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Influence of Central *versus* Peripheral Coordination of Pt and Pd Atoms on Physical–Chemical Properties of Octa–4,5–carboxyphthalocyanines

Nina A. Kuznetsova,[@] Roman A. Bulgakov, Ludmila I. Solovyova,
Ekaterina N. Shevchenko, Oleg L. Kaliya, and Evgeny A. Lukyanets

Organic Intermediates and Dyes Institute, 123995 Moscow, Russia
[@]Corresponding author E-mail: lab32@niopik.ru

New Pt^{II} and Pd^{II} complexes of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine as well as covalent tetraconjugates of diaqua palladium(II) and octacarboxy substituted zinc phthalocyanine were synthesized and characterized by elemental analysis, UV-Vis and IR spectroscopy. Their properties (solubility, absorption and luminescence, singlet oxygen quantum yields and photostability) are herein reported. It was found that introduction of Pd or Pt atom to the phthalocyanine core has a profound effect, while modification of the periphery with four fragments of diaqua platinum or diaqua palladium has only a limited effect on photochemical and photophysical properties of metallophthalocyanines. These data demonstrate the higher sensitivity of the phthalocyanine electronic structure, their singlet and triplet excited states and the probability of transitions between them to modification of the core than of the periphery.

Keywords: Octacarboxyphthalocyanine, platinum, palladium, complex, covalent conjugate, photophysics, photochemistry.

Сравнение влияния центральной и периферической координации атомов Pt и Pd на физико–химические свойства окта–4,5–карбоксифталоцианинов

Н. А. Кузнецова,[@] Р. А. Булгаков, Л. И. Соловьева, Е. Н. Шевченко, О. Л. Калия,
Е. А. Лукьянец

Федеральное государственное унитарное предприятие «Научно-исследовательский институт органических полупродуктов и красителей» (ФГУП ГНЦ «НИОПИК»), 123995 Москва, Россия
[@]E-mail: lab32@niopik.ru

Впервые синтезированы и охарактеризованы данными элементного анализа, электронной, ИК-спектроскопии октакарбоксифталоцианины платины и палладия, а также тетраконъюгат октакарбоксифталоцианина цинка с диаквапалладием. Изучены их спектрально-люминесцентные и фотохимические свойства. Внедрение одного атома Pd или Pt в центр оказывает значительно большее влияние на электронные спектры поглощения, флуоресценцию, генерацию синглетного кислорода и фотостабильность фталоцианина по сравнению с внедрением четырех таких атомов по периферии в виде ковалентно присоединенных фрагментов диаквaплатины и диаквапалладия. Полученные результаты демонстрируют большую чувствительность электронной структуры макроцикла, нижних возбужденных синглетного и триплетного состояний металлофталоцианинов и вероятности переходов между ними к модификации центра, чем периферии.

Ключевые слова: Октакарбоксифталоцианин, платина, палладий, комплекс, ковалентный конъюгат, фотофизика, фотохимия.

Introduction

Phthalocyanines (Pc) are known to have wide application in various areas – as pigments and dyes,[1] non-linear optical materials,[2] gas sensors,[3] catalysts and photocatalysts[4] and as photosensitizers for photodynamic therapy.[5,6] The structure of phthalocyanines can be modified in several ways to adjust their valuable properties. Various substituents can be introduced into the benzene rings (electrophilic substitution, aza-substitution, condensation with the formation of additional rings), while the core can have the central atom or its axial ligands replaced by other ones. The most important of the forementioned structural factors influencing the catalytic and photocatalytic properties is the nature of the complexed metal atom. Notably, some recently developed novel catalysts and photocatalysts are based on bimetallic porphyrins, Pc and their analogs that include a metal ion not only in their core but in the periphery, which is achieved through coordination with the substituents.[7-11] In particular, we had earlier obtained[12,13] a number of bimetallic covalent conjugates of Pt^{II} with phthalocyanines that present interest for the development of novel anti-cancer double action agents that combine photodynamic and catalytic[12] properties of phthalocyanines with the cytotoxicity of platinum.

