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Correlation between thermodynamic stability of zinc(II)tetraphenylporphyrine complexes with neutral molecules and physicochemical properties of the coordinated ligands

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Abstract

The heats of interactions of zinc(II)tetraphenylporphyrine with 30 types of neutral molecules in benzene and carbon tetrachloride were measured using the calorimetric titration method. The thermodynamic characteristics of complex formation were calculated. The satisfactory multiparameter correlation of thermodynamic stability of the molecular complexes formed with physicochemical properties of the neutral molecules (electron pair donor ability, volume, electronic and orientational polarization) was obtained. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the recent years, fundamental significance of donor–acceptor interactions of metalloporphyrines (MPh) with ligand (L) of various nature in organic and biochemical reactions became more obvious. However, the donor–acceptor complexes of MPh with different ligands are not yet studied enough, although these specific interactions play an important role in the processes of breathing, enzyme catalysis, inhibition, biological regulator functions, transport of drugs and toxic compounds, ionic transport [1].

In order to understand the nature of donor–acceptor interactions of MPh–L, it is very important to elucidate what factors, in general, determine electron pair donor and electron pair acceptor properties of the molecules, ascertain the correlations between parameters of initial molecules and their molecular complexes.

The attempts of quantitative estimation of MPh–L donor–acceptor binding were undertaken repeatedly. Most of the works were devoted to studies of donor–acceptor interactions by means of electronic spectroscopy method. Probably it is due to simplicity and accessibility of this method. However, it must be noted that the determination of thermodynamic characteristics from electronic absorption spectra supposes a set of essential assumptions. For example, the thermodynamic characteristics are attributed to basic state, although, it is known that when a system gets the electron excitement energy, the degree of charge transfer from donor to acceptor increases and the

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strength of MPh–L bond changes. Besides, as a rule, the contribution due to changing of medium properties and solvatochromic effects are not taken into consideration. On the one hand, the present assumptions and discrepancies of the values of thermodynamic characteristics obtained by different authors for the same system [2] cause doubt in reliability of application of spectral method to obtain the thermodynamic characteristics of molecular complexes formation. On the other hand, this confirms the necessity of direct calorimetric measurements.

The aim of the present work is the establishment of basic regularities of donor–acceptor interactions of MPh with ligand of different nature. The calorimetric studies of coordinating properties of zinc(II)tetraphenylporphyrine (ZnTPhP) with regards to 30 types of neutral molecules were carried out. By means of calorimetric titration method, the whole set of the thermodynamic characteristics of the processes were studied (K_C, ΔH, ΔS) and stoichiometric composition of the complexes were obtained.

2. Experimental

2.1. Materials

ZnTPhP was synthesized according to techniques [3] and purified chromatographically using Al_2O_3 of the fourth degree of activity, according to Brokman (eluent, benzene). The samples of ZnTPhP were precipitated from hexane and dried under vacuum at 343–353 K to constant mass. The purity of the samples was checked by measuring the electronic absorption spectra. There was a good agreement of our results with literature data [3].

Molecular ligands:

1. butylamine, benzylamine, aniline, diethylaniline, diethylamine, dipropylamine, pipyridine, tributylamine, tribenzylamine, pyridine, *N*,*N*-dimethylamide, hexamethyl phosphoric triamide, dimethylsulfoxide, acetonitrile, benzonitrile, quinoline;
2. oxygen-containing molecular ligands: dimethyl ether of ethylene glycol, tetrahydrofuran, 1,4-dioxane, acetone, cyclopentanone, benzaldehyde, acetophenone, methanol, ethanol, butanol, pentanol, isopropanol, 2-methyl-2-propanol, benzyl alcohol.

The nitrogen-containing molecular ligands were purified according to [4]. The amines were purified directly before using. The nitriles were doubly distillated with anhydrous K_2CO_3. The quantity was purified in accordance with [4]. The amides and dimethylsulfoxide were dried by means of column chromatography method the on activated Al_2O_3 and distillated under vacuum [5].

The oxygen-containing molecules were purified according to well-known techniques, including the removing of hydrogen peroxide compounds on the activated Al_2O_3 by the column chromatography method (for ethers), drying (by chromatography, by molecular shivers 4A), fractional distillation. The hydrogen peroxide content was checked by the reaction with Fe(III)ticynate.

