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Synthesis and Coordination Properties of Nitro Derivatives of 5,15-Diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin

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Abstract—Methods were developed for the synthesis of nitro derivatives of 5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin containing nitro groups at the meso positions of the porphyrin core and at the *para* positions of the phenyl substituents. The formation kinetics of the zinc, copper, and cobalt complexes of the resultant porphyrins in pyridine and in an acetic acid–benzene (7 : 3) mixed solvent was studied. It was found that the properties of the porphyrin ligands are determined both by the electronic effect of the nitro groups and by the effects of spatial distortion of the porphyrin core.

Keywords: synthesis, nitro derivatives, porphyrin, metal complex, kinetics

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INTRODUCTION

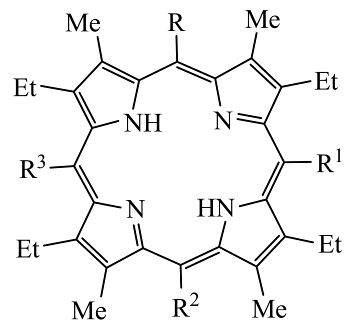
The deformation of the aromatic tetrapyrrole macrocycle was found earlier [1–12] to increase with accumulation of bulky substituents at the meso and beta positions of porphin. A kinetic study of the coordination of such ligands with transition metal salts showed [13–20] that their reactivity is dramatically dependent on the degree of distortion of the planar structure of the tetrapyrrole macrocycle.

To further elucidate how the kinetic parameters of the complexation reactions with 3*d*-metal salts are affected by the structure of the porphyrin molecules we examined here the kinetics of the formation of zinc, copper, and cobalt complexes with 5,15-dipheny-l 3,7,13,17-tetramethyl-2,8,12, 18-tetraethylporphyrin (**1**) and its nitro derivatives (**2–6**) in pyridine and in an acetic acid–benzene (7 : 3) binary solvent. Pyridine was chosen as basic solvent, and acetic acid–benzene, as acidic solvent. Benzene was added to acetic acid for improving the solubility of porphyrins.

EXPERIMENTAL

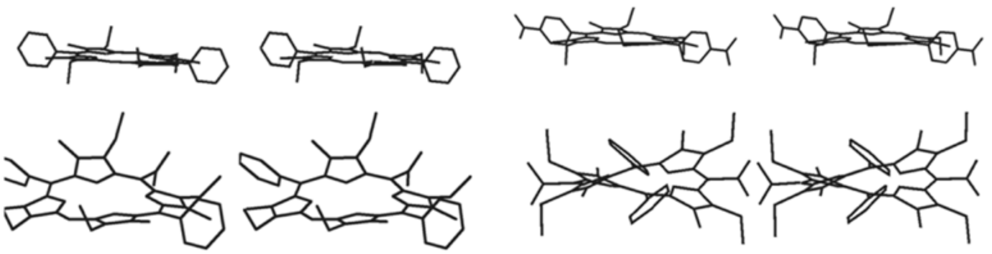
3,7,13,17-Tetramethyl-2,8,12,18-tetraethyl-5,15-diphenylporphyrin (**1**) was synthesized by the technique from [21]; 3,7,13,17-tetramethyl-2,8,12 ,18-tetraethyl-5,15-bis(4'-nitrophenyl)porphyrin (**2**), 3,7,13,17-tetramethyl-2,8,12,18-tetraethyl-5,15-diphenyl-10-nitroporphyrin (**3**), 3,7,13,17-tetramethyl-2,8,12,18-tetraethyl-5,15-diphenyl-10,20-dinitroporphyrin (**4**), 3,7,13,17-tetramethyl-2,8,12,18-tetraethyl-5-phenyl-10-(4'-nitrophenyl)-15-phenyl-10,20-dinitroporphyrin (**5**), and 3,7,13,17-tetramethyl-2,8,12,18-tetraethyl-5,15-bis(4'-nitrophenyl)-10,20-dinitroporphyrin (**6**) were synthesized by the techniques from [19, 21, 22] (Scheme 1).