The current study describes and compares the influence of Pt^{II} and Pd^{II} coordination with the Pc core and periphery on the physico-chemical and photochemical properties of the corresponding complexes. In order to achieve the goal of the study, novel compounds were synthesized – platinum and palladium octacarboxyphthalocyanines ($PtPc^{oc}$ and $PdPc^{oc}$), their properties were compared to the ones of the primary compound $ZnPc^{oc}$, which exerts photodynamic properties, and to covalent peripheral conjugates of $ZnPc^{oc}$ with diaqua platinum and diaqua palladium ($ZnPc^{oc}Pt_4(H_2O)_8$ and $ZnPc^{oc}Pd_4(H_2O)_8$). The compound $ZnPc^{oc}Pd_4(H_2O)_8$ was synthesized in the course of the current study as novel.

The studied phthalocyanine complexes are presented in Figure 1.

Experimental

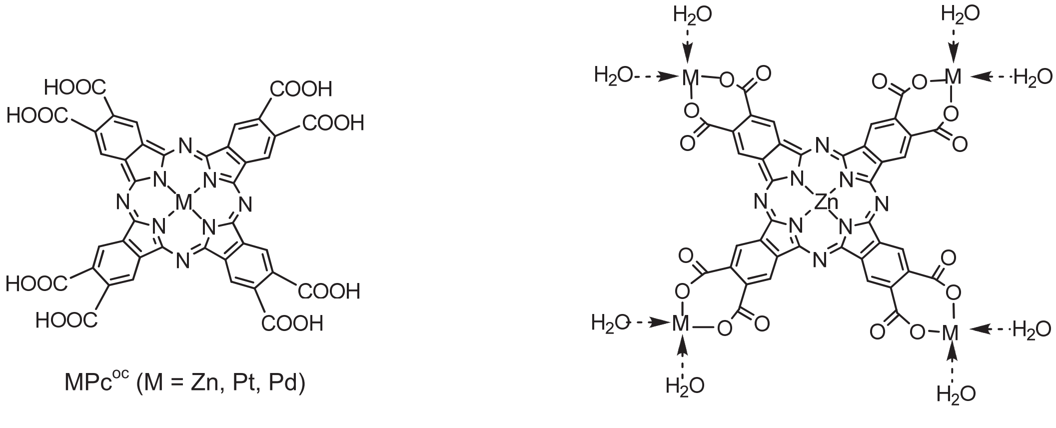
Syntheses

In the current work we used dimethyl sulfoxide (chem.pur., from Spectr-Khim LLC), 1,3-diphenylisobenzofuran and 1,4-diazabicyclo[2.2.2]octane (DABCO) from Fluka, and unsubstituted zinc phthalocyanine from Organic Intermediates and Dyes Institute.

Octasodium salt of zinc 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine ($ZnPc^{oc}Na_8$) and the covalent tetraconjugate of zinc phthalocyanine with diaqua platinum ($ZnPc^{oc}Pt_4(H_2O)_8$) were synthesized by known procedures.[13,14]

Covalent tetraconjugate of zinc phthalocyanine with diaqua palladium ($ZnPc^{oc}Pd_4(H_2O)_8$). The compound was synthesized in an analogous manner to the published procedure[13] for the diaqua platinum conjugate. To a solution of $ZnPc^{oc}Na_8$ (30 mg, 0.02714 mmol) in 3 ml of H_2O was added K_2PdCl_4, which had been obtained immediately before the synthesis from 19.26 mg (0.1086 mmol) $PdCl_2$ and 16.19 mg (0.272 mmol) KCl in 3 ml of H_2O. The reaction mixture was left for 3 hrs at a temperature of about 55 °C. The product was precipitated with a mixture of ethanol and methanol (1:2). The formed precipitate was filtered, washed with a mixture of H_2O:MeOH:EtOH = 1:1:2 and dried in vacuo at 60 °C. Yield – 27.5 mg (68 %). Calculated for $C_{40}H_{24}N_8O_{24}Pd_4Zn$, %: C 32.21; H 1.62; N 7.51. Found, %: C 33.05; H 2.43; N 7.65. UV-Vis (DMSO) λ_{max} nm: 351, 689. IR (KBr) ν_{max} cm^{-1}: 1358, 1447, 1565, 1588, 1620, 1693.

