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Spatial Structure of Molecular Complexes of Zinc(II)tetraphenylporphyrin with Pyridine and Aniline Derivatives

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Abstract—Structure of molecular complexes of zinc(II)tetraphenylporphyrin with 4-dimethylaminopyridine and 4-methoxyaniline has been studied by X-ray diffraction analysis. 4-Dimethylaminopyridine is coordinated almost perpendicular to the porphyrin cycle plane, whereas 4-methoxyaniline is coordinated at lower dihedral angle. The hybridization of aniline nitrogen atom in the crystal depends on donor-acceptor properties and the volume of the substituents in the aromatic ring.

Keywords: pyridine, aniline, tetraphenylporphyrin, X-ray diffraction, rehybriization

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Previously we studied coordination of zinc(II) tetraphenylporphyrin (Zn-TPP) with pyridine and its derivatives in chloroform by means of electron absorption spectroscopy [1, 2]. Provided that steric factor was negligible, linear correlations were found between the complexes stability constant, thermodynamic parameters of the interaction (ΔH^0, ΔS^0, ΔG^0), and red shift of the spectral absorption maximum on the one hand and pK_a of the ligand and σ-constant of the ligand substituent, on the other hand. Moreover, for the mentioned complexation process a linear relationship was observed between ΔH^0 and ΔS^0, the isoequilibrium temperature being 196 K.

In contrast to pyridine-type ligands, complex formation between Zn-TPP and aniline derivatives (except for 4-haloanilines) occurred with zero enthalpy change [3].

In order to elucidate the origin of different coordination behavior of the two classes of nitrogen-containing ligands, we investigated the structure of Zn-TPP complexes with 4-dimethylaminopyridine and 4-methoxyaniline by X-ray diffraction analysis (Table 1; Figs. 1 and 2).

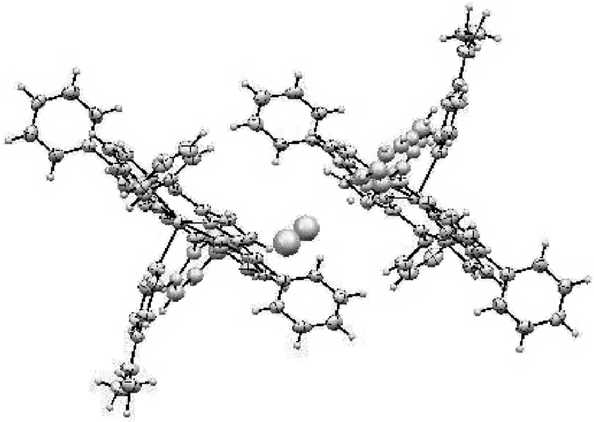
Zn-TPP complex with 4-dimethylaminopyridine exists in two pseudo polymorphic forms: **Ia** and **Ib**. In both forms, the Zn-TPP to ligand ratio was 1 : 1; in one of the forms $0.5H_2O$ co-crystallized with the complex molecule, and one of the benzene rinds was disordered (**Ib** in Fig. 1).

In **Ia** complex (Fig. 1), zinc atom was off the porphyrin ring plane by 0.391 Å and was located at

Table 1. Bond lengths (Å) and angles (deg) in Zn-TPP complexes with 4-dimethylaminopyridine (**Ia**, **Ib**) and 4-methoxyaniline (**II**)

Parameter	**Ia**	**Ib**	**II**
$Zn^1–N^5$	2.00(1)	2.114(5)	2.207(5)
$N^5–C^{45}$	1.29(2)	1.342(9)	1.420(8)
$N^5–C^{49}$	1.47(2)	1.345(7)	–
$N^6–C^{47}$	1.29(2)	1.35(1)	–
$N^6–C^{51}$	1.41(2)	1.470(9)	–
l^a	0.391	0.446	0.22
φ^b	63.53	71.36	23.22
$O^{11}–O^{12}$	–	0.99(5)	–

[a] Distance between the porphyrin plane and Zn atom. [b] Angle between the porphyrin plane and aromatic ring of the ligand.



Ia **Ib**

Fig. 1. Structure of Zn-TPP molecular complexes with 4-dimethylaminopyridine (**Ia**, **Ib**) (in the center: disordered water molecule).

