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Complex Formation between Zinc(II) Tetraphenylporphyrinate and Alkylamines

V. P. Andreev[a], P. S. Sobolev[a], D. O. Zaitsev[a], and V. A. Tafeenko[b]

[a] *Petrozavodsk State University, pr. Lenina 33, Petrozavodsk, 185910 Russia*
e-mail: andreev@petrsu.karelia.ru

[b] *Moscow State University, Moscow, Russia*

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Abstract—Zinc(II) tetraphenylporphyrinate in chloroform forms complexes with primary amines containing up to 18 carbon atoms; the complex with n-octylamine is the most stable. Zinc(II) tetraphenylporphyrinate complex with octanol-1 is more stable than those with other alcohols. Reasons for this highest complex stability have been discussed basing on X-ray diffraction data for the *n*-octylamine complex.

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Previously in the study on complex formation between Zn(II) tetraphenylporphyrinate (Zn-TPP) and *n*-alkylamines in chloroform [1] we demonstrated that the complex stability constant K was an intricate function of RNH_2 alkyl chain length. The most stable complex was formed by *n*-octylamine.

In order to explain the unusual trend in the complexes stability of primary amines, in this work we determined the stability constants of Zn-TPP complexes with series of amines and alcohols at 283–308 K and calculated thermodynamic functions of formation of Zn-TPP complexes with amines (Table 1).

The ΔH^0 values were negative in all cases whereas ΔS^0 were positive for many of complexes (except for those of ammonia and alcohols). Thus, formation of the Zn-TPP complexes with amine was favored by both entropy and enthalpy factors. Analysis of kinetic and thermodynamic parameters of Zn-TPP coordination with *n*-alkylamines (Table 1) revealed that the complexes stability constant K as well as ΔH^0 and ΔS^0 increased in the series from ammonia to *n*-butylamine; in the case of *n*-pentylamine all three parameters they decreased but then were increasing again in going from *n*-pentylamine to *n*-octylamine. Further the observed parameters somewhat decreased; in the cases of C_{12}–C_{18} *n*-alkylamines, the stability constants were close to those of ethylamine and *n*-propylamine.

Note that the changes of K, ΔH^0, and ΔS^0 with increasing alkyl length were somewhat similar in the cases of Zn-TPP coordination with amines and alcohols. However, due to low basicity and weak nucleophilicity of alcohols the complete complex formation of Zn-TPP could only be achieved at a significant excess of the ligand (Table 1). Therefore, the determination of K, ΔH^0, and ΔS^0 in the case of alcohols was questionable: with such excess of alcohol the solvent composition was substantially altered. For example, in the case of 30000-fold excess of alcohol the extinction coefficient ε of the Zn-TPP complex deviated evidently from that in pure chloroform, hence, the determination of K in chloroform from absorbance in chloroform-alcoholic medium could be inaccurate. Nevertheless, the determined Zn-TPP–alcohols stability constants (chloroform, 25°C, Table 1) coincided with those measured in benzene at 24°C [5]. Moreover, the published alcohols basicity values [6–9] are contradictory due to insufficient reliability of quantitative methods of measuring acid-base properties of alcohols in liquid state.

Despite the possible inaccuracy of the data, we previously found a linear correlation between $\log K$ and $\Delta\lambda_{II}$ of alcohols and amines containing the same substituents (for instance, $\log K_{alcohol} = 0.685$, $\log K_{amine} = -1.78$, $r = 0.98$; $\Delta\lambda_{II,alcohol} = 1.39\Delta\lambda_{II,amine} - 13.5$, $r = 0.985$) [1].

The observed trends in the changes of K, ΔH^0, and ΔS^0 values (Table 1) in the case of Zn-TPP coordination with amines along with the ligands

Table 1. Physicochemical parameters of selected primary alcohol and amine ligands and their complexes with Zn(II) tetraphenylporphyrinate (chloroform, 25°C)

