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Thermodynamics of Donor–Acceptor Interaction of Tetraphenylporphyrinatozinc with Amides and Dimethyl Sulfoxide

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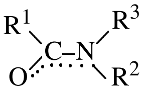
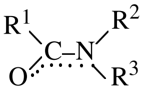
Abstract—Thermodynamic parameters of complex formation of alkylamides and dimethyl sulfoxide with tetraphenylporphyrinatozinc in benzene and carbon tetrachloride were determined by calorimetric titration. The composition of the complexes was also determined. Correlations were found between thermodynamic stability parameters of the complexes and physical parameters of the ligands. The effect of the ligand and solvent nature on the thermodynamics of complex formation was analyzed.

Specific structure of the amide group and its acid–base properties largely determine structural diversity of biologically important protein derivatives [1]. Physical properties of amide groups have been studied to a sufficient extent, especially in the recent years (for reviews, see [2, 3]). Stereochemistry of amides was described in detail. As noted in [2], the structures of amide group in the gas phase and in solution have some specific features which should be taken into account while interpreting the results of studies of compounds possessing such groups. First, the C(O)–N bond in amides has a partially double character as a result of displacement of the unshared electron pair of the nitrogen atom toward π electrons of the C=O bond. Second, amides in solution can exist as *cis* (**A**) and *trans* isomers (**B**) [4].


A


B

In contrast to physical properties of amides, their acid–base properties have been studied to a considerably lesser extent. Despite the wide use of amides in practice as plasticizers for paper, artificial leather, and poly(vinyl chloride), as raw materials in the synthesis of polymers, as extractants for some radioactive materials, and as electron-donor solvents, up to now the problem concerning the basic center in amides has not been solved unambiguously [5]. Analysis of the dependence of ionization potentials on the oxygen and nitrogen atoms upon proton affinity of the base showed [6] that amides in the gas phase are protonated at the oxygen atom. An analogous conclusion was drawn [3, 7] while studying amide hydrochlorides. However, according to the data of [8], protonation of the nitrogen atom predominates in dilute aqueous solutions of acids.

Only a few published data are available on reactions of amides with metals. Saito *et al.* [7] described the IR spectra of tertiary amine complexes with various metals, including alkali metals. The authors presumed that the observed reduction of the $\nu_{C=O}$ frequency relative to free amides indicates coordination at the oxygen atom. According to [3], Li(I) [9], Zn(II) [7], Ni(II), Cr(III), and Co(II) salts coordinate dimethylacetamide, formamide, and *N*-methylacetamide at the oxygen atom.

The results of spectral studies showed that most of the above complexes undergo decomposition by the action of water. However, some complexes, e.g., (dimethylformamido)(pentaammine)cobalt(III), are sufficiently stable, and hydrolysis of the amide ligand occurs by the action of water in alkaline medium. This reaction is essentially similar to enzymatic hydrolysis of peptides [1]. The lack of information on thermodynamic parameters characterizing reactions of amides with metals or their salts leaves no chance to understand the mechanism of a number of biochemical and chemical processes. Despite an obvious significance, there are almost no data on the thermodynamics of amide reactions with inner salts, in particular with porphyrin–metal complexes. Owing to the low solubility of the latter and their chromophoric properties, they are studied mainly by spectral methods (NMR, IR, and electronic absorption spectros-

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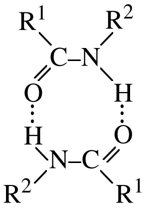
Table 1. Thermodynamic parameters of complex formation between (tetraphenylporphyrinato)zinc(II) and ligands **I**–**VI** in benzene and carbon tetrachloride at 298.15 K

Ligand no.	C_6H_6			CCl_4		
	K_s	$-\Delta H^0$, kJ mol^{-1}	ΔS^0 J mol^{-1} K^{-1}	K_s	$-\Delta H^0$, kJ mol^{-1}	ΔS^0, J mol^{-1} K^{-1}
I	370±21	1.58±0.42	44±12	[a]		
II	838±121	2.20±0.34	49±17	1978±478	1.28±0.36	59±14
III	211±14	26.41±0.56	–44±16	1638±318	5.38±0.54	43±14
	3±7	0.197±0.074	8±6	1232±59	1.65±0.07	54±16
IV	759±205	27.27±0.32	-36±9	2650±345	9.42±0.23	34±9
	526±103	0.884±0.040	49±12	890±77	1.32±0.07	52±18
V	1275±247	39.01±0.78	–71±24	4810±308	15.15±0.61	20±6
	685±64	5.04±0.12	37±6	1200±264	2.56±0.58	50±19
VI	1151±366	16.95±0.78	2±5	2477±265	9.23±0.44	34±7
				1310±240	2.14±0.09	52±13

