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Tetraphenylporphine Zinc(II) Coordination with Primary Amines and Alcohols in Chloroform

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Abstract—Changes in the thermodynamic and kinetic parameters of isoequilibrium coordination of tetraphenylporphine zinc(II) (Zn-TPP) with primary amines in chloroform at 283–308 K follow expanded correlative Taft relation modified for amines. Dependences of stability constants of complexes on shifts of Zn-TPP absorption bands in electronic spectra caused by the reactions with primary amines and the corresponding alcohols are of a linear character, as well as the relations between rate constants of nucleophilic substitution and of complex formation. The formation of molecular complexes with certain amines is accompanied by the appearance of a new absorption band in the electronic spectra near 630 nm.

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Functioning of metal porphines in vivo is connected with the formation of complexes with ligands, the nature of which is insufficiently studied at present owing to complexity of studying intermolecular interactions of low-soluble substances (solubility of metal porphyrins in organic solvents is 10^{-7}–10^{-4} M) and to the limited sensitivity of the majority of physicochemical research techniques.

To use successfully metal porphines in medical practice (in making effective blood substitutes, medical drugs, and transport agents), the information on the effect of the metal porphine nature on its complex-forming properties in relation to electron-donor ligands is necessary.

Synthetic metal porphines are convenient model systems for studying processes occurring in vivo, and (5,10,15,20-tetraphenylporphinato-k^{4}N)zinc(II) (Zn-TPP) is one of the most accessible compounds of this type, therefore it has been chosen for studying coordination with electron-donor ligands of various types. Firstly, Zn-TPP contains a rather simple in structure (in comparison with natural metal porphines) porphyrin part and a biogenic d-metal without a counter ion (unlike Fe^{3+}), which considerably facilitates the interpretation of obtained data. Secondly, unlike metal porphines isolated from biological objects, Zn-TPP can be easily purified and is sufficiently well soluble in organic solvents. Thirdly, unlike manganese-, copper-, and iron-containing porphyrins, Zn-TPP is not prone to participate in redox reactions, and consequently complexes with Zn-TPP do not hinder studying coordination processes. Metal porphines containing zinc (for example, bacteriochlorophyll from *Acidiphillium rubrum* [1]) are found in nature and consequently the data obtained *in vitro* on a model molecule, which we have chosen, are applicable to *in vivo* processes.

We have shown [2–4] that in the absence of steric factor (pyridines, *N*-oxides of pyridines, quinolines, and acridines with substituents in 3 and 4 sites of aromatic rings) linear correlations are observed between kinetic and thermodynamic parameters of the Zn-TPP coordination and nucleophilic substitution reactions with the specified nucleophile ligands. In particular, the shift ($\Delta\lambda$) of absorption bands in the electronic spectra of this metal porphine in chloroform caused by the complex formation linearly correlates with logarithms of stability constants (K) of the complexes, pK_a values of the ligands in water and other solvents, rate constants of S_N reactions, and also with Hammett constants of substituents in a heterocycle.

Table 1. Stability constants (K), thermodynamic constants (ΔG^0, ΔH^0, and ΔS^0) of the formation of Zn-TPP molecular complexes with primary amines in chloroform at 25°C, shifts of maxima of I, II, and Soret absorption bands ($\Delta\lambda$) in Zn-TPP spectra caused by complex formation, $\Sigma\sigma^*$ of substituents, ionization potentials I_p, steric constants, and values of basicity (pK_a) of amines in water at 25°C and in a gas phase (ΔG_B)

Ligand	$K\times10^{-3}$, l mol^{-1}	$\Sigma\sigma^*$ [5, 7]	I_p [8]	E_n [5,7]	$\Delta\lambda$, nm			pK_a (H_2O) [9]	ΔG_B, kcal mol^{-1} [9]	ΔH^0, kJ mol^{-1}	ΔS^0, J mol^{-1} K^{-1}	$\Delta G^{0,a}$, kJ mol^{-1}
					Cope	II	I					
Ammonia	1.55±0.03	1.47	10.15	0.00	9.8	16.2	17.5	9.21	0.0	–21.4±0.2	–11.3±0.8	–18.0
Methylamine	9.2±0.1	0.98	8.97	–0.07	10.2	16.5	18.5	10.62	9.1	–19.8±0.2	8.8±0.7	–22.4
Ethylamine	10.1±0.1	0.88	8.86	–0.36	10.5	16.8	19.1	10.63	11.8	–13.2±0.3	31.1±1.6	–22.8
Propylamine	11.1±0.3	0.86	8.78	–0.39	10.3	16.8	19.7	10.53	13.0	–12.7±0.3	34.6±1.5	–23.0
Isopropylamine	6.3±0.1	0.79	8.72	–0.93	10.0	16.1	17.7	10.63	14.1	–13.2±0.2	28.4±1.5	–21.7
Butylamine	15.2±0.3	0.85	8.71	–0.40	10.7	16.8	19.6	10.59	13.5	–11.9±0.5	40.0±1.7	–23.8
Isobutylamine	12.5±0.3	0.855	8.70	–0.35	10.0	16.6	19.2	10.43	14.0	–12.6±0.3	35.9±1.6	–23.3
sec-Butylamine	9.3±0.2	0.77	–	–1.10	10.1	16.4	18.3	10.56	15.2	–12.7±0.3	33.0±1.4	–22.6
tert-Butylamine	3.5±0.1	0.68	8.64	–1.74	9.8	15.5	17.7	10.45	16.1	–17.9±0.3	7.7±0.9	–20.1
Octylamine	21.7±0.8	0.85	–	–	10.5	16.9	19.1	–	–	–8.3±0.3	54.8±2.4	–24.7
Cyclohexylamine	8.52±0.07	0.83	–	–0.98	10.4	16.6	18.9	–	16.3	–12.3±0.2	33.9±0.7	–22.4
Benzylamine	5.4±0.1	1.20	8.64	–0.38	10.3	16.1	19.1	9.34	–	–16.1±0.1	17.2±0.1	–21.3
Allylamine	7.0±0.1	1.14		–0.20	10.4	16.4	18.3	9.49	11.3	–15.2±0.4	22.4±0.8	–21.9
Propargylamine	2.59±0.06	1.74 [10]			9.5	14.7	16.6	8.15	6.7	–18.4±0.2	3.4±0.4	–19.4
2-Aminoethanol	6.3±0.2	1.18 [10]			10.0	16.3	18.9	9.50 [10, 11]	–	–17.1±0.3	15.2±1.0	–21.6

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

This work is devoted to the study of the Zn-TPP reactions with primary amines (RNH_2) and with alcohol (ROH), where steric factors should be of importance. In such cases expanded Taft Eq. (1) modified for amines [5] is used to describe nucleophilic substitution reactions.