Platinum 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine ($PtPc^{oc}$). A mixture of 0.300 g of 4,5-bis(ethoxycarbonyl) phthalonitrile[14] and 0.090 g of platinum dichloride was heated at 175-180 °C for 1.5 h, the melt was then cooled, treated with 40 ml of ethanol, filtered and then treated with ethanol once again. The crude product was air-dried on the filter, dissolved in a mixture of chloroform with ethanol (10:1 v/v) and passed through a bed of silica gel. The solvent was removed in vacuo. The residue (0.21 g) was introduced into a 10 % aqueous sodium hydroxide solution (5 ml) and stirred for 5 hrs under a constant flow of argon. The reaction mixture was then cooled, the precipitate filtered and treated with 25 % hydrochloric acid. The suspension was filtered, washed with 15 % hydrochloric acid and distilled water to p*H* 3–4 (the phthalocyanine complex was slightly soluble in the washings), pressed and dried. The crude product was washed with ethanol to remove the residual acid and dried. The phthalocyanine complex



MPc^{oc} (M = Zn, Pt, Pd)

$ZnPc^{oc}M_4(H_2O)_8$ (M = Pt, Pd).

Figure 1. Structural formulae of the studied phthalocyanine complexes.

was purified by precipitation from dilute aqueous sodium hydroxide with 50 % acetic acid and then dried over phosphorus pentoxide in vacuo at ambient temperature. The product yielded 0.051 g of PtPc^{oc} (17.5 % on the basis of 4,5-bis(ethoxycarbonyl)phthalonitrile). IR (KBr) ν_{max} cm^{-1}: 1708 (C=O). UV-Vis (0.1% NaOH) λ_{max} nm: 661, 595, 291 (with the relative intensities 1.68:0.38:1); (DMSO) λ_{max} nm: 669, 605 (with the relative intensities 5.1:1). Found, %: C 43.44, 43.29; H 2.05, 1.91; N 10.19, 10.04. $C_{40}H_{16}N_8O_{16}Pt.2H_2O$. Calculated, %: C 43.84; H 1.84; N 10.23.

Palladium 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine (PdPc^{oc}). A mixture of 1.10 g 4,5-bis(ethoxycarbonyl)phthalonitrile and 0.20 g palladium(II) dichloride was heated at 190-195 °C for 2.5 h, the melt was cooled and treated with ethanol and chloroform-ethanol mixture as described above for the platinum complex. After the removal of the solvents the residue was refluxed for 6 hrs in 7 % alcoholic solution of sodium hydroxide. The suspension was filtered and the precipitate washed with hot ethanol (5 portions of 10-15 ml), pressed and stirred with 100 ml of 50 % acetic acid, then the suspension was filtered. The precipitate was consequently washed with 50 % and 10 % acetic acid, pressed, dried on the filter, then continuously stirred in ethanol and filtered until the filtrate was colorless. Thus obtained crude product was purified in an analogous manner to the platinum complex by reprecipitation from sodium hydroxide solution. The product yielded 0.081 g PdPc^{oc} (16.5 %). IR (KBr) ν_{max} cm^{-1}: 1705 (C=O). UV-Vis (DMSO) λ_{max} nm: 680, 612, (relative intensivity 5.4:1). Found, %: C 48.28, 48.37; H 1.91, 1.85; N 11.08, 11.15. $C_{40}H_{16}N_8O_{16}Pd.2H_2O$. Calculated, %: C 48.53; H 1.84; N 11.33.

Materials and Methods

The IR spectra were recorded in KBr pellets on a FSM-1201 FT instrument and the electronic absorption spectra on a Hewlett Packard 8453 spectrophotometer. The light beam intensity was measured with a Thorlabs silicon photodiode.

The kinetics of photodestruction. The kinetic experiments for the phthalocyanine platinum and palladium complexes' photobleaching were conducted using an IS-2-693 photodiode (Tehnoeksan JSC) as the light source, which produced a luminous power of $1.1\cdot10^{17}$ quant·cm^{-2}·s^{-1} in the range of 688-698 nm. A solution of the complex in DMSO was transferred to a standard 1 cm cuvette (optical density for the maximum of the longwave absorption band – 0.7-0.8, C ~$5\cdot10^{-6}$ mol/l) and irradiated while monitoring the photodestruction kinetics by spectrophotometry, recording the changes in the optical density for the Q band maximum.

