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Coordination of Secondary and Tertiary Amines to Zinc Tetraphenylporphyrin

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Abstract—Stability constants of 46 complexes of zinc(II) tetraphenylporphyrin with primary, secondary, and tertiary amines and thermodynamic parameters of their formation (ΔG^0, ΔH^0, ΔS^0) in chloroform at 283–308 K have been analyzed. Probable factors responsible for enhanced stability of the complexes with ligands containing *n*-octyl groups are discussed. The X-ray diffraction data for the 1 : 1 complex of zinc(II) tetraphenylporphyrin with di-*n*-octylamine are given.

Keywords: metalloporphyrins, coordination, coordination compounds, amines, X-ray analysis

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We previously studied [1–5] the complexation of metal porphyrins with aromatic ligands, which can be described by Hammett-type equations log $(k/k_0) = \rho\Sigma\sigma$. However, there are numerous processes where new bond formation involves compounds with variable steric environment of the reaction center. Such processes conform to more complex equations including not only electronic but also other factors. For example, nucleophilic substitution reactions with amines are described by the extended Taft equation (1) modified for that class of nucleophiles [6].

$$\log k = \log k_0 + \rho^*\Sigma\sigma^* + \delta E_N. \qquad (1)$$

Here, k is the reaction rate constant, $\rho^*\Sigma\sigma^*$ is the term reflecting the inductive effect of all substituents on the nitrogen atom, and δE_N reflects the contribution of steric factor (δE_s in the Taft equation).

Taking into account that primary, secondary, and tertiary amines differ very strongly by steric environment of the nucleophilic center, we previously [2, 7–9] studied the complexation of zinc(II) tetraphenylporphyrin (Zn-TPP) with primary amines RNH_2 (**Ia**–**Iy**) [R = H (**a**), Me (**b**), Et (**c**), Pr (**d**), *i*-Pr (**e**), Bu (**f**), *i*-Bu (**g**), *s*-Bu (**h**), *t*-Bu (**i**), pentyl (**j**), isopentyl (**k**), *n*-hexyl (**l**), *n*-heptyl (**m**), *n*-octyl (**n**), *n*-nonyl (**o**), *n*-decyl (**p**), *n*-dodecyl (**q**), *n*-pentadecyl (**r**), *n*-octadecyl (**s**), cyclohexyl (**t**), allyl (**u**), benzyl (**v**), 2-hydroxyethyl (**w**), propargyl (**x**), 2-aminoethyl (**y**)] in chloroform at 283–308 K. The nucleophilic center in **Ia**–**Iy** is most sterically accessible.

It was found that the change of the thermodynamic and kinetic parameters for isoequilibrium coordination with ligands **Ia**–**Iy** fits Eq. (1). The relations between the stability constants of the complexes and shifts ($\Delta\lambda$) of the absorption maxima of Zn-TPP in the electronic spectra due to reaction with primary amines are linear. Linear correlations also exist between the kinetic parameters of nucleophilic substitution reactions (rate constants k) and complexation of Zn-TPP (stability constants K) with primary amines with account taken of electronic factors: $\log K/k = a + \rho^*\Sigma\sigma^*$. Extension of the hydrocarbon chain in unbranched primary aliphatic amines (C_1 to C_{18}) affects the stability constants of Zn-TPP complexes with these ligands in chloroform in a complicated manner: the maximum is observed for *n*-octylamine.

The present work was aimed at studying specific features of the complexation of Zn-TPP with secondary R^1R^2NH [**II**, $R^1 = R^2$ = Me (**a**), Et (**b**), *n*-Pr (**c**), *i*-Pr (**d**), *n*-Bu (**e**), pentyl (**f**), *n*-hexyl (**g**), *n*-heptyl (**h**), *n*-octyl (**i**), cyclohexyl (**j**), benzyl (**k**); R^1R^2NH =

piperidine (**l**), piperazine (**m**), morpholine (**n**), imidazole (**o**); R^1 = Me, R^2 = benzyl (**p**); R^1 = propargyl, R^2 = *n*-Pr (**q**), *n*-Bu (**r**), *i*-Bu (**s**), *t*-Bu (**t**), *n*-octyl (**u**), 2-aminoethyl (**v**)] and tertiary amines $R^1R^2R^3N$ {**III**, $R^1 = R^2 = R^3$ = Me (**a**), Et (**b**), *n*-Bu (**c**), *n*-octyl (**d**), allyl (**e**); $R^1 = R^2$ = Me, R^3 = benzyl (**f**), allyl (**g**), 2-cyanopropyl (**h**), 2-methylpent-4-yn-2-yl (**i**); $R^1 = R^2$ = Et, R^3 = propargyl (**j**); $R^1 = R^2$ = *n*-Pr, R^3 = propargyl (**k**); $R^1 = R^2$ = *i*-Pr, R^3 = Et (**l**); $R^1 = R^2$ = *n*-Bu, R^3 = propargyl (**m**); $R^1 = R^2$ = *n*-heptyl, R^3 = propargyl (**n**); $R^1 = R^2$ = *n*-octyl, R^3 = Me (**o**); $R^1 = R^2$ = *n*-octyl, R^3 = propargyl (**p**); $R^1 = R^2$ = propargyl, R^3 = *n*-Pr (**q**), *n*-Bu (**r**); R^1R^2N = morpholin-4-yl, R^3 = propargyl (**s**); $R^1R^2R^3N$ = 1,4-diazabicyclo[2.2.2]octane (DABCO) (**t**), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**u**)} containing saturated, unsaturated, and aromatic substituents.