Ligand[a]	K, L/mol	ΔG_B, kcal/mol [2]	log P [3]	I_p [4]	$\Delta\lambda_{II}$, nm	ΔH^0, kJ/mol	ΔS^0, J mol^{-1} K^{-1}
Ammonia	1550±25	0.0	–	10.15	16.2	–21.41±0.23	–11.32±0.83
Methylamine	9174±139	9.1	–0.57	8.97	16.5	–19.82±0.22	8.80±0.69
Ethylamine	10142±142	11.8	–0.13	8.86	16.8	–13.18±0.31	31.1±1.6
n-Propylamine	11125±260	13.0	0.48	8.78	16.8	–12.68±0.28	34.60±1.5
n-Butylamine	15213±302	13.5	0.86	8.71	16.8	–11.85±0.51	40.00±1.7
n-Pentylamine	13087±369	13.4	1.49	–	16.8	–13.48±0.37	33.4±1.6
n-Hexylamine	13335±400	13.5	2.06	–	16.9	–13.07±0.13	35.0±0.7
n-Heptylamine	15152±423	13.6	2.57	–	16.9	–12.67±0.41	37.4±1.2
n-Octylamine	21738±808	–	3.09	–	16.9	–8.32±0.28	54.8±2.4
n-Nonylamine	17200±506	–	3.60	–	16.8	–12.76±0.34	38.0±1.2
n-Decylamine	14958±57	–	4.1	–	16.8	–12.85±0.6	36.7±1.9
n-Dodecylamine	10150±150	–	–	–	16.7	–18.20±0.03	15.5±0.01
n-Pentadecylamine	10847±391	–	–	–	16.7	–17.95±0.54	15.5±0.7
n-Octadecylamine	11150±235	–	–	–	16.6	–18.34±0.15	15.9±0.64
Ethylenediamine	19750±232	19.0	–	–	17.3	–11.52±0.16	43.5±1.6
2-Aminoethanol	6340±152		–	–	16.3	–17.3±0.32	15.2±1.0
Methanol	7.32±0.21		–0.74	10.85	9.3	–15.14±0.24	–35.0±1.4
Ethanol	10.11±0.30		–0.30	10.50	9.8	–13.54±0.26	–26.7±1.2
Propanol-1	9.14±0.16		0.25	10.15	9.8	–13.63±0.27	–27.6±1.4
Butanol-1	10.20±0.23		0.84	10.1	9.8	–11.79±0.24	–20.5±1
Heptanol-1	9.50±0.20		2.62	–	9.8	–9.14±0.22	–11.9±0.8
Octanol-1	11.7±0.9		3.07	–	10.2	–10.3±0.24	–15.5±1
Nonanol-1	9.71±0.20		4.02	–	9.8	–9.51±0.34	–13.00±2

[a] Zn(II) porphyrinate was completely transformed into the complex at 1 : 30000 ratio with alcohols and 1 : 1000 ratio with amines. $c_{Zn-TPP} = 2\times10^{-5}$ mol/L; stability constants were determined at (600–5000)-fold excess of alcohols and (0.5–10)-fold excess of amines.

properties (ionization potential I_p and octanol-water partition coefficient log P) suggested that at alkyl substituent shorter than pentyl the inductive effect was the major factor governing the strength of the N→Zn donor-acceptor bond. As the σ* constant is almost the same for the unbranched alkyl groups longer than C_3, further complicated behavior of K, ΔH^0, and ΔS^0 should be due to additional action of other factors (for example, solvation effects). The log P values increased monotonously with the alkyl length (Table 1), therefore, hydrophobicity could not account for the observed trends.

The non-uniform change in kinetic and thermodynamic parameters allowed classification of the ligands into 4 groups (Fig. 1). The lowest point corresponded to ammonia (highest I_p, $\Delta S^0 < 0$); the second group consisted of C_1, C_{12}, C_{15}, and C_{18} *n*-alkylamines; the most numerous group includes C_{2-7}, C_9, and C_{10} *n*-alkylamines; the highest point (*n*-octylamine) forms another single-compound group. The reasons for such distribution are not clear for us, but the maximum values of K, ΔH^0, and ΔS^0 in the case of Zn-TPP complex with *n*-octylamine are remarkable.

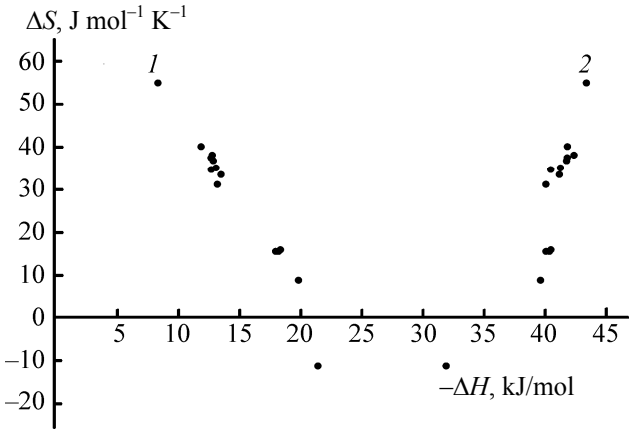
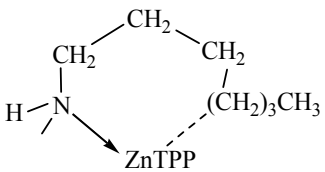