Scheme 1.



1–6

R = R^2 = Ph; R^1 = R^3 = H (**1**), R = R^2 = 4-NO^{2}Ph; R^1 = R^3 = H (**2**), R = R^2 = Ph; R^3 = H; R^1 = NO$_2$ (**3**), R = R^2 = Ph; R^1 = R^3 = NO$_2$ (**4**), R = Ph; R^2 = 4-NO$_2$Ph; R^1 = R^3 = NO$_2$ (**5**), R = R^2 = 4-NO$_2$Ph. R^1 = R^3 = NO$_2$ (**6**).



Stereo images of 3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin and its nitro derivatives.

Porphyrins **1–6** were purified by repetitive column chromatography on silica gel and on alumina. Their individuality was proven by thin-layer chromatography on Silufol plates. The electronic absorption spectra of the porphyrins were identical to those reported in [19, 21, 22].

Zinc(II) acetate (chemically pure grade), copper(II) acetate (analytically pure grade), and cobalt(II) acetate (chemically pure grade) were purified by recrystallization from aqueous acetic acid. $Cu(AcO)_2$ and $Zn(AcO)_2$ were dehydrated by heating at 370–390 K; $Co(AcO)_2$ was dehydrated by refluxing for 3 h with acetic anhydride, followed by filtering off and washing the crystals of the salt on the filter with hexane and drying in a vacuum desiccator over potassium hydroxide.

Pyridine (pure grade) was held over potassium hydroxide and double-distilled with a dephlegmator [15]. Acetic acid (chemically pure grade) was dehydrated by fractional freezing and distilled with a dephlegmator. Benzene (analytically pure grade) was distilled with a dephlegmator. The water content of the solvents, as controlled by the Fischer titration technique [23], was no higher than 0.03%.

The rate of the formation reaction of the metal complexes of porphyrins **1–6** was examined spectro-

Table 1. Effective rate constants of the coordination of porphyrins **1–6** to zinc acetate in pyridine and in the acidic acid–benzene mixed solvent

Porphyrin	Pyridine $C[Zn(OAc)_2] = 3.5\times10^{-3}$ M			Acetic acid–benzene (7 : 3) $C[Zn(OAc)_2] = 3.5\times10^{-3}$ M		
	λ^a, nm	T, K	$k_{eff}\times10^3$, s^{-1}	λ^a, nm	T, K	$k_{eff}\times10^3$, s^{-1}
1	507	Reaction does not proceed during 3 days		574	Reaction is instantaneous upon mixing the solutions	
2	508	318	0.0012±0.0001	626	318	0.44±0.02
		328	0.0034±0.0002		328	0.90±0.03
		338	0.0103±0.0003		338	1.80±0.12
3	564	318	0.078±0.004	543	318	0.033±0.001
		328	0.184±0.005		328	0.120±0.006
		338	0.39±0.02		338	0.41±0.02
4	543	318	0.44±0.02	709	318	0.031±0.001
		328	0.86±0.03		328	0.097±0.004
		338	1.67±0.08		338	0.280±0.008
5	587	318	0.37±0.02	713	318	0.036±0.001
		328	0.78±0.04		328	0.090±0.004
		338	1.55±0.08		338	0.210±0.009
6	586	318	0.48±0.01	586	318	0.042±0.002
		328	0.84±0.03		328	0.100±0.005
		338	1.42±0.04		338	0.225±0.014

[a] (λ) Analytical wavelength.