The samples of monoatomic alcohols were dried by boiling over anhydrous $CuSO_4$ and then doubly distillated over CaO. Further, the samples were dried by metallic Na or Mg, and in some cases, by molecular shivers 3A (e.g. 2-propanol).

The solvent used, benzene and carbon tetrachloride (ultrapure), were dried by means of molecular shivers 4A and distillated. The purity of the solvents was checked by chromatography. It was 99.97%.

2.2. Calorimetry

The studies were carried out by use of automatic ultrasensitive differential titration calorimeter [6] at 298.15 K. The solution of titrant (ZnTPhP in C_6H_6 or CCl_4) was placed into reaction cell. The concentrations of ZnTPhP was varied from 10^{-6} to 10^{-3} mol/kg. The solution of titrant (molecular ligand in C_6H_6 or CCl_4) was placed into the microdosing unit (0.2/0.5 mol/kg). All solutions were prepared by weight. In order to convert a molal concentration scale to molar scale, the solution densities were measured by means of picnometers at 298.15 K.

Primary treatment of the experimental curves of titration consists of determination of single heat effects corresponding to responses of system after injection of separate doses. The heat effect is defined as the product of the peak area and cell constant α. The values of the single heat effects obtained were corrected taking into account the results of titration of pure solvent by the titrant solution. These results allowed to take into consideration the heat effects caused by injection process and ligand dilution. The calculation of the thermodynamic characteristics of complex formation was made with the help of the computer program “CALORY”. The basis of the program is described in [7,8]. For the formation of monoligand complex:

$$\mathrm{MPh_{solv}} + \mathrm{L_{solv}} \overset{K_C}{\leftrightarrow} \mathrm{MPh \cdot L_{solv}} + \mathrm{solv}, \qquad \text{(I)}$$

the equilibrium concentration constant (K_C) is expressed as

$$K_C = \frac{[\mathrm{MPhL}]_n}{[\mathrm{MPh}]_n[\mathrm{L}]_n}, \quad \text{or}$$

$$K_C = \frac{[\mathrm{MPhL}]_n}{([\mathrm{MPh_0}]_n - [\mathrm{MPhL}]_n)([\mathrm{L_0}]_n - [\mathrm{MPhL}]_n)}, \qquad (1)$$

where $[\mathrm{MPh}]_n$, $[\mathrm{MPh}]_n[\mathrm{L}]_n$ are the equilibrium concentrations of the molecular complex, the metalloporphyrine and the ligand, respectively; $[\mathrm{MPh_0}]$ and $[\mathrm{L_0}]$ are the initial concentrations of the metalloporphyrine and the ligand, respectively, after addition of the nth dose of the titrant, where n is the step of the titration.

The heat Q_n absorbed or evolved at addition of the nth dose of the titrant can be calculated as

$$Q_n = \Delta H\, V_n[\mathrm{MPhL}]_n, \qquad (2)$$

where V_n is the volume of reactive mixture.

Combination of Eqs. (1) and (2) gives the expression containing two unknown parameters: K_C and ΔH:

$$\frac{1}{K_C} = \frac{[\mathrm{MPh_0}]_n[\mathrm{L_0}]_n\,\Delta H\, V_n}{Q_n} - [\mathrm{MPh_0}]_n - [\mathrm{L_0}]_n + \frac{Q_n}{\Delta H\, V_n}. \qquad (3)$$

There is a standard graphic method in the program which allows to vary K_C and ΔH and by minimization of the sum of quadratic deviations $\sum(Q_n(\mathrm{exp}) - Q_n(\mathrm{cal}))^2$, to determine the values of the K_C and ΔH at which maximum coincidence of the calculated (Q_n(cal)) and experimental (Q_n(exp)) curves take place. This coincidence, as well as the presence of the inversion point at 1:1 composition testifies about the correct model of the formation of the monoligand complex.

