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Coordination of Zinc Tetraphenylporphyrin with Pyridine Derivatives in Chloroform Solution and in the Solid Phase

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Abstract—Coordination of zinc tetraphenylporphyrin with 2-,3-, and 4-halopyridines, pyridin-2-amine, and pyrimidin-2-amine in chloroform has been studied by spectrophotometry. Protonation and complexation of halopyridines and haloanilines with zinc tetraphenylporphyrin are discussed. According to the X-ray diffraction data, enhanced stability of the 2:2 zinc tetraphenylporphyrin complex with pyrimidin-2-amine in the solid phase and in chloroform solution is likely to be determined by hydrogen bonding between the two ligand molecules involving nitrogen atoms in the pyrimidine ring and amino group.

Keywords: coordination, zinc tetraphenylporphyrin, pyridine derivatives, pyrimidin-2-amine, aniline derivatives, X-ray analysis

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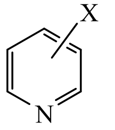
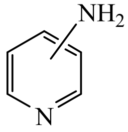
Unlike other aniline derivatives, 3- and 4-haloanilines behave unusually in the complexation with zinc tetraphenylporphyrin (Zn-TPP) in chloroform [1, 2]. For example, the ΔH^0 values of aniline derivatives (except for 4-haloanilines and 2,6-dichloroanilines) are fairly similar ($\Delta H^0_{\text{av}} = -14.7\pm0.1$ kJ/mol; $n = 20$); i.e., their coordination with Zn-TPP (including 3- and 2-haloanilines) is an isenthalpic process, and ΔS^0 is linearly related to log$K$ where K is the stability constant of the complex (Fig. 1a). Of particular interest is the behavior of 4-haloanilines, for which ΔH^0 changes from –13.47 to –15.62 kJ/mol upon complexation with Zn-TPP. These ligands (Fig. 1) show no linear correlation between ΔS^0 and substituent constants σ^+ or between ΔS^0 and log$K$ (ΔG^0), though such correlations are typical of other aniline derivatives. The ΔS^0–σ^+ correlation for 3-haloanilines (Fig. 1b) also deviates from linearity, though to a lesser extent.

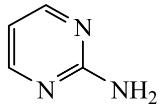
We have compared peculiar features of Zn-TPP coordination with halopyridines **1a**–**1i**, pyridine (**1j**), pyridin-2- and -4-amines **2a** and **2b**, and pirimidin-2-amine (**3**) in chloroform. The coordination of Zn-TPP with 3- and 4-halopyridines was characterized by good linear correlations between log$K$ and $\Delta\lambda$ (shift of the absorption maximum of Zn-TPP due to coordination with n-donor ligand in chloroform), on the one hand, and pK_{a} and Hammett σ-constants, on the other (r = 0.99–0.999) [2, 3]. We have found that the change of ΔH^0 upon coordination of Zn-TPP to pyridine derivative is linearly related to the ligand basicity and Hammett constant σ ($\Delta H^0 = 1895\,\text{p}K_{\text{a}} - 27000$, r = 0.99; $\Delta H^0 = -10580\sigma - 17085$; r = 0.994) and that the absolute value of ΔH^0 increases as pK_{a} of the ligand decreases. The ΔS^0 values are also linear in pK_{a} of the ligands and Hammett constants ($\Delta S^0 = 9.77\,\text{p}K_{\text{a}} - 40.2$, r = 0.99; $\Delta S^0 = -54.68\sigma + 10.79$, r = 0.994). Unlike aniline derivatives, the complexation of Zn-TPP with substituted pyridines is isoequilibrium or isothermodynamic ($\Delta H^0 = 194\Delta S^0 - 19190$, r = 0.9997). The new data obtained in this work for halogen-substituted pyridines are given in Table 1.



1a–**1j**



2a, **2b**



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1, X = 4-Cl (**a**), 4-I (**b**), 3-F (**c**), 3-Cl (**d**), 3-Br (**e**), 3-I (**f**), 2-F (**g**), 2-Cl (**h**), 2-Br (**i**), H (**j**); **2**, X = 4-NH$_2$ (**a**), 2-NH$_2$ (**b**).

