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PHYSICAL CHEMISTRY OF SOLUTIONS

Effect of the Nature of the Tetrapyrrole Macrocycle on the Transmetallation of Zn^{2+} and Cd^{2+} Porphyrins with $PdCl_2$ in Dimethylformamide

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Abstract—Transmetallation of zinc (Zn^{2+}) and cadmium (Cd^{2+}) complexes of 5,10,15,20-tetraphenylporphin, 5,10,15,20-tetra(4-chlorophenyl)porphyrin, 5,10,15,20-tetra(4-methoxyphenyl)porphyrin, tetrabenzoporphyrin, and octaphenyltetraazaporphyrin with $PdCl_2$ in DMF was studied by spectrophotometry. The influence of the nature of the tetrapyrrole macrocycle on the reactivity of Zn^{2+} porphyrins toward palladium chloride in boiling DMF was established. Palladium(II) complexes of 5,10,15,20-tetraphenylporphyrin, 5,10,15,20- tetra(4-chlorophenyl)porphyrin, 5,10,15,20-tetra(4-methoxyphenylporphyrin), and tetrabenzoporphyrin were prepared and identified.

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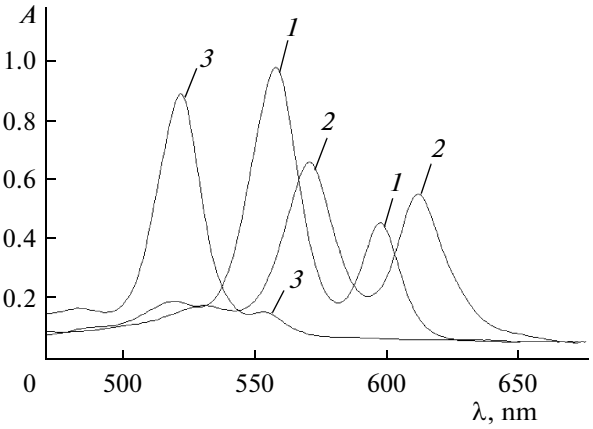
Porphyrins and related tetrapyrrole macrocycles are known to exhibit photochromic and catalytic properties when exist as metal complexes. Of particular interest are porphyrin complexes with palladium, which are widely used in various fields of science and technology for the development of new functional materials [1,2].

A method for the synthesis of palladium (Pd^{2+}) complexes of 5,10,15,20-tetraphenylporphin (PdTPhP) (**I**) and 5,10,15,20-tetra(benzo-15-crown-5)porphyrin by the reaction of the porphyrin ligand with $PdCl_2$ in boiling benzonitrile was reported [3, 4]. Complexes **I** and Pd^{2+} tetrabenzoporphyrin (PdTBP) (**II**) were prepared by a similar procedure in dimethylformamide (DMF) [5, 6].

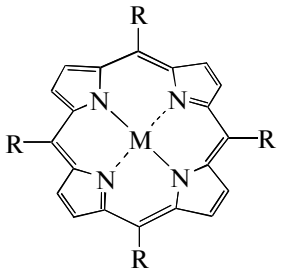


UV–Vis spectra in DMF: (*1*) ZnTPhP, (*2*) CdTPhP, and (*3*) PdTPhP.

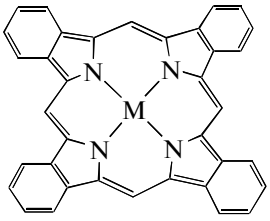
Analysis of published data and our results shows that transmetallation of labile complexes is a promising way for the preparation of palladium complexes with tetrapyrrole macrocycles. In particular, we synthesized PdTBP and Pd^{2+} octaphenyltetraazaporphyrin (PdOPhTAP) (**III**) from Cd and Mg porphyrins [7, 8].

In order to develop efficient methods for the synthesis of Pd^{2+} porphyrins, in this work, we studied the reactions of 5,10,15,20-tetraphenylporphyrin complexes of Zn^{2+} (ZnTPhP) (**VI**) and Cd^{2+} (CdTPhP) (**VII**), 5,10,15,20-tetra(4-chlorophenyl)porphyrin complexes of Zn^{2+} (ZnT(4-ClPh)P) (**VIII**) and Cd^{2+} (CdT(4-ClPh)P) (**IX**), and 5,10,15,20-tetra(4-methoxyphenyl)porphyrin complexes of Zn^{2+} (ZnT(4-OCH_3Ph)P) (**X**) and Cd^{2+} (CdT(4-OCH_3Ph)P) (**XI**) with palladium chloride in DMF. The effect of benzo and aza substitution on the reactivity of Zn^{2+} tetrabenzoporphyrin (ZnTBP) (**XII**), Cd^{2+} tetrabenzoporphyrin (CdTBP) (**XIII**), and Zn^{2+} octaphenyltetraazaporphyrin (ZnOPhTAP) (**XIV**) with $PdCl_2$ in DMF was studied.