If the function Q_n(cal) described Q_n(exp) experimental curve unsatisfactorily, and the inversion point was at 1:2 composition, the calculation of the thermodynamic parameters was carried out for the formation of the biligand complex:

$$\mathrm{MPh_{solv}} + \mathrm{L_{solv}} \overset{K_{C1}}{\leftrightarrow} \mathrm{MPh \cdot L_{solv}} + \mathrm{L_{solv}} \overset{K_{C2}}{\leftrightarrow} \mathrm{MPh \cdot L_{2solv}} + \mathrm{solv}. \qquad \text{(II)}$$

The equilibrium stability constants for the first and second stages of the process are expressed as

$$K_C^1 = \frac{[\mathrm{MPhL}]_n}{[\mathrm{MPh}]_n[\mathrm{L}]_n} = \frac{[\mathrm{MPhL}]_n}{([\mathrm{MPh_0}]_n - [\mathrm{MPhL}]_n - [\mathrm{MPhL_2}]_n)([\mathrm{L_0}]_n - [\mathrm{MPh}]_n - 2[\mathrm{MPhL_2}]_n)} \qquad (4)$$

and

$$K_C^2 = \frac{[\mathrm{MPhL_2}]_n}{[\mathrm{MPhL}]_n[\mathrm{L}]_n} = \frac{[\mathrm{MPhL_2}]_n}{[\mathrm{MPhL_2}]_n([\mathrm{L_0}]_n - [\mathrm{MPhL}]_n - 2[\mathrm{MPhL_2}]_n)}, \qquad (5)$$

where $[\mathrm{MPhL}]_n$, $[\mathrm{MPhL_2}]_n$, $[\mathrm{MPh}]_n$ and $[\mathrm{L}]_n$ are the equilibrium concentrations of molecular complexes, the metalloporphyrine and the ligand, respectively; $[\mathrm{MP_0}]_n$, $[\mathrm{L_0}]_n$ are the initial concentrations of the metalloporphyrine and the ligand, respectively, after addition of nth dose of titrant. The heat Q_n absorbed or evolved in this case can be calculated as

$$Q_n = \Delta H_2\, V_n[\mathrm{MPhL}]_n + \Delta H_2\, V_n[\mathrm{MPhL_2}]_n. \qquad (6)$$

Combining Eqs. (4) and (5), at every iteration, one can get the values of equilibrium concentrations $[\mathrm{MPhL}]_n$ and $[\mathrm{MPhL_2}]_n$. As it follows from Eq. (6), the values of ΔH_1 and ΔH_2 are calculated from linear regression. When the minimum of $\sum(Q_n(\mathrm{exp}) - Q_n(\mathrm{cal}))^2$ function is found, the optimization process is over.

In order to except possible local minima of $\sum(Q_n(\mathrm{exp}) - Q_n(\mathrm{cal}))^2$ function, a profile of the function was plotted and analyzed for the systems studied. The $\sum(Q_n(\mathrm{exp}) - Q_n(\mathrm{cal}))^2$ function is a three-dimensional surface with K_C and ΔH coordinates for the formation of 1:1 complex. If biligand complex is formed, the $\sum(Q_n(\mathrm{exp}) - Q_n(\mathrm{cal}))^2$ function is multi-dimensional surface with ΔH_1, ΔH_2, K_C^1

and K_C^2 coordinates. For the systems studied, the function has a single minimum. It is confirmed by the minimum of dispersion, characterizing the greatest accordance between the calculated and experimental single heat effects. The presence of single minimum testifies its global character and confirms the reliability of the thermodynamic parameters obtained. The calculations of their errors were carried out according to [9].

3. Results

The thermodynamic characteristics of interactions of ZnTPhP with neutral ligands are listed in Table 1. No concentration dependence of the thermodynamic parameters of axial coordination process was obtained.

In accordance to recommendation [11,12], in first approach the value of electronic polarization (P_{el}) may

Table 1
Thermodynamic characteristics of interactions of zinc(II)tetraphenylporphyrine with neutral ligands