Unlike aniline derivatives, the complexation of Zn–TPP with 2-halopyridines showed no linear ΔS^0–log$K$ correlation (Fig. 2a). This may be accounted for by

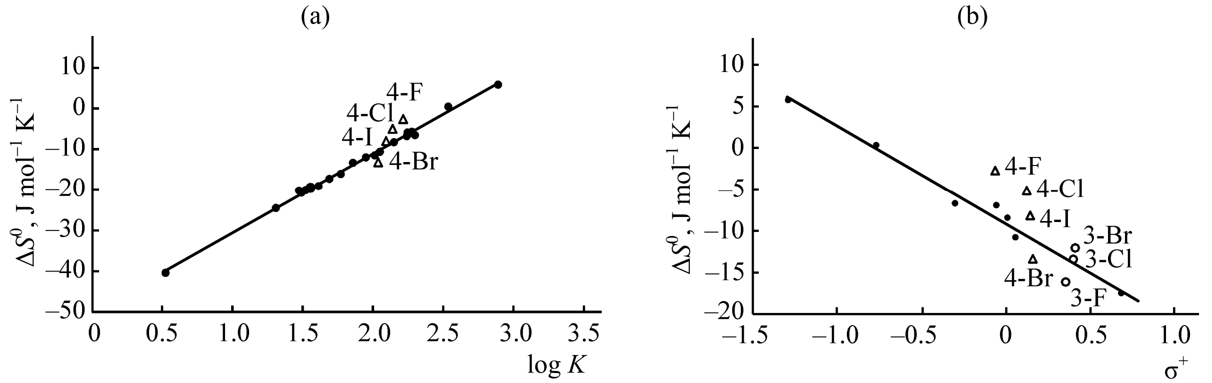

Fig. 1. Plots of ΔS^0 versus (a) $\log K$ and (b) substituent constants σ^+ for the complex formation of Zn-TPP with substituted anilines in chloroform at 25°C; $\Delta S^0 = 19.46\log K - 50.07$; $n = 14$, $r = 0.99$ (X = H, 3-Me, 4-Me, 3-MeO, 4-MeO, 4-NH_2, 3-NO_2, 3-F, 3-Cl, 3-Br, 2-F, 2-Cl, 2-Br, 2-I); $\Delta S^0 = -11.56\sigma^+ - 9.15$; $n = 7$, $r = 0.98$ (X = H, 3-Me, 4-Me, 3-MeO, 4-MeO, 4-NH_2, 3-NO_2) [1, 2].

greater steric hindrances created by the α-substituent for coordination to the pyridine nitrogen atom in comparison to the NH_2 group in substituted anilines. Likewise, no linear correlation was observed between the thermodynamic parameters for coordination of 3-halopyridines and $\log K$, though steric effect of the β- or γ-substituent on the coordination to Zn–TPP should be insignificant (anomalous behaviors of 4-halopyridines and 4-haloanilines are similar). As with aniline derivatives, the points for 3- and 4-halopyridines deviate from the ΔS^0–σ straight line (Fig. 2b) (2-halopyridines are not discussed since there are no appropriate constants σ).

Both 2-haloanilines and 2-halopyridines do not fit linear correlations $\log K$–Δλ and $\log K$–pK_a typical of all 4- and 3-substituted derivatives for which the $\log K$–σ, Δλ–σ, and pK_a–σ correlations are also linear. This may be due to steric factors; however, the gas-phase basicities [5, 6] (GB) of 3- and 4-substituted anilines

Table 1. Stability constants (K), thermodynamic parameters (ΔH^0, ΔS^0) for the formation of Zn-TPP complexes with pyridine derivatives **1a**–**1j**, aminopyridines **2a** and **2b**, and pyrimidin-2-amine (**3**) in chloroform at 25°C, shifts of the absorption maxima (Δλ) in the electronic spectra of Zn-TPP upon complex formation, and substituent constants σ