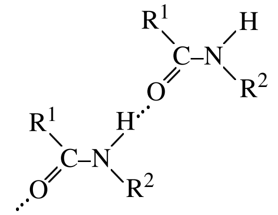
[a] Amide **I** is insoluble in carbon tetrachloride.

copy). However, the application of these methods to systems containing amides is often impossible, for the measured parameters are determined not only by the degree of amide–metal complex interaction but also by experimental conditions, specifically by amide concentration and formation of intermolecular associates.

Amides are known [2] to form three types of associates: hydrogen-bonded dimers **C** and polymers **D** and dipole–dipole dimers **E** [2]. In addition, amides are capable of forming associates with aromatic solvent molecules. In the course of NMR studies, the existence and rotation period of stable and metastable isomers **A** and **B** must be taken into account. All these factors strongly complicate the spectra of amides and make their interpretation difficult.



C



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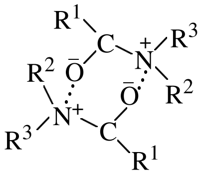
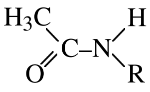
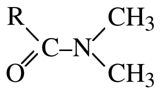


E

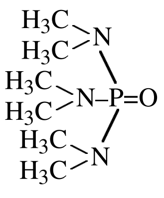
The goal of the present work was to study reactions of primary, secondary, and tertiary amides **I**–**V** and dimethyl sulfoxide (**VI**) (ligand L) with tetraphenylporphyrinatozinc(II) (TPPZn) in benzene and carbon tetrachloride by calorimetric titration.



I, II



III, IV



V

I, **III**, R = H; **II**, R = CH_3; **IV**, R = C_2H_5.

All the above ligands with TPPZn form thermodynamically stable 1 : 1 or 1 : 2 complexes (Table 1). The complex formation is accompanied by heat evolution. The exothermic effect decreases in going from tertiary to secondary and then to primary amides (Table 1). Assuming that the coordination involves the amide nitrogen atom, the greater exothermic effect observed for ligands **III**–**V** may be explained by the inductive effect of the alkyl groups on the nitrogen, which increases the basicity of the nitrogen atom. In this case, steric hindrance and strain due to compression of substituents increase in going from secondary to tertiary amides, which should lead to reduced stability constants of the complexes TPPZn · *n*L (L = **III**–**V**), as compared to TPPZn · L (L = **I**, **II**). No such reduction was observed for the systems under study (Table 1). Therefore, it was reasonable to presume that amides are coordinated to TPPZn through the oxygen atom and that the lower exothermic effect in the reactions with primary and secondary amides is explained by intermolecular association like **C** and **D**.

Table 2. Normalized and natural-scale parameters of ligands **I–IV** and standardized K_s values for the reactions of (tetraphenylporphyrinato)zinc(II) with amides **I–IV** in benzene at 298.15 K

Ligand no.	pK_{BH^+}		V		P_{or}		K_s
	a	b	$cm^3\ mol^{-1}$	b	10^{-5}, m^3	b	b
I	–0.73	–0.011	36.11	–1.272	242.15	–0.995	–0.578
II	–0.49	0.525	60.01	0.842	394.37	1.372	0.971
III	–1.35	–1.395	46.84	–0.323	304.89	–0.020	–1.104
IV	–0.33	0.882	59.00	0.753	283.18	–0.357	0.710

[a] Dimensionless quantity. [b] Normalized values.

Such association is impossible for tertiary amides which are incapable of forming hydrogen bonds. Thus, the interaction of ligands **I** and **II** with TPPZn requires an additional energy for cleavage of L–L hydrogen bonds.

Comparison of the thermodynamic parameters obtained for the systems containing dimethylformamide and *N*,*N*-dimethylacetamide shows that the presence of an alkyl group at the amide carbonyl group favors formation of stronger TPPZn · 2L complexes and increases the exothermic effect of the complex formation. These data also support the assumption that coordination of TPPZn with amides involves the oxygen atom of the latter.

Our results indicate a considerable effect of the medium on the thermodynamics of complex formation. In all cases, replacement of benzene by carbon tetrachloride resulted in formation of more thermodynamically stable complexes and less exothermic process (Table 1). Obviously, the reason is specific features of solvation of tetraphenylporphyrinatozinc(II). As was found previously [10], carbon tetrachloride molecules do not solvate TPPZn in a specific mode, but the cavity in TPPZn appears to be sterically locked by four molecules of the solvent [10]. Benzene and TPPZn give rise to a thermally stable 2 : 1 π-complex (2PhH · TPPZn) [10].