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

Here k is the reaction rate constant, the term $\rho^*\Sigma\sigma^*$ describes the induction effect of all substituents at a nitrogen atom, and δE_N is the effect of the steric factor (δE_s in the Taft equation).

Earlier the application of Eq. (1) to the description of coordination and nucleophilic substitution reactions and the use of the data for seven amines (benzyl-, butyl-, diethyl-, tribenzyl-, tributylamines, aniline, and piperidine) strongly differing in structure have allowed us to deduce dependences (2) and (3) [6] connecting log K in benzene (stability constants were determined by a calorimetric method), $\Sigma\sigma$, E_N, and log k values for the reactions of phenacyl bromide with amines in benzene at 25°C [5].

$$\log K = 3.75 - 0.55\,\Sigma\sigma^* + 0.43E_N,\ r\ 0.961, \quad (2)$$

$$\log K/k = 2.77 + 2.73\,\Sigma\sigma^* - 0.94E_N,\ r\ 0.983. \quad (3)$$

In this case r characterizes the correlation between experimental log K (log K/k) values and values calculated by Eqs. (1)–(3).

The modified correlative Taft relations can be used to predict various physicochemical parameters of the Zn-TPP coordination with primary amines **I** and alcohols **II** on the basis of the electronic spectroscopy data (Tables 1 and 2).

RNH_2	ROH
Ia–Io	**IIb–IIj, IIn–IIq**

R = H (**a**), Me (**b**), Et (**c**), Pr (**d**), *i*-Pr (**e**), Bu (**f**), *i*-Bu (**g**), *s*-Bu (**h**), *t*-Bu (**i**), octyl (**j**), cyclohexyl (**k**), allyl (**l**), benzyl (**m**), 2-hydroxoethyl (**n**), propargyl (**o**), isoamyl (**p**), 2-aminoethyl (**q**).

Experimental stability constants (K) of Zn-TPP molecular complexes with primary amines in chloroform are concentration constants. Taking into account low concentrations of mother substances (2×10^{-5} M for Zn-TPP and 2×10^{-5}–5×10^{-4} M for ligands) and also the absence of ionic species in solution, we can assume that the obtained values differ only slightly from thermodynamic values.

Table 2. Stability constants (K) of Zn-TPP molecular complexes with alcohols in chloroform at 25°C, shifts of the maximum of absorption band II ($\Delta\lambda_{II}$), ionization potentials I_p, and values of $\Sigma\sigma^*$ and E_s of alcohols

Alcohol[a]	K, l mol^{-1}	I_p [8]	$\Delta\lambda_{II}$	$\Sigma\sigma^*$ [7]	E_s [7]
Methylamine	7.3±0.2	10.85	9.3	0.49	0.00
Ethylamine	10.1±0.3	10.50	9.8	0.39	–0.07
Propylamine	9.1±0.2	10.15	9.8	0.375	–0.36
Isopropylamine	6.0±0.2	10.15	9.0	0.300	–0.47
Butylamine	10.2±0.2	10.1	9.8	0.360	–0.39
Isobutylamine	9.4±0.2	10.1	9.5	0.365	–0.93
sec-Butylamine	8.4±0.2	–	9.5	0.28	–1.13
tert-Butylamine	4.6±0.1	9.7	7.6	0.19	–1.54
Isoamine	10.6±0.2	–	10.0		–0.34
Octylamine	11.9±1.1	–	10.2	0.36 [5]	–0.33
Propargylamine	3.0±0.1	–	7.0	1.25 [10]	–

[a] Zn-TPP turns completely to complexes with alcohols at the ratios Zn-TPP:L 1:30000 and 1:150000 in the cases of propargyl and *tert*-butyl alcohols, respectively.

Thermodynamic characteristics of the coordination with Zn-TPP in chloroform (Table 1) were calculated for some primary amines on the basis of the temperature dependence of stability constants in the range of 283–308 K.

The values of ΔH^0 in all cases are negative and ΔS^0 positive (except for ammonia), i.e. the Zn-TPP coordination with primary amines is favored by both enthalpy and entropy factors. The linear relation of free energies should be obeyed in the case of constant activation entropies $\Delta S^{\neq}$ (isoentropy series) or activation enthalpies $\Delta H^{\neq}$ (isoenthalpy series) for chemical reactions and also of entropies ΔS^0 and enthalpies ΔH^0 of complex formations for coordination processes, respectively. However, many reactions, which do not satisfy this condition, nevertheless are well described by Hammett equation because of mutual proportionality of ΔH and ΔS values [12, 13].

In this case, according to Eqs. (4)–(6) at a certain temperature β, the variation of substituents will not result in a change of the process rate, as enthalpy changes are precisely compensated by entropy changes.

$$\Delta(\Delta H) = \beta\Delta(\Delta S), \quad (4)$$

$$\Delta(\Delta G) = \Delta(\Delta H) - T\Delta(\Delta H)/\beta, \quad (5)$$

$$\Delta(\Delta G) = \Delta(\Delta H)\,(1 - T/\beta). \quad (6)$$

The linear relation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is called isokinetic, and that between ΔH^0 and ΔS^0, isoequilibrium or isothermodynamic. In our case of the Zn-TPP complex formation with primary amines ($\Delta H^0 = 198\Delta S^0 - 19390$; r 0.995, n 14; the isoequilibrium temperature equal to the slope ratio of the $\Delta H^0 - \Delta S^0$ dependence [9]) β is 198 K (–75°C).