Analysis of the kinetic and thermodynamic parameters of the complexation of Zn-TPP with secondary amines having unbranched alkyl substituents showed that the stability of the resulting complexes increases in the series Et_2NH < $n\text{-}Pr_2NH$ < $n\text{-}Bu_2NH$ < [$(n\text{-}C_5H_{11})_2NH$, $(n\text{-}C_6H_{13})_2NH$, $(n\text{-}C_7H_{15})_2NH$] < $(n\text{-}C_8H_{17})_2NH$ < Me_2NH (Table 1). Extension of the hydrocarbon chain in the series Me_2NH–$(n\text{-}C_7H_{15})_2NH$ is accompanied by reduction of both ΔH^0 (from –15.04 to –22.57 kJ/mol, due partly to increase of the +*I* effect) and ΔS^0 values (from 22.67 to –12.5 J mol^{-1} K^{-1} as a result of increased steric shielding of the nitrogen atom), which exert opposite effects on the stability of the complexes. However, these variations are so nonproportional to each other (especially in going from dimethylamine to diethylamine) that ligands containing pentyl, *n*-hexyl, and *n*-heptyl groups are almost indistinguishable in nucleophilicity, whereas di-*n*-octylamine and especially dimethylamine form the strongest complexes with Zn-TPP.

Like *n*-octylamine in the series of unbranched alkylamines [7], di-*n*-octylamine possesses specific properties and is characterized by the highest (excludeing dimethylamine) values of *K* (2673 L/mol), ΔH^0 (–12.84 kJ/mol), and ΔS^0 (22.5 J mol^{-1} K^{-1}); the corresponding values for dimethylamine are 6659, –15.04, and 22.67, respectively. Insofar as the ΔS^0 values for both ligands are almost equal, the high stability of the complexes derived therefrom is determined by variation of the enthalpy. However, the nitrogen atom in dimethylamine is sterically accessible, whereas amines containing *n*-octyl substituents are likely to stabilize the complexes with Zn-TPP just due to the unique length of the hydrocarbon chain which gives rise to a chelate-like structure involving the porphyrin aromatic system.

In order to determine steric structure of such adducts we have synthesized 1 : 1 complex **IV** from Zn-TPP and di-*n*-octylamine and studied its structure by X-ray analysis (Fig. 1, Table 2). The distances between the zinc atom and the porphyrin plane (r_1) and nitrogen atom of the di-*n*-octylamine molecule (r_2) in complex **IV** are 0.390 and 2.148 Å, respectively. The corresponding distances in the complexes of Zn-TPP with 2-phenylethylamine (pK_a 9.83 [15]) and (*S*)-α-methylbenzylamine (pK_a 9.08 [15]) are 0.356 and 2.193 Å and 0.211 and 2.256 Å. Taking into account that di-*n*-octylamine is a stronger base than the above two (pK_a ~11, Table 1), we can conclude that the distances r_1 and r_2 depend on the nucleophilicity of the donor not only in solution but also in crystal. Within a single series of compounds, the r_1 values should be proportional to pK_a, and r_2 values, inversely proportional. In fact, as we showed in [8], the r_1 and r_2 distances in the Zn-TPP complex with *n*-octylamine (which is a weaker base than di-*n*-octylamine, pK_a ~ 10.6) are 0.352 and 2.165 Å, respectively. Here, the ligand is linked by the amino nitrogen atom to the zinc atom in one Zn-TPP molecule, while the alkyl terminus is located between the benzene rings and is close to the central part of the porphyrin macrocycle in the neighboring molecule.

The molecule of di-*n*-octylamine in complex **IV** is linked through the nitrogen atom to the zinc atom of one Zn-TPP molecule (Fig. 1b), while its hydrocarbon groups are involved in short intermolecular C–H···C contacts with benzene rings in the neighboring metalloporphyrin molecules (C–H···π interactions).

Thus, *n*-octyl- [8] and di-*n*-octylamines with Zn-TPP form crystalline complexes where the *n*-octyl groups are proximate to the aromatic rings of the neighboring Zn-TPP molecules (intermolecular bonds). We believe that, unlike crystal structure, in chloroform solution at low Zn-TPP and ligand concentrations (10^{-5} to 10^{-4} M) the *n*-octyl group in the complex is also involved in analogous but intramolecular bonds with the porphyrin macrocycle.

Steric factors are very important in the coordination of amines to metalloporphyrin in solution. This is seen especially clearly for amines with branched alkyl groups. For example, the complex of Zn-TPP with diisopropylamine (Table 1) is characterized by the lowest stability constant (*K* = 42.2 L/mol) and ΔH^0 (–27.57 kJ/mol)

Table 1. Stability constants (K) of molecular complexes formed by Zn-TPP with secondary amines and thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) of complex formation (chloroform, 25°C), complexation-induced shifts of the absorption maxima ($\Delta\lambda$), sums of substituent constants σ^* ($\Sigma\sigma^*$), steric constants E_n, and basicities (pK_a) of amines in water at 25°C[a]

