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Crystal Structure of Molecular Complexes of Zinc(II) Tetraphenylporphyrin with Pyridine and Quinoline *N*-Oxides

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Abstract—The structure of molecular complexes of zinc(II) tetraphenylporphyrin (Zn-TPP) with 4-methoxy- and trans-2-(4-dimethylaminostyryl)pyridine and 4-methoxy-, 4-nitro, and 4-chloroquinoline *N*-oxides was studied by X-ray diffraction analysis. Heteroaromatic *N*-oxides, like aniline derivatives, are coordinated at an angle of 26°–32° to the porphyrin ring plane, whereas pyridine ligands are coordinated almost perpendicularly to this plane. It is suggested that just such coordination peculiarities are responsible for the difference in the thermodynamic parameters of Zn-TPP with pyridine-based ligands (linear relationship between ΔH^0 and ΔS^0, high heat effect of the process), and *N*-oxides, aniline derivatives (low ΔH^0 values, quasi-isenthalpic processes).

Keywords: zinc(II) tetraphenylporphyrin, molecular complexes, pyridine and quinoline *N*-oxides, X-ray diffraction analysis

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Previously [1, 2], we studied the coordination of Zn-TPP with pyridine and its derivatives in chloroform by electronic spectroscopy. It was found that in the absence of steric effects linear relationships between the stability constants of the Zn-TPP complexes with pyridine and its derivatives, thermodynamic parameters (ΔH^0, ΔS^0, ΔG^0), coordination-induced red shifts of absorption maxima in the electron absorption spectra of Zn-TPP, basicities (pK_a), and substituent σ-constants are fulfilled. Moreover, the complex formation of Zn-TPP with pyridine and its derivatives in chloroform is characterized by a linear relationship between ΔH^0 and ΔS^0 and the isoequilibrium temperature 196 K.

Unlike observations found for pyridine and its derivatives, the complex formation of Zn-TPP with heteroaromatic *N*-oxides and aniline with substituents in the 2, 3, and 4 positions and at the nitrogen atom (except for 4-halo derivatives) is accompanied by a low heat release and can be considered, to a first approximation, as isenthalpic processes [3, 4].

To gain insight into the reasons for such a strong difference in the coordination behavior of these classes of ligands, we have studied the structure of Zn-TPP complexes with 4-methoxy- and *trans*-2-(4-dimethylaminostyryl)pyridine *N*-oxides (**Ia** and **Ib**) and 4-methoxy- and 4-nitroquinoline *N*-oxides (**IIa** and **IIb**) by X-ray diffraction (XRD) analysis (Table 1, see the figure). The metal porphyrin : ligand ratio in the complexes is 1 : 1.

In the complex of Zn-TPP with 4-nitroquinoline *N*-oxide (**IIb**), the zinc atom deviates from the porphyrin ring plane by 0.226 Å and is 2.186 Å distant from the N→O oxygen atom. The angle between the porphyrin and quinolone rings is 26.00°. The NO_2 group is slightly turned out so that the angle between the quinolone ring and NO_2 group planes is 13.14°.

The structures of the other Zn-TPP complexes with heteroaromatic *N*-oxides are shown in the figure. The angle between the planes of the porphyrin and ligand heteroaromatic ring in all the structures is 26.00°–31.41° (Table 1). The OMe group in the Zn-TPP

Table 1. Bond lengths and bond angles in the 1 : 1 complexes of Zn-TPP with 4-methoxy- and *trans*-2-(4-dimethylaminostyryl)pyridine *N*-oxides (**Ia, Ib**) and 4-methoxy-, 4-nitro-, and 4-chloroquinoline *N*-oxides (**IIa, IIb, IId**)

Parameter	**Ia**	**Ib**	**IIa**	**IIb**	**IId** [a]
N→O bond length, Å	1.316	1.335	1.348	1.303	1.332 O^{11}–N^{51}
Distance between the porphyrin plane and zinc atom, Å	0.360	0.408	0.219	0.226	0.28
Zn–O bond length, Å	2.042 (2.367)	2.091	2.134	2.186	2.129
Angle between porphyrin and ligand aromatic ring planes, deg	27.14	31.41	26.55	26.00	26.58

[a] Data from [4].

complexes with ligands **Ia** and **IIa** forms angles of 4.04° and 2.81° with the heteroring ring planes.

Special attention should be focused on the structure of the Zn-TPP complex with *trans*-2-(4-dimethylaminostyryl)pyridine *N*-oxide (**Ib**), where the angle between the planes of the pyridine and ligand benzene ring is 39.95°, and the dimethyamino group is turned from the phenyl ring plane by 6.70°.