Fig. 1. ΔS^0 as function of ΔH^0 (*1*) and of log *K* (*2*) in the case of primary amines complex formation with Zn(II) tetraphenylporphyrinate (chloroform, 25°C).

Possibly, in contrast to the micelles and membranes formed in water by carboxylic acids and lipids, in the cases of molecular complexes of Zn-TPP with amines in low-polar aprotic chloroform medium the cyclic structures can exist with one (polar) donor-acceptor bond being formed between Zn and the ligand nitrogen atom whereas the second (non-polar) one is due to interaction of the Zn-TPP macrocycle aromatic system and the amine hydrocarbon fragment. The attractive interactions with alkylamine ligand are possible via the CH_3 group as well as via the $(CH_2)_n$ part, similarly to the cases of salts of aromatic and aliphatic acids at the interphase boundary [10].

Probability of such cyclic structures is enhanced in aprotic low-polar solvents and in the gas phase [11].

Aprotic solvent may facilitate formation of cyclic structures involving the interactions with partially positively charged acceptor complexes other than protons, for example, with Zn-TPP. Generally, the most stable structures are five- and six-membered cycles. In the studied case. the chelate structure containing more atoms was likely to form due to attractive interactions between macrocyclic Zn-TPP π-system and the suitable part of the alkyl group.



With increasing alkyl length from C_4 to C_5 another abnormal change of ΔH^0 (from –11.85 to –13.48 kJ/mol) and of ΔS^0 (from 40.0 to 33.4 J mol^{-1} K^{-1}) were observed; those changes were larger that the experimental error but were less significant that in the case of *n*-octylamine. Probably, at that point (C_5 alkyl chain) the increase in *n*-alkylamine chain length allows close contact of Zn-TPP π-system with the farther part of the ligand and the formation of the chelate composition. Due to some reason (likely, of steric origin) the increase of the alkyl chain length to C_9 or more destabilized such conformation.

The *K*, Δλ, ΔH^0, ΔS^0, and ΔG^0 values of Zn-TPP with ethanol were higher than those in the case of methanol. With C_2–C_9 primary alcohols as ligands, no definite trends in the parameters change were found, nevertheless, the complex with *n*-octanol was the most stable.

Spacial structure of Zn-TPP complexes with amines was studied using that with n-octylamine; results of the X-ray diffraction studies are collected in Figs. 2 and 3 and in Table 2.

As seen in Figs. 2 and 3, the ligand is bound to zinc atom of Zn-TPP via nitrogen atom; the alkyl part was located between phenyl rings thus being brought close to the central part of porphyrin macrocycle of the neighboring Zn-TPP molecule.

The distances from Zn atom to the porphyrin plane and to nitrogen of *n*-octylamine were 0.352 and 2.165 Å, respectively. In the Zn-TPP complexes with 2-phenylethylamine (pK_a = 9.83 [1]) and (*S*)-α-methylbenzylamine (pK_a = 9.08 [1]) the corresponding distances were 0.356 and 2.193; 0.211 and 2.256 Å, respectively (Table 3).

Possibly, in $CHCl_3$ medium without other Zn-TPP molecules in the close neighborhood the octyl group could enhance the complex stability due to interaction with the macrocycle, or even facilitate the favorable ligand orientation (for example, in reaction with Pheophorbide A).