Ligand	K, L/mol	$\Sigma\sigma^*$ [10, 11]	E_n [10, 11]	$\Delta\lambda$, nm			pK_a (H_2O) [12]	ΔH^0, kJ/mol	ΔS^0, J mol^{-1} K^{-1}	$-\Delta G^0$, kJ/mol
				Soret	*II*	*I*				
Dimethylamine	6659±139	0.49	–0.47	10.6	16.0	17.8	10.64	–15.04±0.33	22.67±1.2	21.80
Diethylamine	1134 ±22	0.29	–1.98	10.0	14.9	17.2	10.98	–17.73±0.36	–1.03±1.05	17.42
Di-*n*-propylamine	1360±24	0.25	–	10.3	16.2	17.9	11.00	–18.13±0.28	–1.52±0.65	17.87
Diisopropylamine	42.2±0.4	0.11	–3.9	10.1	16.1	17.7	11.05	–27.80±0.4	–63.1±1.7	9.27
Di-*n*-butylamine	1834±25	0.23	–2.04	10.8	16.7	20.0	11.25	–20.34±0.13	–5.92±0.37	18.61
Di-*n*-pentylamine	2067±15	0.23	–2.07	10.7	16.5	17.7	11.18	–21.15±0.35	–7.9±0.8	18.90
Di-*n*-hexylamine	2080±34	0.23	–1.96	10.9	16.6	18.0	11.01	–21.88±0.41	–10.2±1.0	18.92
Di-*n*-heptylamine	2032±36	–	–	10.9	16.6	18.2	–	–22.57±0.42	–12.50±1.02	18.86
Di-*n*-octylamine	2673±98			11.0	16.5	18.4		–12.84±0.21	22.5±1	19.54
Dicyclohexylamine	48.5±0.6	0.19	–	8.4	14.3	16.1	11.25	–16.95±0.8	–24.62±1.3	9.61
Piperidine	49728±1583	0.31	–0.79	11.1	16.7	18.3	11.22	–16.61±0.24	33.8±1.8	26.78
Morpholine	22628±318	1.18	–0.79[b]	9.7	14.7	16.4	8.49	–16.8±0.7	26.7±2.0	24.83
Piperazine	38500±921	–	–0.79[b]	–	15.6	17.2	9.73	–17.18±0.72	30.2±2	26.15
Dibenzylamine	190±4	0.92	–1.50	–	14.4	17.5	8.52	–14.19±0.35	–3.74±0.25	13.09
Benzyl(methyl)amine	5735±91	0.705	–	–	15.8	17.5	4.85	–19.39±0.28	6.48±0.43	21.32
Propargyl(*n*-propyl)amine	2130±70	1.13	–	9.0	14.5	16.8	–	–19.73±1.2	–2.83±1	18.98
n-Butyl(propargyl)amine	449±14			9.4	14.2	15.9		–21.85±0.56	–2.28±1.9	15.2
Isobutyl(propargyl)amine	475 ±5			9.2	14.2	16.3		–15.45±0.24	–0.4±1	15.26
tert-Butyl(propargyl)amine	91±1	0.95	–	8.8	15.5	18.3	–	–21.38±1	–34.5±3	11.7
n-Octyl(propargyl)amine	3810±140	–	–	11.2	17.0	19.5	–	–17.96±0.41	8.3±0.4	20.42
N-Propargylethylenediamine	17643±476	–	–	11.2	17.0	19.5	–	–22.73±0.94	5.1±0.5	24.21
Ethylenediamine	19750±232	–	–	10.5	17.3	19.7	9.98	–11.52±0.16	43.5±1.6	24.49
N,*N*,*N*′,*N*′-Tetramethylethylenediamine	2380±46	–	–	9.6	14.2	17.3	–	–20.48±0.43	–3.82±0.4	19.25
Imidazole	10853±207	–	–	11.0	18.3	20.9	–	–16.26±0.07	22.3±0.21	22.89

[a] ΔG^0 values were calculated by the formula $\Delta G^0 = -RT\ln K_{298}$. Zn-TPP was converted completely into the complex with amine at a Zn-TPP–L molar ratio 1 : 2000 (1 : 10000 for dibenzylamine). [b] The E_n values for morpholine and piperazine were assumed to be equal to –0.79.

