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Molecular Complexes of Phthalocyanine with Organic Solvents

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Abstract—It was established that in crystal solvates and solutions zinc(II)tetra-*tert*-butylphthalocyanine formed stable molecular complexes with benzene and pyridine. The characteristics of the corresponding molecular complexes were estimated. Molecules of electron-donor and aromatic solvents do not break down the zinc(II)tetra-*tert*-butylphthalocyanine associates and do not facilitate intraphase polymorphic transition. A comparative analysis was carried out for the coordinative properties of zinc(II)tetra-*tert*-butylphthalocyanine and its structural analog, zinc(II)tetrabenzoporphyrin, with respect to pyridine in benzene solutions.

The scientific and practical interest to metal complexes of phthalocyanines is caused by their unique properties: high stability, intense color, presence of π-electrons. For instance, phthalocyanines were used in analytical chemistry, in development of pigments and dyes, catalysts, semiconductors [1]. It is a common knowledge that the molecular complexing with macromolecules drastically changes the physico-chemical properties of the latter. However notwithstanding the importance of complexing of phthalocyanine metal derivatives with molecular ligands the information on energy, thermodynamical and thermal stability of the corresponding complexes is virtually absent [2]. Therefore the goal of this study consisted in the investigation of complexing of zinc(II)tetra-*tert*-butylphthalocyanine (**I**) (Zn(*t*-Bu)$_4$Pc) with molecules of organic solvents using the methods of calorimetric titration and thermogravimetry.

The investigation of complexing with participation of phthalocyanines in crystal solvates and saturated solutions is complicated by the occurrence of a con-current process, intraphase polymorphic transition from α- **II** into β-form **III** [3].

The IR spectra of sublimed sample revealed the presence of two polymorphic forms. Therefore a valid analysis of derivatograms obtained for crystal solvates of Zn(*t*-Bu)$_4$Pc with benzene and pyridine (Py) requires an information on the thermal stability of Zn(*t*-Bu)$_4$Pc proper and on the thermal range and energy component of the intraphase transition $\alpha \rightarrow \beta$. For the present study especially interesting thermogravimetric data were published by Elshereafy *et al.* [4] who reported on establishing of the thermal range and activation energy of the intraphase polymorphic transition $\alpha \rightarrow \beta$ in the phthalocyanine metal complexes. However the above transition was followed [4] by variation in the electrochemical properties and not by the characteristic spectral bands. The variations in the electrical conductivity may be caused by the changes in parameters and the order of the crystal lattice of macrocycles. Note that similar extended exothermic peaks on the DTA curves were also observed before [5, 6] in the study
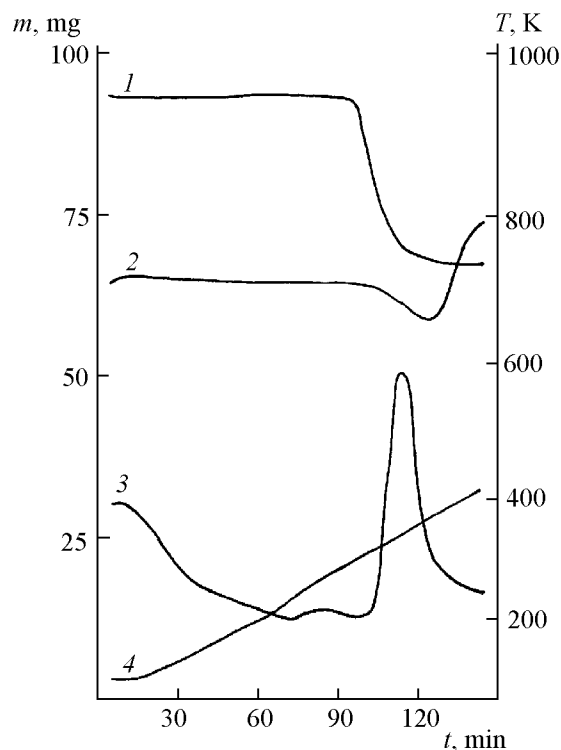