On the assumption that $\Delta H = \Delta H^0$ and $\Delta S = \Delta S^0$ at the isoequilibrium temperature (as well as in the interval 283–308 K) we come to Eq. (7).

$$\Delta G_{198} = \Delta H^0 - T\Delta S^0 = \Delta H^0 - 198\Delta S^0. \quad (7)$$

Hence, for a certain primary amine ($\Delta S^0 = 0$) the ΔG^0 value of its complex formation with Zn-TPP in chloroform will be independent of temperature. In fact, in the case of propargylamine, which has the least ΔS^0 value of 3.35 J mol^{-1} K^{-1} (ΔH^0 –18.44 kJ mol^{-1}) (Table 1), the ΔG^0 value of –19.44 kJ mol^{-1} is the closest to ΔG_{198} –19.39 kJ mol^{-1}, i.e. the temperature variation influences the ΔG value only slightly. At the isoequilibrium temperature the value of K should not depend on a ligand structure, and at its further decrease (the value of ΔS will change its sign) there will be a reversion of the relative stability of complexes. Unfortunately, it is impossible to check independence of ΔG and K values from the structure of primary amines in the isoequilibrium point, because the temperature of chloroform crystallization is –63.5°C.

The characteristics of isoequilibrium points of the Zn-TPP coordination with primary amines in chloroform (β 198 K, ΔG_{198} –19390 J mol^{-1}, this work) and with 3- and 4-substituted pyridines (β 196 K, ΔG_{196} –19100 J mol^{-1}, [4]) are very close to each other. In

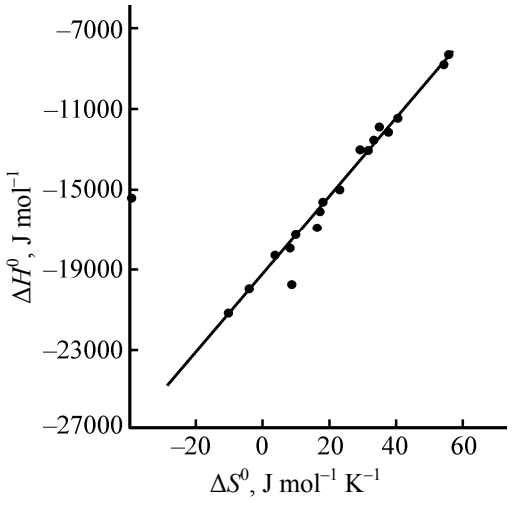

Fig. 1. Dependence of ΔH^0 values on ΔS^0 [$\Delta H^0 = 195\Delta S^o$ - 19270, *n* 21, *r* 0.998; amine **Ib** (below) and 2-chloropyridine are not included in the correlation] for the complex formation of Zn-TPP with primary amines RNH_2 and pyridines XPy (X = 4-NMe_2, 4-Me, 3-Me, H, 3-$CONH_2$, 3-COOEt, 4-CN [4]) in chloroform.

spite of a difference in hybridization states of nitrogen atoms (sp^2 in pyridines and sp^3 in amines) within the limits of these two quite different types of ligands the structural changes do not affect the states of equilibrium between a metal porphine and a complex at the isoequilibrium temperature, as entropy and enthalpy changes of the system in the course of the coordination completely compensate each other. The correlation between ΔH^0 and ΔS^0 involving both amines and pyridines is given in Fig. 1.

Both ΔG^0 and log *K* in the series of primary amines and ammonia (as well as in the case of coordination of pyridines [4]) linearly depend on the ΔH^0 value ($\Delta G^0 = -0.503\Delta H^0 - 29220$, *r* 0.95) and ΔS^0 ($\Delta G^0 = -102\Delta S^0 - 19390$, *r* 0.98) of the Zn-TPP complex formation, however the coordination of 2-chloropyridine (ΔH^0 – 15.42 kJ mol^{-1}; ΔS^0 –39.42 J mol^{-1} K^{-1}; ΔG^0 –3.75 kJ mol^{-1}) with a metal porphine does not obey these regularities because of steric hindrances originating from the halogen atom (Fig. 1).

The analysis of kinetic and thermodynamic parameters of the Zn-TPP coordination with primary amines of unbranched structures (Table 1) shows that the stability of the complexes increases in the series: $NH_3 < CH_3NH_2 < C_2H_5NH_2 < C_3H_7NH_2 < C_4H_9NH_2 << C_8H_{17}NH_2$. Such sequence of *K* variation (in parallel with log *P* values [14] describing the ratio of solubilities of compounds in octane and water; the order of log *P* variation in the methylamine-decylamine series: –0.57, –0.13, 0.48, 0.86, 3.09, 3.60.4.1) points to the fact that apparently the hydrophobic interactions are decisive for butylamine and octylamine (σ* for alkyl groups of an unbranched structure with three and more carbon atoms are practically the same).

The value of ΔH^0 increases from ammonia up to octylamine from –21.4 up to –8.3 kJ mol^{-1}, whereas ΔS^0, from –11.32 up to +54.8 J mol^{-1} K^{-1}, and the variation of stability of Zn-TPP complexes with amines in chloroform is under entropy control, because changes in $T\Delta S^0$ the more exceed ΔH^0, the longer is the length of substituents *R*.

In the case of branching alkyl groups (Table 1) the stability constants of complexes decrease in the following sequence: $BuNH_2$ > *i*-$BuNH_2$> *s*-$BuNH_2$> *t*-$BuNH_2$ and $PrNH_2$ > *i*-$PrNH_2$ in spite of the σ* increase in this series; therewith in both cases ΔH^0 and ΔS^0 decrease as the branching of a chain increases. In the coordination of Zn-TPP the steric factors progressively dominate over electronic factors as the amine alkyl group gets more branched, and the change in *K* is under the entropy control.