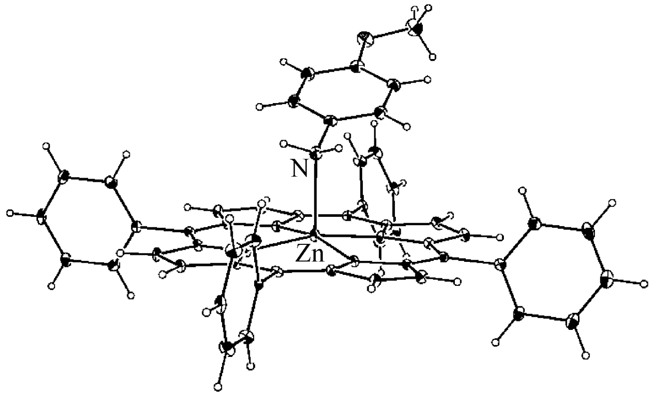


Fig. 2. Structure of Zn-TPP complex with 4-methoxyaniline (**II**).

1.998 Å from the pyridine nitrogen atom; in the case of **Ib** complex the respective distances were 0.446 and 2.114 Å. The angles between porphyrin and pyridine planes were 63.53º (**Ia**) and 71.36° (**Ib**). The dimethylamino group was slightly twisted, the CNC angles between the pyridine ring plane and the dimethylamino group plane were 8.15º (**Ia**) and 2.49° (**Ib**).

In Zn-TPP complexes with other pyridine derivatives [4] the angle between porphyrin and pyridine planes were even closer to 90°: 89.02° (3-amino-), 83.00° (4-amino-), 86.14° [4-(4-dimethylaminostyryl)-], and 88.64° [4-(4-trifluoromethylstyryl)-].

Structure of Zn-TPP complex with 4-methoxy-aniline **II** is given in Fig. 2. In that complex, zinc atom was off the porphyrin ring plane by 0.22 Å and was located at 2.21 Å from the amino group nitrogen atom; the angle between porphyrin and benzene planes was 23.22°.

The values of angles (HNH, 107.53°; HNC 108.48° and 108.47°; HNZn, 108.48° and 108.49°) show that the amino group nitrogen exists in the sp^3 hybridization state when in complex.

In the 1 : 1 Zn-TPP complex with 3-nitroaniline zinc atom was off the porphyrin ring plane by 0.249 Å and was located at 2.214 Å from the amino group nitrogen atom; the angle between porphyrin and benzene planes was 25.98°. The respective angle in Zn-TPP complex with 2-chloroaniline was 31.47° [4].

Hence, Zn-TPP complexes with pyridine and aniline derivatives differ in the angle between porphyrin and the ligand ring planes: 64°–89° in the former case and 23°–32° in the latter case. Probably, just the ability for the π–π interaction between porphyrin and the ligand that determines thermodynamic properties of the complexes with aniline derivatives in chloroform.

Noteworthily, in the solid Zn-TPP complexes the distance between porphyrin cycle and zinc atom was longer in the case of pyridine derivatives, coinciding with the higher basicity of the latter: 4-methoxyaniline, pK_a 5.34 [5, 6], 4-dimathylaminopyridine, pK_a 9.71 [7].

In the case of aniline derivatives, including the 2-substituted ones, the enthalpy change upon complex formation was close to zero; therefore, ΔS^0 of the complex formation was linear with the complex stability constant [3]: $\Delta S^0 = 19.48 \log K - 50.09$ ($r = 0.998$, $n = 18$).

Decrease of the coordination ΔS^0 in the case of aniline derivatives containing primary amino group was in line with the deteriorating electron donor properties of the benzene ring substituents; this could be related to the changes of character of the nitrogen *p*-orbital due to the electron density drift towards the benzene ring ($sp^3 \rightarrow sp^2$ rehybriization). Formation of the N–Zn coordination bond would imply even more significant structural rearrangement to allow for the reverse $sp^2 \rightarrow sp^3$ process.