Ligand	MPh·*n*L	C_6H_6			CCl_4		
		ΔH_0 (kJ/mol)	K_C	ΔS_0 (J/mol K)	ΔH_0 (kJ/mol)	K_C	ΔS_0 (J/mol K)
Butylamine	1:1	−57.21 ± 0.40	1804 ± 101	−130 ± 3	−48.37 ± 0.30	4568 ± 200	−92 ± 8
	1:2	−29.42 ± 0.60	536 ± 16	−46 ± 2	−15.16 ± 0.10	1037 ± 111	7 ± 1
Benzylamine	1:1	−0.21 ± 0.02	496 ± 14	51 ± 4	−0.10 ± 0.01	1827 ± 120	62 ± 12
Aniline	1:1	−7.90 ± 0.06	473 ± 9	25 ± 4	−27.25 ± 0.02	762 ± 22	−36 ± 5
	1:2	−1.57 ± 0.03	240 ± 10	40 ± 6	−25.05 ± 0.02	145 ± 13	−43 ± 8
Diethylaniline	1:1	−0.23 ± 0.03	667 ± 18	53 ± 15	−0.08 ± 0.03	682 ± 20	54 ± 12
Diethylamine	1:1	−44.52 ± 0.30	570 ± 25	−97 ± 8	−16.97 ± 0.40	3148 ± 218	10 ± 1
	1:2	−10.84 ± 0.26	411 ± 15	14 ± 3	−15.08 ± 0.20	187 ± 10	−7 ± 2
Dipropylamine	1:1	−36.89 ± 0.63	1111 ± 114	−65 ± 6	−11.13 ± 0.31	3977 ± 152	32 ± 2
	1:2	−7.09 ± 0.52	875 ± 69	33 ± 4	−1.25 ± 0.05	325 ± 64	44 ± 6
Pipyridine	1:1	−23.27 ± 0.62	1332 ± 28	−18 ± 4	−21.17 ± 0.84	4060 ± 350	−2 ± 5
	1:2	−12.27 ± 0.31	1283 ± 14	18 ± 3	−3.46 ± 0.45	800 ± 142	44 ± 7
Tributylamine	1:1	−3.93 ± 0.62	139 ± 12	28 ± 9	−2.71 ± 0.85	199 ± 41	35 ± 14
Tribenzylamine	1:1	−5.61 ± 0.09	27 ± 13	22 ± 10	−2.39 ± 0.87	69 ± 5	27 ± 12
Pyridine[a]	1:1	−33.38 ± 0.64	3763 ± 553	−44 ± 3	−32.04 ± 0.48	19719 ± 4908	−25 ± 3
N,*N*-dimethylamide	1:1	−2.20 ± 0.34	838 ± 121	49 ± 17	−1.28 ± 0.36	1978 ± 478	59 ± 14
Hexamethylphosphorictriamide	1:1	−39.01 ± 0.78	1275 ± 247	−71 ± 24	−15.15 ± 0.61	4810 ± 308	20 ± 6
	1:2	−5.04 ± 0.12	685 ± 64	37 ± 6	−2.56 ± 0.58	1200 ± 264	50 ± 19
Dimethyl-sulfoxide	1:1	−16.95 ± 0.78	1151 ± 366	2 ± 5	−9.23 ± 0.44	2477 ± 265	34 ± 7
	1:2	–	–	–	−2.14 ± 0.09	1310 ± 240	52 ± 13
Acetonitrile	1:1	−1.08 ± 0.01	260 ± 6	43 ± 6	−6.23 ± 0.01	740 ± 69	34 ± 5
Benzonitrile	1:1	−0.80 ± 0.03	132 ± 13	38 ± 5	−2.04 ± 0.01	175 ± 10	36 ± 5
Quinoline	1:1	−3.131 ± 0.02	1625 ± 412	51 ± 14	−8.78 ± 0.54	631 ± 52	24 ± 9
	1:2	–	–	–	−2.37 ± 0.05	261 ± 15	38 ± 18
Dimethyl ether ethylene glycol	1:1	−1.49 ± 0.02	70 ± 9	30 ± 7	−1.34 ± 0.04	402 ± 13	45 ± 8
Tetrahydrofuran	1:1	−8.22 ± 0.032	453 ± 23	23 ± 5	−3.55 ± 0.01	504 ± 10	40 ± 7
	1:2	−1.88 ± 0.01	37 ± 5	24 ± 4	−2.16 ± 0.01	216 ± 5	37 ± 3
1,4-Dioxane	1:1	−3.57 ± 0.01	1172 ± 106	47 ± 8	−3.05 ± 0.01	1270 ± 102	49 ± 10
	1:2	−3.21 ± 0.01	365 ± 12	38 ± 6	−1.09 ± 0.01	602 ± 75	50 ± 11
Acetone	1:1	−1.55 ± 0.01	124 ± 14	35 ± 6	−2.89 ± 0.01	66 ± 17	25 ± 6
Cyclopentanone	1:1	−0.82 ± 0.06	47 ± 6	29 ± 4	−0.67 ± 0.02	131 ± 13	38 ± 5
Benzaldehyde	1:1	−0.51 ± 0.01	91 ± 14	36 ± 5	−0.28 ± 0.01	138 ± 38	40 ± 9
Acetophenone	1:1	−0.82 ± 0.03	102 ± 13	36 ± 7	−0.43 ± 0.01	110 ± 20	38 ± 11
Methanol	1:1	−13.45 ± 0.02	59 ± 4	−11 ± 5	−13.21 ± 0.04	600 ± 15	9 ± 5
Ethanol	1:1	−4.17 ± 0.08	93 ± 6	24 ± 9	−2.24 ± 0.03	729 ± 12	47 ± 8
Butanol	1:1	−2.60 ± 0.02	194 ± 8	35 ± 10	−2.45 ± 0.03	1563 ± 453	53 ± 4
Pentanol	1:1	−9.83 ± 0.04	409 ± 15	17 ± 8	−8.54 ± 0.02	2497 ± 81	36 ± 7
Isopropanol	1:1	−5.25 ± 0.04	235 ± 11	28 ± 7	−1.00 ± 0.04	1600 ± 354	58 ± 6
2-Methyl-2-propanol	1:1	−4.34 ± 0.04	247 ± 104	31 ± 5	−3.13 ± 0.05	1298 ± 685	49 ± 5
Benzyl alcohol	1:1	−6.01 ± 0.07	48 ± 6	12 ± 4	−2.80 ± 0.07	204 ± 107	35 ± 6