To conclude, studies of complex formation between Zn-TPP and amines or alcohols supported by X-ray diffraction studies of Zn-TPP complex with *n*-octylamine have demonstrated that *n*-octyl group bears some unique structural features resulting in formation of extremely stable chelate and/or intermolecular complexes with porphyrin-containing compounds As compared with other unbranched primary amines, the *n*-octyl-

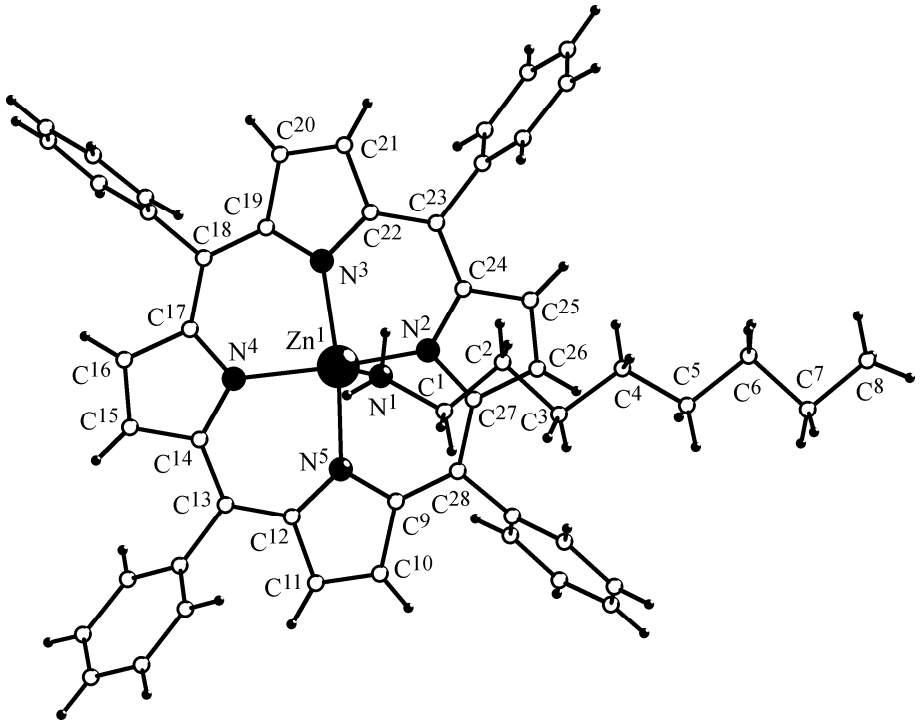


Fig. 2. Spacial structure of Zn(II) tetraphenylporphyrinate complex with *n*-octylamine.

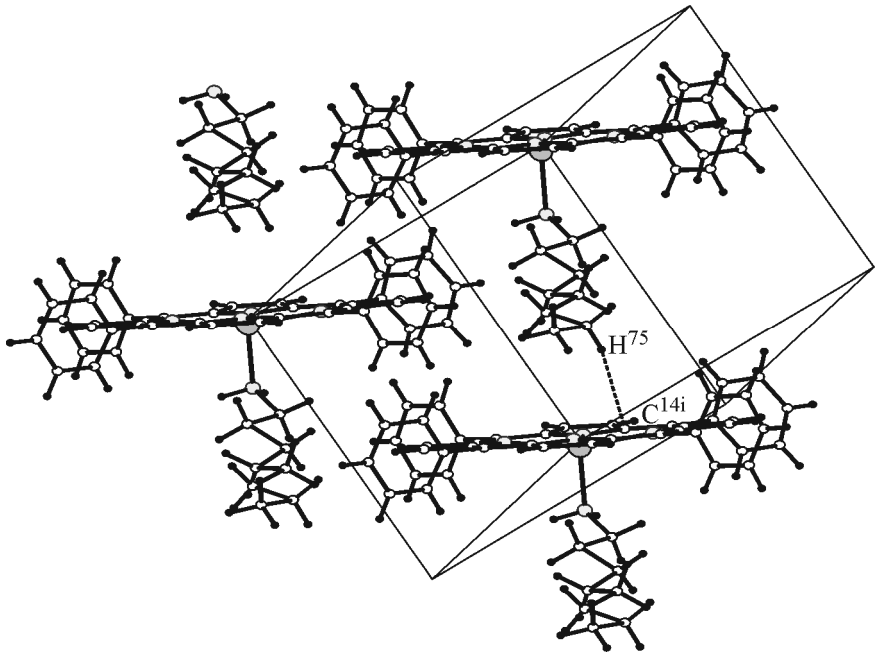


Fig. 3. Fragment of crystal packing of Zn(II) porphyrinate complex with *n*-octylamine. The short intermolecular distance is shown [C^{7}–H^{75}···C^{14i} (1 + *x*, 1 + *y*, 1 + *z*), 2.82 Å], reflecting the C–H···π interaction between octyl group hydrogen and π-system of Zn(II) tetraphenylporphyrinate.

amine complex formed with Zn-TPP in chloroform possessed unusually high ΔS^0 value (54.8 J mol^{-1} K^{-1}) along with relatively low ΔH^0 value (–8.32 kJ/mol) (Table 1).