Analysis of X-ray diffraction data [4] for 124 derivatives of aniline, their salts, and molecular complexes [8] demonstrated that the formation of the new bond

Table 2. X-ray diffraction data for X-substituted anilines [4]

Comp. no.	X	r(C–N), Å	α[a], deg	θ[b], deg	CSD refcode
I	4-NH_2[c]	1.394	112.79	32.61	PDTCNB
II	4-NMe_2	1.409(NH_2) 1.425(NMe_2)	114.96 111.97	43.38 48.81	GILYOP
III	4- OCH_3	1.398	108.78	33.55	PANISD01
IV	4-CH_3	1.400	116.72	25.91	EDACUI
V	H[d]	1.394	110.48	35.40	RAPLEA
VI	4-F	1.395	111.29	37.45	IDAHUR
VII	4-Cl	1.387	114.52	32.61	CLANIC05
VIII	4-Br	1.396	120.93	27.16	PBRANL01
IX	4-I	1.397	117.74	38.93	EJAYET
X	4-NO_2	1.355 1.355	121.02 123.46	4.35 6.97	NANALI02 NANALI21
XI	2-COMe, 4-Br	1.363	120.06	3.26	ICANAB
XII	2-Cl, 3,5-$(NO_2)_2$	1.356	120.01	1.60	RATHAW
XIII	2-Cl, 4,6-$(NO_2)_2$	1.327	121.88	2.40	UCECAG03
XIV	2-NO_2, 5-Cl	1.340	117.43	4.59	RAPKUP
XV	4-Cl, 6-NO_2	1.348	120.00	1.44	WEVNIV
XVI	4-I, 2-NO_2	1.343	120.05	0.75	CAMSOZ
XVII	2,4-I_2, 3-NO_2	1.380	119.99	0	CAMSUF
XVIII	4-I, 2-COO^-	1.346	119.88	0	MAVMEC
XIX	4-CH_3, 2,6-$(NO_2)_2$	1.367	120.00	0	ISAYAC01

[a] The HNH, CNH, or CNC angle. [b] The angle between the planes of benzene ring and amino group. [c] Complex with $(NC)_2C=C(CN)_2$. [d] Complex with 3,4-dichloronitrobenzene.

via the lone-electron pair of nitrogen atom led to the C−N bond elongation from 1.340–1.406 to 1.433–1.485 Å, the bond angle α at the nitrogen atom corresponding to the sp^3 state (≈109°). As far as free aniline and its derivatives are concerned, combined analysis of data r(C–N), α, and θ (angle between the benzene ring and the amino group planes) allows for the estimation of the hybridization state of nitrogen atom: sp^3, α ≈109° and θ = 20°–50°; sp^2, α ≈ 120° and θ ≈ 0°. For instance, in the case of compounds **I–IX** (Table 2) θ was 26°–49°, increasing with higher volume of the neighbor substituents. In the case of hexakis(*N,N*-dimethylamino)benzene (GENFAG) θ reached 89.74°; hence, in that compound nitrogen was found in the sp^3 state. The introduction of nitro group into the ring of 4-methylaniline or introduction of acetyl group into the ring of 4-bromoaniline (Table 2) resulted in shortening of the C–N and in the decrease of θ value (α value approached 120°), evidencing $sp^3 \rightarrow sp^2$ rehybriization of the amino group nitrogen.

In compounds **X–XIX** (Table 2) that contain electron-acceptor groups, θ = 0°–7°, α = 117°–123°, and the C−N bond (1.355–1.380 Å) was shorter than that in compounds **I–IX** (1.387–1.425 Å). Hence, in compounds **X–XIX** nitrogen atom was in the sp^2 state.

Evidently, Zn-TPP coordination with compounds **X–XIX** (sp^2 nitrogen atom) should result in electrons

Table 3. Experimental crystal structure parameters of complexes **Ia**, **Ib**, and **II** and parameters of the structure refinement