[a] [10].

Table 2
The values of physicochemical parameters of neutral ligands and thermodynamic stabilities of the ZnTPhP·*n*L ($n = 1, 2$) molecular complexes expressed in natural scale and corresponding standardized values

Ligand	DN		V		P_{el}		C_6H_6			CCl_4		
		Standardized	S m^3/mol	Standardized	$\times 10^{-5}$ (M^3)	Standardized	P_{or}		K_C	P_{or}		K_C
							$\times 10^{-5}$ (M^3)	Standardized	Standardized	$\times 10^{-5}$ (M^3)	Standardized	Standardized
N-containing ligands												
Butylamine	42	1.011	54.9	−0.293	2.406	−0.334	35.76	−0.413	1.487	20.46	−0.6	0.698
Benzylamine	21	−0.726	66.61	0.084	3.447	0.307	38.97	−0.39	−0.175	38.97	−0.434	−0.056
Aniline	35	0.432	56.38	−0.245	2.98	0.02	46.66	−0.336	−0.204	60.54	−0.241	−0.349
Diethylaniline	33	0.267	99.14	1.132	4.838	1.165	67.04	−0.193	0.042	67.04	−0.183	−0.371
Diethylamine	50	1.673	55.88	−2.61	2.425	−0.322	26.13	−0.48	−0.081	17.32	−0.628	0.307
Dipropylamine	40	0.846	76.34	0.398	3.354	0.25	21.71	−0.511	0.606	21.71	−0.589	0.536
Pipyridine	40	0.846	59.23	−0.153	2.684	−0.163	27.51	−0.47	0.887	77.01	−0.094	0.559
Tributylamine	50	1.673	137.41	2.364	6.163	1.981	12.45	−0.576	−0.628	12.45	−0.672	−0.504
Tribenzylamine	61	2.583	172.54	3.496	9.286	3.906	8.65	−0.603	−0.77	8.65	−0.706	−0.54
Pyridine[a]	33.1	0.275	44.63	−0.624	2.461	−0.3	99.04	0.031	3.975	105.44	0.161	4.869
N,N-dimethylamide	27.8	−0.163	59	−0.161	2.441	−0.312	394.37	2.102	0.26	279.68	1.721	−0.015
Hexamethyl phosphoric triamide	38.8	0.746	12.15	1.551	4.046	0.677	619.01	3.677	0.815	380.12	2.621	0.765
Dimethylsulfoxide	29.8	0.002	44.84	−0.617	2.017	−0.574	311.24	1.519	0.657	371.36	2.542	0.123
Acetonitrile	14.1	−1.297	28.37	−1.147	1.112	−1.131	236.16	0.993	−0.475	238.95	1.356	−0.355
Benzonitrile	11.9	−1.479	60.54	−0.111	3.086	0.085	355.09	1.686	−0.637	330.14	2.173	−0.511
Quinoline	32	0.184	70.23	0.201	2.04	0.661	103.59	0.063	1.259	107.13	0.176	−0.385
O-containing ligands												
Dimethyl ether ethylene glycol	20	−0.809	58.2	−0.187	2.422	−0.324	6.054	−0.621	−0.716	6.054	−0.729	−0.448
Tetrahydrofuran	20	−0.809	46.12	−0.576	2.038	−0.561	5.984	−0.621	−0.229	6.704	−0.723	−0.42
1,4-Dioxane	14.8	−1.239	51.32	−0.408	2.216	−0.451	0.414	−0.66	0.684	0.259	−0.781	−0.21
Acetone	17	−1.057	41	−0.741	1.614	−0.822	15.363	−0.626	−0.647	14.918	−0.65	−0.541
Cyclopentanone	18	−0.974	54.58	−0.303	2.321	−0.368	17.567	−0.54	−0.745	17.567	−0.626	−0.523
Benzaldehyde	16	−1.140	61.01	−0.096	3.103	0.096	15.475	−0.555	−0.689	18.417	−0.618	−0.521
Acetophenone	15	−1.222	73.17	0.296	3.588	0.394	15.701	−0.553	−0.675	17.929	−0.623	−0.529
Methanol	30	0.018	22.31	−1.342	0.823	−1.309	45.98	−0.341	−0.73	59.04	−0.255	−0.394
Ethanol	32	0.184	32.54	−1.013	1.288	−1.023	61.85	−0.23	−0.687	54.28	−0.297	−0.358
Butanol	29	−0.064	53	−0.354	2.217	−0.45	53.71	−0.287	−0.558	59.04	−0.255	−0.129
Pentanol	25	−0.395	73.46	0.305	2.812	−0.084	53.71	−0.287	−0.285	60.44	−0.242	0.128
Isopropanol	36	0.515	42.76	−0.684	1.752	−0.737	59.04	−0.249	−0.506	51	−0.327	−0.119
2-Methyl-2-propanol	38	0.68	52.98	−0.355	2.217	−0.45	56.3	−0.269	−0.491	61.85	−0.229	−0.202
Benzyl alcohol	23	−0.561	59.17	−0.155	3.263	0.194	57.66	−0.259	−0.744	59.76	−0.248	−0.503