Quantum yields of singlet oxygen (Φ_Δ) were determined by relative method using chemical quencher of $^1O_2$ – 1,3-diphenylisobenzofuran (DPIBF). The unsubstituted zinc phthalocyanine (ZnPc), the Φ_Δ of which in DMSO is known (Φ_Δ=0.67), served as a standard. The complex solution (~$5\cdot10^{-6}$ mol/l), containing DPIBF ($3\cdot10^{-5}$ mol/l), was irradiated in the standard cuvette of 1 cm optical layer thickness by light of DKSSh-150 lamp through the glass light filter KS-10 and interference filter with transmittance of 684±25 nm. Light intensity on the sample surface was $2.4\cdot10^{15}$ quantum·cm^{-2}·s^{-1}. The percentage of absorbed light of the sample was estimated by integrating overlapping spectrum of the exciting light and the absorption spectrum of the complexes. Photosensitized oxidation of DFIBF was monitored spectrophotometrically by decrease of maximum absorption at a wavelength of 418 nm. DFIBF initial concentration in all experiments was constant.

To calculate Φ_Δ the following equation was used:

$$\Phi_\Delta = \Phi_\Delta^{ref} \cdot \frac{W \cdot I_{abs}^{ref}}{W^{ref} \cdot I_{abs}},$$

where Φ_Δ^{ref} – the quantum yield of singlet oxygen generation by the reference standard (zinc phthalocyanine); W and W^{ref} – the rates of consumption of DPIBF for sensitization with the studied compound and the standard; I_{abs} and I_{abs}^{ref} – the amount of light quanta absorbed by the sensitizer and the standard, correspondingly.

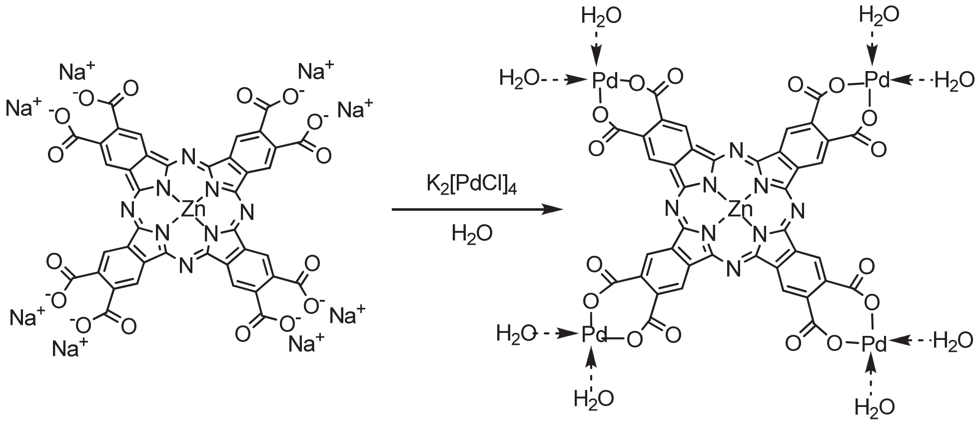
The experimental error for the determination of Φ_Δ was about 10 %.

Results and Discussion

The synthesis of the ZnPc^{oc}Pd$_4$(H$_2$O)$_8$ tetraconjugate was conducted similarly to an earlier developed procedure[13] for the diaqua platinum conjugate (Scheme 1).

The structure of ZnPc^{oc}Pd$_4$(H$_2$O)$_8$ was confirmed by elemental analysis and IR spectroscopy. Comparison of the IR spectrum of ZnPc^{oc}Pd$_4$(H$_2$O)$_8$ with that of the starting ZnPc^{oc} shows significant alterations in the 1500-1700 cm^{-1} range, while the IR spectra of ZnPc^{oc}Pd$_4$(H$_2$O)$_8$ and the previously studied[13] ZnPc^{oc}Pt$_4$(H$_2$O)$_8$ demonstrate a high degree of similarity (Figure 2). On the basis of IR spectra of palladium acetate[16] and analogous platinum conjugates,[11,13] the bands at 1447, 1620 and 1693 cm^{-1} in the spectrum of ZnPc^{oc}Pd$_4$(H$_2$O)$_8$ can be identified as carboxyl group vibrations.

The synthesis of PtPc^{oc} and PdPc^{oc} was performed by fusing 4,5-bis(ethoxycarbonyl)phthalonitrile[14] with platinum or palladium chloride correspondingly with



Scheme 1. Synthesis of covalent tetraconjugate of zinc octacarboxyphthalocyanine with diaqua palladium (ZnPc^{oc}Pd$_4$(H$_2$O)$_8$).