Parameter	**Ia**	**Ib**	**II**
Formula	$C_{51}H_{38}N_6Zn$	$C_{51}H_{39}N_6O_{0.50}Zn$	$C_{51}H_{37}N_5OZn$
M	800.24	809.25	801.23
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Z	2	2	2
a, Å	10.890(9)	11.1528(17)	10.5613(16)
b, Å	11.130(10)	13.238(2)	10.6564(16)
c, Å	17.054(15)	15.004(2)	18.301(3)
α, deg	90.03(2)	71.403(4)	79.447(3)
β, deg	94.09(2)	71.047(3)	86.473(3)
γ, deg	105.54(2)	84.280(4)	78.170(3)
V, Å^3	1986(3)	1985.8(5)	1981.3(5)
d_x, g/cm^3	1.338	1.353	1.343
Radiation	MoK_α	MoK_α	MoK_α
λ, Å	0.71073	0.71073	0.71073
μ, cm^{-1}	0.663	0.665	0.666
T, K	173(2)	173(2)	160(2)
Specimen size, mm	0.22×0.2×0.2	0.2×0.14×0.05	0.1×0.1×0.05
θ, deg (range)	2.21–22.5	2.05–25.0	2.26–25.0
Indexes range			
h	$-11 \le h \le 11$	$-13 \le h \le 13$	$-12 \le h \le 12$
k	$-11 \le k \le 10$	$-15 \le k \le 11$	$-12 \le k \le 12$
l	$-18 \le l \le 18$	$-17 \le l \le 11$	$-21 \le l \le 21$
Reflections: detected/independent (N_1),	10249/5173	10926/6726	15831/6906
R_{int}/ with $I > 2\sigma(I)$ (N_2)	0.3219/1896	0.1148/4151	0.1051/4334
Parameters	368	525	523
R_1/wR_2 over N_1	0.2259/0.2352	0.1554/0.2025	0.1230/0.1866
R_1/wR_2 over N_2	0.0789/0.1796	0.0693/0.1630	0.0658/0.1594
Finesse S	0.857	1.087	1.105
$\Delta\rho_{min}/\Delta\rho_{max}$	–0.442/0.616	–1.035/1.002	–0.802/1.236

shifting from the benzene ring, and the charge delocalization on the nitrogen atom ($sp^2 \to sp^3$ rehybriization accompanying the complex formation). With deterioration of the amino group conjugation with the π-electron system (that is, with more electron-donor substituents), the absolute value of negative ΔS^0 of the Zn-TPP complex formation in chloroform [3] decreased, being close to zero in the case of 4-methoxyaniline and even positive (5.86 J mol^{-1} K^{-1}) in the case of *p*-phenylenediamine. On the contrary, in the case of the complex with 3-niroaniline, $\Delta S^0 = -17.3 \pm 0.62$ J mol^{-1} K^{-1}, and should further decrease in the cases of compounds 10–19. The stability constant of Zn-TPP complex with *p*-nitroaniline (**X**, Table 2) was too low (K = 12.4±0.3 L/mol), and the ΔS^0 value could not be determined.

To conclude, X-ray diffraction data showed that in solid state hybridization type of amino group nitrogen of aniline derivatives was governed by electronic and steric effects of the substituents present in the benzene ring. In the case of anilines with strong electron-acceptor ligands, the formation of the complex with Zn-TPP was accompanied with $sp^2 \rightarrow sp^3$ rehybridization. We suppose that similar changes should occur in the course of the complexes formation in chloroform.

We plan further studies of the above-mentioned complexes by means of gas electron diffraction, as the data collected in the absence of intermolecular interactions will extend the knowledge of the complexes structure.

EXPERIMENTAL

Electron absorption spectra were registered using an SF 2000-02 spectrophotometer. Stability constants of the complexes between Zn-TPP and the studied amines in chloroform were determined as described elsewhere [3]. X-ray diffraction studies of single crystals were performed using the Bruker APEX-II CCD diffractometer. The structures were refined applying the SHELXS-97 and SHELXL-97 software [9]. Basic crystal structure parameters and refinement conditions are collected in Table 3. The structural data were deposited in the Cambridge Crystallographic Data Centre: CCDC 924014 (**Ia**), 924013 (**Ib**), and 924012 (**II**).

Zn-TPP complexes with 4-dimethylaminopyridine (Ia, Ib). Solutions of Zn-TPP (1.47×10^{-5} mol, 10 mg in 10 mL of acetone) and 4-dimethylaminopyridine (1.55×10^{-5} mol, 1.9 mg in 1 mL of acetone) were mixed and kept in the dark till complete solvent evaporation. The formed crystals were washed with hexane (3 × 2 mL) and dried in air.

Zn-TPP complex with 4-methoxyaniline (II). Saturated solutions of Zn-TPP (1.47×10^{-5} mol, 10 mg in 10 mL of acetone) and 4-methoxyaniline (1.9 mg, 1.55×10^{-5} mol in acetone) were mixed and kept in the dark till complete solvent evaporation. The formed crystals were washed with acetone (3 × 2 mL) and dried in air.

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