[a] [10].

Table 3
The standardized physicochemical parameters of the studied amines and thermodynamic stability of molecular complexes ZnTPhP·nL ($n = 1, 2$)

Ligand	DN	V	P_{el}	C_6H_6		CCl_4	
				P_{or}	K_C	P_{or}	K_C
Butylamine	0.133	−0.654	−0.721	−0.097	0.696	−0.686	0.155
Benzylamine	−1.745	−0.374	−0.252	0.021	−0.493	−0.122	−0.357
Aniline	−0.493	−0.618	−0.462	0.304	−0.513	0.536	−0.540
Diethylaniline	−0.672	0.402	0.376	1.052	0.337	0.734	−0.554
Diethylamine	0.849	−0.630	−0.713	−0.450	−0.425	−0.781	−0.130
Dipropylamine	−0.046	−0.142	−0.293	−0.612	0.066	−0.648	0.013
Pipyridine	−0.046	−0.550	−0.596	−0.399	0.267	1.038	0.027
Tributylamine	0.841	1.314	0.974	−0.952	−0.817	−0.930	−0.637
Tribenzylamine	1.833	2.152	2.383	−1.092	−0.919	−1.046	−0.659
Pyridine	−0.663	−0.899	−0.696	2.226	2.475	1.904	2.721

be equal to the value of molecular refraction (R_D). The latter was calculated from additivity principle of atom and group refractions.

The orientation polarization (P_{or}) was used as a measure of charge mobility in ligand molecules. The P_{or} values were calculated as [11,12]

$$P_{or} = \frac{4}{3}\pi N \frac{\mu_0^2}{3RT},$$

where μ_0 is the dipole moment of molecule in corresponding solvent.

In accordance with [13], the volume of ligand was estimated as algebraic sum of Van der Waals volumes and volumes of overlapping of atoms. Gutman's numbers (DN) were used as a measure of electron pair donor ability of the ligand [14].