Owing to the considerable difference between the UV–Vis spectra of the starting compounds and the resulting Pd^{2+} porphyrins (figure, Table 1), it was possible to study transmetallation by spectrophotometry.



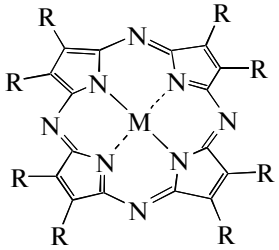
$M = Pd^{2+}$, $R = C_6H_5$ (**I**),
$M = Zn^{2+}$, $R = C_6H_5$ (**VI**),
$M = Cd^{2+}$, $R = C_6H_5$ (**VII**),



$M = Pd^{2+}$ (**II**),
$M = Zn^{2+}$ (**XII**),
$M = Cd^{2+}$ (**XIII**),

$M = Pd^{2+}$, $R = C_6H_4$-4-Cl (**IV**),
$M = Zn^{2+}$, $R = C_6H_4$-4Cl (**VIII**),
$M = Cd^{2+}$, $R = C_6H_4$-4Cl (**IX**),

$M = Pd^{2+}$, $R = C_6H_4$-4-OCH_3 (**V**),
$M = Zn^{2+}$, $R = C_6H_4$-4-OCH_3 (**X**),
$M = Cd^{2+}$, $R = C_6H_4$-4-OCH_3 (**XI**),



$M = Pd^{2+}$, $R = C_6H_5$ (**III**),
$M = Zn^{2+}$, $R = C_6H_5$ (**XIV**).

EXPERIMENTAL

The Zn^{2+} and Cd^{2+} porphyrins (**VI**–**XI**) were synthesized from appropriate porphyrin ligands [9, 10] by the Adler method [11]. The Zn^{2+} and Cd^{2+} porphyrins (**XII**–**XIV**) were prepared by the Linstead method [12, 13]. The transmetallation reactions of Zn^{2+} and Cd^{2+} porphyrins with $PdCl_2$ in DMF were monitored by spectrophotometry and TLC. The spectrophotometric procedure was as follows: samples of equal volume were taken from the reaction mixture at specified intervals and dissolved in specified amounts of DMF, and the solutions were placed in the spectrophotometric cell. The UV–Vis spectra were recorded on a Cary-100 spectrophotometer at 298 K. Electron impact mass spectra were run on an MX-1310 mass-spectrometric setup at an ionizing energy of 70 eV and ionization chamber temperature of 150–200°C. Elemental analysis was performed on a Flash EA 1112 analyzer. The ^1H NMR spectra were recorded on a Bruker AV III-500 instrument, IR spectra were measured on an Avatar 360-FT-IR-ESP instrument for KBr pellets. TLC analysis was performed on Silufol (G/UV_{254}) plates. The solvents were purified by published procedures [14].

Synthesis of Pd^{2+} 5,10,15,20-tetraphenylporphyrin (I). (a) A mixture of complex **VI** (0.05 g) and $PdCl_2$ (0.13 g) in the molar ratio 1 : 10 was dissolved in DMF (20 mL), and the mixture was refluxed for 4 min, cooled, and poured in water. The precipitate was filtered off, washed with water, dried, and chromatographed on alumina with chloroform elution. Yield 0.043 g (0.0598 mmol), 81%. $R_f = 0.78$ (elution with hexane–chloroform (1 : 2)).

^1H NMR (δ, ppm, $CDCl_3$): 8.84 (s, 8 H, pyrrole ring), 8.20 (d, 8H, *ortho*), 7.81 (t, 8H, *meta*), 7.76 (t, 4H, *para*).

The ^1H NMR spectrum of the starting ZnTPhP (δ, ppm, $CDCl_3$): 8.97 (s, 8H), 8.25 (d, 8H), 7.81 (t, 8H), 7.77 (t, 4 H).

(b) Complex **VII** (0.05 g) and $PdCl_2$ (0.037 g) (1 : 3 mol/mol) were refluxed in DMF (20 mL) for 2 min. Yield 0.04 g (0.0556 mmol), 81%. $R_f = 0.78$.