I   **II**   **III**
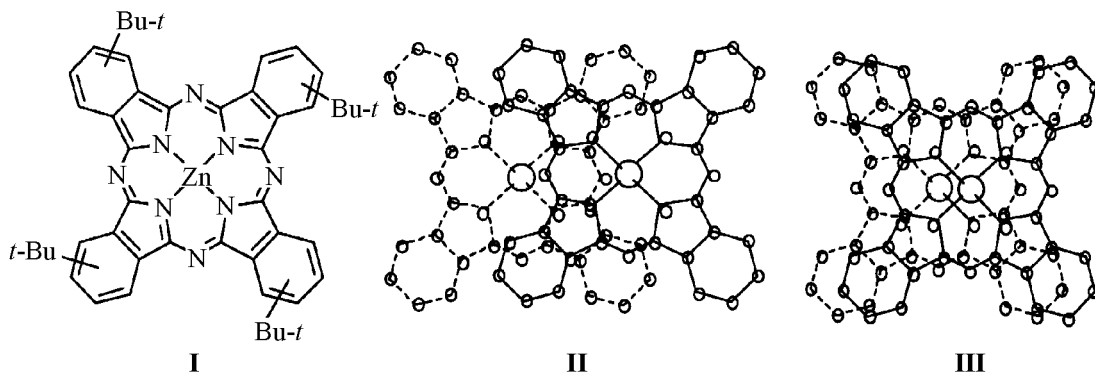
Fig. 1. Thermooxidative degradation of Zn(*t*-Bu)$_4$Pc. (*1*) thermogravimetry, (*2*) differential thermogravimetry, (*3*) differential thermal analysis, (*4*) temperature.

Fig. 2. Derivatogram of Zn(*t*-Bu)$_4$Pc crystal solvate with benzene (the designations see on Fig. 1).

on the thermal stability of metal-porphyrin complexes where the intraphase transitions were not common. In this connection an additional investigation of the thermal stability of Zn(*t*-Bu)$_4$Pc was carried out, and the macrocycle proved to be stable up to 250°C. The derivatogram is presented on Fig. 1. The intermediate control by IR spectroscopy showed that uo to 250°C

Characteristics of specific complexes of Zn(*t*-Bu)$_4$Pc and Zn(II)tetrabenzoporphyrin (ZnTBP) with pyridine and benzene[a]

Molecular complex	Composition	T_p, °C	ΔH_{vap}, kJ mol^{-1}[b]
Zn(*t*-Bu)$_4$Pc–C$_6$H$_6$	1 : 1	71	41.42
ZnTBP–*n*C$_6$H$_6$ [6]	1 : 2	76	150.24
Zn(*t*-Bu)$_4$Pc–*n*Py	1 : 1.5	74	80.08
	1 : 1	94	83.73
	1 : 0.5	134	111.36
ZnTBP–*n*Py [6]	1 : 1	150	83.10

[a] T_p is the breakdown temperature.
[b] ΔH_{vap} values were determined with an error of (0.8–1.5) kJ mol^{-1}.

both polymorphic forms are present in the sample, and during the thermogravimetric experiment their ratio did not virtually change. The assignment of the characteristic bands of the polymorphic forms was done in keeping with suggestions from [3]. At 250°C the spectrum was not reproduced.

No polymorphic transition $\alpha \rightarrow \beta$ within the time of experiment and sufficient heat resistance provided a possibility to study crystal solvates of Zn(*t*-Bu)$_4$Pc with benzene and pyridine. The results are presented in a table. The desolvation of the corresponding Zn(*t*-Bu)$_4$Pc crystal solvates with pyridine and benzene occurs in several stages. At the first stage (15–50°C) the value ΔH_{vap} during evaporation of pyridine or benzene is essentially similar to that of the pure solvent suggesting breakdown of structures built up by universal interactions. A separate peak on the DTG curve at higher temperature corresponds to degradation of the specific molecular complex.

It was established that with benzene formed a complex of Zn(*t*-Bu)$_4$Pc · C$_6$H$_6$ composition. On Fig. 2 a typical example is given of derivatogram obtained in a study of Zn(*t*-Bu)$_4$Pc crystal solvate with benzene. The precise reproducibility of the composition notwithstanding the initial content of

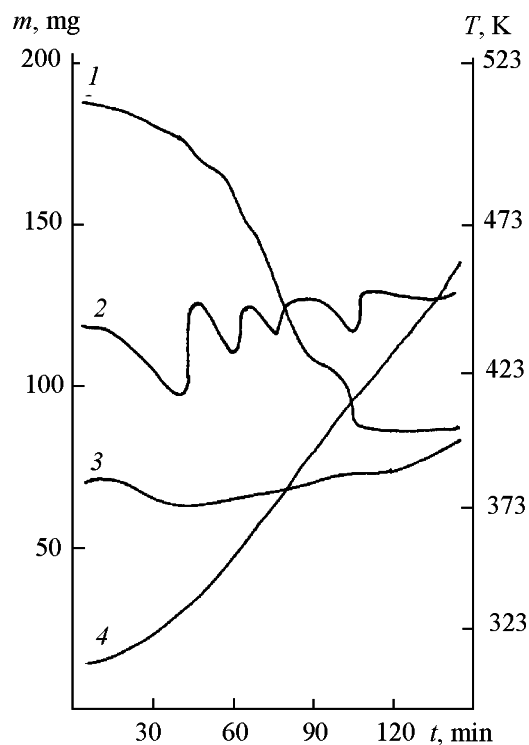**Fig. 3.** Derivatogram of Zn(*t*-Bu)$_4$Pc crystal solvate with pyridine (the designations see on Fig. 1).