According to the XDR data, in the Zn-TPP–**Ib** complex the angle between the pyridine and benzene ring planes is 43.99° and the N→O bond length is 1.275 Å, i.e., at the coordination of the ligand with Zn-TPP the latter bond is elongated, which implies $sp^2 \rightarrow sp^3$ rehybridization of the oxygen atom. In view of the fact that the molecule of ligand **Ib** is planar [5], we can suggest electrostatic repulsion between the sp^3 orbital of the N→O oxygen atom and the *s* orbital of the hydrogen atom at the C=C bond both in the free and Zn-coordinated ligand **Ib**.

At the coordination of Zn-TPP with heteroaromatic *N*-oxides in chloroform [4], the ΔH^0 values for pyridine *N*-oxides with substituents in the 3 and 4 positions and the styryl substituent in the 2 position, as well as for 4-substituted quinolone *N*-oxides are close to each other (ΔH^0_{av} –13.78±0.15 kJ/mol, *n* 22, series A), whereas the ΔH^0 values for 2-methylpyridine, 2-methylquinoline, and 2-styrylquinoline *N*-oxides, too, vary in a narrow range but are much higher (ΔH^0_{av} –12.04±0.18 kJ/mol, *n* 9, series B). Thus, in each of the two series of heteroaromatic *N*-oxides (for aniline with substituents in the 3 and 4 positions, ΔH^0_{av} –14.76±0.14 kJ/mol [3]), the coordination with Zn-TPP is a quasi-isenthalpic process.

As shown in [4], the ΔS^0 of Zn-TPP complex formation with 3- and 4-substituted pyridine and quinoline *N*-oxides in chloroform is proportional to the basicity of the ligands [Eqs. (1) and (2), respectively].

$$\Delta S^0 = 6.67 pK_a + 4.96;\ n\ 11,\ r\ 0.998, \quad (1)$$

$$\Delta S^0 = 7.12\ pK_a + 11.47;\ n\ 4,\ r\ 0.999. \quad (2)$$

Even though the very possibility of coordination is controlled by enthalpy (the main contribution to ΔG^0), the fact that the properties of the ligand and the entropy of its coordination with Zn-TPP vary in parallel suggests an essential effect of the entropy factor on the thermodynamic stability of the complexes.

The structures of the Zn-TPP complexes with heteroaromatic *N*-oxides and aniline derivatives in the solid phase are similar to each other. In the 1 : 1 complexes of Zn-TPP with 3-nitroaniline ([6]; CSD refcode: HAMLAI) and 2-chloroaniline (JIVNIL), the angles between the porphyrin and benzene ring planes are 25.98° and 31.37°, respectively.

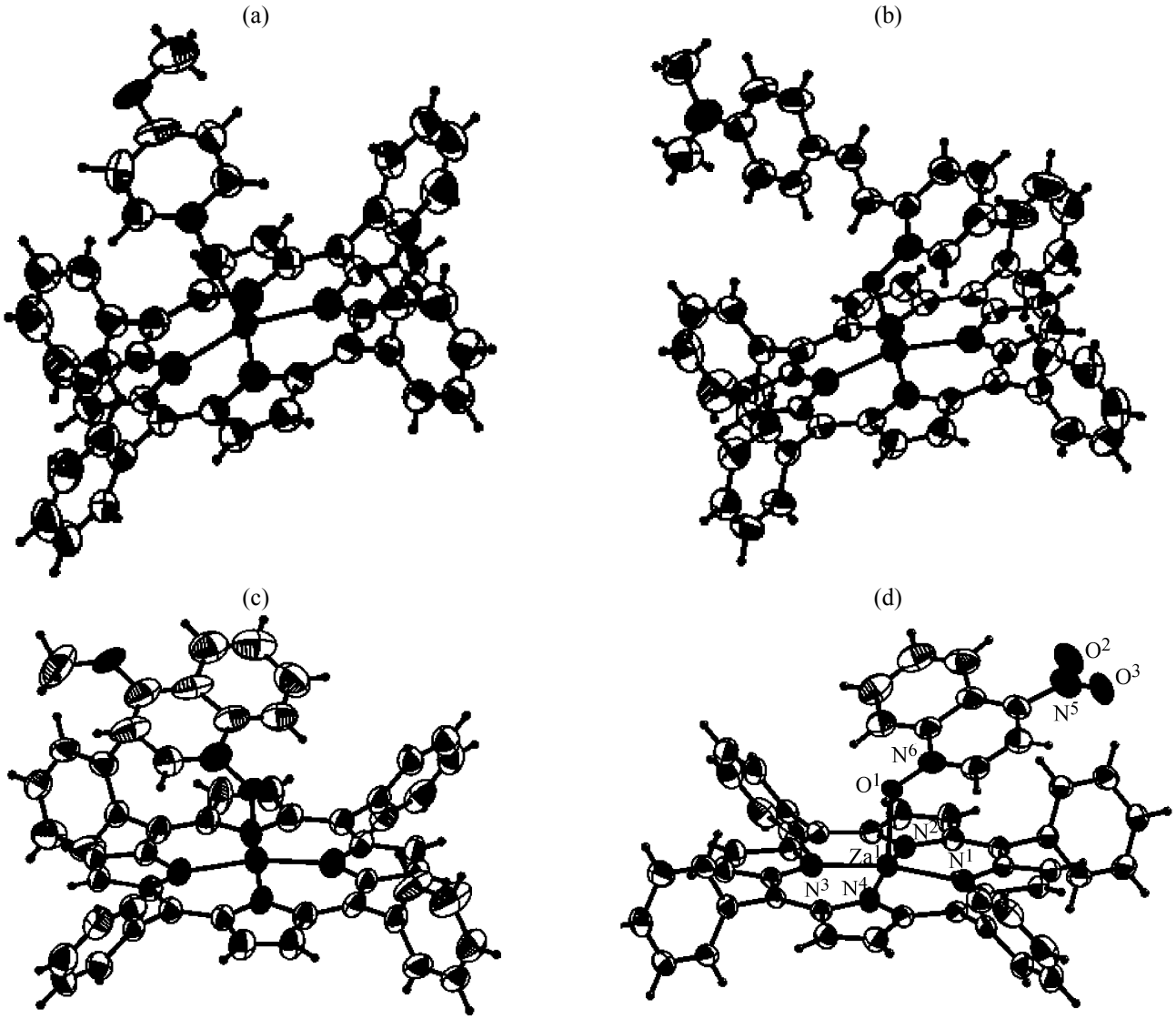
As we showed in [3], the ΔS^0 of the coordination of the members of the isenthalpic series of aniline derivatives, including *ortho*-substituted ligands, with Zn-TPP in chloroform is linearly related to log *K* [Eq. (3)].

