

Reactivity of Rare Earth Metal Porphyrins/Phthalocyanines in Acid Media

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Synthesis, structure, spectral properties and behavior in acid media of acido phthalocyanine complexes $(X)_{n-2}MPc$, double- and triple-decker phthalocyanine and porphyrin complexes $M(HPc)(Pc)$, $M(Pc)_2$, $M_2(Pc)_3$, and $M(P)_2$, $M_2(P)_3$ (M - lanthanide or actinide cation) were explored using UV-visible, IR, NMR spectroscopy and chemical kinetics. Kinetic equations, stoichiometric mechanisms of complexes demetallation and stability- structure relations were established.

Keywords: Phthalocyanines, porphyrins, complexes, double- and triple-deckers, synthesis, demetallation parameters, demetallation mechanism.

Реакционная способность комплексов редкоземельных металлов с порфиринами и фталоцианинами в кислых средах

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Синтез, спектроскопия, молекулярная структура и поведение в кислотах (ацидо)фталоцианинато), (фталоцианинато)/(порфиринато)комплексов лантанидов(III), тория и урана(III)/(IV) двух- и трехпалубного строения изучены с использованием УФ-видимой, ИК, ЯМР-спектроскопии и химической кинетики. Расширено понимание взаимосвязи между структурой и стабильностью комплексов.

Ключевые слова: Фталоцианины, порфирины, комплексы, двух- и трехпалубные комплексы, синтез, условия деметаллирования, механизм деметаллирования.

Introduction

Rare earth metal porphyrins and phthalocyanines, including compounds with double- and triple-decker structure, together with their synthesis and properties, are reviewed in several works.^[1-8] Lanthanide cations having large radius give phthalocyanine complexes of structures $(X)_{n-2}MPC$, $M(PC)_2$, $M_2(PC)_3$ (PC – phthalocyanine dianion). Double-decker porphyrins exist in both in $PM^{II}P$ in the case of Sc, Y, Ln and in $PM^{IV}P$ in the case of cerium, thorium, uranium. Diphthalocyanines (double-decker phthalocyanines) of lanthanides Ln^{3+} could be obtained in both mono-protonated form, $Ln(HPC)(PC)$, where the three-charged Ln^{3+} cation replaces three protons of NH bonds and the fourth proton remains unsubstituted and in an oxidized radical form, $Ln(PC)_2^{\bullet}$, where one π -electron is moved off and the H atom is absent.^[9,10] Double-decker cerium, thorium and uranium porphyrins exist in one form $PM^{IV}P$. Triple-decker porphyrin and phthalocyanine complexes are formed by cations with a formal charge 3+.

Synthesis of metallophthalocyanines with sandwich structure was described for the first time in 1965,^[11] then in 1971 and 1974.^[12,13] The results of works^[14-18] prove a molecular structure of both double-decker and triple-decker rare earth metal phthalocyanines. X-Ray crystallography data for triple-decker complexes are not numerous^[19,20] whereas double-decker complexes including mixed (phthalocyaninato)(porphyrinato) complexes have been studied intensively.^[15-17, 20-28] The results of molecular structure studying by means of density functional theory calculations or by systemizing of vibrational characteristics of bis- and tris-[(na)phthalocyaninato] and mixed (porphyrinato)[(na)phthalocyaninato] complexes^[26,29] were published. Rare earth metal double-decker and triple-decker complexes with different phthalocyanine and porphyrin macrocycles in the same molecule are constructed.^[30-34] Researches of both the first sandwich-type rare earth metal double-decker complexes with *N*-confused porphyrinato and phthalocyaninato ligands^[35] and (phthalocyaninato)/(phthalocyaninato)(porphyrinato) rare earth(III)-cadmium(II) quadruple/quintuple/sextuple-decker complexes have been started.^[36-40]

Spectral and applied properties of the complexes are studied as a rule. Porphyrin and phthalocyanine double- and triple-decker complexes exhibit promising properties such as high stability of neutral and oxidized forms, solubility in organic solvents and ability to self-organization in solid layers.^[41-44] Lanthanide/actinide porphyrin/phthalocyanine complexes with double- and triple-decker structures can be used as components of new materials. Functional substitution of sandwich-type complex molecules lead to new functional molecular materials as optically active materials, FETs, SMMs.^[45-54] From the point of possibility of practical use of the compounds, their stability to chemical, thermal and photochemical influence is very important. Intensive studying^[55,56] clearly revealed high stability and its dependence on molecular structure for porphyrin/phthalocyanine acido metal complexes. However, despite the synthesis and structural investigations of numerous porphyrin/phthalocyanine rare earth metal double-decker and triple-decker complexes, less attention has been devoted to their chemical stability.

Synthesis, structure, spectra and behavior in acid media of acido(phthalocyaninato), bis/tris(phthalocyaninato) and bis/tris(porphyrinato) rare earth(III) complexes were explored in the present work. The greatest attention is given to consideration of the ways of increasing the phthalocyanine complex stability. Kinetics and mechanisms of dissociation (demetallation) of the complexes are under discussion. We hope that the present results will attract interest for the creation of new functional materials based on rare earth multiple-decker complexes with phthalocyanine/porphyrin ligands.

Experimental

Complexes of lanthanides $(X)LnPC$ were synthesized from Li_2PC and corresponding lanthanide salt in a molar ratio 1:2.5 in boiling DMSO during 15–20 min.^[57] Reaction mixture was cooled and diluted with a double volume of water. A residue was filtered, washed with water and air-dried. An yield was *ca.* 90 %. Li_2PC was synthesized from H_2PC and butyllithium.

A mixture of $(X)LnPC$, $LnPC_2H$, Ln_2PC_3 complex compounds with different content of individual complexes depending on the metal nature is obtained when synthesizing lanthanides phthalocyanines according to traditional methods.^[10,58] That is when heating *o*-phthalonitrile with a rare earth metal salt in 8:1 molar ratio at 563 K during 1 hour. A product was dissolved in 500 mL of DMF and filtered. A solution was chromatographed on alumina (40/250) using ethanol. Two areas were obtained. The compounds of the first green and the second blue areas ($LnPC_2H$ and Ln_2PC_3 respectively) isolated by ethanol evaporating were dissolved in DMF and purified separately by second chromatography on alumina using ethanol.

$LnPC_2^{*59}$ can be synthesized using method^[60] by interaction of 10 g of *o*-phthalonitrile with lanthanide acetate at 560-570 K during 1 hour. The blue-green product was endured in vacuum at 620 K for 1 hour, and then dissolved in DMF (150 ml) with addition of hydrazine hydrate. The solution was filtered and was undergone electrolysis with constant current in a cell with graphite cathode and Pt anode. The crystals obtained were filtered, washed with acetone and dried at the temperature of 370 K in air. Electron absorption spectra of stable Ln diphthalocyanines in concentrated sulfuric acid have one wide band in the 400 nm region: λ_{max} , nm (log ϵ) in 17.7 M H_2SO_4 are equal to 442 (4.47); 443 (4.51); 410 (4.32); 410 (4.00); 407 (4.00) for Nd, Pr, Sm, Eu and Gd complexes correspondingly.

Syntheses of double- and triple-decker actinide porphyrins are shown below in Results and Discussion.

Th(TPP)₂. Electronic absorption spectrum (ethanol) λ_{max} nm: 657, 596, 556 and 516 with decreasing intensity in a number III > II > IV > I. IR (200–400 cm^{-1}) ν cm^{-1} : vibrations of pyrrole rings 252 (ν Ln-N, δ C-C-N), 384 (δ C-C-N, ν C-N), 395 (ν C-N); Th-N 436. Found C, (71.8 \pm 0.8); N, (7.2 \pm 0.3); H, (3.5 \pm 0.2); Th, (16.1 \pm 0.3) %. Calc. for Th(TPP)₂, C, 72.51; N, 7.69; H, 3.87; Th, 15.92 %.

Th₂(TPP)₂. Visible electronic absorption spectrum (benzene) λ_{max} nm: 699, 589, 549, 516 with decreasing intensity in a number III > IV > I > II. Found C, (67.9 \pm 0.7); N, (6.9 \pm 0.3); H, (3.5 \pm 0.2); Th, (20 \pm 2); Calc. for Th₂(TPP)₂, C, 68.86; N, 7.30; H, 3.68; Th, 20.16 %.

U^{IV}(TPP)₂. Electronic absorption spectrum (ethanol) λ_{max} nm (log ϵ): 595.3 (4.03), 556.9 (4.33), 516.0 (4.01), 422.5 (4.84). IR (KBr) ν cm^{-1} : vibrations of pyrrole rings 802 (γ (C-H)), 997, 1008 (ν (C-C)), δ (C-H), ν (C-N)), 1372, 1388 (ν (C-N)), 1442 (ν (C=N)), 2870, 2930 (ν (C-H)); vibrations of benzene rings 706, 724, and 754 (γ (C-H)), 1072 and 1160, 1178 (δ (C-H)), 1527, 1578, 1600 (ν (C=C)), 3050, 3090 (ν (C-H)); vibrations of the U-N bonds 430. ¹H NMR ($CDCl_3$) δ ppm: 8.93 (m, 8 H, $J_{HH} = 10.1$ Hz, *o*-C₆H₅); 8.19 (s, 16 H, C₄H₂N); 7.74 (t, 8 H, $J_{HH} = 7.75$ Hz, *m*-C₆H₅); 7.72 (t, 8 H, $J_{HH} = 7.44$ Hz, *p*-C₆H₅); 7.52 (t, 8 H, $J_{HH} = 6.82$ Hz, *m*-C₆H₅); 6.70 (m, 8 H, *o*-C₆H₅). Found: U, 16.1 %. Calc. for U^{IV}(TPP)₂: 16.26 %.