For $PdC_{44}N_4H_{28}$ anal. calcd. (%): C, 73.48; N, 7.79; H, 3.93.

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

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

IR (ν, 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).

Pd^{2+} tetrabenzoporphyrin (II) was synthesized by a modification of a reported procedure [7]. A mixture of complex **XIII** (0.05 g) and $PdCl_2$ (0.14 g) (molar ratio 1 : 10) in DMF (80 mL) was refluxed for 10 min and cooled, the precipitate was filtered off, and the filtrate was poured in water. The precipitate was filtered off, washed with water and ethanol, and chromatographed on alumina (elution with pyridine–diethyl ether (1 : 4)). The yield of complex **II** was 0.037 g (0.06 mmol), 75%. $R_f = 0.62$ (elution with diethyl ether).

For $PdC_{36}H_{20}N_4$ anal. calcd. (%): C, 70.31; N, 9.11; H, 3.28.

Found (%): C, 70.25; N, 9.07; H, 3.24.

^1H NMR (δ, ppm, [D_6] DMSO): 11.30 (s, 4H), 9.93 (s, 8H), 8.32 (s, 8H).

IR (ν, cm^{-1}): 2922, 2847 (ν_{C-H}, $-C_6H_4$), 1727, 1606, 1568 ($\nu_{C=C}$, $-C_6H_4$), 1460 ($\nu_{C=N}$), 1430, 1372, 1323 (ν_{C-N}), 1257, 1122 (δ_{C-H}, $-C_6H_4$), 1066, 1011 (γ_{C-C}, δ_{C-H}), 831 (γ_{C-H}, pyrrole ring), 755, 706 (γ_{C-H}, $-C_6H_4$), 454 (ν_{Pd-N}).

Synthesis of Pd^{2+} 5,10,15,20-tetra(4-chlorophenyl)porphyrin (IV). (a) Complex **VIII** (0.05 g), $PdCl_2$ (0.11 g) (1 : 10 mol/mol) in DMF (10 mL) was refluxed for 5 min. Yield 0.041 g (0.0478 mmol), 78%. $R_f = 0.89$.

Table 1. UV–Vis spectra of Pd^{2+}, Zn^{2+}, and Cd^{2+} porphyrins

Compound	Solvent	Band I	Band II	Soret band
		λ, nm (logε)		
PdTPhP	$CHCl_3$	555 sh	523 (4.43)	415 (5.47)
PdTPhP	DMF	554 sh	522 (4.41)	415 (5.44)
ZnTPhP	DMF	598 (4.29)	558 (4.62)	423 (5.70)
CdTPhP*	DMF	614 [0.218]	572 [0.253]	431 [2.72]
PdT(4-ClPh)P	$CHCl_3$	555 sh	524 (4.42)	416 (5.43)
PdT(4-ClPh)P	DMF	554 sh	523 (4.40)	415 (5.40)
ZnT(4-ClPh)P*	DMF	598 [0.23]	559 [0.41]	421 [2.84]
CdT(4-ClPh)P*	DMF	615 [0.14]	573 [0.22]	434 [2.68]
PdT(4-OCH_3Ph)P	$CHCl_3$	558 (3.64)	525 (4.44)	419 (5.43)
PdT(4-OCH_3Ph)P	DMF	560 (3.63)	525 (4.39)	419 (5.40)
ZnT(4-OCH_3Ph)P*	DMF	603 [0.25]	561 [0.31]	422 [2.79]
CdT(4-OCH_3Ph)P*	DMF	622 [0.38]	576 [0.32]	431 [2.91]
PdTBP	DMF	606 (4.97)	556 (3.80)	408 (5.18)
ZnTBP	DMF	624 (5.05)	577 (4.20)	425 (5.48)
CdTBP	DMF	629 (5.02)	585 (4.23)	433 (5.53)
PdOPhTAP[8]	$CHCl_3$	616 (4.28)	560 (3.83)	350 (4.26)
ZnOPhTAP	$CHCl_3$	637 (5.11)	580 (4.36)	375 (5.05)

* Relative intensities are presented.

(b) Complex **IX** (0.05 g) and $PdCl_2$ (0.03 g) (1 : 3 mol/mol) were refluxed in DMF (10 mL) for 2 min. Yield 0.04 g, 81%. $R_f = 0.89$.