As future direction of this work, we plan the investigation of structure of various metal porphyrinates complexes with octyl-containing primary,

Table 2. X-ray diffraction data on Zn(II) porphyrinate complex with *n*-octylamine

Parameter	Value
Empirical formula	$C_{52}H_{47}N_5Zn_1$
M	807.34
Crystal size, mm,	0.15×0.12×0.12
T, K	296
Crystal system	Triclinic
Space group	*P*1
a, Å	10.6305(2)
b, Å	10.8344(2)
c, Å	11.0428(2)
α, deg	117.2320(10)
β, deg	103.638(2)
γ, deg	90.870(2)
V, Å^3	1087.79(3)
Z	1
d_{calc}, g/cm^3	1.232
μ	
θ_{max}, deg	68
h, *k*, *l* ranges	–12.12; –13.10; –8.13
Number of independent reflections	5408
Number of reflections with [$I > 2\sigma(I)$]	4571
Number of refined parameters	551
$R(F^2)$	0.067
$R_w(F^2)$	0.17
Quality	1.03
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	0.58, –0.66

secondary, and tertiary amines as well as ethylenediamine derivatives in solution and in solid phase by spectroscopy methods.

EXPERIMENTAL

The amines were distilled over alkali, the alcohols were dried and distilled over barium oxide. Physical constants of the purified substances coincided with the corresponding published data. Electron absorption spectra were registered using SF-2000-02 spectrophotometer. Stability constants of Zn(II) tetraphenylporphyrinate complexes were determined as described in [1].

Table 3. Bond lengths and bond angles in Zn(II) porphyrinate complex with *n*-octylamine

Bond	*d*	Угол	φ
Zn^1–N^1	2.165(8)	$H^{60}N^1H^{61}$	105.9
Zn^1–N^2	2.063 (8)	$Zn^1N^1C^1$	128(1)
Zn^1–N^3	2.070 (6)	$Zn^1N^1H^{60}$	105.4
Zn^1–N^4	2.092 (6)	$Zn^1N^1H^{61}$	105.5
Zn^1–N^5	2.086 (7)	$H^{60}N^1C^1$	105
N^1–C^1	1.46 (2)	$H^{61}N^1C^1$	105
		$N^1C^1C^2$	108(2)

Gaseous ammonia, methylamine, or ethylamine (produced by heating of their hydrochlorides with calcium hydroxide and passed through anhydrous NaOH and $CaCl_2$) were bubbled through chloroform. The ligand concentration was determined by back titration: excess of HCl (0.01 mol/L) was added to aliquot of the chloroform solution, and the sample was titrated with NaOH (0.01 mol/L) in the presence of phenolphthalein. The stability constants of the formed complexes were determined in mixtures of Zn-TPP and the ligand solutions corresponding to the calculated molar ratio of the components.

Thermodynamic parameters of the complex formation were calculated by graphic method assuming that the ΔH and ΔS values were constant at 288–308 K (283–298 K in the cas of gaseous ligands) [12]: $\ln K_T = -\Delta H^0_{298}/RT + \Delta S^0_{298}/R$.

X-ray diffraction studies were performed using StadiVari Pilatus 100K STOE diffractometer (CuK_α, equipped with multilayer thin-film ellipsoidal FOX3D HF Xenocs monochromator). Data collection, determination and refining of the crystal cell parameters were performed using STOE X-Area software package. The main X-ray diffraction parameters are collected in Table 2. The structural data were deposited in Cambridge Crystallographic Data Center (CCDC 912709).

The structure was solved by the direct method (SHELXS-97 software [13]). Positions and thermal parameters of non-hydrogen atoms were refined under full-matrix approximation. Positions of hydrogen atoms were calculated and refined under isotropic approximation applying the *rider* model. Molecular structures were prepared using DIAMOND software [14].

Zn(II) tetraphenylporphyrinate complex with *n*-octylamine. Saturated hot solution of Zn(II) tetraphenylporphyrinate in 10 mL of acetone (containing 10 mg, 1.47×10^{-5} mol of Zn-TPP) was mixed with *n*-octylamine (2 mg, 1.55×10^{-5} mol) solution in chloroform. The mixture was left in air in dark place at room temperature. The precipitated crystals were washed with acetone (3×2 mL) and dried in air.

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