Primary amines with alkyl groups have practically equal basicity values, and in this case (unlike pyridines with substituents in 3 and 4 sites) a correlation of stability constants and thermodynamic parameters with pK_a is absent. However, when a carbon atom hybridization is changed ($sp^3 \rightarrow sp$), the basicity of amines (in accordance with the electronegativity increase) considerably decreases and a possibility to reveal the specified regularities appears. For example, in the series $CH_3CH_2CH_2NH_2$, $CH_2{=}CHCH_2NH_2$, $HC{\equiv}CCH_2NH_2$ a basicity and a stability constant *K* decrease (from 10.53 to 8.15 pK_a units and from 11125 to 2591 l mol^{-1}, respectively). Values of ΔH^0 and ΔS^0 decrease in the same sequence (from –12.68 to –18.44 kJ mol^{-1} and from 34.60 to 3.35 J mol^{-1} K^{-1}, respectively), but the factor defining a relative stability of Zn-TPP complexes with primary amines is still the entropy factor connected with the number of degrees of freedom in a ligand molecule (the rigidity of a molecule and the spacial accessibility of the nitrogen atom increase from propyl- to propargylamine). Analogous changes in pK_a, *K*, ΔH^0, and ΔS^0 also occur in passing from cyclohexyl- to benzylamine (Table 1).

The study of correlation (8) (except for octylamine) (Fig. 2) has shown that a similar pattern is observed in all the cases: as Σσ* increases up to 0.9 in the series of saturated amines, the decrease in absolute values of E_N

exceeds the decrease in +*I* effect, log *K* and log ($K/\Delta\lambda$) values increase, however further they start to decrease as Σσ* increases.

$$\log K - \Sigma\sigma^* \text{ and } \log (K/\Delta\lambda) - \Sigma\sigma^*(\Delta\lambda_{\mathbf{I}}, \Delta\lambda_{\mathbf{II}}, \Delta\lambda S^0_{ret}). \quad (8)$$

Too large decrease in log *K* and log ($K/\Delta\lambda$) values for ammonia seems to be caused by a low polarizability of the molecule. The values of I_p, pK_a, and ΔG_B for ammonia (which does not belong to primary amines) considerably differ from such values for other ligands (Table 1).

Taking into consideration the steric factors, except for those of amines (I_n and I_o) with unknown E_N values, we obtain Eqs. (9)–(11) (n = 12) for primary amines.

$$\log K = 5.64 - 1.57\Sigma\sigma^* + 0.525E_N,\ r\ 0.915, \quad (9)$$

$$\log (K/\Delta\lambda_{\mathbf{II}}) = 4.37 - 1.52\Sigma\sigma^* + 0.503E_N,\ r\ 0.915, \quad (10)$$

$$\Delta\lambda_{\mathbf{II}} = 18.3 - 1.49\Sigma\sigma^* + 0.888E_N,\ r\ 0.845. \quad (11)$$

The application of Eq. (1) with the data for nine primary amines **Ib–Ie, Ih, Ik–Iq** has allowed us to deduce Eqs. (12)–(14) connecting the stability constants of the Zn-TPP complexes (determined by the spectrophotometric method) and rate constants (k) of nucleophilic substitution reactions with phenacyl bromide in benzene at 25°C [5].

$$\log k = -0.504 - 2.01\Sigma\sigma^* + 1.04E_N,\ r\ 0.95, \quad (12)$$

$$\log K/k = 5.49 + 1.06\Sigma\sigma^* - 0.74E_N,\ r\ 0.870, \quad (13)$$

$$\log (\Delta\lambda_{\mathbf{II}}/k) = 1.77 + 1.97\Sigma\sigma^* - 1.02E_N,\ r\ 0.95. \quad (14)$$

Only allyl- and benzylamine (they are away from saturated amines in Fig. 2) do not obey the linear correlation with Σσ*. After eliminating them from the correlations we derive Eqs. (15)–(17) (n = 7, **Ib–If, Ih, Ik**).

$$\log k = -2.89 + 0.552\Sigma\sigma^* + 0.688E_N,\ r\ 0.99, \quad (15)$$

$$\log K/k = 8.63 - 2.31\Sigma\sigma^* - 0.263E_N,\ r\ 0.98, \quad (16)$$

$$\log (\Delta\lambda_{\mathbf{II}}/k) = 4.06 - 0.95\Sigma\sigma^* - 0.686E_N,\ r\ 0.99. \quad (17)$$

The results obtained allow us to make a preliminary conclusion that the Zn-TPP coordination and the S_N reactions involving primary amines can be described by Eq. (1). The effects of steric factors for similar ligands should be similar, and they can be excluded from equations, if ratios of values related to different processes are used (for example, the exclusion of E_N from Eqs. (15), (16) gives the equation: $y = a\Sigma\sigma^* + b$, r 0.92–0.97). The fact that allylamine and benzylamine do not obey these simple regularities points to an important role of similar electronic effects in these molecules.

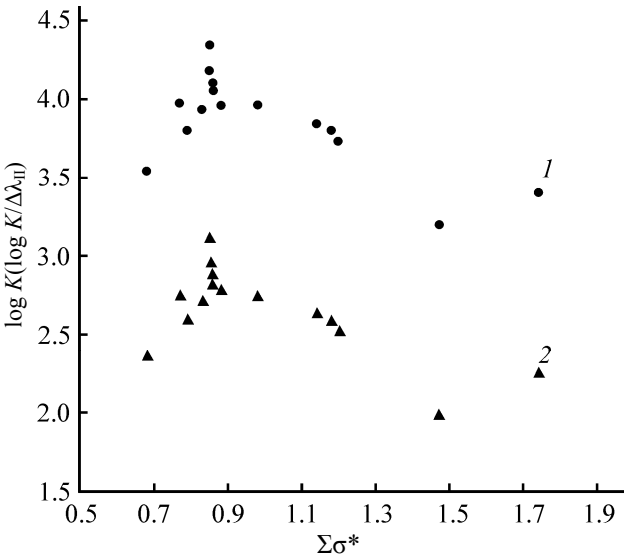

Fig. 2. Dependences (*1*) log *K*–Σσ* and (*2*) log ($K/\Delta\lambda_{II}$)–Σσ* for the complex formation of Zn-TPP with compounds **Ia–Ii, Ik–Io** in chloroform at 25°C.

