Octacarboxyphthalocyanines – compounds of interesting spectral, photochemical and catalytic properties

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Introduction

Phthalocyanines are a family of chemical compounds that are structural analogues of porphyrin [1]. The properties of phthalocyanines depend both on the character of ligand (Pc), peripheral substituents, as well as on central metal atom. Type of substituents, their arrangement and number determine many of phthalocyanine properties, including spectral [1], catalytic and electrocatalytic ones [2], as well as electric properties [1]. Phthalocyanine complexes were initially used as dyes and pigments due to their intensive colour [3], however, they might be also used as laser dyes, molecular semiconductors, catalysts, electrocatalysts [1,3] as well as photosensitizers in antitumour photodynamic therapy (PDT) [4]. Unsubstituted phthalocyanines exhibit very low solubility in most of commonly used organic solvents – it is a result of strong π–π interactions of phthalocyanine macrorings in crystalline state [1]. On the one hand, low solubility is a desired quality in compounds used as pigments, but on the other hand this limits many of their other potential applications and obstructs testing of solutions. Therefore, mainly substituted phthalocyanines are currently studied – their properties depend on the type of substituents, their number and their arrangement within Pc ligand.

This article presents synthesis methods of octacarboxyphthalocyanines (Fig. 1), their UV-Vis absorption spectra and selected photochemical and catalytic properties. Carboxyl groups give this compounds solubility in many polar solvents.
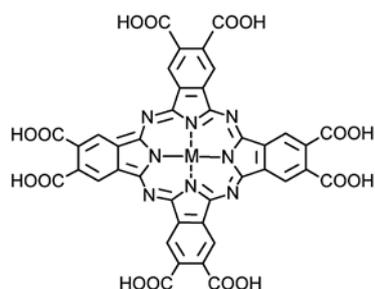

Fig. 1. Formula of octacarboxyphthalocyanine, M–metal

Experimental part

The synthesis of copper, zinc and cobalt 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines was described previously in [5÷7]. Instruments: Spectrophotometer Unicam UV 300, England; Spectrophotometer Perkin Elmer Fluorescence MPF-3. UV-Vis absorption and emission spectra were measured in quartz cuvettes of width of studied layer equal to 10.00 mm. For testing catalytic activity of CoPcOC, the oxygen sensor CTN-920.S, Elsent S.C, Poland was used; as well as multifunctional microcomputer instrument CX-551, Elmetron, Poland and thermostated measurement cell. The solutions were thermostated, $T = 24,5 \pm 0,5°C$. During measurements system was tightly sealed, without access to atmospheric oxygen.

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Synthesis of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines

The literature describes few methods of synthesis of octacarboxyphthalocyanines. The synthesis proposed by Boston et al. [8] consists of two steps. The first step involves obtaining tetraimide derivative of metal phthalocyanine as a result of cyclic tetramerization of 1,2,4,5-tetracyanobenzene (TCB) in the presence of appropriate metal salt (e.g. chloride) in ethylene glycol. The second step involves base hydrolysis of formed imide to carboxyl derivative. The syntheses conducted by Authors have led to the conclusion that this method is effective for obtaining CuPcOC, while its application for synthesis of CoPcOC and NiPcOC gives number of by-products. Moreover, proposed conditions for hydrolysis of imides are too drastic – complexes undergo decomposition. Imide derivatives of some metal phthalocyanines might be also obtained using reaction of pyromellitic acid anhydride, metal chloride, urea and catalyst i.e. DBU (1,8-diazabicyclo[5.4.0] undec-7-ene) [9]. Wöhrle et al. [10] have presented three-step synthesis of metal octacarboxyphthalocyanines. The first step consists of synthesis of non-metal octacyanophthalocyanine, $H_2Pc(CN)_8$ from TCB in the presence of lithium propanolate, the second step – metal incorporation into Pc macroring, i.e. synthesis of octacyanophthalocyanine of respective metal, while the third step involves base hydrolysis of metal octacyanophthalocyanine to respective octacarboxyl derivative. A certain disadvantage of this method lies in the difficulty of achieving full metalization of $H_2Pc(CN)_8$ to $MPc(CN)_8$ for some metals. Starting from TCB and anhydrous salt of respective metal it is possible to obtain directly metallic octacyanine derivative ($CoPc(CN)_8$, $FePc(CN)_8$) using aprotic solvent (e.g. sulfolane)[11]. One can also use in this reaction a catalyst in form of DBU. Obtained octacyanophthalocyanines might be subjected to base hydrolysis giving carboxyl derivatives. Authors have synthesized CoPcOC in such way with yield equal to approx. 25%. The article [12] describes multi-step synthesis of octacarboxyphthalocyanine H_2PcOC obtained finally as a result of base hydrolysis of respective ester derivative. In this case, starting substrate was pyromellitic acid anhydride.