$U^{III}_2(TPP)_3$. Electronic absorption spectrum (benzene) λ_{max} nm (log ϵ): 657.9 (4.40), 599.5 (4.36), 462.1 (5.12), 422.3 (5.16). IR (KBr) ν cm $^{-1}$: vibrations of pyrrole rings 808 (ν (C-H)), 1000, 1016 (ν (C-C)), δ (C-H), ν (C-N)), 1375, 1380 (ν (C-N)), 1445 (ν (C=N)), 2875, 2950 (ν (C-H)); vibrations of benzene rings 704, 710, and 728 (ν (C-H)), 1080 and 1158, 1185 (δ (C-H)), 1528, 1550, and 1580, 1608 (ν (C=C)), 3070, 3100 (ν (C-H)); vibrations of the U-N bonds 436. 1H NMR (CDCl $_3$) δ ppm: 9.97(d); 8.42 (m); 8.24(s); 7.76 (t); 7.74 (t); 7.71 (t); 7.68 (t); 7.49 (t); 7.02 (d); 6.72 (d). Found: U, 19.8 %. Calc. for $U^{III}_2(TPP)_3$: 20.57 %.

The kinetics of complex dissociation reactions was studied spectrophotometrically in the acid solvents of variable composition by the concentrations excess method. The experiment was carried out in a thermostatically controlled glass cell at the temperature of 298 K and higher. The temperature was measured to ± 0.1 K. Changes in the absorbance of the solution were measured at the operating wavelengths. The effective rate constants of dissociation (k_{obs} , s $^{-1}$) obtained under the conditions of large excess of solvated protons with respect to the complex concentration were calculated by the first-order equation (1):

$$k_{obs} = \frac{1}{\tau} \ln \frac{A_0 - A_\infty}{A_\tau - A_\infty} \quad (1)$$

Here A_τ , A_0 , A_∞ are absorbances observed at present time, when $\tau = 0$, and when a reaction had terminated, respectively*. The reaction order with respect to the acid concentration was determined from the log k_{ef} vs. [log C_{HX}] plots as the slope of the regression line in three-five independent experiments. The activation parameters E and ΔS^\ddagger of the complex dissociation were calculated using the Arrhenius equation and the basic equation of the transition state theory reduced to the form (2), respectively. Numerical value of ΔS^\ddagger was determined as the arithmetic mean of one calculated for all investigated temperatures. E and ΔS^\ddagger were obtained with an accuracy 2–9 kJ/mol and 8–28 J/(mol·K), respectively.

$$\Delta S^\ddagger = 19.1 \log kT + E/T - 19.1 \log T - 205 \quad (2)$$

Results and Discussion

Acido Phthalocyanine Metal Complexes (X) $_{n-2}$ MPc

Varying acido ligand nature could change stability of the coordination compounds of this type.^[61] The study was carried out for both complexes of one and the same metal with a set of acido ligands X $^-$ (Cl $^-$, Br $^-$, AcO $^-$)^[62] and

complexes of different metal cations of one type with one and the same X $^-$.^[33]

Until now only a few crystal structures with trivalent metals have been described. In lutetium(III) monophthalocyanine derivative [(H $_2$ O) $_2$ (AcO)Lu III (Pc)]H $_2$ O·CH $_3$ OH the coordination geometry is a slightly distorted square antiprism.^[63] The donor atoms consist of four isoindole nitrogens of the phthalocyanine ring, two oxygen atoms of one acetate anion, and two oxygens of two water molecules. Acetate anion and two water molecules are at the same side of the macrocycle. The four Lu–N iso-bond distances range from 2.333 to 2.359 Å with a mean value of 2.345 Å. The four isoindole nitrogen atoms of the phthalocyanine ring are coplanar. The Lu atom lies 1.26 Å away from the 4 N-iso mean plane.

(X)LnPc give molecular solutions in ethanol (10 $^{-5}$ –10 $^{-4}$ mol/l). A long wave absorption band ($\pi \rightarrow \pi^*$ transition) position in UV-vis spectra of the complexes in this solvent as in other organic solvents (Table 1) is practically independent on metal and acido ligand nature.

This points to the existence of particles [(C $_2$ H $_5$ OH) $_{n-2}$ LnPc] $^+$ in the solution, where n is the maximum coordination number of Ln at given conditions (Figure 1). Thus, ethanol is the fit medium for investigating the dissociation of the complexes in the presence of acid.

[(C $_2$ H $_5$ OH) $_{n-2}$ LnPc] $^+$ dissociation leads to formation of H $_2$ Pc soluble in the reaction mixture, sediment formation is not observed during the reaction process:

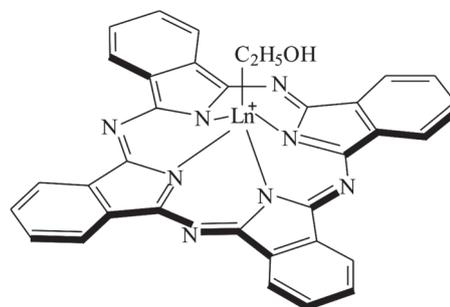
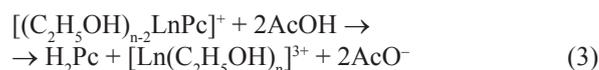


Figure 1. Structure of lanthanide (Tb–Lu) phthalocyanines in the ethanol solution.

Table 1. A long wave absorption band position (λ_{max}^1 , nm) in UV-vis spectra of (X)LnPc a .

Solvent	(AcO)TbPc	(AcO)DyPc	(AcO)HoPc	(AcO)ErPc	(AcO)TmPc	(Cl)YbPc	(AcO)LuPc
Ethanol		670.6				670.6	
DMSO	676.9	674.9	678.6	674.6	673.4	677.5	673.8
PhH	671.5	671.9	672.6	672.6	677.5	674.3	674.3
Acetone	667.9	667.8	670.2	666.8	666.7	666.7	663.1
Py	675.2	675.4	674.4	674.4	675.7	674.4	674.4
PhCN	719.1	720.5	719.0	719.0	718.4	716.9	714.9
	691.2	690.6	691.2	691.2	691.2	691.2	691.2
CHCl $_3$	675.2	671.6	671.3	676.8	675.7	676.7	675.3

^a λ_{max}^1 is equal to 671.5 and 669.2 nm for (Cl)CePc in ethanol and (AcO)GdPc in DMSO.

* For numerical values of effective rate constants of dissociation, see Online Supplementary Materials.

The k_{obs}^{298} values for Tb–Yb complexes (Table 1S) derived from extrapolation of k_{obs} -temperature dependence are changing non-linearly with changing AcOH content in a wide range of the mixed solvent compositions (Figure 2, Tables 1S, 2S). That is why it is impossible to find a total kinetic equation for reaction (3) and true values of the rate constants k . The $k_{obs}^{298} - f(C_{AcOH}^0)$ dependence for labile cerium and praseodymium phthalocyanines (Table 2S) is linear from 0 to 0.04 mole fractions of AcOH in ethanol:

$$-dC_{(X)LnPc} / d\tau = k_{obs} \cdot C_{(X)LnPc} = k \cdot C_{(X)LnPc} \cdot C_{AcOH} \quad (4)$$

In this case a value of tangent of inclination angle of straight line in $k_{obs}^{298} - f(C_{AcOH}^0)$ coordinates can be used as a universal (in regard to mixed solvent composition) criterion of the complex stability. Its value is equal $k = K_a \cdot k'$, K_a – acid ionization constant of AcOH in ethanol, k' – the rate constant of elementary reaction between (X)LnPc and AcOH. UV-vis spectra of phthalocyanine complexes with rare earth elements from Tb to Lu do not change when boiling the ethanol solutions of the compounds during a

long time. This allows extrapolation of $k_{obs}^{298} - f(C_{AcOH}^0)$ dependencies at $C_{AcOH}^0 > 0.04$ mole fractions. Tangent of inclination angle of tangent line to curve drawn through the origin (tg α) has the same meaning as $K_a \cdot k'$ parameter in the case of phthalocyanine complexes with elements from La to Gd. Thus, using tg α values proportional to k value for Tb–Lu phthalocyanine complexes we obtain the dependence of the physical-chemical parameter of the complex from the lanthanide ordinal number (Z) through the lanthanides row. That is shown in Figure 3. According to Figure 3 data the phthalocyanine lanthanides stability changes with Z growth through concave curve with “gadolinium fracture” directed down. It must be pointed out that k_{obs}^{298} dependence from Z for the same solvent composition has analogous view. The dependence under consideration has “canonical” type in a whole^[60] in spite of the complex composition of the investigated compounds and is analogous to the dependencies obtained when studying the stability of Ln^{3+} complexes with chelate and simple molecular ligands. It is known^[64,65] that “gadolinium fracture” is connected with peculiarities of Ln^{3+} f -shells and namely is determined by contributions of spin and orbital angular moments of motion quantity of the base