(c) Tetra(4-chlorophenyl)porphyrin (0.05 g) and $PdCl_2$ (0.035 g) (1 : 3 mol/mol) were refluxed in DMF (20 mL) for 1 min. Yield 0.043 g (0.050 mmol), 76%. $R_f = 0.89$.

For $PdC_{44}N_4H_{24}Cl_4$ anal. calcd. (%): Cl, 16.56; Pd, 12.41.

Found (%): Cl, 16.61; Pd, 12.39.

^{1}H NMR (δ, ppm, $CDCl_3$): 8.83 (s, 8H), 8.11 (d, 8H), 7.77 (d, 8H).

IR (ν, cm^{-1}): 2923 (m), 2846 (w), 1906 (w), 1739 (w), 1637 (w), 1541 (w), 1487 (s), 1449 (w), 1352 (m), 1256 (w), 1092 (s), 1013 (s), 885 (w), 806 (s), 716 (m), 506 (m).

Synthesis of Pd^{2+} 5,10,15,20-tetra(4-methoxyphenyl)porphyrin (V). (a) Complex **X** (0.05 g) and $PdCl_2$ (0.11 g) (1 : 10 mol/mol) were refluxed in DMF (15 mL) for 5 min. Yield 0.04 g (0.048 mmol), 77%. $R_f = 0.81$.

(b) Complex **XI** (0.05 g) and $PdCl_2$ (0.031 g) (1 : 3 mol/mol) were refluxed in DMF (15 mL) for 2 min. Yield 0.039 g (0.046 mmol), 79%. $R_f = 0.81$.

(c) Tetra(4-methoxyphenyl)porphyrin (0.05 g) and $PdCl_2$ (0.036 g) (molar ratio 1 : 3) were refluxed in DMF (30 mL) for 20 s. Yield 0.041 g (0.049 mmol), 72%, $R_f = 0.81$.

For $PdC_{48}N_4H_{36}O_4$ anal. calcd. (%): C, 68.70; N, 6.68; H, 4.32.

Found (%): C, 68.84; N, 6.63; H, 4.27.

^{1}H NMR (δ, ppm, $CDCl_3$): 8.86 (s, 8H), 8.10 (d, 8H), 7.30 (d, 8H), 4.11 (s, 12H).

IR (ν, cm^{-1}): 2927 (m), 2830 (w), 2029 (w), 1607 (s), 1506 (s), 1462 (m), 1353 (s), 1289 (m). 1249 (s), 1175 (s), 1111 (w), 1016 (s), 799 (s), 714 (m), 608 (m), 500 (w).

RESULTS AND DISCUSSION

Transmetallation of Zn^{2+} tetraphenylporphyrin with Cu^{2+} in boiling pyridine and Cd^{2+} and Hg^{2+} tetraphenylporphyrins with Zn^{2+} in pyridine at 25°C was described in detail [15]. It was show that the exchange with Hg^{2+} tetraphenylporphyrin is 17 times faster than with Cd^{2+}.

The studies carried out upon sampling showed that the reaction of Zn porphyrin (**VI**) with $PdCl_2$ taken in 1 : 3 molar ratio in boiling DMF gives Pd porphyrin (**I**) within 15 min. The UV–Vis spectrum of the sample taken from the reaction mixture after 15 min and dissolved in DMF exhibits bands with $\lambda_I = 554$, $\lambda_{II} = 522$ nm, while the bands for starting **VI** with maxima at 598 and 558 nm (figure) have disappeared. The hypsochromic shift of the Soret band in the UV–Vis spectrum of **I** with respect to Zn porphyrin in DMF was 8 nm (Table 1). When the reaction time increased to 20 min, the UV–Vis spectral pattern of complex **I** did not change. Under similar conditions, the degree of conversion of chloro and methoxy derivatives of Zn^{2+} porphyrins to the corresponding Pd porphyrins was ~25–30%. The

UV–Vis spectra of samples in DMF exhibit, apart from the bands with maxima at 555, 524 and 558, 525 nm for the reaction products, also the bands for the starting Zn chloro and methoxy porphyrins at $\lambda_{max} = 598$, 559 and 603, 561 nm. As the reaction time was increased to 1 h, the product yield increased but still no complete transformation of the starting metal porphyrins to the final products took place. The observed decrease in the reactivity of Zn tetraphenylporphyrin upon the substitution is probably due to enhancement of the N ⟶ M σ-bond (+C effect in the case of **VIII**, +J effect in **X**). As the salt amount is increased to a 10-fold excess, the deactivating effect of substituents is levelled up and Pd porphyrins (**I**, **IV**, and **V**) are formed in boiling DMF after 4–5 min.