Authors' experience proves that the choice of appropriate synthesis method depends to a great extent on character of metal. While choosing synthesis path, one shall also consider possibility of by-product formation, e.g. phthalocyanine oligomers or polymers, and possibility of incomplete metallization of phthalocyanine macroring or incomplete hydrolysis of respective substituents to carboxyl groups. Copper, cobalt and nickel octacarboxyphthalocyanines exhibit very high chemical and thermal stability. However, some derivatives are unstable in alkaline environment. They undergo slow decomposition even if there is only small access of oxygen and light (e.g. H_2PcOC, ZnPcOC or MnPcOC). In order to purify octacarboxyphthalocyanines, very often it is necessary to carry out continuous solvent extraction and sometimes use preparative (column) chromatography.

UV-Vis absorption spectra and association

UV-Vis spectra of octacarboxyphthalocyanine typically have two absorption areas: B in 300-400 nm range, and Q, in 550-800 nm range (Fig. 2). It is also possible to distinguish bands corresponding to transitions requiring higher energies: N and L [5÷7,13]. For complexes of some metals, e.g. Mn, Co and Fe additional bands appear in 450-550 nm range corresponding to charge transfer transitions, CT. Octacarboxyphthalocyanines usually exhibit strong tendency for stacking association (multimerization) in solutions. Molecules might interact with each other via delocalized macroring π electrons and additionally by specific interactions, e.g. hydrogen bonds. The most important factors affecting aggregation are: pH, concentration, temperature, solution polarity [5, 6, 13]. Monomeric forms of octacarboxyphthalocyanines give in Q range intensive and narrow band at λ_{max} approx. 680–690 nm. For spectra of metal phthalocyanines (of D_{4h} symmetry of electron system) there is one intensive and narrow Q_{0-0} band in 650–750 nm range, while for non-metal derivatives – D_{2h} symmetry – the band in Q area splits into two: Q_x and Q_y (Fig. 2).
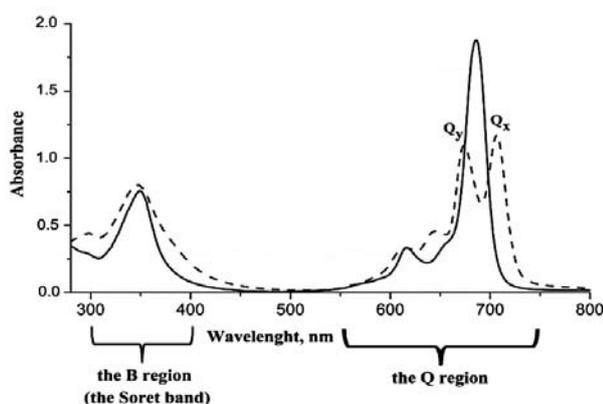

Fig. 2. UV-Vis spectrum of H₂PcOC and CuPcOC, buffered solutions of pH≈7

The association causes appearance of broadened band, typical for dimers, at λ_{max} approx. 630–650 nm, which with increasing multimerization degree undergoes hypsochromic shift. The Soret (B) band also undergoes blue shift, but to a smaller extent [5, 6, 13].

Monomeric forms of octacarboxyphthalocyanines (catalytically and photochemically active) might be easily obtained by alkalization of environment. However, for some (fluorescent) compounds in alkaline solutions their slow decomposition occurs. This fact have motivated decision to study the impact of cationic surfactants, selected quaternary ammonium salts on association of octacarboxyphthalocyanines. Addition of this salts practically does not change pH of the solution. The influence of hydrocarbon chain length in tetraalkylammonium ion (methyl-, ethyl-, butyl-) was studied, as well as influence of type of salt anion (bromide, iodide, chloride ion) on UV-Vis spectra of aqueous solutions of CuPcOC. The spectral changes induced by added salts, Authors attribute to tetraalkylammonium cations. Furthermore, the influence of alkyl chain length in cation was observed. The biggest changes in spectrum are caused by tetrabutylammonium salts. While the effect of anion type (Br⁻, Cl⁻ and I⁻) is practically negligible. Depending on concentration of tetrabutylammonium bromide (TBABr) the spectrum of monomeric or associated form of CuPcOC is obtained (Fig. 3). Increase of salt concentration causes gradual disassociation. There is a decrease of band intensity at ≈645 nm, that shall be attributed to associates (mainly dimer) present in the solution, while intensity of monomer band at $\lambda_{max} \approx 690$ nm increases. TBABr causes also batochromic shift of this band from $\lambda_{max} = 684$ to 694 nm and B band, from 350 to 357 nm.
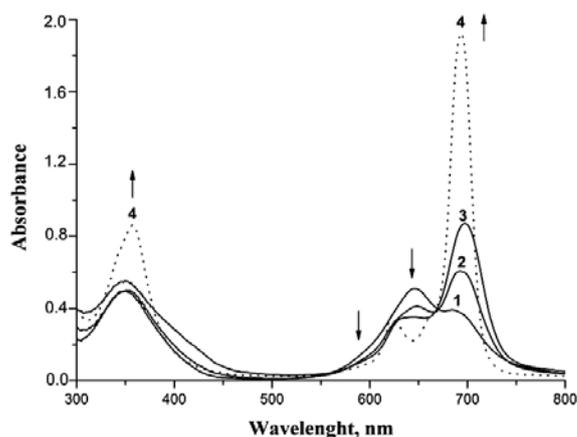

Fig. 3. Effect of TBABr concentration on spectrum of aqueous solutions of CuPcOC; $c=1.1\times10^{-5}$ mol/dm³; c_{TBABr}, mol/dm³: 1) 0.01; 2) 0.045; 3) 0.06; 4) 0.09

The observed spectral changes might be explained by interaction of tetraalkylammonium cations with carboxyl groups of CuPcOC. This causes disassociation and stabilization of ionized, monomeric form of the phthalocyanine.