It was been known that a construction of multiparameter regression using the standardized variables has incontestable advantages. In contrast to usual regression variables, the standardized variables are expressed in comparable units. Hence, coefficients of the standardized variables indicate the influence of every variable on change of function. Therefore, the function $y_i(K_C)$ and variables x_{ij} (DN, P_{or}, P_{el}, V) were standardized by using the following equations [15]:

$$y_i = \frac{y_i - \bar{y}_i}{S_{y_i}}, \quad x_{ij} = \frac{x_{ij} - \bar{x}_{ij}}{S_{x_{ij}}},$$

where S_{y_i} and $S_{x_{ij}}$ are the standard deviations of the function and variables defined as

$$S_{x_{ij}} = \sqrt{\frac{\sum(x_{ij} - \bar{x}_{ij})^2}{m-1}}.$$

The values of function $y_i(K_C)$ and variables x_{ij} (DN, P_{or}, P_{el}, V) expressed in natural scale and the corresponding standardized values are listed in Table 2.

Table 4
The standardized physicochemical parameters of the ethers, aldehydous, ketones studied and thermodynamic stability of molecular complexes ZnTPhP·nL ($n = 1, 2$)

Ligand	DN	V	P_{el}	C_6H_6		CCl_4	
				P_{or}	K_C	P_{or}	K_C
Dimethyl ether ethylene glycol	1.456	0.052	−0.247	−1.754	−0.568	−1.726	1.749
Acetone	−0.104	−1.429	−1.310	0.293	1.258	−0.011	−0.777
Cyclopentanone	0.416	−0.259	−0.380	0.777	−1.346	0.501	−0.289
Benzaldehyde	−0.624	0.294	0.648	0.317	0.142	0.665	−0.236
Acetophenone	−1.144	1.342	1.287	0.367	0.514	0.571	−0.447

Statistical treatment of the data obtained was realized with the help of program of multilinear regression analysis. The degree of the influence of every variable on thermodynamic stability was estimated by the values of dispersion of adequacy (S_{ad}). These data are also listed in Tables 2–4.

4. Discussion

As it can be seen from the data, the studied molecular complexes in general have low thermodynamic stabilities. Therefore, in accordance to the classification proposed in [16], the complexes of ZnTPhP with neutral ligands are weak. In addition to the contribution caused by transfer or displacement of charge from ligand to metal ion and sterical factor, the polarizational interactions are very important. That is why the correlation analysis was made taking to account electronic and orientational polarization.

ZnTPhP forms 1:1 and 1:2 complexes with the ligands studied (Table 1). In the case of formation of 1:2 complexes, the authors [17,18] have proposed to operate by the characteristics of the former added molecule only.

The correlation of the thermodynamic stability of the complexes formed with ligand properties in benzene may be expressed as

$$K_C = (-0.094 \pm 0.100)\mathrm{DN} + (-0.023 \pm 0.100)V + (0.96 \pm 0.07)P_{el} + (0.01 \pm 0.06)P_{or} \tag{7}$$

$R = 0.95; \qquad S_{ad} = 0.32.$

In carbon tetrachloride:

$$K_C = (-0.098 \pm 0.100)\mathrm{DN} + (0.026 \pm 0.100)V + (0.96 \pm 0.06)P_{el} + (-0.011 \pm 0.060)P_{or} \tag{8}$$

$R = 0.95; \qquad S_{ad} = 0.324.$

Taking into account the assumption about insignificance of coordination of the second ligand molecule, it may be suggested that the Eqs. (7) and (8) describe adequately the K_C dependence on ligand properties. However, the regression coefficients and dispersion of adequacy show that the Eqs. (7) and (8) cannot be used for predictions. Probably, it may be connected with domination of different factors (electrostatic, polarizational, etc.) at the formation of ZnTPhP complexes with neutral ligands of different nature.

In order to test of this supposition, the correlations of the thermodynamic stabilities of the ZnTPhP complexes with amine (Eqs. (9) and (10)), ethers, aldehydous and ketones (Eqs. (11) and (12)) were obtained. The standardized parameters are listed in Tables 3 and 4.