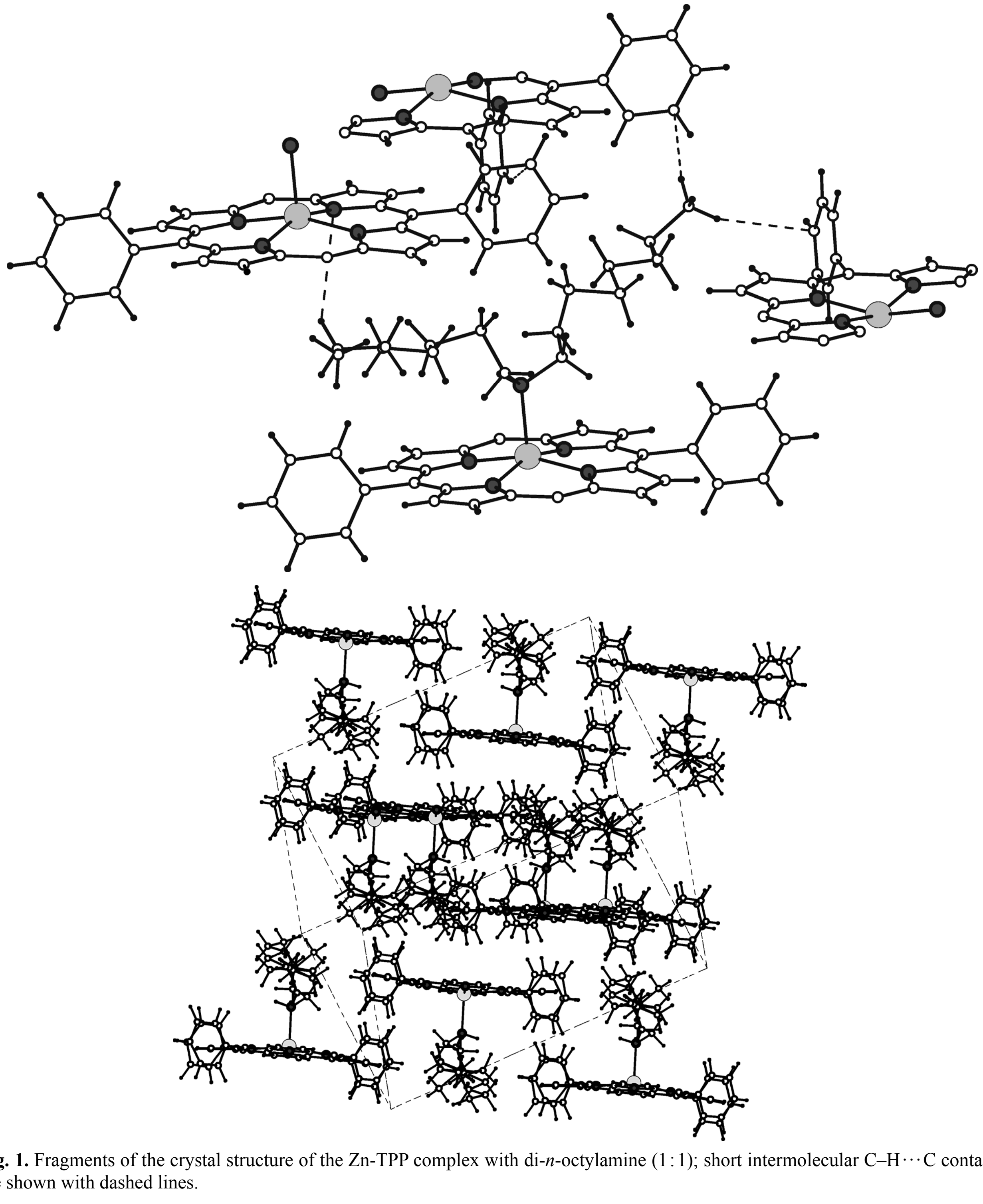


Fig. 1. Fragments of the crystal structure of the Zn-TPP complex with di-*n*-octylamine (1 : 1); short intermolecular C–H···C contacts are shown with dashed lines.

and especially ΔS^0 values (–63.1 J mol^{-1} K^{-1}; the difference from the ΔS^0 value for dipropylamine is 62 J mol^{-1} K^{-1}). By contrast, the nitrogen atom in heterocyclic amines is even more sterically accessible than in dimethylamine (ΔS^0 = 26.7–33.8 J mol^{-1} K^{-1}), and their complexes with Zn-TPP are exceptionally stable. In going from piperidine to piperazine and then to morpholine the stability constant (in keeping with increase of electronegativity of atoms in the series C < N < O) decreases from 49700 to 22600. The complex of Zn-TPP with the tertiary heterocyclic amine 1,4-diazabicyclo[2.2.2]octane is especially stable (K =

105 000 L/mol, $\Delta S^0 = 46.3$ J mol^{-1} K^{-}). Even imidazole gives rise to a more stable complex ($K = 10\,853$ L/mol, $\Delta S^0 = 22.3$ J mol^{-1} K^{-1}) than those derived from other secondary and tertiary acyclic amines (Tables 1, 3).

Introduction of electron-withdrawing substituents [cf. Me(Bzl)NH and Bzl_2NH, n-PrN(H)$CH_2C{\equiv}CH$ and n-PrN$(CH_2C{\equiv}CH)_2$] and increase of the size of the alkyl group [cf. *n*-propyl(propargyl)amine and *tert*-butyl(propargyl)amine] lead to reduction of ΔS^0 and stability constant (Tables 1, 3).

Analysis of the kinetic and thermodynamic parameters for the complexation of Zn-TPP with unbranched trialkylamines (Tables 1, 3) showed that the stability of the resulting complexes [$Et_3N < (n\text{-}Bu)_3N < (n\text{-}C_8H_{17})_3N < Me_3N$] is related to the alkyl chain length in the same manner as for secondary amines [$Et_2NH < (n\text{-}Bu)_2NH < (n\text{-}C_8H_{17})_2NH < Me_2NH$]. Here, the formation of the most stable complex with trimethylamine can readily be rationalized by high steric accessibility of the nitrogen atom ($\Delta S^0 = 8$ J mol^{-1} K^{-1}), and small difference in the stabilities of the complexes derived from Et_3N and $(n\text{-}Bu)_3N$ may be attributed to opposite variations of the electronic (ΔH^0) and steric (ΔS^0) factors; however, the behavior of tri-*n*-octylamine in the complex formation with Zn-TPP is as unusual as those of *n*-octylamine [1, 2] and di-*n*-octylamine (Table 1). From the viewpoint of electronic and steric factors (the +*I* effects of *n*-butyl and *n*-octyl groups should be almost similar, but longer substituents should hamper coordination to zinc to a stronger extent due to large number of degrees of freedom and possible conformers), the coordination of tri-*n*-octylamine to Zn-TPP should be less effective. Nevertheless, the complex of Zn-TPP with tri-*n*-octylamine is almost four times more stable than that with tri-*n*-butylamine (the complex of Zn-TPP with di-*n*-octylamine is more stable than the complex with di-*n*-butylamine by a factor of 1.5). It should be noted that the complexes formed by Zn-TPP with *n*-octyl-(propargyl)amine and di-*n*-octyl(propargyl)amine are approximately twice as stable as those derived from *n*-propyl(propargyl)amine amd di-*n*-butyl(propargyl)-amine. Probable factors responsible for such behavior of amines containing *n*-octyl groups were discussed by us previously [8, 9].