Rate constants of reactions of saturated primary amines **Ib–Id, If, Ih** with 2,4-dinitrobenzenesulfonyl chloride [15] in benzene at 25°C [Eqs. (18), (19)], and of amines **Id–Ii** with 2,4-dinitrochlorobenzene at 30°C [16] in ethanol [Eqs. (20), (21)] and dioxane [Eqs. (22), (23)] closely follow not only modified Eq. (1), but also the usual Taft equation.

$$\log K/k = -6.50\ \Sigma\sigma^* + 11.07,\ r\ 0.993, \quad (18)$$

$$\log (\Delta\lambda_{\mathbf{II}}/k) = -6.29\ \Sigma\sigma^* + 8.09,\ r\ 0.975, \quad (19)$$

$$\log K/k = -10.5\ \Sigma\sigma^* + 14.34,\ r\ 0.997, \quad (20)$$

$$\log (\Delta\lambda_{\mathbf{II}}/k) = -13.37\ \Sigma\sigma^* + 13.93,\ r\ 0.993, \quad (21)$$

$$\log K/k = -4.46\ \Sigma\sigma^* - 11.1,\ r\ 0.96, \quad (22)$$

$$\log (\Delta\lambda_{\mathbf{II}}/k) = -7.35\ \Sigma\sigma^* - 10.65,\ r\ 0.975. \quad (23)$$

Good correlations are observed between log K/k and Σσ* and also between log ($\Delta\lambda_{\mathbf{II}}/k$) and Σσ* values in spite of the fact that the E_N value is absent from the equations. Hence, the sensitivity (δ) of the Zn-TPP coordination and of the nucleophilic substitution reactions to the steric difficulties caused by saturated primary amines is the same in both cases.

The possibility of using simple relations log K/k–Σσ* and log ($\Delta\lambda/k$)–Σσ* (similar to Hammett-Taft equations) in the presence of a great amount of experimental information collected in coordination and

organic chemistry (stability constants of molecular complexes of metal porphines and rate constants of S_N reactions) will essentially facilitate the calculation of previously unknown σ* values and the understanding of general regularities of the formation of donor-acceptor bonds. Litvinenko et al. [17] assumed on the ground of mathematical calculations that E_S constants (analogs of E_N in the expanded Taft equation) are not universal for different reaction series. The use of our equations containing log K/k, log ($\Delta\lambda/k$), and log ($\Delta\lambda/K$) allows us to avoid this problem due to the absence of steric constants in an explicit form and to detect easily ligands with an abnormal mechanism of coordination, which deviate from linear correlations.

Tabulated values of E_S and E_N in modified equations [7, 18] may be not universal, because when using kinetic parameters (K and k) it is necessary to take into consideration not only electronic and steric factors, but also others, for example, hydrophobic interactions. Otherwise, the calculation of new E_N values by means of biparametric equations will result in its various (wrong) values depending on a type of a reaction series.

Probably, for primary amines RNH_2 and alcohols ROH with similar structures and close in size nitrogen and oxygen atoms (a similarity of $\Sigma\sigma^*$ and E_N, E_S), the stability constants should have similar dependences on electronic ($\Sigma\sigma^*$), steric (E_N and E_S), and other factors. We have constructed the dependences log $K_{alcohol}$–log K_{amine} at 25°C and $\Delta\lambda_{II\ alcohol}$–$\Delta\lambda_{II\ amine}$ (Fig. 3) on the basis of Tables 1 and 2. They appeared to be linear. For saturated alcohols, as well as in the case of amines, the stability constant has the minimal value in the case of the Zn-TPP coordination with *tert*-butyl alcohol and the maximal, with octyl alcohol.

Thus, it is possible to calculate parameters of a complex formation with alcohols on the basis of kinetic data on the coordination of Zn-TPP with primary amines and vice versa. It appears that this principle should be obeyed also for such types of ligands as secondary amines R_2NH and ethers R_2O.

The analysis of sparse published X-ray structural data (Table 3, [20]) on the Zn-TPP (1:1) molecular complexes with phenols, anilines, alcohols, amines, pyridines, and also on the Zn-tetrakis(4-chlorophenyl) porphin complexes with benzyl alcohol and (S)-α-methylbenzylamine, and on the Zn-tetrakis(4-bromophenyl)porphine complexes with (R)-α-methylbenzylamine shows that they can be separated in two groups. In the n,ν-complexes of anilines and phenols (Fig. 4a) (probably, with participation of π,π interactions) an angle of 24°–34° is formed between a metal-porphine plane and a ligand aromatic ring. In the complex with Zn-octaethylporphine 3-aminopyridine is coordinated through the nitrogen atom of the NH_2 group, the angle being equal to –21.20°, whereas the other pyridines (Fig. 4b) are oriented almost perpendicularly (80°–89°), and amines and alcohols (in view of a zigzag-like conformation of a hydrocarbon chain), along the axial metal-porphine axis. It is possible that these are special features of the orientation of a metal porphine and a ligand, which cause similar regularities in the thermodynamic and kinetic behavior of pyridines, amines, and alcohols on the coordination with Zn-TPP. Our study has shown that, as distinct from pyridines and amines, the coordination Zn-TPP with anilines in chloroform is isoenthalpic.