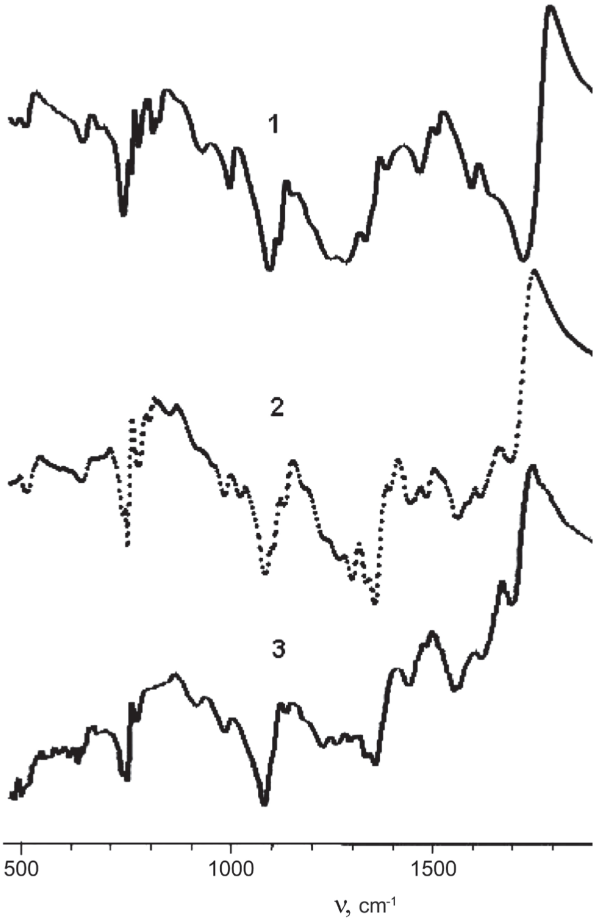
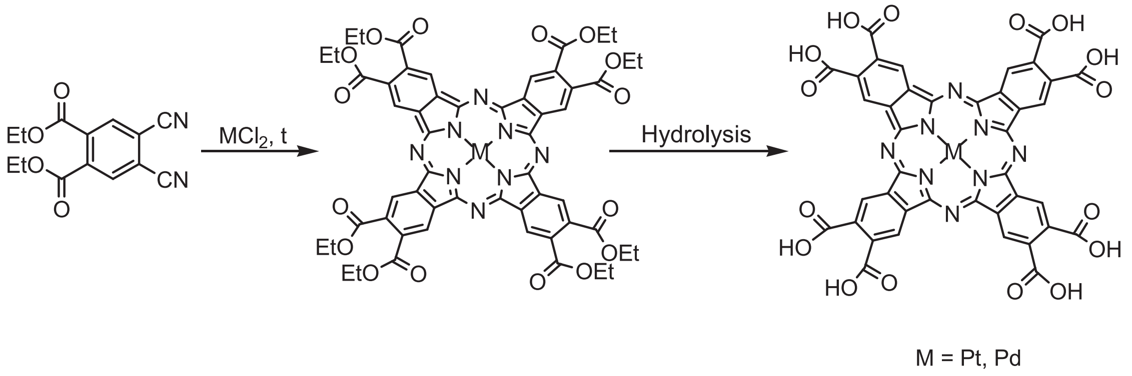


Figure 2. IR spectra: 1 – $ZnPc^{oc}$, 2 – $ZnPc^{oc}Pd_4(H_2O)_8$, 3 – $ZnPc^{oc}Pt_4(H_2O)_8$.

subsequent saponification of the reaction product containing octaethyl ester of the respective metal 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine and the products of its partial hydrolysis, followed by acidification of the formed $PtPc^{oc}$ or $PdPc^{oc}$ sodium salts (Scheme 2). The obtained complexes are soluble in water, phosphate buffer, dilute aqueous alkali, ethanol in the presence of organic bases (triethylamine) and in aprotic polar solvents (dimethyl sulfoxide, dimethyl formamide).

The maxima of the longwave absorption Q-bands of the studied metal complexes lie in the range of 669-698 nm (Table 1). It can be seen (Figure 3A) that in the MPc^{oc} series the transition from Zn to Pt results in a substantial (30 nm) hypsochromic shift of the longwave Q-band in the electronic absorption spectrum. At the same time the transition from $ZnPc^{oc}$ to its peripheral tetraconjugate $ZnPc^{oc}M_4(H_2O)_8$, regardless of the significant structural changes caused by the introduction of four diaqua platinum or diaqua palladium fragments, does not influence the Q-band position. However, as it is demonstrated in Figure 3B, its vibrational satellite (Q_{0-1}) has a considerable but identical for both of the complexes shortwave shift, which probably is caused by the alterations in their skeletal vibrations.

