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Статья

Synthesis of Stable Dimeric Phthalocyanine *J*−Type Complexes and Investigation of Their Nucleophilic Properties

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Dedicated to Professor Gelij Vasilievich Ponomarev on the Occasion of his 75th Birthday

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Metallation of the low-symmetry 2-hydroxy-9(10),16(17),23(24)-tri-tert-butylphthalocyanine (ligand) with zinc and magnesium acetate salts in the medium of n-hexanol has resulted in obtaining the thermally stable dimeric J-type complexes constructed from identical macrocycles with a parallel orientation and geometrical rotation by an angle of 130–132 deg. Thermoanalytical study has demonstrated high stability (up to 450 °C) of dimeric complexes, and spectropotentiometry has identified significant differences in their nucleophilic properties as well.

Keywords: Phthalocyanine, *J*-type dimer, thermal analysis, spectropotentiometry.

Синтез стабильных димерных фталоцианиновых комплексов *J*−типа и исследование их нуклеофильных свойств

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Путем металлирования низкосимметричного лиганда 2-гидрокси-9(10),16(17),23(24)-три-трет-бутил-фталоцианина ацетатами цинка или магния в среде н-гексилового спирта получены термически стабильные димерные комплексы J-типа, построенные из идентичных макроциклов с параллельной ориентацией и гео-метрическим разворотом на угол 130-132°. Термоаналитические исследования показали высокий предел ста-бильности комплексов цинка и магния (вплоть до 450 °C), а при помощи спектропотенциометрии выявлены существенные различия в их нуклеофильных свойствах.

Ключевые слова: Фталоцианин, димер *J*-типа, термоанализ, спектропотенциометрия.

Introduction

Phthalocyanines and related macrocyclic compounds have long attracted the interest because of the unique features of their structure. Phthalocyanine complexes have great potential for use in different areas such as electrochromic devices, chemical sensors and catalysts, nonlinear optical materials as well as the sensitizers for photodynamic cancer therapy.[1,2] Self-organization of the phthalocyanines to form ordered aggregates of nanoscale level opens up the possibility of creating advanced materials with desired linear and nonlinear optical properties. Two types of ordered assemblies – *H*- and *J*- have been known today, with their diversity being depended on the direction of the dipole moment of the interacting monomer components in the process of transition from the ground to the excited states. [3] According to the Kasha's molecular exciton theory,[4] if the angle between the polarization direction of the monomer and the line passing through the center of the aggregate (*e.g.* slip angle), is more than 54.7°, such aggregate (*H*-type) demonstrates the presence of an additional band in the UV-Vis spectrum which is blue-shifted towards the major intense band (*Q*-band). When the slip angle is less than 54.7°, in the UV-Vis spectrum of aggregates (*J*-type), an additional band is red-shifted with respect to the *Q*-band. A principal difference in the spectral properties of both types of aggregates consists in the fact that *J*-aggregates are well fluorescent, while *H*-aggregates are not.[5] The formation of aggregates with ordered structure is due to a number of factors, mainly, the nature of the solvent, complexing metal and peripheral substituents as well. Thus, UV-Vis spectroscopy has demonstrated the transformation of the monomeric phthalocyanine complexes bearing four peripheral aryloxy substituents to the *J*-type aggregates upon addition of pyridine to the solutions in chloroform.[6] In the case of the monomeric complexes with only one peripheral polar substituent (*e.g.* low-symmetry phthalocyanines), instead of aggregates the dimers of similar structure are formed.[3,7] Dimers and aggregates of *J*-type are of interest for a number of studies, and only to date they were able to be isolated from the solutions as individual compounds. So, we have synthesized, for the first time, of thermally stable dimeric *J*-type phthalocyanine complexes and studied of axial coordination and peripheral functionalization processes as well.[8-10] The present work is devoted to the study of nucleophilic properties of the *tert*-butyl substituted phthalocyanine complexes of *J*-type using spectropotentiometric titration.