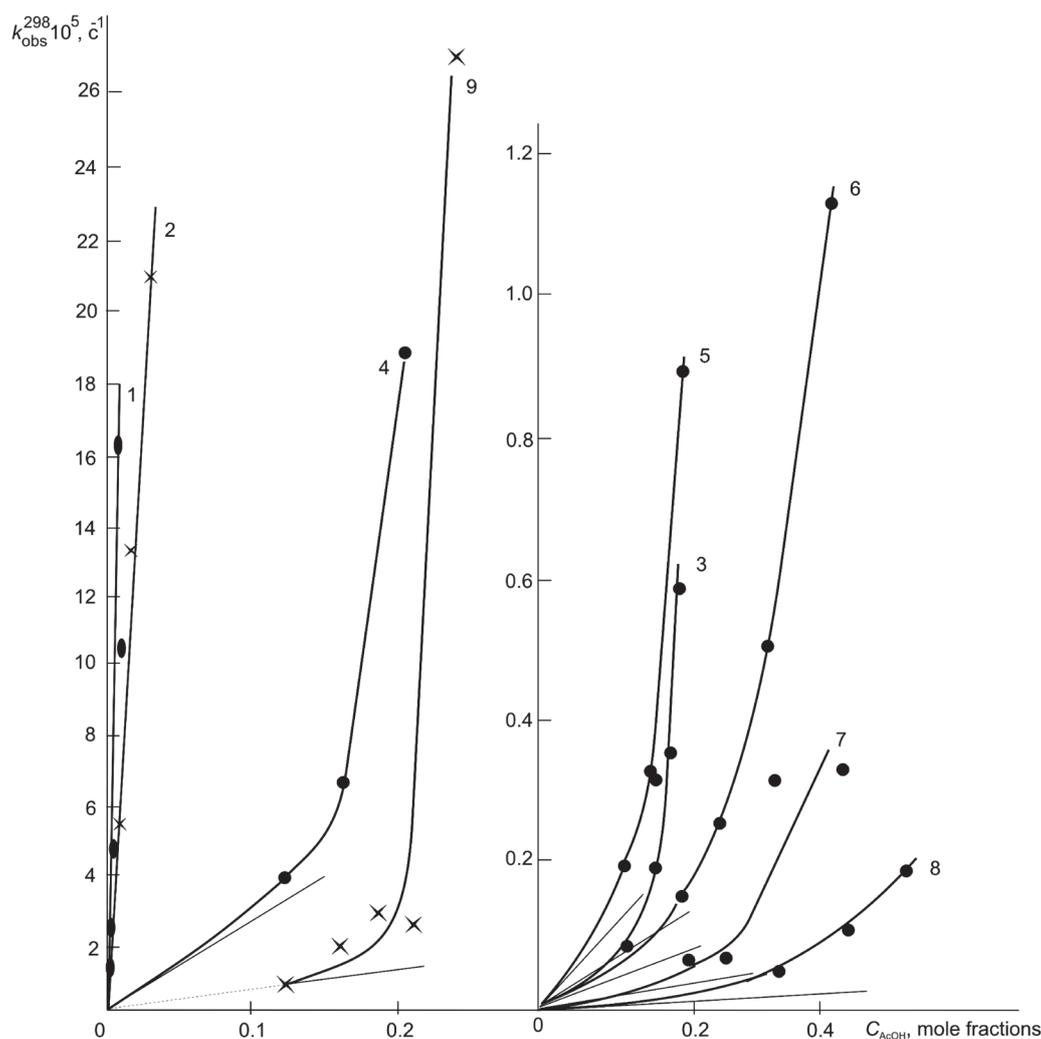


Figure 2. Dependences of dissociation rate constants of (X)MPc on initial AcOH concentration. M: 1 – Ce, 2 - Pm, 3 - Tb, 4 – Dy, 5 – Ho, 6 – Er, 7 – Tm, 8 – Yb, 9 – Y (for Ce and Pm $k \cdot 10^3$).

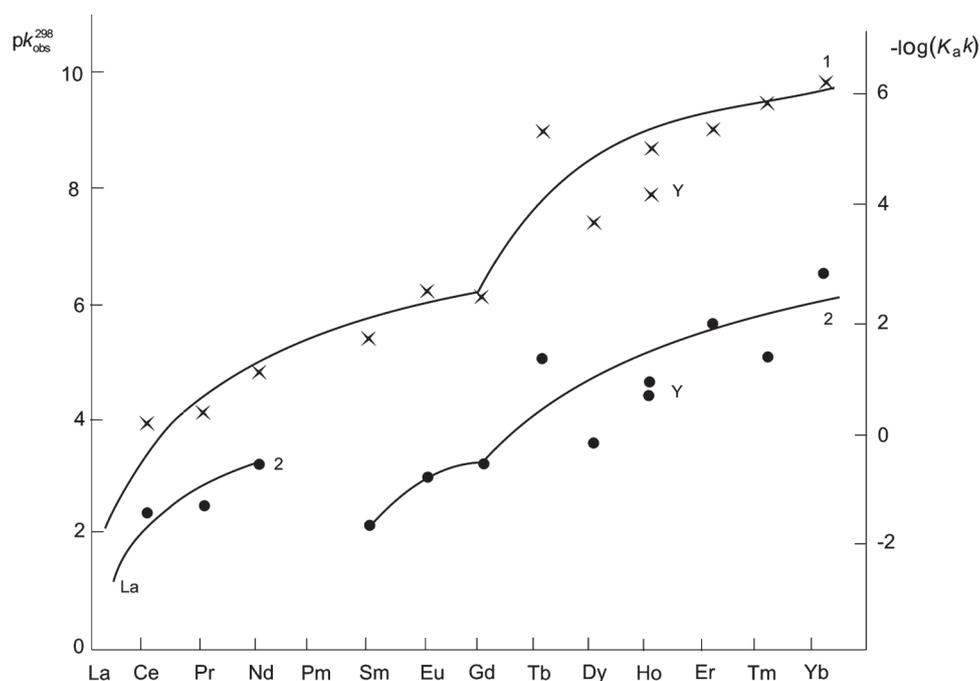


Figure 3. Dependences of $\log(K_a \times k)$ (1) and pK_{obs}^{298} in ethanol-25% AcOH (2) on lanthanides number. The pK_{obs}^{298} in ethanol-1% AcOH are shown for La–Pr.

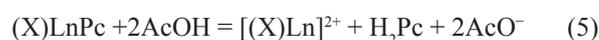
lanthanide cation states. Detailed analysis of the dependency in Figure 3 shows that un-monotonous character of complex stability changing in lanthanides row is connected not only with the presence of partially filled f -orbitals in $(X)LnPc$ but with action of supplementary factors in the cases of complexes of Ce^{3+} and Tb^{3+} as well. Sharp increase in kinetic stability at the beginning of every sub-group – from La to Ce and from Gd to Tb – is the evidence of participation of $4f^l$ - and $4f^8$ -electrons in dative π -bond $Ln \rightarrow N$ in the complex. This could be connected with striving of the pointed atoms for stable f^0 and f^7 configurations correspondingly and with presence of vacant π -orbital of low energy in the macrocycle.

The considered data show that rare earth element phthalocyanines are not pure ionic complexes. Covalent contribution to donor-acceptor interaction is carried out with participation of the $4f$ -orbitals as well as the external s -orbitals. The last is proved by comparison of stability of M^{3+} cation complexes with closed the s^2p^6 outer shell without f -orbitals (Al^{3+} , Sc^{3+} , Y^{3+}) and La^{3+} , Gd^{3+} , Lu^{3+} cation complexes with the f^0 , f^7 and f^14 electron configurations. The stability series made with the help of acidities of media where the complexes dissociate with a measurable rate (Tables 1S, 2S,^[66,67]) is the following: $Al > Sc > Y > La < Gd < Lu$. The complexes in the series are settled according with Z increase. Deviation from monotony for Gd and Lu complexes is obviously connected with the so-called “ f -effect”^[67] which is a decrease in energy of outer s -orbitals and their participation in formation of covalent bonds with the ligand orbitals.

Dependence of the dissociation rate of gadolinium and dysprosium phthalocyanines with a set of different acido ligands X⁻ upon X⁻ nature (Figure 4) is the evidence of the acido ligand presence in the coordination shell of Gd and Dy (Figure 5). The dissociation rate increases in a series:

$(OAc)GdPc < (Br)GdPc < (Cl)GdPc$, corresponding to the electronegativity parameter of X⁻ donor atom.