The quantum yields of fluorescence (Φ_{fl}) and singlet oxygen generation (Φ_Δ) of the studied compounds demonstrate that an internal heavy atom effect exists, which depends on the position of Pt and Pt (in the core or in the periphery of the macrocycle). This effect is evident in enhancement of spin forbidden intersystem transitions, resulting in fluorescence quenching, increasing the yield and decreasing the lifetime of triplet states. The spin-orbit perturbations introduced by heavy atoms allow the transitions between states of different spin multiplicities. It should be noted that internal heavy



Scheme 2. Synthesis of platinum and palladium octacarboxyphthalocyanines (MPc^{oc}, M = Pt, Pd).

Table 1 Spectral-fluorescent properties and quantum yields for singlet oxygen generation for MPc^{oc} and covalent conjugates of $ZnPc^{oc}$ with diaqua platinum and diaqua palladium in DMSO.

Compound	λ_{max}^{abs}, nm	λ_{max}^{fl}, nm	Φ_{fl}	Δ
$ZnPc^{oc}$	698	708[17]	0.24[17]	0.56[17]
$PdPc^{oc}$	680	-	-	0.78±0.08
$PtPc^{oc}$	669	-	-	0.81±0.08
$ZnPc^{oc}Pd_4(H_2O)_8$	698	714	0.12	0.60±0.05
$ZnPc^{oc}Pt_4(H_2O)_8$	698	713[13]	0.16[13]	0.51[13]

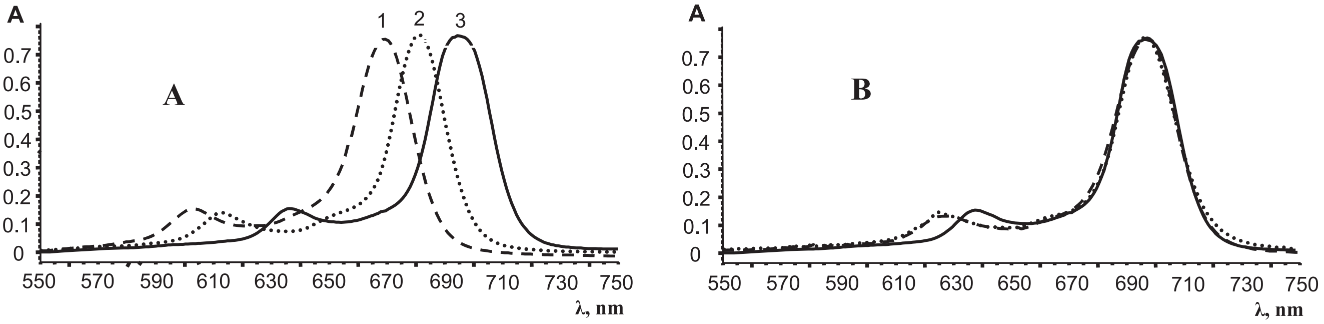


Figure 3. Electronic absorption spectra, **A**: ZnPc^{oc} (——), PdPc^{oc} (·······), PtPc^{oc} (- - - - -); **B**: ZnPc^{oc} (——), ZnPc^{oc}Pd$_4$(H$_2$O)$_8$ (·······) and ZnPc^{oc}Pt$_4$(H$_2$O)$_8$ (- - - - -).

atom effect for phthalocyanines is currently described only by a few publications in contrast to this effect for porphyrins (*e.g.* the review by Solovyov and Borisevich[18]).

Compound ZnPc^{oc} in DMSO when excited by the visible light exhibits fluorescence with Φ_{fl} = 0.24 quantum yield.[17] The transition to PtPc^{oc} and PdPc^{oc} results in a complete quenching of the phthalocyanine fluorescence due to the heavy atom effect. At the same time, incorporation of four heavy atoms of Pt or Pd into the structure of ZnPc^{oc} in the periphery of the macrocycle (transition to ZnP^{oc}Pt$_4$(H$_2$O)$_8$ and ZnPc^{oc}Pd$_4$(H$_2$O)$_8$) has a greatly less influence on Φ_{fl}, which still decreases but not more than 2 times. The data in Table 1 demonstrate that effect of structural changes of the ZnPc^{oc} periphery on the position of the fluorescence maximum is insignificant.

