-butoxyphenyl)porphyrinate (X). Porphyrin **VI** (0.1 g) and PdCl₂ (0.2 g) in a molar ratio of 1 : 10. Reaction time: 1 min. Yield: 0.08 g (0.0794 mmol, 76%). $R_f = 0.73$.

For PdC₆₀N₄H₆₀O₄ anal. calcd. (%): C, 71.51; N, 5.56; H, 6.01.

Found (%): C, 71.49; N, 5.52; H, 5.98.

Mass spectrum (m/z): 1007.3 ($I_{rel} = 83%$) [M⁺].

IR (cm⁻¹): 3039 w, 2956 m, 2926 m, 2870 w, 1607 s, 1505 s, 1465 m, 1353 m, 1285 m, 1243 s, 1174 s, 1107 w, 1074 w, 1009 m, 798 w, 714 w, 643 w, 543 w, 452 w.

Palladium(II) 5,10,15,20-tetraphenylporphyrinate (XI). Porphyrin **I** (0.1 g) and PdCl₂ (0.29 g) in a molar ratio of 1 : 10. Reaction time: 2 h. Yield: 0.08 g (0.111 mmol, 73%). $R_f = 0.78$.

For PdC₄₄N₄H₂₈ anal. calcd. (%): C, 73.48; N, 7.79; H, 3.93.

Found (%): C, 73.46; N, 7.77; H, 3.90.

Mass spectrum (m/z): 718.1 ($I_{rel} = 87%$) [M⁺].

IR (cm⁻¹): 3053 w, 3016 w, 2923 m, 2852 w, 1803 w, 1598 m, 1538 w, 1490 w, 1441 m, 1353 m, 1311 w, 1209 w, 1177 w, 1075 m, 1015 s, 836 w, 796 m, 752 m, 701 m, 667 w, 528 w, 466 w.

Palladium(II) 2,3,7,8,12,13,17,18-octaethylporphyrinate (XII). Porphyrin **II** (0.1 g) and PdCl₂ (0.33 g) in a molar ratio of 1 : 10. Reaction time: 2 min. Yield: 0.09 g (0.141 mmol, 75%). $R_f = 0.73$.

For PdC₃₆N₄H₄₄ anal. calcd. (%): C, 67.63; N, 8.74; H, 6.95.

Found (%): C, 67.61; N, 8.77; H, 6.92.

Mass spectrum (m/z): 636.1 ($I_{rel} = 69%$) [M⁺].

IR (cm⁻¹): 3049 w, 2958 s, 2926 m, 2867 w, 1738 w, 1671 w, 1553 w, 1452 m, 1388 w, 1310 w, 1263 m, 1233 s, 1154 s, 1142 m, 1107 w, 1057 m, 989 m, 937 w, 832 m, 753 m, 732 m, 715 m, 608 w, 457 w.

RESULTS AND DISCUSSION

The reduction of Pt⁴⁺ to Pt²⁺ occurs during the reactions of H₂PtCl₆ with compounds **I**, **II**, **V**, and **VI**. We found that in the reaction of compound **I** with H₂PtCl₆ in boiling phenol, porphyrinate **III** is formed ~15 times more rapidly than in the with K₂PtCl₄ in boiling benzonitrile [9]. It is worth mentioning that the reactivity of the tetrapyrrole macrocycle toward Pt⁴⁺ decreases substantially (maximally sixfold) under the inductive effect of electron-releasing substituents arranged in the both *ms*- (**I**, **V**, **VI**) and β - (**II**) positions of the molecule. According to the mechanism of porphyrin coordination by metal cations in nonaqueous media [10], metal porphyrins are formed due to the bimolecular collision of the porphyrin ligand and solvated salt. The rate of the complexation process depends on two factors, namely, (1) the strength of the N–H bonds of the reaction center of the porphyrin and (2) coordination interaction between the metal cation and nitrogen atoms of the porphyrin. The effect of these factors depends on the specifics of the process. The decrease in the complexation rate observed on going from **I** to **II**, **V**, and **VI** indicates that the strength of the N–H bonds of the porphyrin ligand makes the key contribution to the energy of the transition state. Electron-releasing substituents increase the density of the N–H bonds, thus decreasing the reactivity of the tetrapyrrole macrocycle to Pt⁴⁺. This is confirmed by the consecutive increase in the time of formation of porphyrinates **III**, **VII**, and **VIII** with an increase in the number of the alkyloxy groups (*n*) in the phenyl fragments (*n* = 0 (**III**), 1 (**VII**), 4 (**VIII**)).

The fact that the formation rate of palladium(II) porphyrinates **IX**, **X**, and **XI** in the reactions of the corresponding ligands with PdCl₂ in dimethylformamide changes in the opposite direction indicates that the coordination interaction of the metal cation with the nitrogen atom of the porphyrin makes the key contribution to the energy of the transition state of the complex formation process. The electron-releasing substituents increase the electron density on the tertiary nitrogen atoms of the macrocycle, thus enhancing the coordination interaction of the cation of the solvate complex with the porphyrin in the transition state. The latter is accompanied by an increase in the reaction rate (maximally by ~120 times).

The synthesis of palladium(II) octaethylporphyrinate (**XII**) needs special attention. The reaction of octaethylporphine **II** with PdCl₂ in boiling dimethylformamide yields porphyrinate **XII** in 75% yield. No forma-

tion of side dihydroporphyrins was observed under these conditions, unlike in [6].

The data of the electronic absorption, mass, and IR spectra and elemental analysis match completely to the structures of the synthesized compounds. The hypsochromic shift of the absorption bands in the electronic absorption spectra of the platinum(II) and palladium(II) porphyrinates (**III**, **IV**, **VII–XII**) relative to the metal porphyrins containing the metal ion with a closed electronic shell (for instance, zinc(II)) is caused by the strong $d_{\pi}-e_g(\pi^*)$ type π -dative interaction between the metal ion and porphyrin macrocycle; the shift increases on going from the palladium to platinum complexes (see the table).

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