Summary Gd^{III} and Dy^{III} complex dissociation equations (equation 5) and rate equations (6 and 7 for Gd and Dy complexes correspondingly) are found:



$$-dC_{(X)GdPc} / d\tau = kC_{(X)GdPc} \cdot (C_{AcOH}^0)^2 \quad (6)$$

$$-dC_{(X)DyPc} / d\tau = kC_{(X)DyPc} \cdot C_{AcOH}^0 \quad (7)$$

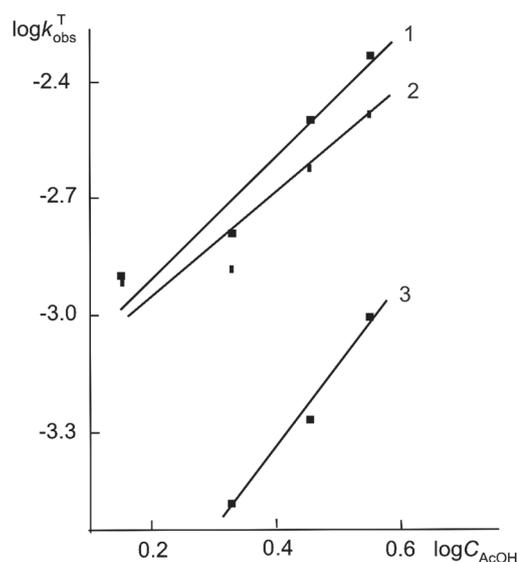


Figure 4. Dependences of dissociation rate constants of $(X)GdPc$ on initial AcOH concentration at 313 K. X = Cl (1), Br (2), OAc (3).

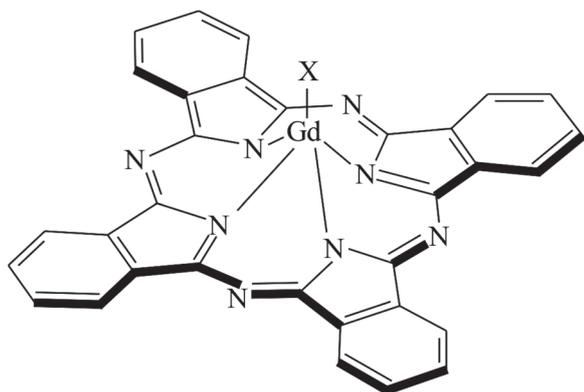
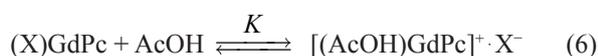
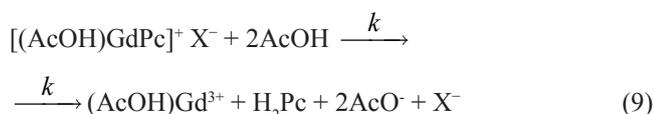


Figure 5. Structure of gadolinium phthalocyaninates in the solution.

Kinetic data for Gd^{III} complexes indicate the equilibrium stage of acido ligand dissociation with its ousting to the second coordination sphere in contrast with Dy^{III} complexes:



The limiting stage of M-N (N – the donor macrocycle atoms) bonds dissociation is differed in case of two complexes:



Through the above mentioned series the dissociation rate constant value are changing in 24.4 and 2.4 times for Gd and Dy complexes correspondingly. Presence of dative π -bonds halogen – lanthanide or O-Ln (for acetic complexes) is obviously the reason for the low sensitivity of the Dy complex dissociation rate to counter ion X⁻. Kinetic stability of (X)DyPc (k^{298}) is in 4.30 and 44 times (for X = AcO⁻, Br and Cl⁻ respectively) higher as compared with (X)GdPc due to reverse dative Dy-N π -bonds and the closer position of Dy cation to the macrocycle plane because of “lanthanide pressure” effect.

Thus, the complex stability could be changed in a necessary direction by acido ligand changing.

Phthalocyanine Double-Deckers

Double-decker structure of diphthalocyanine complexes of lanthanides was confirmed with X-ray crystallography data for NdPc₂.^[14] According to these data Nd atom in the molecule is situated between two parallel phthalocyanine ligands, which are turned to 45° about each other. Each of eight Nd-N bond distances equals to 2.39–2.49 Å. One of the phthalocyanine ligands has saucer-like conformation and the other is planar. The metallodiphthalocyanines exist in different crystalline modifications. For instance, α -tetragonal and β -monoclinic forms of Nd(Pc)₂ and β -monoclinic and

γ -orthorhombic forms of Sn(Pc)₂ are known.^[68-70] Nd(Pc)₂ also crystallizes in orthorhombic γ -form. Nowadays there is also information about structures of Er^{III}(Pc)₂,^[16] Ce^{IV}(Pc)₂^[17] and others.

Data on sandwich complexes the structure of which is studied by X-ray crystallography are listed in [2]. From the results, it is seen that the structure of double-decker phthalocyanine complexes for all the investigated compounds has the same type. The metal atom is coordinated by eight isoindole nitrogen atoms (N-iso) and is situated between two phthalocyanine macrocycles. Macrocycles undergo distortion and become non-planar but saucer-shaped with benzene rings bent outward. The distortion degree as well as M-N-iso distances and rotation of the macrocycles with respect to one another are determined by nature and radius of the metal cation.

The results of the first quantitative investigations of stability in solutions of lanthanides phthalocyanines with composition lanthanide ion-phthalocyanine 1:2 were published in^[59]. Diphthalocyanines of metals could be obtained in two forms.^[9,10] In this part the properties of sulfuric acid solutions and dissociation reactivity of oxidized diphthalocyanines of Sc, Y, Pr, Nd, lanthanides from Sm to Lu (Figure 6) are systematically considered. Properties of oxidized Ln diphthalocyanines are changing essentially when going along a series from La to Lu. That is why La and Y sub-groups will be described separately.

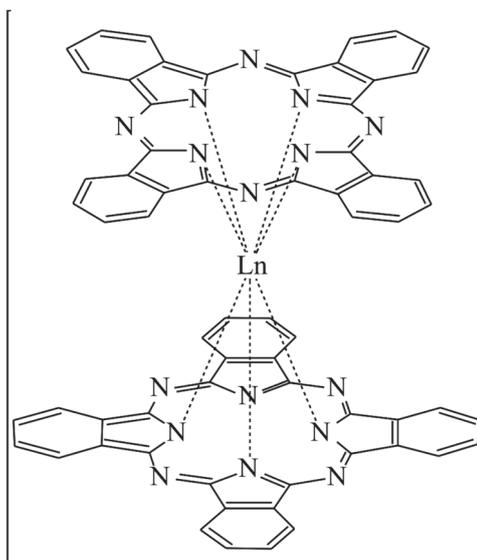
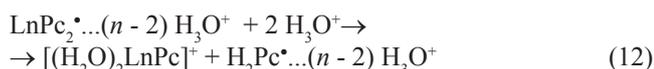
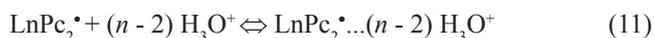


Figure 6. Structure of oxidized diphthalocyanines LnPc.

When sulfuric acid solutions of the complexes are kept at temperatures higher than 338 K (Sm, Eu, Gd) or 300 K (Pr, Nd) a gradual decrease of LnPc₂[•] concentration is observed, there are no other colored forms in the solutions according to UV-vis spectra. Reprecipitation of the reaction mixture during the reaction process ($\tau_{1/2}$) to ice gives the same result. The dissociation process is accompanied with rapid destruction of the macrocycle. Table 3S shows values of effective rate constants, energy and entropy of dissociation activation of lanthanides diphthalocyanines in concentrated H₂SO₄.

An order of diphthalocyanines $\text{LnPc}_2\cdot$ dissociation on $[\text{H}_3\text{O}^+]$ (n) changes when temperature changing and depends upon metal cation nature (Table 2). For the same complex n value is smaller at the higher temperature. At 298 K the reaction order decreases in a series: $\text{Eu} > \text{Gd} > \text{Sm} > \text{Pr}$, Nd , that is in a reverse succession compared with $\log k^{298}$ and E values changing.

It can be supposed that the first order on $\text{LnPc}_2\cdot$ and high variable order on H_3O^+ are connected with the following elementary reactions:



The total process rate is limited by reaction (12). $\text{LnPc}_2\cdot$ transformation to mono-phthalocyanine complex (reactions 11, 12) is a result of solvo-protolytical dissociation of Ln-N bonds under the action of H_3O^+ cations but not owing to splitting one of two macrocycles of $\text{LnPc}_2\cdot$.

Like monophthalocyanine complexes dissociation in ethanol-AcOH mixtures, the rate of diphthalocyanine complexes dissociation in sulfuric acid decreases in the lanthanides row. Gd complex is an exception. This is connected with peculiarities of structure of electron f -shells of the metal cation and essential covalence of the complexes.

When $\text{LnPc}_2\cdot$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$) concentration in sulfuric acid solution growing from $2 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ mol/l the UV-vis spectrum changes (Figure 7, compare curves 3 and 1). Absorption band of the diphthalocyanine $\text{LnPc}_2\cdot$ (420 nm) is shifted bathochromically and decreases in intensity with the complex concentration growth. High-energy absorption bands (838, 775 nm) become more intensive. This spectrum is characteristic for dimer diphthalocyanine complexes^[10,71] which also undergo dissociation in concentrated acid solutions (Figure 7).