$$\Delta S^0 = 19.48 \log K - 50.09;\ n\ 18,\ r\ 0.998. \quad (3)$$

The ΔS^0 of the coordination of Zn-TPP with aniline derivatives containing primary amino groups (like with heteroaromatic *N*-oxides) decrease in parallel with decreasing electron-donor (increasing electron-acceptor) properties of substituents in the benzene ring [Eq. (4)]. This can be ascribed [7] to the gradual increase in the *p*-contribution to the lone pair orbital of the nitrogen atom due to electron density displacement to the benzene ring and, as a result, $sp^3 \rightarrow sp^2$ rehybridization of the nitrogen atom.

$$\Delta S^0 = -11.56\sigma^+ - 9.15;\ n\ 10,\ r\ 0.98. \quad (4)$$

Complex formation should affect the steric environment of the reaction center (the ligand molecules become more planar), whereas N–Zn coordination leads to structural reorganization and induced the reverse process, specifically $sp^2 \rightarrow sp^3$ rehybridization.



Structures of 1 : 1 complexes of Zn-TPP with *N*-oxides of (a) 4-methoxypyridine (**Ia**), (b) *trans* -2-(4-dimethylaminostyryl)pyridine (**Ib**), (c) 4-methoxyquinolinea (**IIa**), and (d) 4-nitroquinoline (**IIb**). The thermal ellipsoids are drawn at a 50% probability level.

Our analysis of the data for aniline derivatives, their salts, and molecular complexes, available in the Cambridge Structural Database over 1970–2010 [7], shows that the formation of a new bond, involving the lone electron pair of the aniline nitrogen leads to the elongation of the C–N bond from 1.340–1.406 to 1.433–1.485 Å. The nitrogen bond angles α of ~109° suggest sp^3 hybridization of this atom. The values of the C–N bond lengths and the α and τ (the angles between the amino group and aromatic ring planes) angles in free ligands allow the estimation of the degree of the sp^3 (α ~ 109°, τ 20°–50°) and sp^2 (α 120°, τ 0°) hybridization of the nitrogen atom. Nitro substitution in the benzene ring of aniline and 4-methyl-, 4-methoxy-, 4-iodo-, and 4-chloroaniline, as well as COMe substitution in the benzene ring of 4-bromoaniline decreases the C–N bond length and the τ angle (α is close to 120°), which implies $sp^3 \rightarrow sp^2$ rehybridization of the NO_2 nitrogen atom.