An opposite situation is observed for complexation of the tetraphenylporphin ligand and its derivative with $PdCl_2$ in DMF [5]. According to published data [16], electron-donating substituents, which increasing the electron density on the tertiary nitrogen atoms of the macrocycle, enhance the coordination interaction of the solvato complex cation with porphyrin in the transition state, and the reaction rate thus increases. Our studies demonstrated that the introduction of chlorine atoms (+C effect) and electron-donating methoxy groups (+J effect) in the *para*-position of the tetraphenylporphin benzene rings increases the rate of complexation with $PdCl_2$ in DMF by ~2 orders of magnitude as compared with the starting porphyrin [5].

It is known [17] that benzo and aza substitution stabilize Zn porphyrins. This was also supported by our studies. The degree of conversion of Zn tetrabenzoporphyrin (**XII**) to Pd(II) porphyrin at 1 : 10 molar ratio of the reactants in boiling DMF at the reaction time of 1 h is only ~25%. Zinc octaphenylporphyrin (**XIV**) does not form the corresponding palladium porphyrin(III) even on long-term refluxing (2 h) with a 20-fold excess of $PdCl_2$.

On going from the covalently bonded Zn porphyrins to less stable ionic Cd porphyrins [17], the rate of metal exchange with Pd increases. Irrespective of the chemical modification of the macrocycle, the rates of formation of Pd^{2+} porphyrins (**I**, **IV**, **V**) in boiling DMF almost coincide. The transmetallation of Cd porphyrins (**VII**, **IX**, **XI**) by $PdCl_2$ in DMF at lower temperature has not been studied. Palladium tetrabenzoporphyrin is formed in boiling DMF ~5 times more slowly than complex **I** at 1 : 10 molar ratio of the reactants. Cd^{2+} octaphenyltetraazaporphyrin is not formed by the Linstead method [13]. Cd^{2+} octaphenyltetraazaporphyrin formed from the corresponding ligand and cadmium acetate in DMF is unstable in the solid state. During the isolation, the complex is converted to the octaphenyltetraazaporphyrin ligand. Therefore, it is expedient to obtain Pd^{2+} octaphenyltetraazaporphyrin from Mg octaphenyltetraazaporphyrin [8].

Table 2. Effect of the nature of the tetrapyrrole macrocycle on the transmetallation of Zn^{2+} and Cd^{2+} porphyrins by $PdCl_2$ in boiling DMF

Starting compound	Reactant molar ratio	Reaction time
ZnTPhP	1 : 3	15 min
CdTPhP	1 : 3	2 min
ZnT(4-ClPh)P	1 : 3	15 min–degree of conversion ~ 25%
CdT(4-ClPh)P	1 : 3	2 min
ZnT(4-OCH_3Ph)P	1 : 3	15 min–degree of conversion ~30%
CdT(4-OCH_3Ph)P	1 : 3	2 min
ZnTPhP	1 : 10	4 min
ZnT(4-ClPh)P	1 : 10	5 min
ZnT(4-OCH_3Ph)P	1 : 10	5 min
ZnTBP	1 : 10	1 h–degree of conversion ~25%
CdTBP	1 : 10	10 min
ZnOPhTAP	1 : 20	2 h–no reaction
MgOPhTAP*	1 : 20	1 h

* Data from [8].

The data from elemental analysis, UV–Vis, IR, and NMR spectroscopy fully correspond to the structures of the synthesized compounds. The hypsochromic shift of the UV–Vis bands of Pd^{2+} porphyrins (**I**–**V**) with respect to the starting Zn^{2+} and Cd^{2+} porphyrins (**VI**–**XIV**) can be attributed to strong π-dative interaction between the metal ion and the porphyrin macrocycle of the d_π–$e_g(\pi^*)$ type (Table 1). In the ^{1}H NMR spectrum of Pd tetraphenylporphyrin, the signals of the pyrrole rings and *ortho*-protons are shifted upfield by 0.13 and 0.05 ppm relative to the spectrum of the starting Zn porphyrin.

The obtained results indicate that in the case of tetrapyrrole macrocycles that are usually prepared by template cyclotetramerization as metal porphyrin complexes, the palladium complexes are conveniently synthesized via transmetallation of their labile complexes (Table 2). In the case of tetrapyrrole macrocycles that are readily formed as free ligands, it is more expedient to use the complexation of the porphyrin ligand with the metal cation classical for porphyrins.

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