Ligand	K_{298}, L mol^{-1}	σ [4]	$\Delta\lambda_{\text{Soret}}$	$\Delta\lambda_{II}$	$\Delta\lambda_{I}$	$-\Delta H^0$, kJ/mol	ΔS^0, J mol^{-1} K^{-1}
1a	6495±40	0.227	10.5	14.1	16.8	22.02±1.60	–0.9±5.5
1b	2105±45	0.18	9.4	14.5	17.0	14.91±0.11	13.6±0.5
1c	1065±15	0.337	8.8	13.8	14.9	20.88±0.07	–12.1±0.3
1d	1010±13	0.373	8.7	13.6	15.7	17.48±0.1	–1.37
1e	967±30	0.391	8.5	13.9	16.0	15.76±0.15	4.35±0.9
1f	1680±25	0.352	9.1	14.4	16.5	14.28±0.13	13.8±0.3
1g	5.7±0.16	–	–	12.8	14.9	13.89±0.76	–32.1±1.7
1h	4.5±0.1	–	7.2	12.4	14.5	15.42±0.35	–39.4±1.5
1i	1.71±0.7	–	–	11.7	14.0	9.54±0.13	–27.1±0.6
1j	3520±150	0	9.8	15.0	18.2	17.29±0.17	8.9±0.6
2a	17460±380	–0.66	12.1	17.5	20.7	10.50±0.44	46±2
2b	670±30	–	–	14.2	15.8	17.81±0.36	–5.5±1.5
3	910±30	–	–	11.6	11.8	17.33±0.72	–1.5±2.3

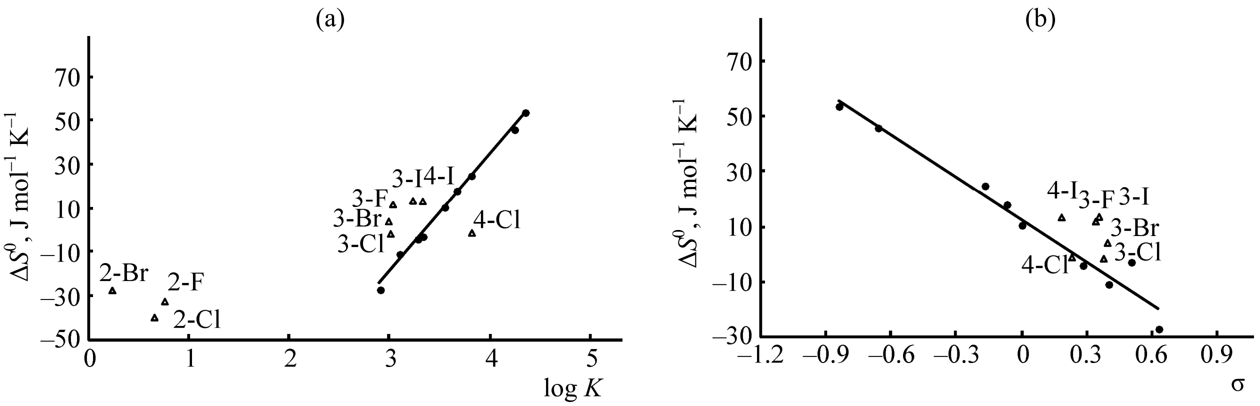

Fig. 2. Plots of ΔS^0 versus (a) log$K$ and (b) substituent constants σ^+ for the complex formation of Zn-TPP with substituted pyridines in chloroform at 25°C; $\Delta S^0 = 53.85\log K - 180.74$; $n = 9$, $r = 0.998$; $\Delta S^0 = -51.36\sigma - 12.5$; $n = 9$, $r = 0.98$; X = 4-NH_2, 4-NMe_2, 4-Me, H, 4-CN, 4-COMe, 3-Me, 3-$CONH_2$, 3-COOEt.