Earlier we have found that log K values for Zn-TPP complexes with pyridines and N-oxides of pyridines in chloroform and $\Delta\lambda$ values of absorption bands in EAS caused by Zn-TPP coordination with these ligands, save 2-chloropyridine (K 4.50±0.10 l mol^{-1}; $\Delta\lambda S^0_{ret}$ of 7.2 nm; $\Delta\lambda_{II}$ 12.4 nm; $\Delta\lambda_{I}$ 14.5 nm), depend linearly on pK_a of these ligands in various solvents. However, in the case of primary saturated amines, which we used, it is impossible to construct such correlation owing to a narrow range of their basicity variation (0.2 pK_a unit [9]). It is the more so for alcohols, because the published data are highly inconsistent owing to the absence of reliable methods of quantitative determination of relative acid–base characteristics of these compounds in liquid phases [26–29].

The correlation log $K/\Delta\lambda$–$\Sigma\sigma^*$ for alcohols (Table 2) in general is similar to the correlation for amines (Fig. 2). Points for *tert*-butyl, *sec*-butyl, and isopropyl alcohols deviate from the set of other points to a greater extent, the greater are steric hindrances in a ligand at the oxygen atom. However the regularities involving shifts of absorption bands (I, II, and Soret bands) in the EAS caused by the Zn-TPP coordination with alcohols are not so consistent as in the case of amines, which results from much greater errors in the determination of low K and $\Delta\lambda$ values. The use of (3–15)×10^4-fold excess of alcohols for the determination of extinction coefficients (ε) of their complexes with Zn-TPP (2×10^{-5} M) possibly makes unjustified the use of this parameter for the calculation of stability constants in chloroform. Nevertheless the values of

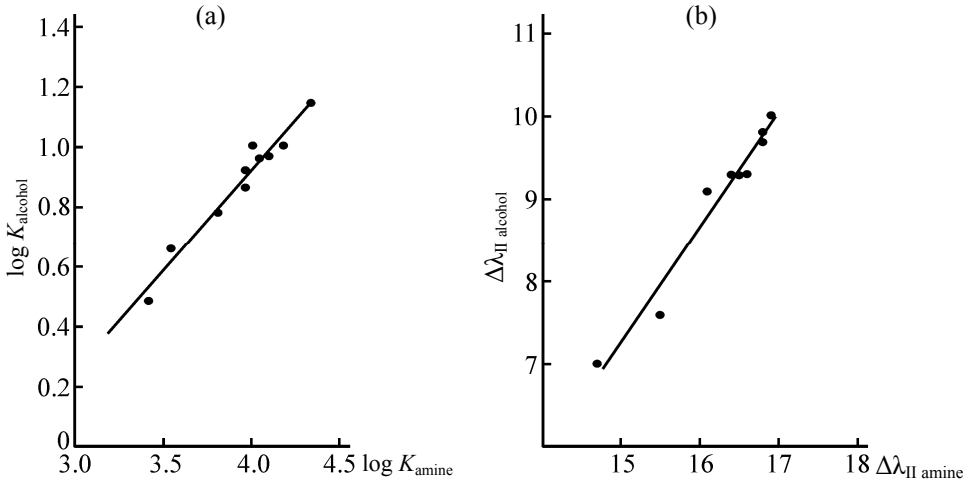

Fig. 3. Dependences: (a) $\log K_{alcohol}$–$\log K_{amine}$ ($\log K_{alcohol} = 0.675 \log K_{amine} - 1.78$, r 0.98) and (b) $\Delta\lambda_{II\ alcohol}$–$\Delta\lambda_{II\ amine}$ ($\Delta\lambda_{II\ alcohol} = 1.39\ \Delta\lambda_{II\ amine} - 13.5$, r 0.985) for Zn-TPP complex formation with amines **Ib–It** and **Io** and alcohols **IIb–IIt** and **IIo** in chloroform at 25°C.

Table 3. Axial *n*, *v*-complexes of Zn-porphines with amines, pyridines, alcohols, and phenols [19]

Metal porphine	Ligand	CSD refcode[a]	Ligand pK_a [9, 20–24]	Coordination center	r_1, Å[b]	r_2, Å[c]	θ, deg[d]
Zn-Tetraphenylporphine	2-Phenylethylamine	HAMMIR	9.83	$-NH_2$	0.356	2.193	–
Zn-Tetraphenylporphine	(S)-α-Benzylamine	HALWOG	9.08	$-NH_2$	0.211	2.256	–
Zn-Tetraphenylporphine	3-Aminopyridine	BORJEY	6.04	–N=	0.443	2.128	89.02
Zn-Tetraphenylporphine	4-Aminopyridine	BORJIC	9.12	–N=	0.369	2.089	83.00
Zn-Tetraphenylporphine	4-(4-Dimethylaminostyryl)pyridine	YEHQOS		–N=	0.382	2.153	86.14
Zn-Tetraphenylporphine	4-(4-Trifluoromethylstyryl)pyridine	YEHQUY	–	–N=	0.408	2.160	88.64
Zn-Tetraphenylporphine	Pyrazine	HALTOD		–N=	0.293	2.210	80.40
Zn-Tetraphenylporphine	3-Nitroaniline	HAMLAI	2.46	$-NH_2$	0.249	2.214	25.43
Zn-Tetraphenylporphine	2-Chloroaniline	JIVNIL	2.64	$-NH_2$	0.000	2.460	31.37
Zn-Tetraphenylporphine	3-Penten-2-ol	HALXOH	–	–OH	0.246	2.267	
Zn-Tetraphenylporphine	4-Chlorophenol	HAMFUW	–	–OH	0.122	2.329	33.29
Zn-Tetraphenylporphine	2,4-Dichlorophenol	JIVNOR	–	–OH	0.003	2.479	32.55
Zn-Tetraphenylporphine (composition 1:2)	2,4,5-Trichlorophenol	HALWEW	–	–OH	0.000	2.496	24.46
Zn-Tetrakis(4-bromophenyl)-porphine	(R)-α-Methylbenzylamine	XAMHAU	9.08	$-NH_2$	0.371	2.227	
Zn-Tetrakis(4-chlorophenyl)porphine	(S)-α-Methylbenzylamine	ZITMIY	9.08	$-NH_2$	0.378	2.204	
Zn-Tetrakis(4-chlorophenyl)porphine	Benzyl alcohol	ZITMOE	–	–OH	0.248	2.188	
Zn-Octaethylporphine	Pyridine	EPOPZN10	5.21	–N=	0.396	2.200	85.07
Zn-Octaethylporphine	3-Aminopyridine	BORJOI	6.04	$-NH_2$	0.330	2.245	21.20
Zn-Dodecaphehylporphine	3-Aminopyridine	BORKAV	6.04	–N=	–	2.124	–
Zn-Dodecaphehylporphine	4-Aminopyridine	BORKEZ	9.12	–N=	–	2.065	–