Experimental

General

In this work, all the solvents and reagents obtained from Aldrich® were utilized without purification. Synthesis and analytical characteristics of dimeric complex **2a** were described earlier.[8,9] UV-Vis spectra of phthalocyanines **2a**,**b** were recorded on a Hitachi U-2900 spectrophotometer in the range of 190-1100 nm, using 1 cm thickness quartz cuvette and tetrahydrofuran as a solvent. ^{1}H NMR spectrum (500 MHz) of **2b** was registered on a Bruker Avance III 500 MHz spectrometer. Mass spectra were recorded on

an Autoflex II device (MALDI-TOF method, no matrix). Differential calorimetric analysis (DSC) was performed on a differential scanning calorimeter Netzsch DSC 204 F1 Phoenix® under argon at a heating rate of 10 °C/min in the range of 100-600 °C. Quantum chemical calculations were carried out by the DFT method using PBE[11] density functional and cc-pVDZ[12] basis set with the program PRIRODA.[13] *tert*-Butyl substituents were replaced with the hydrogen atoms in order to reduce calculation time.

Spectropotentiometry

Analytical studies were performed with the specially designed cell.[14] The protonation equilibria have been investigated at 298 K by titration of complex **2b** with perchloric acid in methanol, and the processes have been controlled with the UV-Vis spectroscopy. The glass electrode was graduated in aqueous buffer solutions according to the equation (1), adjusted for the change of the activity coefficient of the proton in methanol.[15]

$$pH_{MeOH} = pH_{H_2O} + 2.34 \qquad (1)$$

$$B + H^+ \underset{\longleftarrow}{\overset{K_{b1}}{\longrightarrow}} + HB^+ \qquad (2)$$

$$HB^+ + H^+ \underset{\longleftarrow}{\overset{K_{b2}}{\longrightarrow}} + H_2B^{2+} \qquad (3)$$

$$A_t = \frac{A_{0(B)} + A_{0(HB^+)} \cdot K_{b_1} \cdot 10^{-pH} + A_{0(H_2B^{2+})} \cdot K_{b_1} \cdot K_{b_2} \cdot 10^{-2pH}}{1 + K_{b_1} \cdot 10^{-pH} + K_{b_1} \cdot K_{b_2} \cdot 10^{-2pH}} \qquad (4)$$

$$A_t = \frac{A_{0(B)} + A_{0(HB^+)} \cdot K_{b_1} \cdot 10^{-pH}}{1 + K_{b_1} \cdot 10^{-pH}} \qquad (5)$$

A_t – is the current value of optical density of the solution on the analytical wavelength; $A_{0(B)}$, $A_{0(HB^+)}$ and $A_{0(H_2B^{2+})}$ – are optical densities of the components corresponding to the analytical concentration of phthalocyanine; K_{b1} and K_{b2} – are the constants of reactions (2) and (3).

To the spectropotentiometric cell the solution of phthalocyanine **2b** in methanol (90 mL) with the given optical density (*A* = 1.05 a.u.) was placed. The solution was thermostated at 298 K to achieve stable indications of the p*H*-meter followed by recording the UV-Vis spectrum. Then, an aqueous solution of HClO$_4$ was added to change p*H* of the solution by 0.03 units. After the equilibrium has been reached, the p*H* values were registered, with the corresponding UV-Vis spectra being recorded. This procedure was repeated until the experiment has been completed. Calculation of the equilibrium protonation constants in the equations (2) and (3) were determined by adjusting the parameters in equation (4) using the SigmaPlot® software package. Equation (5) is the special case when a single protonation being observed.

Synthesis

Bis(2-hydroxy-9(10),16(17),23(24)-tri-tert-butylphthalo-cyanine) complex of Mg (complex 2b). To a solution of ligand **1** (250 mg, 0.36 mmol) in *n*-hexanol (5 ml) lithium methoxide (70 mg, 1.79 mmol) was added, and the reaction mixture was refluxed for 20 min. After that, Mg(OAc)$_2$·4H$_2$O (150 mg, 0.72 mmol) was added to the solution and the refluxing was continued for 30 min. After completion of the reaction (UV-Vis control), the solvent was removed under vacuum, with the residue being washed with methanol followed by chromatographic separation of the phthalocyanine products on a crosslinked polymer BIORAD® Bio-Beads SX-1 using tetrahydrofuran as an eluent to give 160 mg (62 %) of the target compound **2b**. MS (MALDI-TOF), *m/z*: 1440 [M]+. ^{1}H NMR