Zn(*t*-Bu)$_4$Pc and C$_6$H$_6$ in the crystal solvate, and low energy and heat resistance indicate that in Zn(*t*-Bu)$_4$Pc crystal solvates with benzene a π–π complex and not an insertion complex is formed [7].

It should be noted that the results obtained (see the table), namely, the composition of the specific Zn(*t*-Bu)$_4$Pc complex with benzene and its relatively low stability energy are somewhat unexpected for the specific π–π benzene complexes with metal-porphyrin compounds in the absence of steric hindrances from bulky substituents at the macroring are as a rule stable and have 1:2 composition [8]. As an example we cited in the table the previously obtained results [6] on the specific complexes with benzene of the close structural analog of Zn(*t*-Bu)$_4$Pc, Zn(II)tetra-benzoporphyrin (ZnTBP).

Although the π–π complexes are obviously important, theoretical concepts of their nature and the driving force of π–π complexing are now in the course of transformation and development. It is assumed [8] that the total energy of interaction between two molecules (E_{tot}) in the π–π-complex may be described by expression (1):

$$E_{tot} = E_{att} + E_{ind} + E_{disp} + E_{rep}, \qquad (1)$$

where E_{att}, E_{ind}, E_{disp}, and E_{rep} are the contributions to the total energy of electrostatic attraction, inductive, dispersion forces, and electrostatic repulsion respectively.

This model of π–π-interaction evidently is more complete than those assumed before: it is solvato-phobic considering association to occur due to hydro-phobic effect and to the gain in the enthropy component of the interaction, also it is donor-acceptor model of interaction. These theories do not explain quite a number of features, for instance, the lack of maximum π–π overlapping of electronic orbitals of the interacting molecules, the rigid geometrical requirements, and no reciprocal rotation of the molecules. The developed theory [8] where the observed π–π interactions actually result from π–σ bonding prevailing over π–π repulsion permits an explanation of the above mentioned features. This conclusion is in agreement with the results of the X-ray diffraction study of complexes between macro-cycles and aromatic molecules (benzene, toluene, *o*-, *m*-, *p*-xylenes, 1,2,5-trinitrobenzene) [9]. Just the same, none of the theories mentioned can explain the observed significant difference in the characteristics of complexes obtained from structural analogs, zinc(II)tetrabenzoporphyrin and zinc(II)tetra-*tert*-butylphthalocyanine. This fact is apparently due to the specific structural features of the crystalline lattice of the latter. Presumably the aromatic molecules do not break down associates in either polymorphic form, α or β, of the zinc(II)tetra-*tert*-butylphthalo-cyanine.

IR spectra taken before and after the thermogravi-metric experiment supported this assumption, for the presence of both polymorphic forms was observed.

Interesting results were obtained at thermogravi-metric analysis of Zn(*t*-Bu)$_4$Pc crystal solvates with pyridine. Certain peaks on the DTG curve (Fig. 3) correspond to high ΔH_{vap} values, exceeding two times that of the pure pyridine. This fact allows a conclu-sion on breakdown of solvate structures built up by specific interactions. IR spectroscopic monitoring showed that in the initial Zn(*t*-Bu)$_4$Pc crystal solvates with pyridine and in Zn(*t*-Bu)$_4$Pc after the thermo-gravimetric experiment both polymorphic forms were present; thus the addition of the electron-donor solvent did not facilitate the intraphase polymorfic transition and did not destroy the associates. Note the noninteger values of the molar ratio Zn(*t*-Bu)$_4$Pc: pyridine (see table). The pyridine is an aromatic electron-donor solvent, therefore between Zn(*t*-Bu)$_4$Pc and pyridine may operate both the π–π mechanism

and donor-acceptor interaction of the unshared electron pair of pyridine nitrogen with the central metal atom of the phthalocyanine complex. The electron absorption spectra of $Zn(t\text{-Bu})_4Pc$ in benzene taken before and after addition of the 10-fold molar excess of pyridine evidence the donor-acceptor character of $Zn(t\text{-Bu})_4Pc$ interaction with pyridine since the first absorption band of $Zn(t\text{-Bu})_4Pc$ suffers a red shift ($\Delta\lambda$ 4 nm).