In benzene:

$$K_C = (1.18 \pm 0.05)\mathrm{DN} + (-1.86 \pm 0.10)V + (0.34 \pm 0.10)P_{el} + (0.28 \pm 0.05)P_{or} \tag{9}$$

$R = 0.999; \qquad S_{ad} = 0.041.$

In carbon tetrachloride:

$$K_C = (1.52 \pm 0.10)\mathrm{DN} + (-2.64 \pm 0.20)V + (0.6 \pm 0.10)P_{el} + (5.37 \times 10^{-3} \pm 8.9 \times 10^{-2})P_{or} \tag{10}$$

$R = 0.999; \qquad S_{ad} = 0.04.$

In benzene:

$$K_C = (-1.67 \pm 0.20)\mathrm{DN} + (-0.71 \pm 0.60)V + (-0.36 \pm 0.7)P_{el} + (-1.10 \pm 0.20)P_{or} \tag{11}$$

$R = 0.994; \qquad S_{ad} = 0.227.$

In carbon tetrachloride:

$$K_C = (0.61 \pm 8.3 \times 10^{-2})\mathrm{DN} + (-0.36 \pm 0.20)V + (0.96 \pm 0.30)P_{el} + (-0.62 \pm 7.9 \times 10^{-2})P_{or} \tag{12}$$

$R = 0.999; \qquad S_{ad} = 8.4 \times 10^{-2}.$

The values of regression coefficients and the dispersion of adequacy obtained show that the Eqs. (9)–(12) describe adequately the K_C dependence on physicochemical properties of ligands. Moreover, the parameters characterizing electron pair donor abilities of ligands and their volumes, are dominant for the aliphatic and aromatic amines. But for oxygen-containing ligands, the polarization characteristics play a main role.

It must be noted that, in general, the coordination of molecular ligands by ZnTPhP is more exothermic in benzene, while the stability constants are greater in carbon tetrachloride. This fact, probably, can be explained by peculiarities of solvation of ZnTPhP in these solvents.

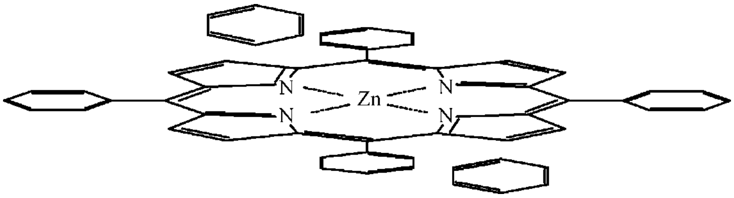

Fig. 1. Schematic illustration of ZnTPhP·$2C_6H_6$ π–π complex.

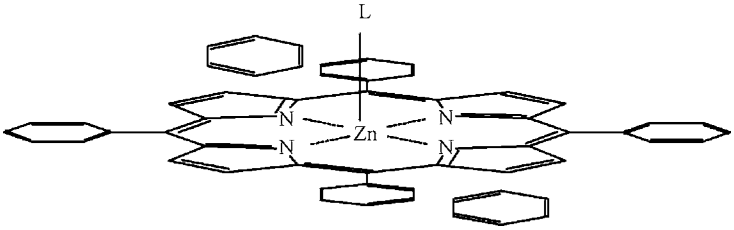

Fig. 2. Schematic illustration of ZnTPhP·$2C_6H_6$·L axial complex.

Earlier, it was shown that molecules of ZnTPhP do not interact with CCl_4 molecules specifically, but reactive cavity is found to be blockaded by four CCl_4 molecules. ZnTPhP forms the energy and thermally stabilized complex ZnTPhP·$2C_6H_6$ [19].

Therefore, it is obvious that the interaction of ZnTPhP·$2C_6H_6$ (Fig. 1) with electron pair donating ligands yields the formation of the axial complex ZnTPhP·$2C_6H_6$·L (Fig. 2) for the systems studied. This is supported by the greater exothermal effect of the process in benzene then that in carbon tetrachloride (Table 1). If the process of removing or forcing out of molecules of benzene from ZnTPhP·$2C_6H_6$ complex will precede the process of axial coordination, the exothermal effect in C_6H_6 will reduce in comparison to CCl_4.

Thus, the results presented here show that in addition to electron pair donating properties, the polarization effects and sterical accordance of interacting molecules are very important in the processes of complex formation of conformational rigid macromolecules (metalloporphyrines) with molecular ligand.

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