The value of Φ_Δ is an important parameter that defines the possibility of the use of the compounds as photocatalysts. All the studied phthalocyanine complexes were found to efficiently generate $^1O_2$ in DMSO when excited with visible light. Figure 4 demonstrates the data from one of the experiments aimed at sensitization by the studied metal complexes of the photo-induced discoloration of the $^1O_2$ scavenger (diphenylisobenzofuran, DPIBF) in DMSO. As it is seen, when PtPc^{oc} was used as the photosensitizer for $^1O_2$ formation and visible light with wavelengths close to the Q-band maximum was used, the absorption of DPIBF (λ_{max} = 418 nm) rapidly decreased. The Q-band of PtPc^{oc} does not change, which testifies its considerable photostability. The singlet oxygen quencher – DABCO – decreased the rate of the photosensitized DPIBF oxidation, thereby confirming the participation of $^1O_2$ in the current process.

The Φ_Δ values were measured as relative to the ZnPc standard. The results (Table 1) demonstrate that substitution of the central atom in ZnPc^{oc} from Zn to the heavier Pt and Pd result in a significant increase of Φ_Δ. It is known that $^1O_2$ is formed as the result of energy transfer from the sensitizer in triplet excited state to molecular oxygen, therefore increased Φ_Δ values testify the increased triplet states yield, *i.e.* the manifestation of the heavy atom effect. On the other hand, the change in Φ_Δ when the periphery of the macrocycle is modified with four fragments including the same heavy atoms, is insignificant and does not exceed the experimental error relative to the value of $\Phi_\Delta = 0.56\pm0.05$ for the parent ZnPc^{oc}. It should be noted that in[10] incorporation of diaqua platinum fragments into silicon octacarboxyphthalocyanine resulted in a significant increase of Φ_Δ from 0.26 to 0.56. We did not observe such a notable effect in the case of ZnPc^{oc} apparently due to the fact that φ_Δ for compound ZnPc^{oc} already reaches 0.56.

Thus, the data on fluorescence and the quantum yield of singlet oxygen collected in the present study show that introduction of Pt and Pd into the phthalocyanine core

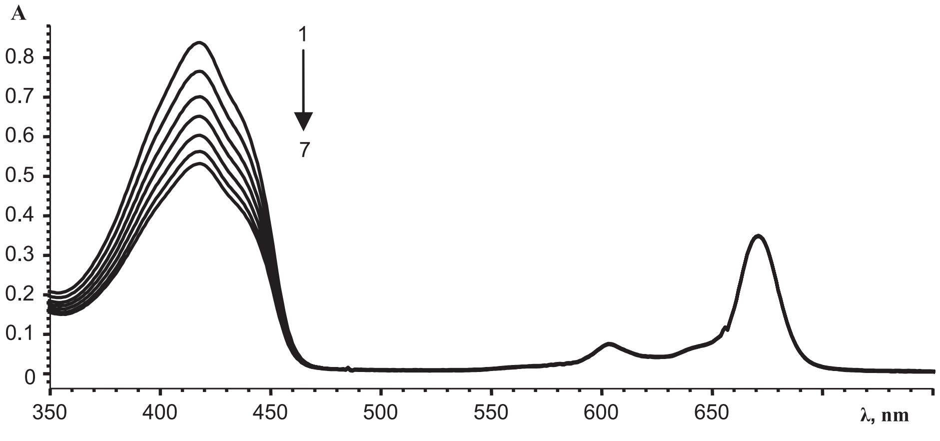


Figure 4. Spectral changes in the course of DPIBF oxidation in DMSO, with sensitization by the complex PtPc^{oc} (λ_{excit} = 684±25 nm): The curves **1**–**7** correspond to 0; 10; 20; 30; 40; 50; and 60 s of irradiation time. The Soret band of the complex (λ_{max} = 339 nm) does not interfere with kinetic measurements of photooxidation of DPIBF at its absorption maximum (418 nm).

is a much stronger factor for spin-orbital perturbations than introduction of the same metals to the periphery of the macrocycle. Similar behavior has been reported for porphyrins as well:[19,20] bonding of heavy halogen atoms to pyrrole rings of the conjugated system of the porphyrin increases the probability of intersystem transitions much more than peripheral substitution of phenyl rings for tetraphenylporphyrin. This is understandable because for both porphyrins and phthalocyanines the S_1~~>T_1 intersystem crossing occurs with the involvement of states belonging to the π,π^*-type, and when the heavy atom is positioned further from the core π-electron system to the periphery, the effect of π-orbits perturbation weakens.