Thus, the results of our studies on the complexation of Zn-TPP with alcohols and primary [8], secondary, and tertiary amines and nucleophilic substitution reactions of pheophorbide *a* with primary amines [8] and X-ray diffraction data for the complexes of Zn-TPP with *n*-octyl- [8] and di-*n*-octylamines led us to conclude that the *n*-octyl group possesses a unique ability to form stable intra- and/or intermolecular bonds with porphyrin systems. This conclusion is also based on anomalously high ΔS^0 values for the complexes of Zn-TPP with *n*-octylamines in chloroform and relatively low absolute values of ΔH^0 as compared to analogous amines containing *n*-alkyl groups with different numbers of carbon atoms (Tables 1, 3).

Table 2. Bond lengths and bond angles in the complex of Zn-TPP with di-*n*-octylamine

Bond	*d*, Å	Angle	ω, deg
$Zn^1–N^1$	2.148(7)	$N^2Zn^1N^1$	99.6(2)
$Zn^1–N^2$	2.073 (3)	$N^3Zn^1N^1$	100(2)
$Zn^1–N^3$	2.064 (3)	$N^4Zn^1N^1$	97.8(2)
$Zn^1–N^4$	2.057 (3)	$N^5Zn^1N^1$	99.7(2)
$Zn^1–N^5$	2.065 (3)	$Zn^1N^1C^{46}$	119.8(6)
$N^1–C^{46}$	1.46 (1)	$Zn^1N^1C^{54}$	115.1(6)
$N^1–C^{54}$	1.47 (1)	$N^1C^{54}C^{55}$	111(1)

The ΔS^0 value decreases from 8.0 to –45.1 J mol^{-1} K^{-1} in the series $Me_3N < Et_3N < (n\text{-}Bu)_3N$. Obviously, branching of alkyl group and further increase of steric load in the series of saturated tertiary amines should be accompanied by reduction of the stability constants of the corresponding complexes. In fact, the stability constant for the complex with ethyl(diisopropyl)amine ($K = 4.78$ L/mol) is the lowest among the examined amines due primarily to steric hindrances to the coordination ($\Delta S^0 = –83.3$ J mol^{-1} K^{-1}).

Insofar as the propargyl group is close to methyl in steric effect on the nitrogen atom, the behavior of tertiary β-acetylenic amines is determined by electronic factors to a stronger extent than the behavior of saturated tertiary amines. The complexes become more stable as the length of the alkyl group R increases (Et < *n*-Pr < *n*-Bu; increase of +*I* effect. Simultaneously, ΔS^0 increases from –42.6 to –19.8 J mol^{-1} K^{-1}. The presence of a compact morpholine fragment (ΔS^0 = 6.56 J mol^{-1} K^{-1}) gives rise to especially sharp increase of the stability constant ($K = 1025$ L/mol).

However, addition of diisopropyl(propargyl)amine to a solution of Zn-TPP in chloroform induces no appreciable variation of the electronic absorption

Table 3. Stability constants (K) of molecular complexes formed by Zn-TPP with tertiary amines and thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) of complex formation (chloroform, 25°C), complexation-induced shifts of the absorption maxima ($\Delta\lambda$), sums of substituent constants σ^* ($\Sigma\sigma^*$), steric constants E_n, and basicities (pK_a) of amines in water at 25°C[a]