[a] CSD refcode is the reference to the Cambridge Structural Database. [b] r_1 is the distance from a macrocycle plane to a zinc atom. [c] r_2 is the distance from a zinc atom to a ligand coordination center. [d] θ is the angle between planes of a metal porphine and a ligand aromatic ring.

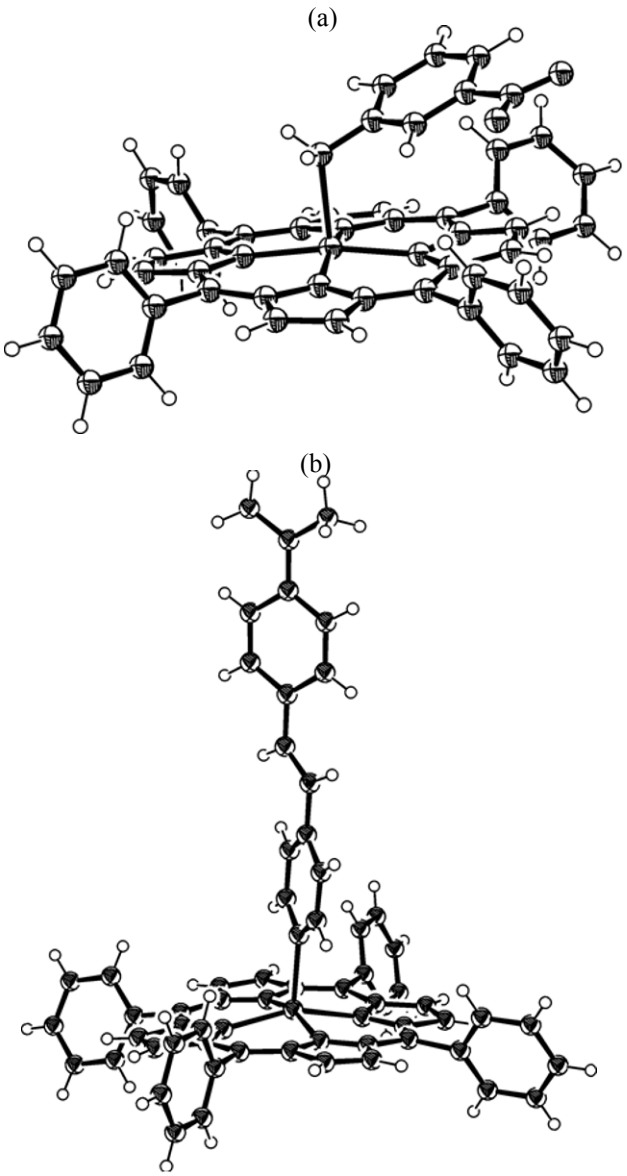

Fig. 4. Molecular complexes of Zn-TPP with (a) 3-nitroaniline (HAMLAI) and (b) 4-(4-dimethylaminostyryl)-pyridine (YEHQOS).

stability constants in chloroform, which we have determined (Table 2), agree with the published data found by a spectrometric method for Zn-TPP coordination with alcohols in benzene at 24°C [30]. In benzene (as well as in chloroform) also complexes of the composition 1:1 are formed, and the stability constant varies for analogous ligands within the limits of 4.0–11.5, taking the minimal value for *tert*-butyl alcohol and the maximal for octyl alcohol.

Quite different pattern is observed for the stability constants of Zn-TPP complexes with alcohols