The results obtained facilitate the interpretation of thermogravimetric data on $Zn(t\text{-Bu})_4Pc$ crystal solvates with pyridine. It was established that the α and β polymorphic forms were retained in the crystal solvates. Therefore it is more proper to discuss not the interaction with molecules of $Zn(t\text{-Bu})_4Pc$ but with associates of zinc(II)tetra-*tert*-butylphthalocyanine. It is likely that the interaction of the α and β polymorphic forms of $Zn(t\text{-Bu})_4Pc$ results in molecular complexes of different composition and heat resistance. Apparently the blocked from one side reactive center of the α-form of $Zn(t\text{-Bu})_4Pc$ provides molecular complexes with pyridine of $2Zn(t\text{-Bu})_4Pc$: 2Py composition whereas the interaction of the β-form with pyridine results in complexes $2Zn(t\text{-Bu})_4Pc$:4Py. It was not possible to carry out thermogravimetric study on individual forms of $Zn(t\text{-Bu})_4Pc$ crystal solvates for we did not succeed in chromatographic separation of α- and β-polymorphic forms.

Calorimetric investigation of coordinative properties of $Zn(t\text{-Bu})_4Pc$ toward pyridine in benzene medium showed that in benzene formed a thermodynamically stable complex $Zn(t\text{-Bu})_4Pc$–Py. The following thermodynamical characteristics of the process under study were obtained: ΔH -9.22 ± 1.38 kJ mol^{-1}, K 332 ± 1, ΔG -14.392 ± 0.4 kJ mol^{-1}, ΔS 17.3 ± 5 J mol^{-1} K^{-1}.

The thermodynamical stability and energy characteristics of interaction between the central metal atom and electron-donor ligands is known to be governed by the strength of the σ-bonds metal–macroring. The smaller coordination space of phthalocyanines as compared to porphyrins positively affects the stability of phthalocyanine metal complexes, i.e., the partial positive charge on the zinc atom in the phthalocyanine complex is more compensated than that of the zinc atom in the porphyrin one. Obviously this is just the reason why $Zn(t\text{-Bu})_4Pc$ has worse coordinative properties than zinc(II)tetrabenzoporphyrin [10].

EXPERIMENTAL

Compound **I** was prepared by procedure [11] with subsequent sublimation in a vacuum. The purity was checked by electron absorption spectra well consistent with the published data [11].

The solvents, benzene and pyridine of "specially pure" grade, were subjected to additional purification: drying with molecular sieves (4 Å)followed by fractional distillation. The purity of solvents checked by chromatography attained 99.98%. Water content was determined by Fischer's method, and in all solvents used it did not exceed 0.02%.

Calorimetric measurements were carried out on automatic differential calorimeter for titration [12]. Into the cell was placed the titrant solution of $Zn(t\text{-Bu})_4Pc$ in benzene which was prepared by weight. The concentration of zinc(II)phthalocyanine in various runs was in the limits from 10^{-6} to 10^{-4} mol kg^{-1}. The titrant charged into the feeder was pyridine solution in benzene of 0.02–0.5 mol kg^{-1}. The concentrations were recalculated into molar concentrations after measuring the densities of the corresponding solutions at 298.15 K with the use of pycnometers.

The primary treatment of experimental data consisted in the evaluation of the individual thermal effect values corresponding to the system response at addition of separate portions. The value was calculated as the product of the corresponding peak area by the cell constant α $[Qn(\text{exp})]$. The obtained individual values of thermal effect were subjected to correction taking into account the results of blank run at each step of titration. In the blank run the titrant was introduced into pure solvent, and this measurement permitted accounting for the thermal effect at introduction and dilution of the titrant solution. The thermodynamic characteristics of the processes under study were calculated on PC using software of KALORY type [13]. The thermodynamic characteristics calculated for the processes under study are standard values since they are obtained in organic solvents at 298.15 K and in the concentration range used (10^{-8}–10^{-4} mol kg–1) they are independent of metal-phthalocyanine complex and ligand concentrations.

Thermogravimetric measurements were performed on derivatograph 1000 D MOM (Hungary). The samples of zinc(II)phthalocyanine crystal solvates were prepared by slow crystallization from saturated solutions similarly to procedure described in [6, 14]

for preparation of crystal solvates of porphyrins and phthalocyanines metal complexes designed for differential scanning calorimetry and X-ray diffraction study. The experimental procedure and calculations were described in detail before [14].

Spectral monitoring was carried out on spectrophotometer Specord M-80 on pellets 3 mm in diameter, consisting of a mixture of $Zn(t\text{-}Bu)_4Pc$ and KBr in 1:100 ratio. The pressure at pelletizing was 6000 kg cm^{-2}, Integration time was 3 min.

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