Ligand	K, L/mol	$\Sigma\sigma^*$ [10, 11]	E_n [10, 11]	$\Delta\lambda$, nm			pK_a (H_2O) [12]	ΔH^0, kJ/mol	ΔS^0, J mol^{-1} K^{-1}	$-\Delta G^0$, kJ/mol
				Soret	*II*	*I*				
Trimethylamine	2634±146	0.00	–1.54	8.8	15.4	16.9	9.76	–17.06±0.29	8±0.6	19.5
Triethylamine	7.93±0.12	–0.30	–3.80	8.8	13.9	16.6	10.65	–16.81±0.6	–38.71±1.4	5.13
Tri-*n*-butylamine	12.0±0.2	–0.39	–4.50	9.3	15.1	17.6	10.89	–19.65±0.57	–45.1±2.2	6.15
Di-*n*-butyl(*n*-octyl)amine	–	–	–	10.8	14.9	18.5	–	–	–	–
Tri-*n*-octylamine	42.6±1	–0.39	–4.39	–	15.9	18.3	–	–13.73±0.4	–14.58±0.9	9.39
Benzyl(dimethyl)amine	908±25	0.215	–2.23	9.4	14.1	16.3	8.93	–18.17±0.34	–4.31±0.3	16.89
1,1-Dimethylbutyn-2-yl(dimethyl)amine	27.5±1.1	0.21	–	10.9	12	16.7	8.91 [13]	–14.83±0.5	–21.94±1.6	8.29
Triallylamine	14.05±0.15	0.48	–	9	14.2	16.7	8.31	–15.33±0.45	–29.50±1.90	6.54
Allyl(dimethyl)amine	2320±60	0.16	–	9.8	14.5	16.3	–	–17.27±0.45	6.47±0.4	19.2
Ethyl(diisopropyl)amine	4.78±0.13	–0.48	–	8.5	15.1	17.4	–	–28.56±0.95	–83.3±4	3.87
Methyl(dioctyl)amine	169.5±3	–	–	9.7	14.8	17.4	–	–17.16±0.6	–14.7±1.3	12.71
DABCO	105000±1700	–	–	9.2	15.4	17	–	–14.85±0.65	46.3±1.5	28.63
N,*N*-Dimethylamino-propionitrile	800±32	–	–		11.2	13.3	–	–25.34±0.2	–30±1	16.55
Diethyl(propargyl)amine	22.8±0.7	0.56	–	10.0	15.2	17.3	7.76 [14]	–20.56±0.46	–42.6±1.4	7.74
Propargyl(di-*n*-propyl)amine	31.5±0.5	0.52	–	9.4	14.5	17.4	–	–16.91±0.4	–28.0±1.0	8.54
Di-*n*-butyl(propargyl)amine	5.2±0.2	0.50	–	–	16.2	18.8	–	–18.97±0.7	–49.5±0.6	4.08
Di-*n*-heptyl(propargyl)amine	5.1±0.11			10.1	16.0	18.1		–19.92±0.75	–52.2±2.4	4.03
Di-*n*-octyl(propargyl)amine	6.3±0.2			10.3	16.4	18.4		–17.6±0.41	–43.6±2	4.54
4-Propargylmorpholine	1025±25	1.45	–	–	14.2	17.7	–	–15.33±0.01	6.56±0.06	17.17
Dipropargyl(*n*-propyl)amine	6.7 ±0.31	1.40	–	–	–	–	–	–19.13 ± 0.7	–48.3 ± 2.4	4.71
n-Butyl(dipropargyl)amine	25.9±0.4				12.6			20.04±0.24	–40.3±0.9	8.06

[a] ΔG^0 values were calculated by the formula $\Delta G^0 = -RT\ln K_{298}$.

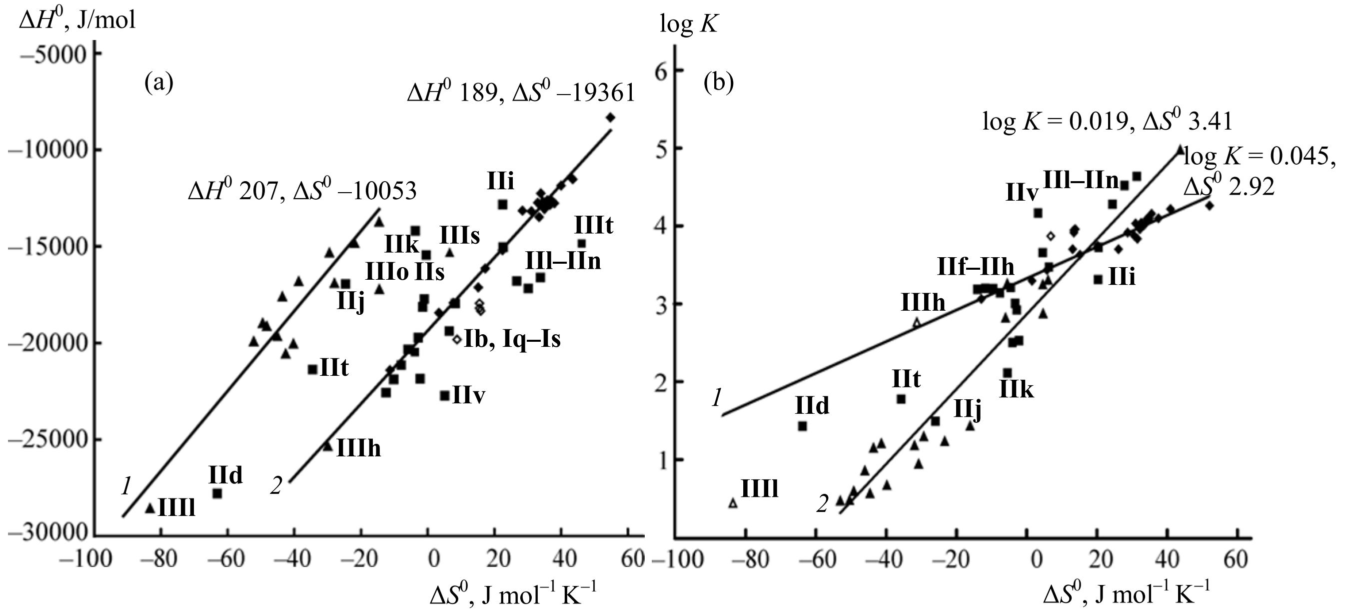


Fig. 2. Plots of (a) ΔH^0 and (b) $\log K$ versus ΔS^0 for the complexation of Zn-TPP with primary (rhombs), secondary (squares), and tertiary (triangles) amines in chloroform at 25°C. Straight lines *1* for primary amines were drawn with exclusion of amines **Ib** and **Iq**–**Is** (dark rhombs), and straight lines *2* for tertiary amines were drawn (a) for **IIIb**–**IIIe**, **IIIi**–**IIIo**, **IIIq**, and **IIIr** and (b) for the same amines with exclusion of **IIIh** and **IIIl** (triangles).