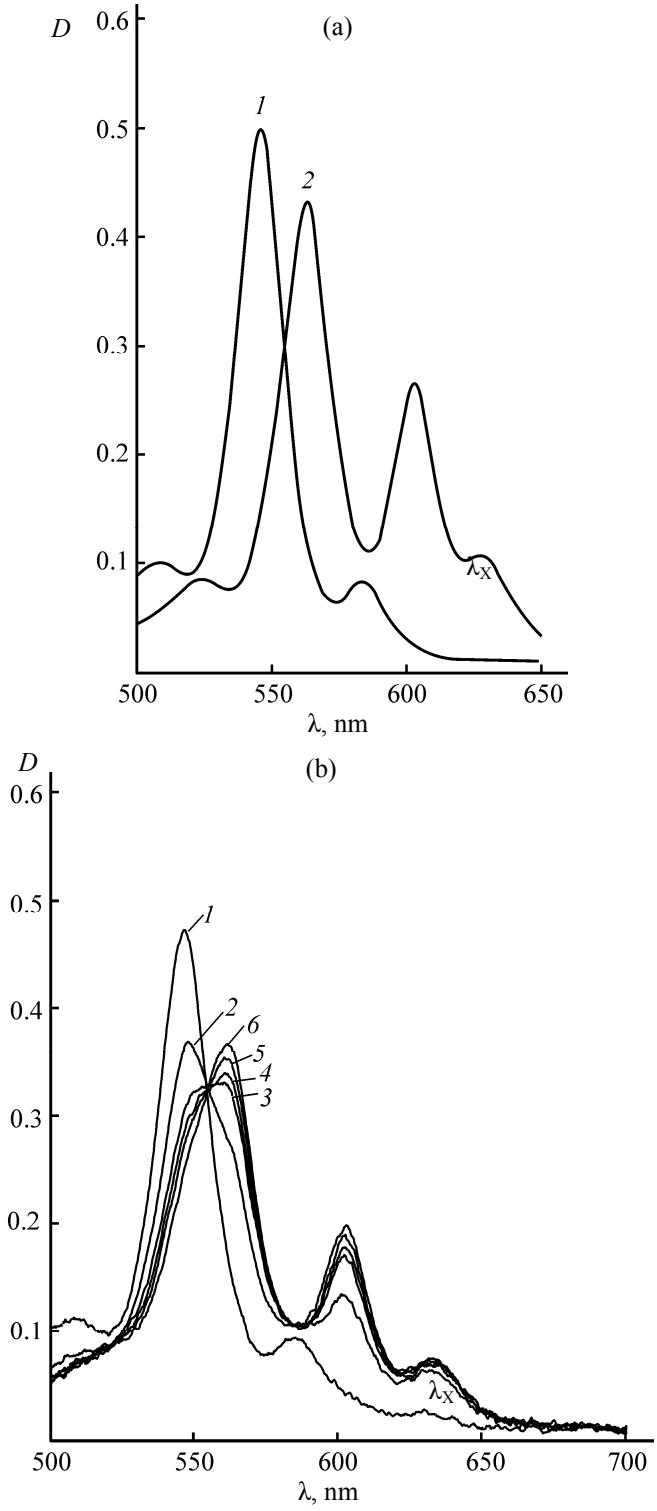

Fig. 5. EAS in chloroform. (*1*) Zn-TPP and solutions containing (a) methylamine and (b) tributylamine. Zn-TPP-L ratio: (a) 1:4500 (*2*); (b) 1:1014 (*2*), 1:1522 (*3*), 1:2029 (*4*), 1:2536 (*5*), 1:3043 (*6*); c_{ZnTPP} 2×10^{-5} M; λ_X are bands of unknown origin appearing on the formation of complexes with ammonia and certain primary, secondary, and tertiary amines.

determined by calorimetric titration in benzene and carbon tetrachloride at 25°C [6], which are $\times 10^{-50}$ and 100–300-fold higher than the corresponding values determined by the spectrometric method in chloroform. They do not obey the correlations described in this paper (however a linear dependence is observed between log $K_{benzene}$ and log K_{CCl4} values for the majority of ligands). We can assume that the incongruence of numerical values of stability constants and the absence of simple correlations between them are caused by the fact that the calorimetric method records an algebraic sum of heat effects of all equilibrium processes between Zn-TPP and various molecular complexes. At the same time the spectrometric method recognizes only complexes, which are formed with changes in EAS.

It is necessary to note in conclusion that in addition to the shifts of maxima of Zn-TPP absorption bands in electronic spectra to the long-wave region (Fig. 5), the coordination of this metal porphine with certain amines is connected with the appearance of the band (λ_{max} ~633 nm), which was not earlier described in the literature. When Zn-TPP is dissolved in alcohols and in chloroform-alcohol mixtures, no new absorption bands were observed. We have not detected any new absorption bands when studying complex formation of Zn-TPP with pyridines, anilines, and N-oxides of pyridines, quinolines, and acridines. It is possible that, owing to the maximal basicity of saturated amines among the mentioned types of compounds and to the spacial accessibility of a nitrogen atom, they form with Zn-TPP charge-transfer complexes whose charge-transfer bands lie in the long wavelength region. We shall pay special attention to get an understanding of this phenomenon.

Thus, the use of Taft equation and modified Eq. (1) and the availability of kinetic characteristics of complex formation of Zn-TPP with amines in chloroform allow us predicting the behavior of these nucleophiles (bases) in nucleophilic substitution reaction in other solvents. To determine relative nucleophilicity order for Lewis bases even weaker (softer) than alcohols (for example, mercaptans) the application of a softer acceptor by Pearson's classification (Hg-TPP) is expedient.

The offered new scale of basicity-nucleophilicity based on log K and $\Delta\lambda$ can be used also for predicting various parameters of enzymatic processes involving metal porphines and amines of various spacial structures [31].

The determination of the limits of Taft's equation application in coordination, organic, and biological chemistry, and also a theoretical substantiation of the appearance of the earlier unknown absorption band in the electronic spectra of Zn-TPP complexes with certain amines in chloroform shall be a subject of further work.

EXPERIMENTAL

Amines were distilled over an alkali, alcohols were dried and distilled over barium oxide. Ethanol was additionally dried and distilled over metal sodium, and propane-2-ol was boiled for 30 min and distilled over a fresh portion of metal magnesium. Their physical constants coincided with the published data. Electronic spectra were taken on an SF 2000-02 instrument. Stability constants of Zn-TPP complexes with amines and alcohols in chloroform were determined as described in [3].

Gaseous ammonia, methylamine, and ethylamine obtained by heating their hydrochlorides with calcium hydroxide and passed through anhydrous NaOH and $CaCl_2$ were passed through chloroform. Concentrations of bases were determined by back titration: to an aliquot of chloroform solution an excess of 0.01 M hydrochloric acid was added, and unreacted acid was titrated by 0.01 M NaOH solution in the presence of phenolphthalein. Stability constants of Zn-TPP complexes were determined in mixtures of metal porphine and ligand solutions in chloroform with calculated mole ratios.

Thermodynamic parameters of complex formation were calculated by a graphical method with accounting for formula (24) (the first Uhlich approximation [32]), assuming that ΔH and ΔS values remain constant in the narrow temperature range under study 288–308 K (for gaseous ligands **Ia–Ic** 283–298 K).

$$\ln K_T = -\Delta H^0_{298}/RT + \Delta S^0_{298}/R. \quad (24)$$

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