Tb, Dy, Ho, Er, Tm diphthalocyanines are stable in 16-18 M H_2SO_4 at 298 K and in 100 % H_2SO_4 even at 400 K. In more diluted H_2SO_4 (12 M) $\text{LnPc}_2\cdot$ dissolve with destruction. When heating the diphthalocyanine solutions in 16-18 M H_2SO_4 a progressive decrease of intensity of the visible absorption band is observed. Dissociation rate constants grow with temperature increasing and with lowering H_2SO_4 concentration (Table 4S). $\log k_{\text{obs}}^T$ Values (Table 3) are proportional to $\log[\text{H}_3\text{O}^+]^n$ values.

Data of Tables 2, 3 show that the reaction orders on $[\text{H}_3\text{O}^+]$ (n) is higher 2 in the most cases and varies when varying metal nature. n value is higher when higher pK value of diphthalocyanine dissociation. State of Pr-Tm diphthalocyanines concentrated H_2SO_4 was studied by UV-vis and NMR spectroscopy in order to determine the causes of increasing the dissociation reaction order. UV-vis spectra of lanthanides diphthalocyanines of La and Y sub-groups have large differences (Table 4).

Spectra of freshly prepared sulfuric acid solutions of diphthalocyanines of lanthanides of the first group contain intensive absorption bands at 700-900 nm (Figure 8). In several hours at the room temperature (or several minutes

Table 2. Kinetic characteristics of lanthanides diphthalocyanines in 17.7 M H_2SO_4 (n – order on $[\text{H}_3\text{O}^+]$).

T, K	n		$-\log k$		T, K	n		$-\log k$		n	$-\log k$	
	NdPc ₂ ·	PrPc ₂ ·	SmPc ₂ ·	EuPc ₂ ·		GdPc ₂ ·						
298	3.2	6.4	3.2	6.4	298	4.4	8.9	6.6	10.6	6.0	9.8	
308	1.95	5.15	2.0	5.2	338	3.6	7.2	2.7	6.2	2.8	6.2	
318	1.4	4.2	1.4	4.2	348	3.3	6.7	2.9	6.15	2.7	5.8	
					358	3.7	6.9	2.4	5.4	2.07	4.9	

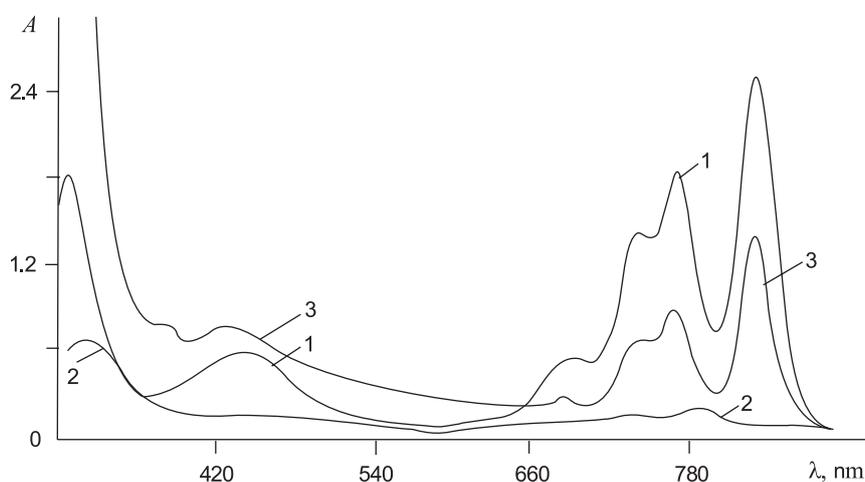


Figure 7. Electron absorption spectra of $[\text{NdPc}_2\cdot]$ in 17.7 M H_2SO_4 for $[\text{NdPc}_2\cdot] \cong 1 \cdot 10^{-4}$ (1, 2) and $2 \cdot 10^{-5}$ (3) mol/l at 298 K; time: 1 and 3 – 0; 2 – 24 hours.

Table 3. Reaction order on $[H_3O^+]$ (n) and rate constants for $LnPc_2^{\bullet}$ dissociation reaction in concentrated H_2SO_4 .

Diphthalocyanine	T, K	n	$-\log k$
$TbPc_2^{\bullet}$	338	4.1	7.6
	348	5.4	9.0
	358	4.5	7.8
$DyPc_2^{\bullet}$	338	5.6	9.4
	348	7.3	11.2
	358	7.3	10.9
$HoPc_2^{\bullet}$	338	5.2	9.3
	348	6.7	10.8
	358	5.0	8.4
$ErPc_2^{\bullet}$	338	2.2	6.4
	348	5.9	10.1
	358	6.6	10.5
$TmPc_2^{\bullet}$	338	4.3	9.3
	348	4.6	9.4
	358	5.7	10.2

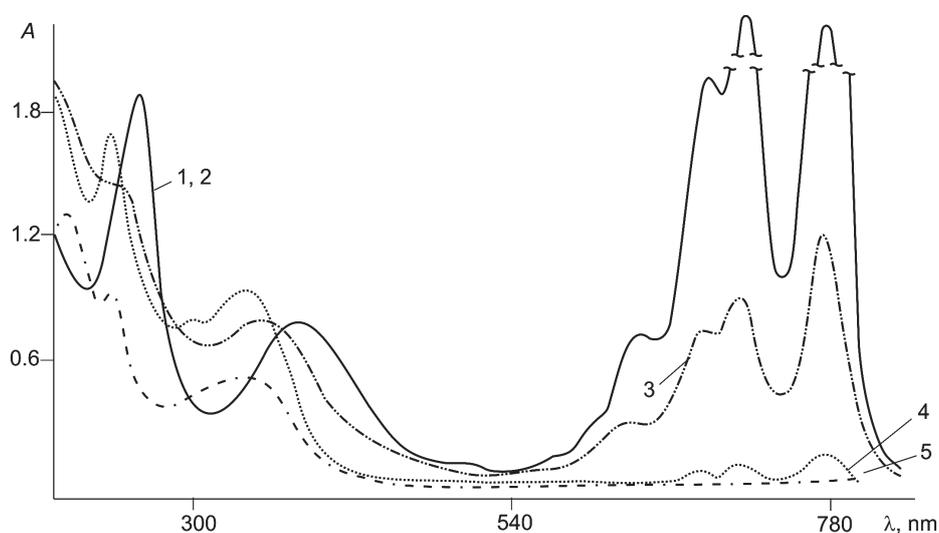
at 320 K) the spectra of Sm, Eu, Gd complexes change and become analogous in character to spectra of complexes of lanthanides from Tb to Lu ($LnPc_2^{\bullet}$) (Table 4).

Number of bands in spectra of Pr and Nd complexes does not change in time but the intensity of the absorption bands decreases because of the complex dissociation (Table 3S). The transformation of diphthalocyanine spectra in time is obviously connected with formation of dimers of diphthalocyanines in freshly prepared solutions. According to opinion of the author of [27] $LnPc_2^{\bullet}$ complexes exist as dimers in a solid state. The dimers transfer to monomeric diphthalocyanines $LnPc_2^{\bullet}$ when dissolving in concentrated H_2SO_4 , which has high dielectric constant. This is the cause of the spectra changing in time or when heating. Spectral data (Table 4, Figure 8) show that the complexes of lanthanides of the second row half are less inclined to dimer formation what could be connected with their larger susceptibility to unpaired electron delocalization as compared with the complexes of La sub-group. Thus, in dissociation conditions the complexes exist as the monomeric sandwich molecules (radicals). Proton absence, *i.e.* $LnPc_2H$ particles absence is shown by 1H NMR spectra investigations. Signals are not observed in D_2SO_4 solutions.

Table 4. Position (λ_{max}) and intensity ($\log \epsilon$) (in brackets) of adsorption bands in $LnPc_2^{\bullet}$ UV-vis spectra in 17.7 M H_2SO_4 .

Diphthalocyanine	λ_{max}						
	I	II	III	IV	V	VI	VII
$PrPc_2^{\bullet}$	837 (5.16)	775 (5.02)	745 ^a	690 ^a	443 (4.51)	305 (4.90)	250
$NdPc_2^{\bullet}$	837 (5.11)	775 (4.96)	745 ^a	690 ^a	442 (4.47)	305 (4.85)	250
$SmPc_2^{\bullet}$	–	783 (3.26)	–	–	410 (4.32)	–	250
$EuPc_2^{\bullet}$	–	–	–	–	410 (4.00)	–	250
$GdPc_2^{\bullet}$	–	–	–	–	407 (4.00)	315 ^a	250
$TbPc_2^{\bullet}$	–	–	–	–	397 (4.43)	285 (4.78)	250
$LuPc_2^{\bullet}$	–	–	–	–	395 (4.60)	285 (4.83)	253 (4.99)

^a shoulder

**Figure 8.** Electron absorption spectra of freshly prepared solutions of diphthalocyanines in 17.2 M H_2SO_4 . 1 – Pr, 2 – Nd, 3 – Sm, 4 – Ho, 5 – Yb. $[LnPc_2^{\bullet}] = 2 \cdot 10^{-5}$ mol/l.