spectrum. The reason is *–I* effect of the propargyl group and cumulative action of steric factors of the substituents, which strongly reduce nucleophilicity of the nitrogen atom. It should be emphasized that introduction of substituents into amine molecules already containing bulky substituents [e.g., in going from *tert*-butylamine to *tert*-butyl(propargyl)amine and from diisopropylamine to ethyl(diisopropyl)amine] leads to a strong reduction of ΔS^0 and *K*.

Unlike primary amines, the complexation of Zn-TPP with secondary and especially tertiary amines does not conform to a common linear relation between the ΔS^0 and ΔH^0 values (Fig. 2), which is likely to result from sharp increase of steric hindrances to coordination in the series $RNH_2 < R_2NH < R_3N$. In fact (Fig. 2a), many points for secondary and tertiary amines are located between straight lines *1* (primary amines) and *2* (most sterically hindered tertiary amines; ΔS^0 = –14.6 to –83 J mol^{-1} K^{-1}). Exceptions are cyclic secondary (piperidine, piperazine, morpholine) and tertiary amines (DABCO) (ΔS^0 = 27–46 J mol^{-1} K^{-1}), as well as *N*-propargylethylenediamine (ΔS^0 = 5.1 J mol^{-1} K^{-1}), owing to positive change of the entropy upon formation of complexes by Zn-TPP and ligands with a rigid cyclic structure or capable of chelating.

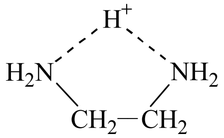
The $\log K$—ΔS^0 dependence cam also be represented as two straight lines shown in Fig. 2b. The points for secondary cyclic amines **IIl**–**IIn** and *N*-propargylethylenediamine (**IIv**) appear above these lines, while the points for ligands with strongly shielded nitrogen atom [ethyl(diisopropyl)amine (**IIIl**), diisopropylamine (**IId**), and *tert*-butyl(propargyl) amine (**IIf**)] are located in the bottom part of the plot between straight lines *1* and *2*.

The behavior of ethylenediamine and its derivatives in the complexation with Zn-TPP deserves special consideration. The stability constant of the Zn-TPP complex with ethylenediamine (*K* = 19750 L/mol, pK_a 9.98 [16]) is thrice as high as that for the complex with 2-aminoethanol (*K* = 6340 L/mol, pK_a 9.50). Furthermore, it exceeds those found for more basic (pK_a 10.6) ethyl- (*K* = 10142 L/mol), *n*-propyl- (*K* = 11125 L/mol), and *n*-butylamine (*K* = 15213 L/mol). In addition, the stability constant changes insignificantly upon introduction of an electron-withdrawing propargyl group (*K* = 17643 L/mol for *N*-propargylethylenediamine); introduction of the same substituent into *n*-propylamine molecules leads to fivefold reduction of the stability constant of the corresponding complex [*K* = 2130 L/mol for propargyl(*n*-propyl)amine]. These findings may be interpreted

Table 4. Crystallographic data for the complex of Zn-TPP with di-*n*-octylamine

Parameter	Value
Formula	$C_{60}H_{63}N_5Zn_1$
Molecular weight	919.52
Crystal dimensions, mm	0.034, 0.02, 0.17
Temperature, K	295
Crystal system	Triclinic
Space group	P-1
a, Å	12.0648(3)
b, Å	12.3300(3)
c, Å	18.9311(4)
α, deg	82.449(2)
β, deg	89.514(2)
γ, deg	67.179(2)
V, Å^3	2570.43
Z	2
d_{calc}, g/cm^3	1.188
μ	0.980
θ_{max}, deg	66
Ranges of h, k, l	–9, 14; –14, 14; –22, 22
Number of independent reflections	8586
Number of reflections with $[I > 2\sigma(I)]$	3727
Number of variables	650
$R(F^2)$	0.059
$R_w(F^2)$	0.139
Goodness of fit	0.76
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	0.31, –0.52

assuming formation of chelate complexes from Zn-TPP and ethylenediamine and its *N*-propargyl derivative via coordination of both nitrogen atoms of the ligand to the zinc atom. It should be noted that increased stability of ethylenediamine in gas phase and aprotic solvents (not in water) may be rationalized by formation of stable bridged structures [12].



In fact, the stability constant of the complex with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**IIIu**) (K = 2380 L/mol; due to the presence of tertiary amino groups ligand **IIIu** is characterized by a low ability to form chelates with Zn-TPP) is almost similar to those of the complexes with trimethylamine (K = 2634 L/mol) and allyl(dimethyl)amine (K = 2320 L/mol).

It should be emphasized that, like the hydrocarbon moiety of *n*-octylamines (which is spatially close to the aromatic fragments of the neighboring metalloporphyrin molecules), 1,3-diaminopropane and 1,4-diaminobutane (analogs of ethylenediamine) form crystalline 2 : 1 complexes with Zn-TPP [17, 18], where both nitrogen atoms of the ligand are axially coordinated to the zinc atoms of two metalloporphyrin molecules.