According to the X-ray diffraction data, aromatic solvent molecules in π-complexes with metal porphyrins can be located either above the *trans*-pyrrole fragments of the macroring or directly above the the cavity. The greater exothermic effect of complex formation in benzene indicates formation of a mixed complex like TPPZn · $2C_6H_6$ · *n*L; otherwise, the ligand coordination (which is accompanied by decomposition of the 2PhH · TPPZn complex) in benzene would be characterized by a lesser exothermic effect than in carbon tetrachloride. Thus, the state of the cavity turns out to be important for conformationally rigid macrocycles (such as metal porphyrinates).

It should be noted that the stability of the TPPZn · *n*L complexes in the examined solvents decreases in the amide series **V** > **IV** ≥ **II** > **I** > **III**. It is seen that the complex TPPZn · **III** is characterized by the lowest thermodynamic stability. Unlike the other amides, ligand **III** contains no hydrocarbon group at the carbonyl group. Obviously, the observed low K_s value for the complex TPPZn · 2**III** cannot be explained by the absence of electron-donor groups in ligand **III**, for this fact should necessarily be reflected in the enthalpy component of the TPPZn–amide interaction. Presumably, the TPPZn · *n*L complexes with ligands **I**, **II**, and **IV** are additionally stabilized by attractive interaction between the π system of TPPZn and methyl groups of the amides. An analogous strong effect of attractive interactions between metal porphyrinates and electron-donor ligands on the stability of complexes derived therefrom was repeatedly noted in the literature [11].

The existence of correlations between the properties of complexes and physicochemical parameters of their components makes it possible to estimate the effect of those parameters and elucidate driving forces of complex formation. The use of multiparameter correlations for donor–acceptor interaction between metal porphyrinate and electron-donor ligand requires that the electron-donor power of the ligand be determined. Unfortunately, we have found no published data on gas-phase proton affinities for the ligands under study (except for compounds **III** and **IV**). Other empirical parameters characterizing the electron-donor power and including effect of the medium, i.e., Gutmann donor numbers (*DN*) [12] and basicity constants pK_{BH^+} [13], are also available for a few ligands (Tables 2, 3). Therefore, in the present study we drew correlations for two groups of the ligands. Acetamide is poorly soluble in CCl_4, so that we failed to determine thermodynamic parameters for complex forma-

Table 3. Normalized and natural-scale parameters of ligands **III**–**VI** and standardized K_s values for the reactions of (tetraphenylporphyrinato)zinc(II) with amides **III**–**VI** in benzene and carbon tetrachloride at 298.15 K

Ligand no.	*DN*		*V*		P_{or} (C_6H_6)		K_s (C_6H_6)	P_{or} (CCl_4)		K_s (CCl_4)
	kJ/mol	a	cm^3 mol^{-1}	a	10^{-5}, m^3	a	a	10^{-5}, m^3	a	a
III	111.45	–0.751	46.84	–0.597	304.89	–0.467	–1.332	298.61	–0.671	–0.929
IV	116.48	0.534	59.00	–0.212	283.18	–0.602	–0.188	280.14	–1.037	–0.180
V	162.57	1.457	112.15	1.470	619.01	1.496	0.890	380.12	0.941	1.418
VI	124.86	–0.172	44.84	–0.661	311.24	–0.427	0.631	371.36	0.768	–0.308

[a] Normalized values.

tion of acetamide with TPPZn, and the corresponding multiparameter correlation in carbon tetrachloride was not drawn.

By analysis of the quantities given in Tables 1 and 2 we obtained correlation (1) between the thermodynamic stability of TPPZn · L complexes (L = **I**–**IV**) in benzene and ligand properties:

$$K_s = (0.7361 \pm 6.4 \times 10^{-4})\,pK_{BH^+} + (0.2196 \pm 9.1–10^{-4})V + (–0.2916 \pm 7.8 \times 10^{-4})P_{or};$$
$$S_{ad} = 8.6 \times 10^{-4};\ R = 1. \quad (1)$$

Here, K_s is the normalized equilibrium constant; V is the normalized van der Waals volume, P_{or} is the normalized orientational polarizability, S_{ad} is the remainder variance, and R is the normalized electronic polarizability.