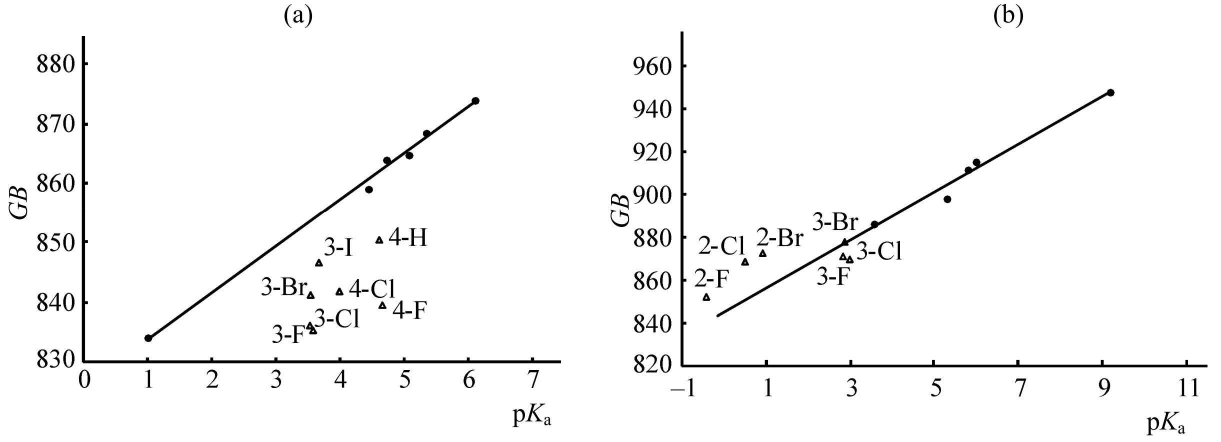

Fig. 3. Plots of the gas-phase basicities (*GB*) of (a) aniline (triangles, X = H, 4-F, 4-Cl, 3-F, 3-Cl, 3-Br, 3-I); circles (X = 4-Me, 4-OMe, 4-NH_2, 3-Me, 3-NO_2, 2-Me) and (b) pyridine derivatives (triangles, X = 3-Cl, 3-Br, 3-I, 2-F, 2-Cl, 2-Br; circles, X = H, 4-NH_2, 4-Me, 3-Me, 3-$CONH_2$) versus pK_a in water at 25°C; (a) GB = 7.80pK_a + 826; $r = 0.998$; $n = 6$; (b) GB = 11.2 pK_a + 845; $r = 0.99$; $n = 5$) [5, 6].

(Fig. 3a; no data for 2-substituted derivatives are given, except for 2-methylaniline) and, to a lesser extent, of 2- and 3-halopyridines (Fig. 3b; the data for 4-halopyridines are not given) also displayed no linear correlation with pK_a.

Taking into account the lack of steric effect of 3- and 4-substituents and of essential intermolecular interactions in the gas phase, the electronic factors of halogens are determined by specific rules depending on the solvent.

All monosubstituted anilines (X = 4-NH_2, 4-OMe, 4-Me, 4-F, 4-Cl, 4-Br, 4-I, H, 3-Me, 3-OMe, 3-NO_2, 3-F, 3-Cl, 3-Br, 2-F, 2-Cl, 2-Br) and pyridines (X = 4-NMe_2, 4-NH_2, 4-Me, 4-CN, 4-COMe, 4-Cl, 4-I, H, 3-Me, 3-$CONH_2$, 3-COOEt, 3-F, 3-Cl, 3-Br, 3-I, 2-F, 2-Cl) fit well the linear correlation $\Delta\lambda$–pK_a (anilines: $\Delta\lambda_{II} = 0.99\text{p}K_a + 9.72$; $n = 17$, $r = 0.96$; pyridines: $\Delta\lambda_{II} = 0.58\text{p}K_a + 12.3$; $n = 17$, $r = 98$), though the $\Delta\lambda$ values were measured in chloroform while pK_a values were determined in water. Presumably, both these solvents essentially and similarly level unusual properties (static polarization effect) of halogen atoms via dynamic polarization of base molecules.

The thermodynamic behaviors of the two ligand series demonstrated considerably stronger differences: the complexation of Zn-TPP with aniline derivatives (except for 4-haloganilines) is an isenthalpic process, whereas the complexation with pyridine derivatives (except for 2-, 3-, and 4-halopyridines) is isothermodynamic, and all halopyridines do not fit linear correla-

Table 2. Basicity constants of haloanilines and halopyridines in water (pK_a) and stability constants of their complexes with Zn-TPP in chloroform (K, 25°C)

Halogen position	Haloanilines, pK_a (H_2O) [2, 9], $K_{Zn\text{-}TPP}$ [2]				Halopyridines pK_a (H_2O) [10, 11], $K_{Zn\text{-}TPP}$ [2]			
	F	Cl	Br	I	F	Cl	Br	I
4	4.65, 164	3.98, 138	3.88, 109	3.79, 124	– –	3.83, 6495	3.78, –	4.06, 2105
3	3.57, 59	3.57, 72	3.53, 89	3.61, –	2.97, 1065	2.84, 1010	2.84, 967	3.25, 1680
2	3.20, 41	2.64, 36	2.53, 33	2.55, 31	0.44, 57	0.72, 4.5	0.90, 1.71	1.82, –

tions ΔH–ΔS, as well as linear correlations of ΔH and ΔS with $\log K$, $\Delta\lambda$, pK_a, and σ.