Table 2. Effective rate constants of the coordination of porphyrins **1–4, 6** to copper acetate in pyridine and in the acetic acid–benzene mixed solvent

Porphyrin	Pyridine $C[Cu(OAc)_2] = 2.5\times10^{-3}$ M			Acetic acid–benzene (7 : 3) $C[Cu(OAc)_2] = 3.5\times10^{-4}$ M		
	λ^a, nm	T, K	$k_{eff}\times10^5$, s^{-1}	λ^a, nm	T, K	$k_{eff}\times10^3$, s^{-1}
1	507	318	2.23±0.13	532	298	5.1±0.4
		328	5.2±0.3		308	14±0.6
		338	12.0±0.6		318	29.5±1.2
2	559	318	1.24±0.07	534	298	10±0.6
		328	2.32±0.11		308	22.5±0.8
		338	4.7±0.3		318	50.3±1.2
3	521	298	44±3	606	298	2.49±0.12
		308	79±4		308	6.03±0.3
		318	136±8		318	13.6±1
4	573	288	210±10	564	298	1.08±0.04
		298	340±17		308	3.0±0.15
		308	520±30		318	8.8±0.6
		318	790±50			
6	Reaction is instantaneous upon mixing the solutions			562	298	0.945±0.056
					308	3.0±0.12
					318	8.84±0.44

[a] (λ) Analytical wavelength.

photometrically on a Hitachi U-2000 instrument in ground-glass-joint thermostatted cells over the temperature range from 228 to 338 K. The temperature fluctuations were within 0.1 K.

The spectra of all the reaction systems exhibited clear isobestic points. During each experiment, 15–25 measurements of the optical density of the solution at a certain wavelength were made at fixed time intervals. The root mean square error in determining the effective rate constants (k_{eff}) did not exceed 5%. Tables 1–6 summarize the kinetic parameters of the formation reactions of zinc, copper, and cobalt complexes of porphyrins **1–6**.

RESULTS AND DISCUSSION

Molecular mechanics (MM+ force field) calculations of the geometric structure showed that porphyrin **1** (see figure) has a planar structure of the porphyrin macrocycle. The introduction of two nitro groups to the *para* positions of the phenyl substituents caused a saddle-shaped macrocycle distortion from planarity. The structure of porphyrin **3** is much more strongly affected by the introduction of a nitro group to the meso positions of the macrocycle. The inclusion of the second nitro group in the opposite meso position of porphyrin **4** leads to a sharp distortion of the structure of the macrocyclic core. These structural features of the porphyrins characteristically affect their reactivity towards metal salts in nonaqueous solutions.

Complexation of porphyrins **1–6** with zinc, copper, and cobalt acetates $[M(AcO)_2]$:

$$H_2P + M(AcO)_2 \rightarrow MP + 2AcOH \qquad (1)$$

adheres to kinetic equation (2):

$$d[H_2P]/dt = -k[H_2P][M(AcO)_2]^n. \qquad (2)$$

Here H_2P is porphyrin, MP, metalloporphyrin, and k, rate constant of reaction (1). The formation reaction of zinc, copper, and cobalt complexes of the porphyrins of interest shows the first order with respect to the ligand. This is confirmed by the linearity of the $\log\,[C^0(H_2P)/C(H_2P)]$–$t$ plots $[C^0(H_2P)$ and $C(H_2P)$ are

Table 3. Effective constants of the coordination of porphyrins **1–6** to cobalt acetate in pyridine and in the acetic acid–benzene mixed solvent

Porphyrin	Pyridine $C[Co(OAc)_2] = 2.5\times10^{-3}$ M			Acetic acid–benzene (7 : 3) $C[Co(OAc)_2] = 3.5\times10^{-4}$ M		
	λ^a, nm	T, K	$k_{eff}\times10^3$, s^{-1}	λ^a, nm	T, K	$k_{eff}\times10^3$, s^{-1}
1	508	Reaction does not proceed during 3 days		622	318	0.46±0.02
					328	1.4±0.7
					338	3.84±0.15
2	508	318	0.023±0.001	626	318	0.74±0.04
		328	0.076±0.003		328	2.08±0.08
		338	0.24±0.01		338	5.2±0.3
3	521	318	0.211±0.019	670	318	0.040±0.002
		328	0.50±0.02		328	0.153±0.006
		338	1.10±0.05		338	0.501±0.018
4	703	308	1.60±0.07	713	318	0.109±0.004
		318	3.56±0.14		328	0.322±0.016
		328	7.07±0.03		338	0.90±0.05
5	693	308	2.15±0.11	709	318	0.12±0.03
		318	4.14±0.18		328	0.302±0.015
		328	8.4±0.4		338	0.71±0.03
6	618	Reaction is instantaneous upon mixing the solutions		701	318	0.174±0.008
					328	0.40±0.02
					338	0.85±0.04