Non-constant order on $[H_3O^+]$ of reaction (12) does not allow using pK_{obs}^{298} value for comparative estimation of the complex stability. Because of this, the pK_{obs}^{298} values for the same H_2SO_4 concentration for different complexes are shown in Figure 9.

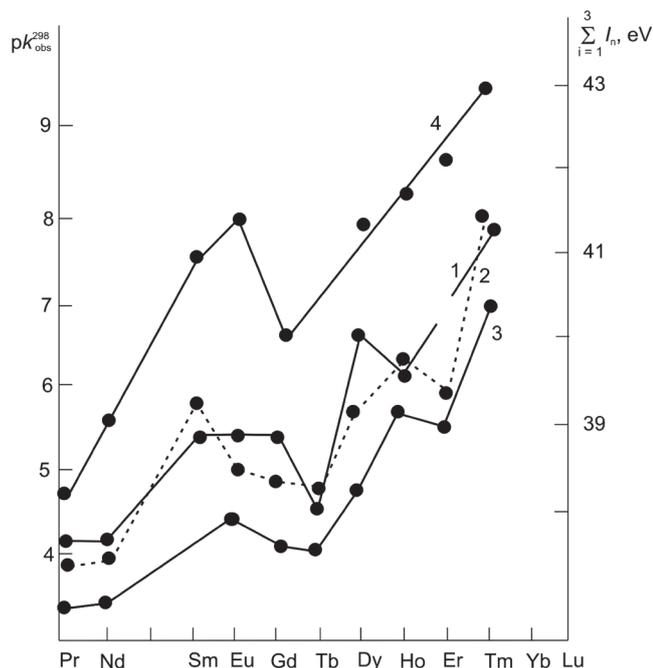


Figure 9. Dependence of pK_{obs}^{298} for $LnPc_2^*$ dissociation in H_2SO_4 (1-3) and summarizes the third potential of ionization of rare earth metals (4) on lanthanides number. $[H_2SO_4]$, mol/l: 17.7 (1), 16.9 (2), 15.9 (3).

The character of $pK_{obs}^{298} - Z$ dependence is the same as ionization potential changing in the lanthanides row (Figure 9). A deep minimum for Gd and Tb complexes is observed in all the investigated media. Eu complex is kinetically more stable than neighboring $GdPc_2^*$. Thus it could be concluded that, firstly, lanthanides diphthalocyanines must be regarded to covalent complexes and, secondly, that f -orbitals of metal take part in covalent Ln-N interaction. Complex of Gd (f^7) is essentially less stable than $EuPc_2^*$ in which one electron is needed to addition of metal f -orbital to stable f^7 state. The last apparently promotes an electron density transfer from macrocycle π -orbitals to metal (dative π -bond $N \rightarrow Ln$). It ought to point out that “tetrad effect” found for dissociation of sulfur derivatives of lanthanide phthalocyanines in acid aqueous media^[27] is not corroborated by the data presented here.

Substituted double-decker lanthanide phthalocyanines are recently in increasing interest owing to their possibility to possess the intensive absorption and $4f$ luminescence in near-infrared range.^[72,73]

Triple-Decker Metallophthalocyanines

Maximum Ln_2Pc_3 yield is achieved in the reaction of *o*-phthalonitrile with a rare earth metal chloride in 6:1 mole ratio at 563 K during 1 hour (Experimental, ^[74]). The reaction mixture was cooled, dissolved in DMF and undergone preparative chromatography procedure on Al_2O_3 . Two well divided zones of green and blue colors were observed. Every product has individual UV-vis and IR spectra. Green zone consists of sandwich structures $LnPc_2H$ (Figure 10a) described in^[9]. Compounds of blue zone are triple-decker metallophthalocyanines (Figure 10b). Each of two metal

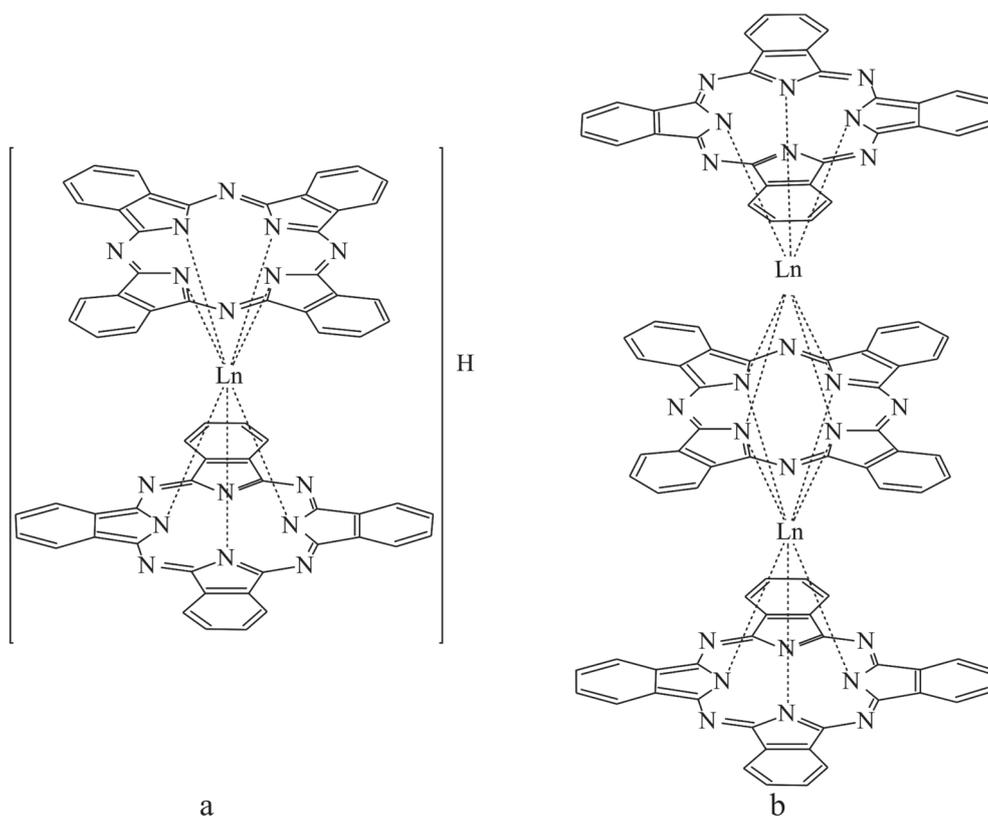


Figure 10. Structure of H-containing diphthalocyanines $LnPc_2H$ (a) and triple-decker metallophthalocyanines Ln_2Pc_3 (b).

atoms is covalently bound with two macrocycles. Two equivalent each other external macrocycles are not adequate to the third, central macrocycle. This structure is confirmed by all the obtained experimental data described below.

As a whole data about triple-decker phthalocyanine complexes structure are not numerous. There are structural data on $\text{In}_2(\text{Pc})_3$,^[75] Lu complex with tetra-15-crown-5-phthalocyanine^[18] and few heteroleptic porphyrin/phthalocyanine complexes.^[76] The first structure reported for a heteroleptic triple-decker crown-phthalocyaninato complex was represented in the work^[77] on an example of a complex $(\text{Pc})\text{Sm}[(15\text{C}5)_4\text{Pc}]\text{Sm}(\text{Pc})$. The central ligand in Lu complex is turned to 43.7° about external ligands. Average distance between macrocycle planes is 2.923 \AA . Lu atoms are localized between the ligands. Average distances between Lu atoms and coordinating N atoms of external ligands are equal 2.305 \AA . Analogous distances to the central ligand N atoms are much larger (2.560 \AA). According to the X-ray data,^[77] $(\text{Pc})\text{Sm}[(15\text{C}5)_4\text{Pc}]\text{Sm}(\text{Pc})$ has a symmetrical structure with two Sm atoms located at a nonbonding Sm-Sm distance of $3.5111(4) \text{ \AA}$. The distances between the samarium and nitrogen atoms are determined as $2.613(3)$ and $2.599(3) \text{ \AA}$ for the central bridging crown-substituted macrocycle and as $2.372(3)$, $2.385(3)$, $2.397(3)$ and $2.395(3) \text{ \AA}$ for the outer Pc ligands. The average twist angle of distorted square antiprisms is equal to 43° .

^{13}C NMR spectrum shows more than 4 signals of carbon,^[78] *i.e.* there are macrocycles of two types in the

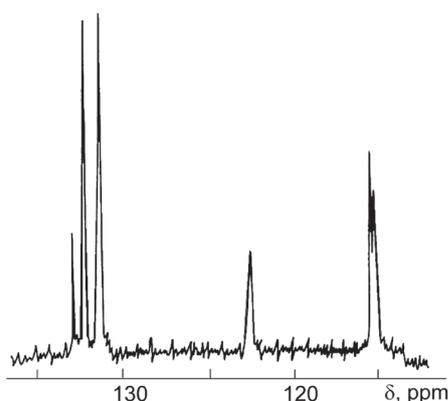


Figure 11. ^{13}C NMR (b) spectra of Tm_2Pc_3 in CDCl_3 , Bruker AM-500, 125.7 MHz.