Analysis of a few published and our own X-ray diffraction data [2, 7] on 1:1 molecular complexes of Zn-TPP with pyridine, phenol, aniline, pyridine *N*-oxide, and quinoline *N*-oxide derivatives allowed us to divide these complexes into two groups. The crystal structure of *n*,ν-complexes derived from pyridine is characterized by almost orthogonal orientation of the pyridine ring with respect to the macrocycle plane (the corresponding dihedral angle is 80°–89°), whereas other ligands are oriented at an angle of 24° to 34°. Probably, just these structural features are responsible for the specific thermodynamic and kinetic behaviors of pyridine derivatives (isoequilibrium process), as well as of anilines and heteroaromatic *N*-oxides (isenthalpic process), upon coordination to Zn-TPP.

Unusual behavior of halogen derivatives is likely to be related in part to the fact that, unlike carbon, nitrogen, and oxygen atoms constituting other substituents on the pyridine ring and belonging to the same period of the Periodic Table, halogen atoms belong to different periods of the Periodic Table (though derivatives with fluorine atom of the second Period also behave unusually; Figs. 1–3). Differences in the size of halogen orbitals are considerably larger; therefore, peculiarities of static (electronic effects) and dynamic polarization [solvation with water (pK_a) and chloroform ($\log K_{Zn\text{-}TPP}$)] of molecules containing halogen atoms cannot be rationalized in a simple manner. For example, the unusual basicity order of 4-haloanilines (Table 2; F > Cl > Br > I, where the fluorine atom is the strongest electron donor) in water is explained assuming greater contribution of the +*M* effect than of the –*I* effect which decreases in the opposite direction [8]. In fact, this order is generally retained for the complexation of Zn-TPP with not only 4-haloanilines but also 4-halopyridines in chloroform (Tables 1, 2). Exceptions are 4-iodoaniline (for which the stability constant K is higher than for 4-bromoaniline) and 4-iodopyridine (maximum pK_a value). The K values (Tables 1, 2) for 4-fluoroaniline (164 L/mol) and 4-chloropyridine (6495 L/mol) are higher than those for aniline (141 L/mol [2]) and pyridine (3520 L/mol [2]), respectively. In the case of 2-haloanilines and 2-halopyridines, the stability constants change in keeping with the general trend (F > Cl > Br > I).

However, there are also other differences in the behaviors of halogen-substituted anilines and pyridines. The orders of variation of pK_a and $K_{Zn\text{-}TPP}$ for 2- and 4-substituted anilines (+*M* effect is the major factor), depending on the halogen nature (except for 4-iodo- and 4-bromoanilines), are almost similar. 3-Iodoaniline has the maximum basicity among 3-haloanilines (no +*M* effect), but the basicity order of the other compounds remains almost unchanged. However, the order is reversed upon coordination to Zn-TPP (data for 3-iodoaniline are lacking).

Substituted anilines:

pK_a (H_2O)	$K_{Zn\text{-}TPP}$,
4-F > 4-Cl > 4-Br > 4-I	4-F > 4-Cl > 4-I > 4-Br
3-I > 3-F = 3-Cl > 3-Br	3-Br > 3-Cl > 3-F
2-F > 2-Cl > 2-Br = 2-I	2-F > 2-Cl > 2-Br > 2-I

There are some peculiarities in the halopyridine series. All iodopyridines are the most basic (no pK_a value of 4-fluoropyridine is available), while the basicity and stability constant orders for the other derivatives are similar. Exceptions are pK_a values of 2-halopyridines (reverse order) and stability constants $K_{Zn\text{-}TPP}$ for 3-halopyridines (the highest value is observed for 3-iodopyridine).

Table 3. Bond lengths and dihedral angles in Zn-TPP complexes **4**–**6** with pyrimidin-2-amine, acetone, and water

Parameter	**4**	**5**	**6**
Zn–N (Zn–O) bond length, Å	2.252	2.249	2.439
Deviation of the zinc atom from the porphyrin plane, Å	0.341	0.353	–
Dihedral angle between the porphyrin and extra ligand planes, deg	85.50	83.07	90

Substituted pyridines:

pK_a (H_2O)	$K_{Zn\text{–}TPP}$
4-I > 4-Cl > 4-Br	4-Cl > 4-I
3-I > 3-F > 3-Cl = 3-Br	3-I > 3-F > 3-Cl > 3-Br
2-I > 2-Br > 2-Cl > 2-F	2-F > 2-Cl > 2-Br

Thus, static polarization (electronic effects) cannot completely rationalize variation of the stability constants and thermodynamic parameters determined by us. We plan to contunue studying anomalous behavior of halogen derivatives of pyridine, aniline, phenol, and heteroaromatic *N*-oxides.