In anilines containing alkyl substituents (positive effects: hyperconjugation for alkyl substituents in the *ortho* and *para* positions and inductive effect for alkyl substituents in all positions of the benzene ring) and functional groups that exhibit +*M* effect, the τ angle is 22°–49°, and it increases with increasing volume of the

Table 2. Crystal data, experimental details, and structure refinement parameters for Zn-TPP complexes with heteroaromatic *N*-oxides **Ia, Ib, IIa**, and **IIb**

Parameter	**Ia**	**Ib**	**IIa**	**IIb**
Empirical formula	$C_{50}H_{35}N_5O_2Zn$	$C_{59}H_{44}N_6OZn{\cdot}2CHCl_3$	$C_{54}H_{37}N_5O_2Zn$	$C_{53}H_{34}N_6O_3Zn$
M	803.2	1157.11	853	868.23
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	*P*21/*c*	*P*-1	*P*-1	*P*-1
Z	8	2	2	2
a, Å	14.8337(2)	11.4412(2)	10.4166(2)	10.3080(2)
b, Å	36.2040(4)	13.3102(2)	13.5191(2)	13.4128(2)
c, Å	15.6493(2)	20.0847(3)	16.1245(3)	15.7420(2)
α, deg	90.00	73.9660(10)	68.3470(10)	70.323(2)
β, deg	107.9540(10)	87.7650(10)	84.5570(10)	86.238(2)
γ, deg	90.00	69.5740(10)	75.188(2)	77.030(2)
V, Å^3	7995.03(17)	2749.18(8)	2040.34(6)	1996.98(6)
d_x, g/cm^3	1.335	1.398	1.389	1.444
Radiation wavelength, Å	1.54186	1.54186	1.54186	1.54186
μ, cm^{-1}	1.229	3.680	1.239	1.305
T, K	295	295	295	295
Sample dimensions, mm	0.15×0.08×0.08	0.08×0.05×0.05	0.12×0.05×0.04	0.12×0.06×0.06
θ, deg	<70	<69	<68	<72
Number of unique reflections	15042	8973	7122	7475
$I > 2\sigma(I)$	5168	5186	2713	4826
Number of refined parameters	1098	679	560	520
R	0.058	0.073	0.059	0.044
GOF	0.73	0.88	0.72	0.86
$\Delta\rho_{min}/\Delta\rho_{max}$	0.66/–1.29	1.21/–1.09	0.72/–0.63	0.38/–0.53

neighboring substituents [up to 89.74° in the hexa (dimethylamino)benzene]. Vice versa, with increasing number of –*M* functional groups in the benzene ring [NO_2, COOH, COOR, C≡CH, C≡N, C(H)=O, and C(R)=O], this angle decreases (0°–7°), the molecule becomes more planar, and the nitrogen atom eventually changes its hybridization to sp^2.

Consequently, according to the Cambridge Crystallographic Database, the hybridization of the amino nitrogen in aniline derivatives in the solid phase is controlled by the electronic and steric effects of substituents in the benzene ring.

The angles between porphyrin and pyridine ring planes in solid Zn-TPP complexes with pyridine ligands [6] are close to 90° [3-amino (BORJEY) 89.02°, 4-amino (BORJIC) 83.00°, 4-(4-dimethylaminostyryl) (YEHQOS) 86.14°, 4-(4-trifluoromethylstyryl) (YEHQUY) 88.64°]. For the coordination of Zn-TPP with pyridine derivatives in chloroform [2], a linear dependence (5) was obtained. This result implies that this process (unlike that observed with aniline derivatives and heteroaromatic *N*-oxides) is isoequilibrium and isothermodynamic.

$$\Delta H^0 = 196.12\Delta S^0 - 19100;\ r\ 0.9999. \quad (5)$$

Thus, the small angle between the metal porphyrin macroring and ligand aromatic ring planes in solid Zn-TPP complexes with heteroaromatic *N*-oxides and aniline derivative (unlike complexes with pyridine ligands) does not prevent π–π bonding between these planes (such interactions are possible in solutions, too).

It can be suggested that just such structural differences in the molecular complexes govern the thermodynamic features of coordination with the studied ligands.

EXPERIMENTAL

Complexes of Zn-TPP with heteroaromatic *N*-oxides Ia, Ib, IIa, IIb. A mixture of acetone solutions of Zn-TPP (1.47×10^{-5} mol, 10 mg in 10 mL) and pyridine or quinoline *N*-oxide (1.55×10^{-5} mol in 1 mL) was kept in the dark in air at room temperature. The crys-tals that formed were washed with acetone (3 × 2 mL) and dried in air.

X-ray diffraction analysis of single crystals was performed on a StadiVari Pilatus 100K STOE diffractometer (CuK_α radiation). Data collection, processing and refinement of unit cell parameters, and processing of diffraction data were performed using STOE X-Area software. The principal crystal data, measurement conditions, and structure refinement parameters are listed in Table 2. The structures were solved by the direct method using SHELXS-97 software[8]. The geometric and thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares using anisotropic temperature factors. Hydrogen atoms were located and refined isotropically using the *rider* model. The graphic representation of molecules in crystal was performed using DIAMOND software [9].

The structural data were deposited in the Cambridge Crystallographic Data Center [CCDC 991715 (**IIb**), 912709 (**Ia**), 912706 (**Ib**), 912707 (**IIa**)].

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