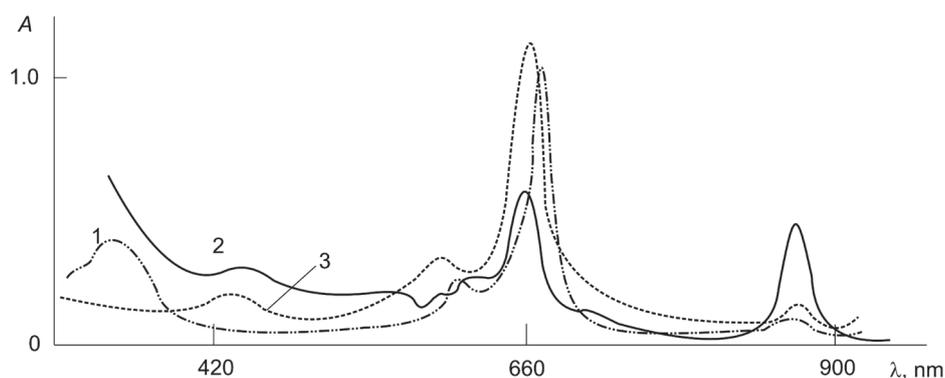


Figure 12. UV-vis spectra of (X) TmPc (1), TmPc_2H (2) and Tm_2Pc_3 (3) in benzene.

sample (one central and two equal each other external macrocycles) (Figure 11).

UV-vis spectra of complexes LnPc_2H and Ln_2Pc_3 differ from those of $(\text{X})\text{LnPc}$ (Figure 12). Typical UV-vis spectrum of metal phthalocyanine in organic solvent has long-wave maximum in the region $670\text{--}700 \text{ nm}$ ($\pi \rightarrow \pi^*$ transition,^[79] Q band) and its oscillation component of lower intensity about 610 nm . Intensive Soret band is disposed at $330\text{--}390 \text{ nm}$ (B band). In the lanthanides row the UV-vis spectra show low dependence from Ln and acido-ligand nature (Table 1). This differs the complexes with 1:1 composition from double- and triple-deckers (Table 4,^[80,81]). Both LnPc_2H and Ln_2Pc_3 exhibit typical features of the electronic absorption spectra for rare earth double- and triple-decker complexes with the new low-intensity absorption appearing at *ca.* 420 nm and hypsochromically shifted Q band at *ca.* 660 nm . The band observed in near IR at *ca.* 870 nm in such neutral solvent as benzene is also attributed to the double- and triple-decker complex absorption not only for oxidized double-decker LnPc_2^+ but for neutral LnPc_2H ^[82] and triple-decker $\text{Ln}_2(\text{PcR}_4)_2$ ($\text{R} = \text{dinaphto}[1,2\text{-}e:1',2'\text{-}g]\text{-}1,4\text{-dioxocine}$ group, $\text{P} = 5,10,15,20\text{-tetrakis}(4\text{-chlorophenyl})\text{porphyrin}$ dianion).^[76] ZINDO calculations of molecules, cations and anions of simpl ZnPc using 16-orbital model and data of magnetic circular dichroism^[83,84] show that highly symmetric ZnPc demonstrates the orbital degenerated main state: two boundary HOMO are degenerated. When the removal of one electron, on the example of the transition from ZnPc to the ZnPc^+ , takes place, the similar degeneracy lifting and the appearance of new bands of $\pi \rightarrow \pi^*$ transition within the occupied shells ($\pi^* \rightarrow \pi^*$ transition in the case of ZnPc^+) together with bathochromic shifted Q bands at 958 and 925 nm , a band of second $\pi \rightarrow \pi^*$ transition at $300\text{--}450 \text{ nm}$ and B_1 , B_2 and $n \rightarrow \pi^*$ bands are observed. Assumption of two equilibrium redox ($\text{LnPc}_2/\text{LnPc}_2\text{H}$) or acid-base ($\text{LnPc}_2^-/\text{LnPc}_2\text{H}$) form in benzene solution of considered LnPc_2H is not confirmed due to experimental data. A view of spectra 2 and 3 in Figure 12 at *ca.* 420 and 870 nm stays same after treatment of benzene solution by means of DMF-hydrazine hydrate or HCl.

IR-spectra of the obtained compounds correspond to metallophthalocyanines spectra.^[85] There are differences in IR spectra of TmPc_2H and Tm_2Pc_3 in the region of $\nu(\text{CH})$ benzene rings vibrations: $\nu(\text{CH}) = 2816, 2920, 2984, 3080 \text{ cm}^{-1}$ for TmPc_2H and $2784, 2800, 2968, 3010, 3040,$

Table 5. Kinetic parameters of dissociation of LnPc₂H complexes forming during Ln₂Pc₃ dissolving in 15.9 M H₂SO₄.

Complex	$k_{obs}^{298K} \cdot 10^3, s^{-1}$			$E,$ kJ/mol	$\Delta S^\ddagger,$ J/mol·K
	338 K	348 K	358 K		
Sm ₂ Pc ₃	0.73±0.02	1.60±0.08	2.6±0.1	63±13	-125±39
Gd ₂ Pc ₃	0.88±0.09	1.7±0.1	2.80±0.09	58±8	-140±22

Table 6. Kinetic parameters of dissociation of Th₂TPP₃ in ethanol-acetic acid solvents.

C ⁰ _{AcOH} , %	$k_{obs} \cdot 10^3, s^{-1}$				$E,$ kJ/mol	$\Delta S^\ddagger,$ J/mol·K
	298 K	333 K	343 K	353 K		
60	0.80±0.02	1.64±0.02	1.95±0.02	2.32±0.02	16.6±0.5	-256±2
50	0.50±0.02	0.996±0.03	1.17±0.02	1.39±0.04	16.2±0.8	-262±3
40	0.31±0.01	0.60±0.01	0.70±0.01	0.83±0.01	15.5±0.9	-268±3

3080 cm⁻¹ for Tm₂Pc₃, IR-spectrum of triple-decker Tm₂Pc₃ contains larger number of bands than TmPc₂H spectrum. This could be connected with the presence of one more phthalocyanine ligand.

Triple-deckers Ln₂Pc₃ dissociate in the mixed ethanol-H₂SO₄ (20:1) solvent at 298 K giving double-deckers LnPc₂H and H₂Pc. The last is insoluble in the experimental conditions and falls to sediment blue-green in color during several hours. Low stability of Ln₂Pc₃ complexes in comparison with LnPc₂ is obviously connected with mutual pushing off the macrocycles in the coordination sphere of the triple-decker complexes.

Rates of Ln₂Pc₃ dissociation in H₂SO₄ are equal to the rates of the corresponding LnPc₂H complexes dissociation. Observed kinetic parameters for dissociation of LnPc₂H complexes forming during Ln₂Pc₃ dissolving (Table 5) are close to the values^[59] obtained for LnPc₂H synthesized according to traditional method.^[9,58]

Ln₂Pc₃ complexes are not dissolved in water or undergo dissociation in it. They are weakly dissolved in the coordinating solvents. Thus the initial complex is not ionic compound as authors of works^[9,58,86,87] suppose. Analogous conditions of dissociation (ethanol-H₂SO₄ mixtures) of Ln₂Pc₃ complexes (to LnPc₂H and H₂Pc) and their monophthalocyanine (X)LnPc analogs (to Ln³⁺, X⁻ and H₂Pc) is one more evidence of the covalent nature of donor-acceptor bonds in Ln₂Pc₃.

Double- and Triple-Decker Actinide Porphyrins

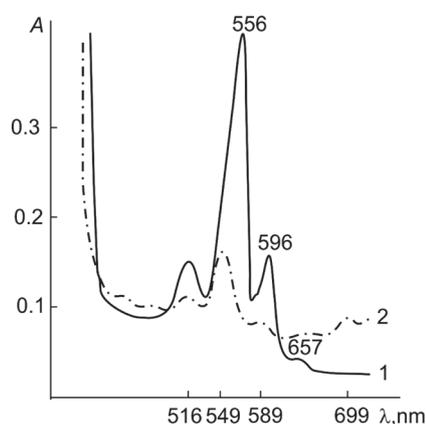
U^{IV} and Th^{IV} double-decker complexes were obtained by reaction of H₂TPP or H₂OEP with diethyl amide metal complexes.^[19,88,89] Triple-decker thorium(III) tetraphenylporphyrin with structure analogous to Ln₂Pc₃ (Figure 10b) was obtained for the first time by the authors of the present work in 1991.^[90]

The coordination geometry of Th(TPP)₂ is a distorted square-antiprism where the thorium center is displaced by 1.47 Å from each of the porphyrin N₄ planes; the porphyrin N₄ planes are therefore separated by 2.94 Å.^[91] In analogous octaethylporphyrin complex Th(OEP)₂ the two porphyrin planes are separated by 2.89 Å in a nearly perfect square-antiprismatic coordination geometry around the thorium center. The porphyrin macrocycles, held in such close

proximity, interact electronically as shown by a blue shift in the porphyrin Soret band and by unusually low oxidation potentials relative to related monoporphyrin species.^[91]

Thorium(IV) complexes Th^{IV}(TPP)₂ and Th^{III}(TPP)₃ differ in solubility, UV-vis spectra (Figure 13) and reactivity with acids (Table 6).^[90] Th(TPP)₂ is soluble in ethanol whereas triple-decker complex Th₂(TPP)₃ is insoluble in one. UV-vis spectra of both complexes have specific features compared to spectra of (X)ThTPP. There is an additional intensive band at 426 nm in Th(TPP)₂ spectrum and a wide band at 699 nm with low intensity in Th₂(TPP)₃ spectrum. The Soret bands in both spectra are bathochromically shifted and split in two with λ_{max} equal 411 and 398 nm. Visible absorption bands in Th(TPP)₂ spectrum are bathochromically shifted as compared to those of Th₂(TPP)₃. Analogous regularities is observed for Ce(OEP)₂ and Ce₂(OEP)₃ complexes.^[79] Appearance of wide absorption bands in the region higher than 650 nm in spectra of metalloporphyrins with two and more macrocycles the authors of^[92] explain by resonance interaction of the porphyrin ligands.