We attempted to elucidate peculiar features of the coordination of Zn-TPP with pyridin-2-amine (**2b**) and pyrimidin-2-amine (**3**) that are key intermediate products in the synthesis of many biologically active compounds and medicinals. The stability constants and thermodynamic parameters for the complexation of Zn-TPP with ligands **2b** and **3** are given in Table 1.

The stability constants of the complexes formed by Zn-TPP with pyridin-2-amine (**2b**) and pyrimidin-2-amine (**3**) were much higher than those found for 2-halopyridines, and the complexation with these ligands was characterized by more negative ΔH^0 values and less negative values. The ΔS^0 values were positive for pyridine (**1i**) and, especially for pyridin-4-amine (**2a**) (Table 1) having higher pK_a values (5.29 and 9.17 [2]).

Pyridin-2-amine (**2b**), in keeping with its higher basicity {pK_a 6.86 (5.23) [12]} relative to pyrimidin-2-amine (**3**) {(pK_a 3.54 (1.30) [12]}, showed higher nucleophilicity in the coordination to metal porphyrins. However, the stability constant of the Zn-TPP complex with pyrimidin-2-amine (**3**) is slightly higher. In order to rationalize these findings, the structure of crystalline Zn-TPP adduct **4** was studied by X-ray analysis. According to the X-ray difraction data (Fig. 4a, Table 3), isolated complex **4** contains solvent (acetone) molecule and has the composition Zn-TPP–pyrimidin-2-amine–acetone 1:2:1. Protons of the acetone molecule interact with the benzene π-system. One endocyclic nitrogen atom of pyrimidin-2-amine forms a dative bond with the zinc atom, so that the latter deviates by 0.341 Å from the porphyrin macrocycle plane (Table 3). The Zn–N bond length is 2.252 Å, and the porphyrin macrocycle and pyrimidine ring form a dihedral angle of 85.50°. The other endocyclic pyrimidine nitrogen atom and the amino group are involved in intermolecular hydrogen bonding to form a centrosymmetric dimer (Fig. 4a) through N–H···N hydrogen bonds (N···N 2.061 Å). The pyrimidine rings in the dimer lie in one plane, and the amino group is turned through an angle of 8.91° with respect to the pyrimidine ring.

The X-ray diffraction data (Fig. 4a) suggest that, as in the crystalline state, the formation of centrosymmetric dimer is responsible for the enhanced stability of complex **4** in chloroform. Analogous intermolecular hydrogen bonds are formed in nature between complementary base pairs in DNA helix. Such dimerization via hydrogen bonding is impossible for the Zn-TPP complex with pyridin-2-amine since the latter lacks second endocyclic nitrogen atom.

We failed to isolate a complex of Zn-TPP with pyridin-2-amine from acetone solution; instead, crystalline 1:1 adduct **5** of Zn-TPP with acetone was formed (Fig. 4b). The crystal packing of **5** is represented by a two-layer structure like cell membrane, where weakly polar metal porphyrin molecules are linked through H^{25} aromatic hydrogen atoms of one layer and C^9 and N^3 of the other layer. More polar acetone molecules are located at the outer side of the porphyrin systems and are coordinated to zinc, thus forcing the latter out of the porphyrin macrocycle by 0.353 Å. The Zn–O bond length is 2.249 Å, and the dihedral angle between the macrocycle and acetone planes is 83.07°.