(CCl$_4$+4% DMSO-*d*$_6$) δ ppm: 1.1–1.9 (m, 54H, C(CH$_3$)$_3$), 7.2–8.4 and 8.6–9.7 (two m, ∑ 24H, Ar), 9.8–10.1 (br. s, 2H, OH). UV-Vis (THF) λ$_{max}$ nm: 289, 349, 625, 673, 696.

Results and Discussion

Interaction of 2-hydroxy-9(10),16(17),23(24)-tri-*tert*-butylphthalocyanine ligand (**1**) with the zinc and magnesium acetate salts in the presence of lithium methoxide has resulted in corresponding dimeric complexes **2a,b** being obtained.

In the MALDI-TOF mass spectra of target compounds only molecular ions peaks were observed with *m/z* 1522 (for complex **2a**) and 1440 (for complex **2b**), indicating a high stability of the compounds even under strong laser radiation, required for desorption ionization during recording the spectra (Figure 1a), while no fragmentation was detected. High stability of dimeric complexes **2a,b** is due to the intramolecular π-π- interactions and coordination bonds between the central metal ions and oxygen of the OH groups.[9] Thus, according to the thermoanalytical studies, stability of dimeric complex **2a** was found to be in the same range as that for the corresponding monomeric derivative (250–450 °C), with a significant energy barrier (>100 kcal/mol) being illustrated by the theoretical study of a hypothetical degradation process. The curve of differential scanning calorimetry (DSC, Figure 1b) reveals two peaks corresponding to the partial elimination of the peripheral *tert*-butyl groups conjugated with the irreversible dissociation of the dimer to form monomer, and complete destruction of the phthalocyanine macrocycle.[9] For magnesium complex **2b**, the first destruction stage is observed over a wider range (250–400 °C) than that for a similar zinc complex (250–350 °C), which may be due to the more advanced potential energy surface (PES) of the macrocycles slippage.[17] Preliminary analysis has revealed the greater number of local minima that, along with a larger distortion of the structure makes it difficult to destroy of the dimeric molecule. Thus, complex **2b** is characterized by minimal distance between the oxygen and magnesium atoms (2.25 Å), that leads to ion displacement from the plane of the macrocycle and distortion of the geometry of the latter (Table 1, Figure 1c). The total stabilization energy of the structure of complex **2b** was calculated to be 17.1 kcal/mol (ΔE$_{total}$), that is more than 2 times higher compared to **2a**.[8] For this reason, magnesium
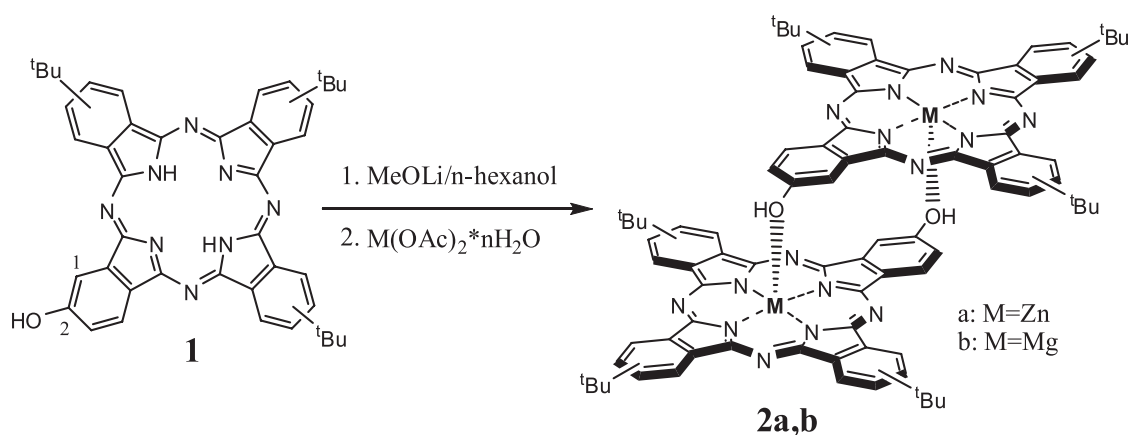
Scheme 1. Synthesis of dimeric *J*-type complexes **2a**,**b**.