Th(TPP)₂ dissociates in ethanol-AcOH as well as in benzene-AcOH solutions with acid content 50–90 vol. %. Th₂(TPP)₃ dissociates with measurable rate in the same mixtures with lesser acid content (25–60 vol. %) (Table 6). Like in the case of Ln₂Pc₃ the triple-decker Th complex is less stable compared with Th(TPP)₂.

**Figure 13.** UV-vis spectra of Th(TPP)₂ in ethanol (1) and Th₂(TPP)₃ in benzene (2).

Triple-decker uranium complex with tetraphenylporphyrin (H_2TPP) was synthesized and studied for the first time in the laboratory of the authors in 2003.^[93] The reaction between H_2TPP and $UO_2(OAc)_2$ in molar ratio 1:10 in a refluxing benzonitrile medium during 19 hours yields two complexes $U(TPP)_2$ and $U_2(TPP)_3$. The complexes can be isolated by thin layer chromatography (Al_2O_3) using benzene-chloroform (1:4) mixture. Individual complexes can be obtained also after the reaction mixture dissolving in ethanol after liquid chromatography on an Al_2O_3 column with $CHCl_3$. Complex $U(TPP)_2$ is soluble in ethanol whereas $U_2(TPP)_3$ complex stays in a solid phase. Filtration gives a green-violet solid residue of $U_2(TPP)_3$ (18 % yield). After ethanol evaporation from the filtrate a pink-violet powder of $U(TPP)_2$ is obtained (14 % yield).

$U^{IV}(TPP)_2$ and $U^{III}_2(TPP)_3$ are stable in air and have spectral and chemical properties which are in agreement with a 1:2 and 2:3 uranium/tetraphenylporphyrin ratios. An analogous synthetic procedure in phenol gives double- and triple-decker uranium tetraphenylporphyrins mixture in 3 hours and 40 minutes.

The NMR spectrum of the double-decker complex agrees with the literature data for $Th^{IV}(TPP)_2$ ^[88] and $Ce^{IV}(TTP)_2$ (TTP – tetratolylporphyrin dianion).^[94] The NMR spectrum of the triple-decker complex shows ten peaks what is in accord with ten kinds of protons: two – C_4H_2N (one inner and two outer macrocycles), two – $p-C_6H_5$, three – $o-C_6H_5$, and three – $m-C_6H_5$.

Double-decker and triple-decker complexes have different UV-vis and IR spectra. The IR spectra of double- and triple-decker complexes are more complicated in regions 700 (γ C-H of benzene rings), 800 (γ C-H of pyrrole rings), 990–1010 (δ C-H, ν C-C, ν C-N of pyrrole rings), 1540–1550 cm^{-1} (pyrrole ring stretching) than these of lanthanide monoporphyrinates (X) $Ln^{III}TPP$.^[95] The frequencies of vibrations $\nu(U-N)$ (430 and 436 cm^{-1} for $U^{IV}(TPP)_2$ and $U^{III}_2(TPP)_3$ respectively) are higher than $\nu(Ln-N)$ (Ln : Sm–Lu, 421–429 cm^{-1}), which is connected with growth of the strength constant of U-N bond in the complexes of double- and triple-decker structures. There are no bands at 212–216 cm^{-1} ($\nu(M-Cl)$, $(M-O)$) in $U^{IV}(TPP)_2$ and $U^{III}_2(TPP)_3$ spectra because of the absence of acido ligands X^- (Cl^- or $C_6H_5O^-$) in the complexes.

UV-vis spectra of both uranium complexes have specific features (Figures 14, 15). There are additional wide band at 657.9 nm of low intensity and an intensive band at 462 nm in $U^{III}_2(TPP)_3$ spectrum as compared with (X) $Ln^{III}TPP$ spectra. An extra band at 462 nm may be due to a porphyrin-to-uranium(III) charge-transfer transition. This could be connected with striving of the two uranium atoms with a coordination number of 8 for stable $f^4(a_{2u}^1t_{1u}^3)$ configuration in the complex.

The double-decker $U^{IV}(TPP)_2$ complex has a "normal" metalloporphyrin UV-vis spectrum. Absorption bands in the visible region $Q(0,0)$ are bathochromically shifted as compared to those of (X) $Ln^{III}TPP$. For example for (Cl) $Lu^{III}TPP$, λ_{max} ($\log \epsilon$) are 585(3.5), 547(4.0), 510(3.6), 416(5.5) nm in ethanol.^[95] No band is found between 450 and 500 nm in $U^{IV}(TPP)_2$ spectrum. Analogous regularities were observed for $Ce^{IV}(OEP)_2$ and $Ce^{III}_2(OEP)_3$ complexes for which the crystal structure determination was described.^[80]

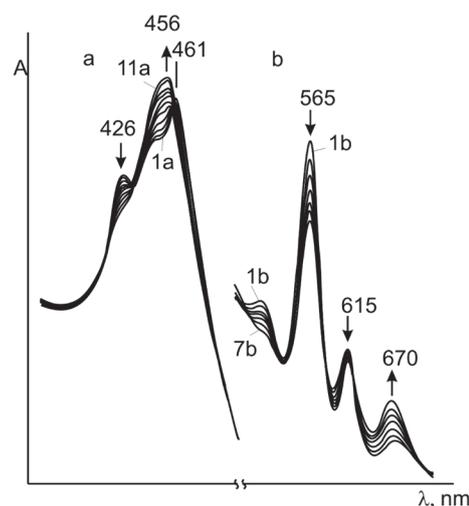


Figure 14. UV-vis spectra during dissociation of $U^{III}_2(TPP)_3$ (a) in benzene – 40 (%) AcOH, 308 K, 0 – 1 hour and $U^{IV}(TPP)_2$ (b), in ethanol – 55 (%) AcOH, 353 K, 0 – 4 hours. Curve 1a corresponds to $U^{III}_2(TPP)_3$, 1b – $U^{IV}(TPP)_2$, 11a – $U^{IV}(TPP)_2 + H_4TPP^{2+}$, 7b – $(AcO)_2U^{IV}TPP + H_4TPP^{2+}$.

Appearance of wide absorption bands in the region higher 650 nm in the spectra of metalloporphyrins with two and more macrocycles was explained^[92] by resonance interaction of the porphyrin ligands. The corresponding broad bands in the double-decker complex $U^{IV}(TPP)_2$ is between 950 and 1000 nm.

Chemical properties of double- and triple-decker porphyrin complexes are essentially different. The complexes $U^{IV}(TPP)_2$ and $U^{III}_2(TPP)_3$ dissociate with a spectrophotometrically measured rate only in the presence of AcOH in concentrations higher 40 %. $U^{IV}(TPP)_2$ dissociates in mixed ethanol-AcOH solvent at 330–350 K, whereas $U^{III}_2(TPP)_3$ dissociates in benzene-AcOH media and 300–320 K. The dissociation rate constants of formally the first order (k_{obs}^{298K}) at a 50% AcOH concentration in the mentioned solvents are equal 10^{-4} and $0.5 \cdot 10^{-3} s^{-1}$ for $U(TPP)_2$ and $U_2(TPP)_3$, respectively. Taking in to account that the reactivity of the complexes changes greatly when changing from one mixed solvent to another,^[96] it is possible to note an enormous difference in stability of the double- and triple-decker complexes. The UV-vis absorption spectra of $U^{IV}(TPP)_2$ and $U^{III}_2(TPP)_3$ during dissociation process (Figure 14) show a series of bands smoothly passing from the spectrum of the initial complex to another form of the complex: $(AcO)_2U^{IV}(TPP)$ and $U^{IV}(TPP)_2$, respectively. The spectra of the reaction mixtures contain in addition absorption bands of free porphyrin in protonated form H_4TPP^{2+} . The bands at 456 and 670 nm correspond to H_4TPP^{2+} . The reaction products were identified by UV-vis spectra after extracting the products from the reaction mixture, their purifying from AcOH traces and column chromatography on Al_2O_3 with $CHCl_3$. The double-decker complex band at 516.0 nm (Figure 15) is absent in the absorption spectrum of product of its dissociation $(AcO)_2U^{IV}TPP$ (Figure 14). The UV-vis spectrum of $(AcO)_2U^{IV}TPP$ is in agreement with the literature data for (Cl) $U^{IV}TPP$.^[89]

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