In view of the above stated, of particular interest is ligand competition for coordination sites in the complexation with Zn-TPP. Therefore, while studying

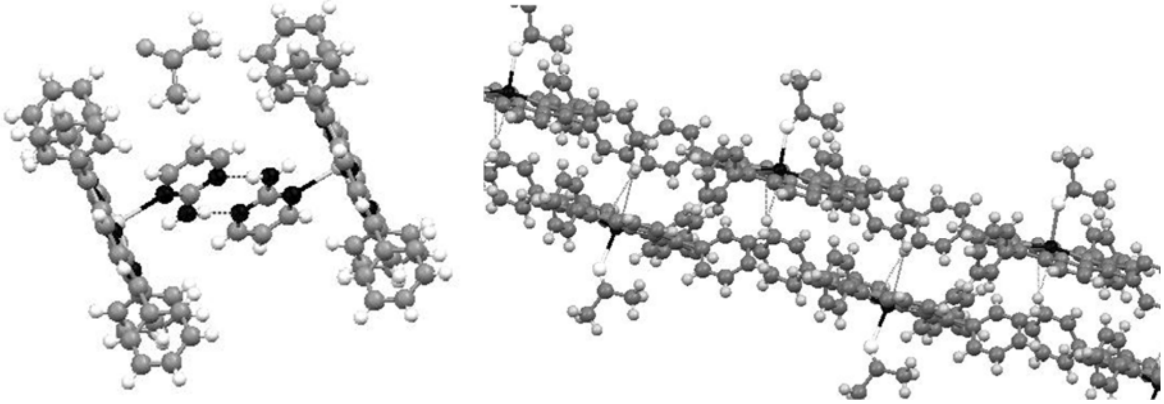

Fig. 4. (a) Structure of complex **4** formed by zinc tetraphenylporphyrin with pyrimidin-2-amine according to the X-ray diffraction data (black circles indicate nitrogen atoms; acetone molecule is shown at the top) and (b) steric arrangement of molecules **4** and acetone molecules in the crystal packing (black circles indicate nitrogen atoms, and white circles indicate acetone oxygen atoms).

complex formation of Zn-TPP with *n*-donor ligands in solution and obtaining crystalline complexes for X-ray analysis, we selected chloroform as solvent incapable of participating in strong specific interaction. Nevertheless, even low-boiling chloroform can be included into crystals, as it was observed, e.g., for the 2 : 1 complex of Zn-TPP with *p*-phenylenediamine [1].

The use of acetone which always contains some water (if no special purification was performed) makes the situation more complicated. As stated above, from a solution in acetone we isolated crystalline complex **4** of Zn-TPP with pyrimidin-2-amine, whereas acetone complex **5** with Zn–O dative bond was isolated in the presence of pyridin-2-amine. Our attempts to obtain Zn-TPP complexes with 4-aminobenzaldehyde and ethyl 4-dimethylaminobenzoate from acetone solution in both cases resulted in the isolation of previously unknown adduct **6** of Zn-TPP with water at a ratio of 1 : 1 (Fig. 5, Table 3). Unlike the complex with acetone, complex **6** in crystal has a multilayer structure where the porphyrin units are linked not only directly to each other (Fig. 5) but also to water molecules located on the fourfold inversion axis and statistically positioned below or above the porphyrin plane, so that a pseudo symmetry center appears.

Thus, neither the basicity of halogen-substituted anilines and pyridines in water or gas phase nor their coordination to Zn-TPP in chloroform can be interpreted with the aid of only electronic factors. The anomalous behavior of these ligands is essentially determined by solvation. Unlike aminopyridines, aminopyrimidines are capable of forming H-bonded associates in the complexation with metal porphyrins both in the solid phase and in solution. This may elucidate mechanisms of interaction of pyrimidine drugs with heme-containing proteins, as well as coordination processes *in vivo* involving metal porphyrins used as photosensitizers in photodynamic therapy of cancer.

EXPERIMENTAL

The electronic absorption spectra were measured on an SF 2000-02 spectrophotometer. The stability constants of Zn-TPP complexes with pyridine derivatives and pyrimidin-2-amine in chloroform were determined according to the procedure described in [1]. The thermodynamic complex formation constants were determined by the graphical method using formula (1) (first Ulich approximation) [13] and assuming that ΔH

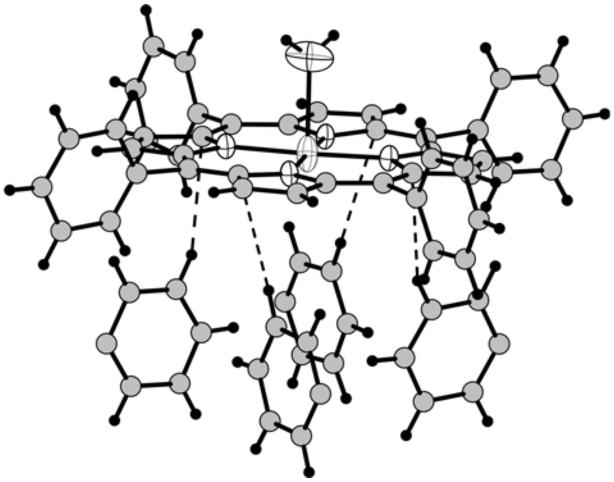

Fig. 5. Structure of complex **6** formed by zinc tetraphenylporphyrin and water according to the X-ray diffraction data.