Table 1. The geometrical parameters of the DFT-optimized models of dimeric complexes **2a,b**, in which the *tert*-butyl groups were replaced with the hydrogen atoms to reduce a calculation time.

Property	Model[a]	
	A	**B**
Symmetry point group	C$_2$	C$_2$
Type of a dimer	*J*	*J*
Angle of slippage, deg.	22.8	20.4
Tilt angle, deg.	12.1	16.7
The angle of relative rotation of the macrocycles, deg.	130.4	131.9
The distance between the central metal ion of the first macrocycle and O atom of the OH group of the second one, Å	2.67	2.25
The distance between the centroid of a macrocycle and the complexing metal ion, Å	0.13	0.42
The distance between the macrocycles, Å	3.87	3.82
The angle between the planes that pass through the macrocycle and the isoindoline fragment bearing OH group of the same macrocycle, deg.[b]	12.8	15.7

[a] The models **A** and **B** correspond to compounds **2a** and **2b** respectively.
[b] Denotes the distortion of the macrocycle.

dimeric complex is more stable than the corresponding zinc complex **2a**.

The specific structure of the dimeric *J*-type complexes **2a,b** results not only in their high stability. Study of their spectral properties with the UV-Vis spectroscopy has revealed a number of features, which are not peculiar for monomeric derivatives. In particular, the presence of additional band (*J*-band), which is red-shifted with respect to the *Q*-band (Figure 1d), confirms the fact that dimers **2a,b** refer to a *J*-type; at the same time the fluorescence studies of **2a** proved the presence in the structure of coordination bonds Zn···O.[9] However, the study of the nature of intramolecular interactions of the macrocycles we consider as a separate problem. So, the possibility of mutual displacement of the macrocycles, which previously was observed during the scanning the PES of their slippage, was then confirmed in the study of the fluorescent properties of dimer **2a** and the corresponding monomer.[9] This result explains, in particular, a reduction in fluorescence quantum yield of the dimers as compared to monomers. Slippage of the macrocycles is thermodynamically fixed near the global minimum on the PES corresponding to model structures **A** and **B** (Figure 1c).[16] With this molecular structure, when the distance between

the macrocycles does not exceed 4 Å (see Table 1), the specific intermolecular contacts, or π-π- interactions, could be observed. Thus, study of the protonation equilibrium with the spectropotentiometric method showed that the phthalocyanine macrocycles in dimer **2a** represent an uniform molecular system.[17] Similar investigations were carried out for complex **2b**. The results are shown in Figure 2 and Table 2.

Table 2. The basicity constants (K_b) of dimers **2a,b** at 298 K.