The photostability of the studied complexes was evaluated by the kinetics of their photobleaching in DMSO saturated with air for excitation of their Q-bands (Figure 5). Introduction of heavy metals to the structure of phthalocyanines increases the stability of the complexes towards radiation and this effect for Pt and Pd being incorporated into the macrocyclic core is far greater than the one for the introduction of Pt and Pd to the periphery. It is notable that the heavier Pt atom inhibits the photobleaching of the macrocycle to a greater extent than Pd.

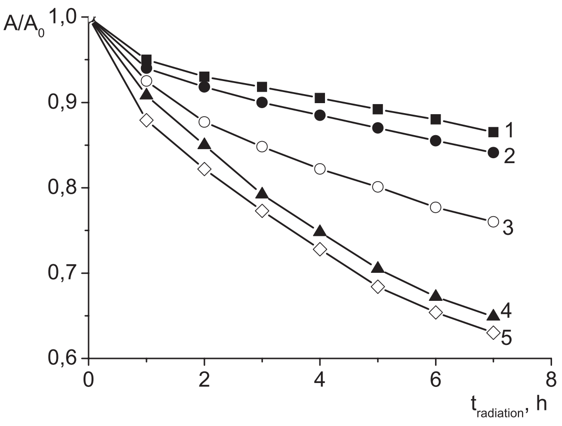


Figure 5. Kinetic curves for the photobleaching in air-saturated DMSO: **1** – PtPc^{oc}, **2** – PdPc^{oc}, **3** – ZnPc^{oc}Pt$_4$(H$_2$O)$_8$, **4** – ZnPc^{oc}Pd$_4$(H$_2$O)$_8$, **5** – ZnPc^{oc}. Concentration ~$5\cdot10^{-6}$ mol/l, λ_{exc} = 688–698 nm (IS-2-693 photodiode). Data were collected for λ_{max}^{abs} (Table 1).

Photodestruction of phthalocyanines is known to proceed via different competing mechanisms. The contribution of each to the overall process depends on the structure of a phthalocyanine and on the medium.[21] We have earlier demonstrated that the contribution of singlet oxygen to oxidation of the basic compound ZnPc^{oc} is not high in an aqueous medium.[21] As the efficiency of photodestruction in the series of the studied compounds does not increase with increased Φ_Δ and is on the contrary decreased, it can be concluded that in the case of Pt and Pd complexes with MPc^{oc} in DMSO the contribution of singlet oxygen to photooxidation is not significant and the mechanism is of the radical type. The formation of radicals is known to proceed generally via triplet states, the increased probability of formation of those in the presence of a heavy metal seemingly presumes more intensive photodestruction. However, the primary photochemical processes that result in the formation of radicals are bimolecular[22] and the bimolecular reaction rate is defined not by the probability of formation of T_1 state but by its stationary concentration (the T_1 level population) which depends on the ratio of its formation and deactivation rates (intersystem transitions S_1~~>T_1 and T_1~~>S_0). Depending on the alteration of the rates of these processes, induced by the heavy atom, the population of the T_1 level can either decrease or increase. It seems that when MPc^{oc} form chelate complexes with heavy atoms of Pt and Pd the deactivation of T_1 is more accelerated and the population of the highly reactive T_1 state is lowered, which is the most probable cause of the increased photostability of the complexes.

Conclusions

Octacarboxyphthalocyanines PdPc^{oc} and PtPc^{oc} as well as ZnPc^{oc}Pd$_4$(H$_2$O)$_8$ tetraconjugate were synthesized as novel compounds. The compounds were characterized by elemental analysis, electronic and IR spectroscopy, their spectral, luminescent and photochemical properties were studied. The properties of PdPc^{oc} and PtPc^{oc} were compared to the ones for ZnPc^{oc} peripheral diaqua platinum and diaqua palladium covalent conjugates. It was found that substitution of one atom (Zn) in the macrocyclic core for Pd or Pt has a much greater influence on electronic absorption spectra, fluorescence, generation of singlet oxygen and photostability of Pc compared to incorporation of four same atoms into the periphery in the form of diaqua platinum and diaqua palladium, which says for the greater sensitivity of the electronic structure of the central aromatic ring, the lowest excited singlet and triplet states of phthalocyanines and the probability of transitions between them to the modification of the core than to modification of the periphery.

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