[a] (λ) Analytical wavelength.

the initial and the current concentrations of the porphyrin, respectively]. Kinetic experiments were carried out under at least hundredfold excess of the metal acetates over porphyrin, which allowed calculating the effective constants (k_{eff}) of reaction (1) by Eq. (3).

$$k_{eff} = (1/t)\ln[(A_0 - A_\infty)/(A - A_\infty)]. \quad (3)$$

Here, A_0, A, A_∞ are the optical densities of the solution at the initial moment, at time t, and at the end of the reaction, respectively.

The rate constants k_{n+1} were calculated by Eq. (4).

$$k_{n+1} = k_{eff}/C^n[Me(AcO)_2], \quad (4)$$

where n is the reaction order with respect to the salt.

We found earlier that the reaction order with respect to copper acetate in the acetic acid–benzene (7 : 3) mixed solvent is 0.5 [19], and that in pyridine, 0.4 [25]; the reaction order with respect to $Co(AcO)_2$ and $Zn(AcO)_2$ in pyridine and in the acetic acid–benzene (7 : 3) binary solvent was estimated at unity [18, 26].

The activation energy of the metalloporphyrin formation reactions was calculated using the Arrhenius equation (5).

$$k = Ae^{-E/RT}. \quad (5)$$

The pre-exponential factor (A) was calculated by Eq. (6)

$$\ln A = \ln k_{1+n} + E/RT. \quad (6)$$

The kinetic data on the formation of zinc, copper, and cobalt complexes of porphyrins **1–6** in pyridine possessing weakly basic properties (Tables 1–6) show that, with increasing nonplanarity of the tetrapyrrole aromatic macrocycle, the reaction rate tends to increase, and the activation energy and the pre-

Table 4. Kinetic parameters of the reaction of coordination of porphyrins **1–6** to zinc acetate in the acetic acid–benzene (7 : 3) mixed solvent and in pyridine

Porphyrin	Acetic acid–benzene (7 : 3)			Pyridine		
	$k_1^{318}\times10^3$, L mol^{-1} s^{-1}	E_a, kJ/mol	A, s^{-1}	$k_1^{318}\times10^3$, L mol^{-1} s^{-1}	E_a, kJ/mol	A, s^{-1}
1	Reaction is instantaneous upon mixing the solutions			Reaction does not proceed during 3 days		
2	126±3	62±1	1.94×10^9	0.322 ±0.013	100±1	8.2×10^{12}
3	9.4±0.4	110±2	1.11×10^{16}	22.2±1.1	72±1	1.5×10^{10}
4	10.2 ±0.4	78±2	6.67×10^{10}	126±8	57±1	2.9×10^8
5	8.9±0.3	98±2	1.13×10^{14}	106±5	64±2	3.5×10^7
6	12.4±0.5	74±1	1.74×10^{10}	137±4	48±1	1.06×10^7

Table 5. Kinetic parameters of the reaction of coordination of porphyrins **1–4**, **6** to copper acetate in the acetic acid–benzene (7 : 3) mixed solvent and in pyridine

Porphyrin	Acetic acid–benzene (7 : 3)			Pyridine		
	$k_{1.5}^{298}$, L mol^{-1} s^{-1}	E_a, kJ/mol	A, s^{-1}	$k_{1.5}^{298}$, L mol^{-1} s^{-1}	E_a, kJ/mol	A, s^{-1}
1	0.360±0.014	64±2	5.97	0.245±0.014	74±1	35×10^7
2	0.63±0.04	62±2	4.67	0.132±0.009	60±3	94×10^4
3	0.157±0.011	66±1	5.82	14.9±0.9	44±1	25×10^4
4	0.068±0.003	85±1	5.42	87±5	33±2	22×10^3
6	0.190±0.008	82±1	4.49	Reaction is instantaneous upon mixing the solutions		