Complex	lgK_{b1}	lgK_{b2}
2a[18]	4.56±0.03	3.40±0.02
2b	4.81±0.03	–

Upon acidification of methanol solution of **2b** with the perchloric acid in the area preceding the titration curve the blue-shifting of the absorption bands was observed (Figure 2) which is not associated with the protonation of a dimeric chromophore. A possible reason for this is that the protolytic processes could affect the extracoordination sphere of the magnesium cation. Under the experimental
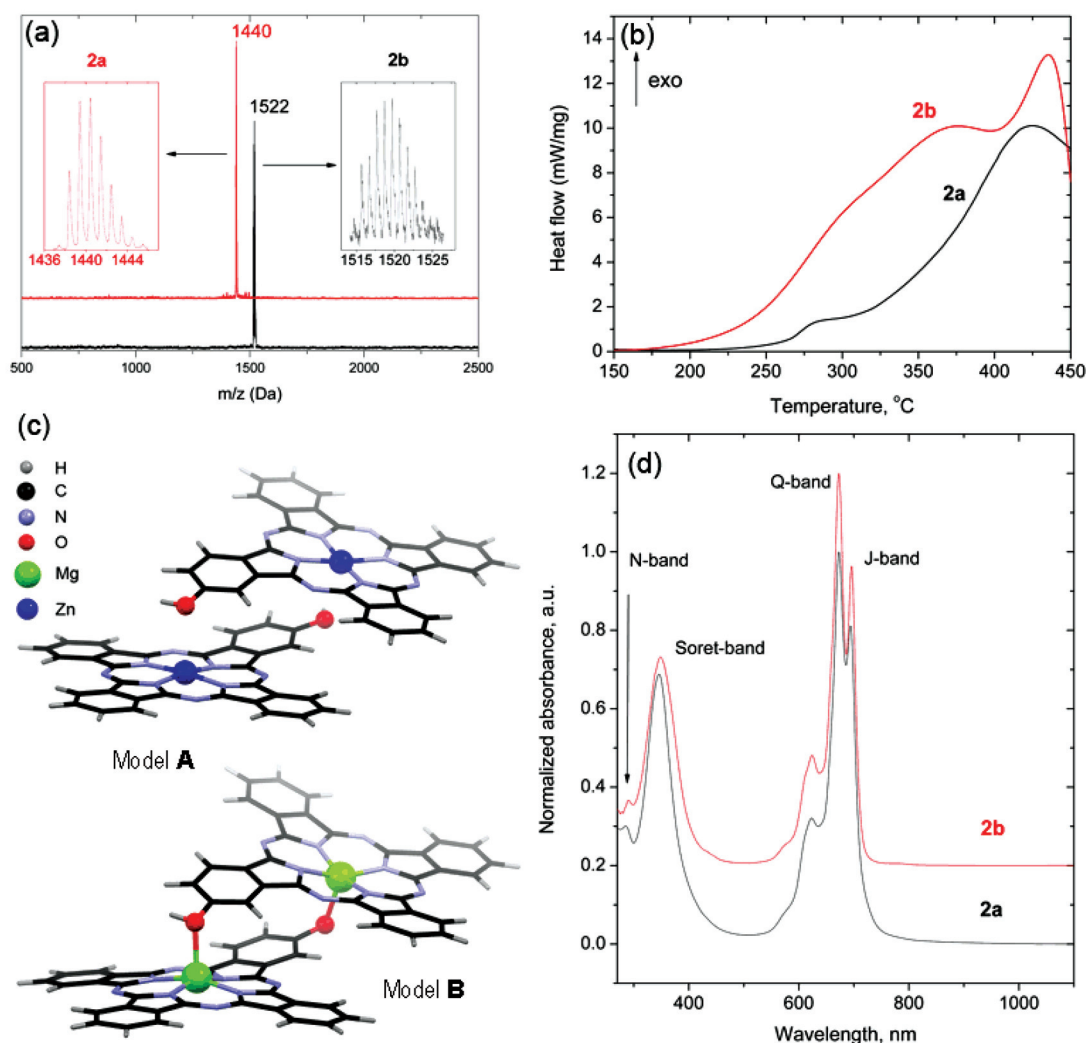