Analysis of the quantities given in Tables 1 and 3 allowed us to draw correlations (2) and (3) (for benzene and carbon tetrachloride, respectively) between the thermodynamic stability of TPPZn · L complexes (L = **III**–**VI**) and ligand properties:

$$K_s = (3.5820 \pm 1.3 \times 10^{-3})DN + (–0.0463 \pm 1.1 \times 10^{-3})V + (–2.8484 \pm 1.1 \times 10^{-3})P_{or};\ S_{ad} = 5.0 \times 10^{-4},\ R = 1; \quad (2)$$

$$K_s = (1.2436 \pm 1.3 \times 10^{-3})DN + (0.8569 \pm 1.1 \times 10^{-3})V + (–1.1050 \pm 1.6 \times 10^{-3})P_{or};\ S_{ad} = 5.0 \times 10^{-4},\ R = 1. \quad (3)$$

The values of R and S_{ad} indicate that Eqs. (1)–(3) satisfactorily describe thermodynamic stability of the corresponding complexes. The significance of each parameter in the above equations was estimated by their successive exclusion. The results showed that the stability of TPPZn · L complexes is determined mainly by the electron-donor power and orientational polarizability of the amide molecule; the ligand volume turned out to be less significant. It should be noted that orientational polarizability reflects orientation of fixed dipoles which, in keeping with published data [4], are oriented toward the oxygen atom in amide molecules. The significance of P_{or} together with the insignificant contribution of V may be regarded as further evidence of the assumption that amides are coordinated to (tetraphenylporphyrinato)zinc(II) through the oxygen atom.

The above correlation equations are unlikely to possess a predictive power, for they have been drawn for a small number of amides.

EXPERIMENTAL

(Tetraphenylporphyrinato)zinc(II) (TPPZn) was synthesized and purified by the procedures described in [14]; its purity was checked by the electronic absorption spectra. The ligands (L): acetamide (**I**), *N*-ethylacetamide (**II**), dimethylformamide (**III**), *N*,*N*-dimethylacetamide (**IV**), hexamethylphosphoric triamide (**V**), and dimethyl sulfoxide (**VI**) were purified by column chromatography on activated Al_2O_3 and subsequent vacuum distillation [15]. Acetamide was purified according to the recommendations given in [15]; its purity was checked by thermogravimetry using an MOM-1000D derivatograph (Hungary); its melting point coincided with that given in [5]. Benzene and carbon tetrachloride of ultrapure grade were additionally purified by drying over 4Å molecular sieves, followed by fractional distillation. Their purity was checked by chromatography (it was 99.98%). The concentration of water was determined according to Fischer (it was no more than 0.02%).

The study was performed using an automatic differential titration calorimeter [16]. Its dosing unit was charged with a solution of appropriate ligand (c = 0.2–0.3 mol/kg), and the cell was charged with a solution of TPPZn (10^{-7}–10^{-3} mol/kg). Molal concentrations were recalculated into molar concentrations using the solution densities measured at

298.15 K by the volumetric method. The thermodynamic parameters: stability constants K_s (expressed in the molarity units) and ΔH^0 for reactions of TPPZn with ligands L were calculated from the experimental titration curves with the aid of KALORY program [17]. In order to exclude possible local minima of the function $\Sigma(Qn_{\text{exp}} - Qn_{\text{calc}})^2$ (where Qn_{exp} is the experimental dependence of the heat effect upon the number of doses, and Qn_{calc} is the same but calculated theroretically), the corresponding function profile was built up and analyzed for each system. In all cases, the function $\Sigma(Qn_{\text{exp}} - Qn_{\text{calc}})$ had the only minimum, as followed from the dependence of the corresponding profile. Here, the variance minimum indicated the best agreement between the calculated and experimental unit heat effects. The presence of a single minimum pointed to its global character and confirmed the reliability of the calculated thermodynamic parameters.

Multiparameter correlation equations were drawn as follows. In keeping with the recommendations given in [18], the ligand volume was estimated as algebraic sum of the van der Waals volumes of particular atoms and bonds. As a measure of charge mobility in the ligand molecules we used orientational polarizability calculated according to [19].

Statistical treatment of the results was performed following a multilinear regression analysis program. The quality of the correlations was estimated through the multiple correlation coefficient R and remainder variance S_{ad}.

Physicochemical parameters of the ligands and thermodynamic parameters of complex formation were standardized according to [20]. Multiparameter regresions with normalized variables (Tables 2, 3) make it possible to estimate the significance of each particular parameter directly from the regression coefficient [20].

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