Table 4. Crystallographic parameters of Zn-TPP complexes **4**–**6**

Parameter	**4**	**5**	**6**
Formula	$C_{48}H_{33}N_7Zn{\cdot}C_3H_6O$	$C_{47}H_{34}N_4OZn$	$C_{44}H_{30}N_4OZn$
Molecular weight	831.26	736.15	696.09
Crystal dimensions, mm	0.12×0.08×0.05	0.18×0.14×0.12	0.10×0.08×0.04
Temperature, K	295	295	295
Crystal system	Triclinic	Monoclinic	Tetragonal
Space group	*P*-1	*P*2$_1$*C*	*I*-4
a, Å	11.0531(4)	14.8542(6)	13.3969(3)
b, Å	11.6587(5)	17.5725(6)	13.3969(3)
c, Å	17.6689(8)	14.3296(7)	9.6671(2)
α, deg	96.684(3)	90	90.00
β, deg	93.792(3)	96.646(4)	90.00
γ, deg	107.994(3)	90	90.00
V, Å^3	2138.22	3715.26	1735.02
Z	2	4	2
d_{calc}, g/cm^3	1.291	1.316	1.332
μ, mm^{-1}	1.161	1.242	1.298
$\Theta_{\max}$, deg	72.8	69.2	72.0
h, *k*, *l* ranges	–12.3, –13.14, –21.11	–17.17, –21.17, –7.11	–15.16, –7.16, –11.11
Number of independent reflections	7979	6840	3735
Number of reflections with $I > 2\sigma(I)$	5058	2931	1252
Number of variables	560	480	120
$R(F^2)$	0.037	0.052	0.047
$R_w(F^2)$	0.078	0.11	0.124
Goodness of fit	0.89	0.81	1.016
$\Delta\rho_{\max}/\Delta\rho_{\min}$ ($\bar{e}$/Å^3)	0.25/–0.34	0.30/–0.28	0.33/–0.45

and Δ*S* remain constant in the examined narrow temperature range (273–313 K).

$$\ln K_T = -\Delta H^0_{298}/RT + \Delta S^0_{298}/R. \quad (1)$$

(Pyrimidin-2-amine)(5,10,15,20-tetraphenylporphyrinato)zinc(II) (4). A hot saturated acetone solution (10 mL) containing 10 mg (1.47×10^{-5} mol) of Zn-TPP was mixed with a solution of pyrimidin-2-amine (1.55×10^{-5} mol) in the same solvent, and the mixture was left to stand at room temperature in the dark on exposure to air. The crystals were filtered off, washed with acetone (3×2 mL), and dried in air.

Complexes **5** and **6** were synthesized in a similar way using pyridine-2-amine and 4-aminobenzaldehyde or ethyl 4-(dimethylamino)benzoate, respectively.

The X-ray diffraction data for complexes **4**–**6** were obtained on a STOE StadiVariPilatus 100K diffractometer (CuK_α radiation, GeniX^{3D}CuHF generator, microfocus X-ray tube, Xenocs FOX3D HF multilayer thin film ellipsoid monochromator). The data were collected and processed using STOEX-Area software. The principal crystallographic parameters of complexes **4**–**6** are given in Table 4. The structures were solved by the direct method implemented in SHELXS-97 [14]. The positional and thermal parameters of non-hydrogen atoms were refined in full-matrix anisotropic approximation. The positions of hydrogen atoms were calculated and refined in isotropic approximation according to the riding model. The molecular structures were plotted using DIAMOND [15]. The X-ray diffraction data were deposited to the Cambridge Crystallographic Data Centre [CCDC entry nos. 1521215 (**4**), 1521213 (**5**), 1521216 (**6**)].

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