Figure 1. MALDI-TOF mass spectra (a), DSC curves (b), DFT-optimized models (c) and UV-Vis spectra in THF (d) of dimeric complexes **2a,b**.
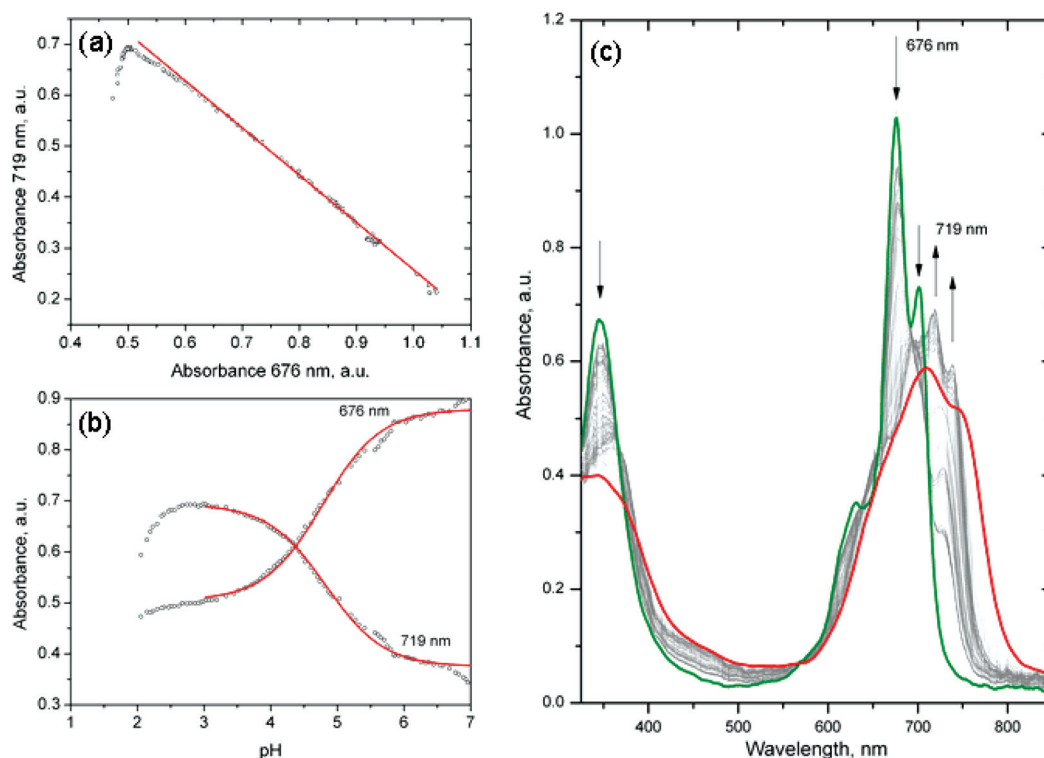
Figure 2. The results of the spectropotentiometric titration of **2b** with perchloric acid in methanol: (a) – correlation dependence of the optical densities at different absorption maxima, (b) – titration curves (the experimental dependencies are shown as dots, and the model titration curves are represented as a solid line), (c) – the changes in the UV-Vis spectra in the range of p*H* from 7 to 2.

conditions we were able to fix only 90 % of the titration curve, then **2b**, probably, begins to collapse as a result of further protonation. The dimeric complex is singly protonated according to equation (2) (see *Experimental*). This is indicated by the family of isosbestic points at 360, 635, 692 and 711 nm respectively, while the linear correlation confirms the presence of only one balance between a pair of light absorbing centers of **2b** and **2b**·H⁺. Titration curve obeys the equations (2) and (5) for the first protonation stage and, therefore, the only macrocycle in **2b** is subjected to the protonation. Spectrophotometric protonation constants of dimers **2a,b** in methanol at 298 K are shown in Table 2. Comparison of lgK_{b1} values for **2a,b** gives an indication of slightly higher basicity of exocyclic *meso*-N atoms of the magnesium dimer (lgK_{b1} = 4.81) in respect with the same of zinc dimer (lgK_{b1} = 4.56), that is associated with a stronger ionic bond character of Mg–N compared to Zn–N. Absence of the second protonation stage of **2b** could serve as a confirmation of the chemical destruction of the complex, since we failed to isolate this compound with the initial spectral characteristics upon deprotonation. We should note only that the phthalocyanine dimeric structure is retained in the presence of strong acid. The study of this phenomenon will be continued in our future works.

Conclusions

In this paper, a new thermally stable dimeric phthalocyanine complex of *J*-type (compound **2b**) was obtained. It is

shown that the thermal stability of the *J*-type phthalocyanine dimers depends on the nature of the complexing metal, but in general, the high thermal stability of these compounds is due to their structural features. Spectropotentiometric study has revealed that despite the higher thermal stability of the magnesium dimeric complex compared to the corresponding zinc derivative, the chemical stability of a former is substantially lower. According to the quantum chemical calculations, the dimeric structures are characterized by the relative shifting of the macrocycles resulted in unusual spectral properties of the complexes.

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