Table 6. Kinetic parameters of the reaction of coordination of porphyrins **1–6** to cobalt acetate in the acidic acid–benzene (7 : 3) mixed solvent and in pyridine

Porphyrin	Acetic acid–benzene (7 : 3)			Pyridine		
	$k_2^{318}\times10^3$, L mol^{-1} s^{-1}	E_a, kJ/mol	A, s^{-1}	$k_{1.5}^{298}$, L mol^{-1} s^{-1}	E_a, kJ/mol	A, s^{-1}
1	131.4±0.6	94±1	3.7×10^{14}	Reaction does not proceed during 3 days		
2	212±4	86±2	2.8×10^{13}	6.6±0.2	104±2	8.1×10^{14}
3	11.4±0.4	112±1	2.9×10^{16}	60±3	74±2	8.7×10^{10}
4	28.6±1.1	98±2	3.7×10^{14}	457±19	65±1	2.2×10^{10}
5	34.3±1.7	78±2	2.3×10^{11}	1190±60	58±2	4×10^9
6	49±2	72±2	3.2×10^{10}	Reaction is instantaneous upon mixing the solutions		

exponential factor tend to decrease. The highest reactivity in the formation reactions of the metal complexes was exhibited by porphyrins **4, 6** whose aromatic macrocycles are distorted maximally due to the presence of nitro groups at the meso positions. Porphyrin **6** is more active in the complexation reaction than porphyrin **5**. This is apparently due to the fact that the latter is more strongly solvated in the initial state than in the transition state due to the presence of an electron-withdrawing substituent (NO_2) in the *para* position of the phenyl core.

A different situation is observed in the reaction of complexation of porphyrins **1–6** with zinc, copper, and cobalt acetates in the acetic acid–benzene (7 : 3) mixed solvent (Tables 1–6). Highly distorted porphyrins exhibit extremely low reactivity in complexing. The distortion effect leads to increased basicity of the tertiary nitrogen atoms which form strong hydrogen bonds with the acetic acid molecules blocking the coordination center of the porphyrin. Slight acceleration of the complexation reaction on changing from **5** to **6** is apparently due to the fact that the distortion effect and the *–I* effect of the NO_2 groups in the phenyl cores have mutually opposite impacts on the rate of the metalloporphyrin formation reaction. Due to its negative induction effect the nitro group slightly acidifies the NH bonds of the porphyrin, thereby facilitating their stretching in the transition state.

The rate of the complexation reactions for planar porphyrin **1** and slightly distorted porphyrin **2** with $Zn(AcO)_2$, $Cu(AcO)_2$, and $Co(AcO)_2$ in the binary acetic acid–benzene (7 : 3) solvent is several orders of magnitude higher than that in pyridine. This is associated with stabilization of the first solvation shell of the salts on changing from acetic acid to pyridine [26, 27].

Depending on the nature of the salt cation, the rate of the metalloporphyrin formation reaction in acetic acid increases in the series: $Zn^{2+} < Co^{2+} < Cu^{2+}$. As already noted, the reaction of formation of the copper complexes proceeds faster compared to those in the case of the cobalt and zinc complexes. This can be obviously explained by the manifestation of the Jahn-Teller effect, responsible for the square-pyramidal configuration of the coordination sphere with two substantially stretched and weakened M–Solv bonds, taken by the copper(II) solvate complexes. It was found [28] that the main contribution to the activation energy of the coordination reactions of porphyrins comes from the energy spent in deformation and stretching of the M–Solv bonds of the solvate complexes and NH bonds of the porphyrins. Deceleration of the complexation upon changing from cobalt acetate to zinc acetate is also associated with the specific composition and structure of the solvation shells of $Co(AcO)_2$ and $Zn(AcO)_2$ [26].

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