Interestingly, the stability constant of the Zn-TPP complex with propargyl(*n*-propyl)amine (K = 2130 L/mol), in spite of electron-withdrawing effect of the $CH_2C{\equiv}CH$ group, is higher than that of the complex with di-*n*-propylamine (K = 1360 L/mol). Presumably, the propargyl group in which the three carbon atoms are arranged linearly causes less hindrance to coordination than does *n*-propyl group.

In summary, we have shown that the complexation of zinc tetraphenylporphyrin with secondary and tertiary amines in chloroform, as well as nucleophilic substitution reactions with the same amines, can be described on the basis of electronic and steric factors. On the other hand, high stability of some complexes may be rationalized assuming formation of chelate structures with multidentate ligands. We believe that, as in the complexation of Zn-TPP with aromatic ligands (pyridines, pyridine and quinoline *N*-oxides, anilines) and primary amines and alcohols, which fits the Hammett equation, the examined model system can be very useful for elucidation of specific features of various nucleophilic processes involving sterically hindered secondary and tertiary amines and alcohols. In particular, variations of the electronic spectra of Zn-TPP ($\Delta\lambda$ values) should provide quantitative information on not only electronic but also steric effects of substituents in the ligand.

In our further studies we plan to find out factors responsible for the specific behavior of *n*-octyl substituents in complex formation and nucleophilic substitution reactions with metalloporphyrins and to apply the modified Taft equation to describe the complexation of Zn-TPP with secondary and tertiary amines.

EXPERIMENTAL

Propargylamines were synthesized according to the procedure described in [19]. All amines, except for propargylamines, were distilled over alkali.

The stability constants of Zn-TPP complexes with amines in chloroform were determined as described in [1]. Gaseous dimethyl- and trimethylamine were prepared by heating the corresponding hydrochlorides with potassium hydroxide, passed through anhydrous NaOH and $CaCl_2$, and then passed through chloroform. The ligand concentration was determined by back titration: a definite amount of chloroform solution was treated with excess 0.01 M aqueous HCl, and the remainder of the latter was titrated with 0.01 M aqueous sodium hydroxide in the presence of phenolphthalein. The stability constants of the Zn-TPP complexes with dimethyl- and trimethylamines were determined in mixtures of chloroform solutions of the metalloporphyrin and ligand with a known molar ratio.

The electronic absorption spectra were recorded on an SF 2000-02 spectrophotometer. The IR spectra were measured in the region 4000–600 cm^{-1} on Shimadzu IR Prestige-21 and Perkin Elmer Paragon 1000 FTIR spectrometers. The ^1H NMR spectra were taken from solutions in $CDCl_3$ on a Bruker WM 400 instrument using tetramethylsilane as internal reference. The high-resolution mass spectra (electrospray ionization) were obtained on a Bruker micrOTOF 10 223 instrument.

X-Ray analysis of a single crystal of complex **IV** was performed on a StadiVari Pilatus 100K STOE diffractometer (CuK_α radiation). The data were acquired and processed, and the unit cell parameters were determined and refined, using STOE X-Area software. The principal crystallographic parameters are given in Table 4. The structure was solved by the direct method sing SHELXS-97 [20]. The positions and thermal parameters of nonhydrogen 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 [21]. The X-ray diffraction data were deposited to the Cambridge Crystallographic Centre (entry no. CCDC 987479).

The thermodynamic parameters of complex formation were determined graphically with account taken of formula (2) (first Ulich approximation [22]), assuming that ΔH and ΔS remain constant within the examined narrow temperature range (288–308 K or 283–298 K for gaseous ligands).

$$\ln K_T = -\Delta H^0_{298}/RT + \Delta S^0_{298}/R. \tag{2}$$

***N*-*n*-Octylprop-2-yn-1-amine (IIu).** A solution of 12.9 g (16.5 mL, 0.1 mol) of *n*-octylamine in 40 mL of hexane was cooled in an ice–water bath, and a solution of 6 g (4 mL, 0.05 mol) of propargyl bromide in 10 mL of hexane was added under stirring. The mixture was left to stand for 24 h at room temperature, the precipitate of *n*-octylamine hydrochloride was filtered off, the solvent was removed from the filtrate under reduced pressure, and the residue was distilled in a vacuum. Yield 70%, bp 76–78°C (1 mm). IR spectrum, ν, cm^{-1}: 3310 v.s, 2924 v.s, 2854 v.s, 2103 v.w, 1458 v.s, 1348 w, 1328 m, 1247 w, 1116 s, 978 w, 903 m, 835 v.w, 723 w, 644 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (3H, Me, J = 6.0 Hz), 1.1–1.5 m (12H), 2.10 t (1H, ≡CH, J = 2.4 Hz), 2.62 t (2H, CH_2N, J = 6.0 Hz), 3.25 d (2H, $CH_2C≡$, J = 3.0 Hz). Mass spectrum, m/z: 168.1752 [M + H], 206.1910 [$M + H + C_3H_2$], 130.1590 [$M + H - C_3H_2$]. Found, %: C 78.97; H 12.65; N 8.37. $C_{11}H_{21}N$. Calculated, %: C 78.91; H 12.55; N 8.54.

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

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