Photochemical properties

In the last years phthalocyanines have been studied intensively in terms of their application as photosensitizers in antitumour photodynamic therapy (PDT) [4, 14]. Phthalocyanines are among most promising second generation photosensitizers [4]. In comparison to porphyrins (first generation photosensitizers), phthalocyanines absorb more intensely light of higher wavelengths (approx. 650) than porphyrins and have higher molar absorptivity. Due to the fact that light depth of penetration in tissue increases with wavelength, this allows to treat lesions located deeper in the body. Phthalocyanine complexes with Zn^{2+}, Al^{3+}, Ga^{3+} and Si^{4+} ions show high quantum yield of triplet state and therefore allow to achieve high quantum yield in generation of singlet oxygen and other reactive and cytotoxic oxygen forms [4, 14]. Phthalocyanine association quenches fluorescence. Numerous studies confirm that only monomeric forms of phthalocyanines exhibit strong fluorescence that ensures obtaining cytotoxic oxidising media [4, 6, 14]. The higher hydrophobicity of compounds (photosensitizers), the higher their tendency for association in aqueous solution. While phthalocyanines with polar substituents undergo hydration more easily and electrostatic repulsion (at least partially) prevents aggregation. In this aspect, especially interesting are phthalocyanines containing sulfo and carboxyl groups [6, 14].
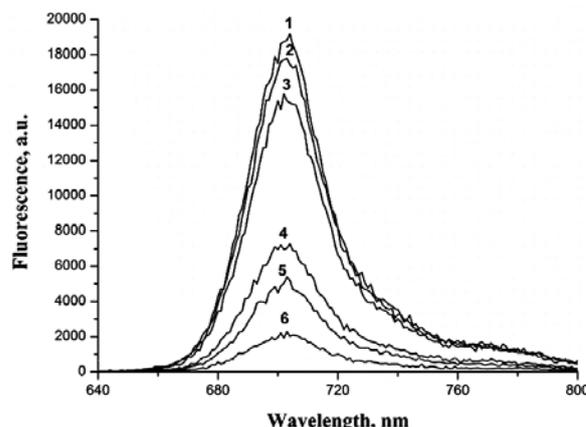

Fig. 4. Influence of ZnPcOC concentration on fluoroscence spectrum of aqueous solutions; c ×10⁶ mol/dm³: 1) 7.5; 2) 9.0; 3) 12.5; 4) 17.0; 5) 20.0; 6) 30.0; $\lambda_{ex} = 350$ nm

Due to the presence of carboxyl groups, ZnPcOC exhibits solubility in aqueous solutions i. e. biological systems as well as in organic solvents (DMF, DMSO). Fluorescent molecular entity is monomeric form of ZnPcOC [6]. But in water it undergoes association quenching fluoroscence. Figure 4 presents fluoroscence spectra of aqueous solutions. With the increase of ZnPcOC concentration gradual decrease of fluoroscence intensity occurs, as well as very clear decrease of I/c value (Fig. 5).
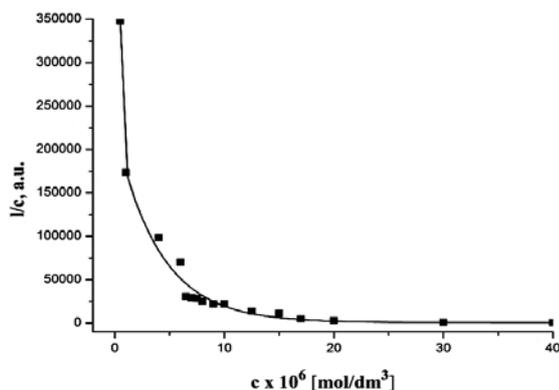

Fig. 5. Dependence of I/c from ZnPcOC concentration,
λ_{emis} = 703 nm, λ_{ex} = 350 nm

In the range of ZnPcOC concentrations from 0.5 to 5.0 μmol/dm^3, the increase of concentration causes sharp decline (approx. 14 times) in value of I/c. The analysis of UV-Vis absorption spectra shows that in this concentration range apart from associates absorbing at λ_{max} approx. 630 nm, there is a relatively high percentage of monomeric form of studied phthalocyanine (λ_{max} approx. 690 nm). In the range of concentration over 5.0 μmol/dm^3 value of I/c still decreases, but not as sharply as in previous case, approaching constant near-zero value. The curve shape might be explained by decrease of concentration of monomeric form of phthalocyanine and increase of content of non-fluorescent associates (multimers). Such strong decrease in solution luminescence indicates however, that apart from association, other factors play some role e.g. concentration effect. Association of ZnPcOC in aqueous solutions can be greatly reduced or completely prevented by increasing pH of solution.

Catalytic properties

Phthalocyanines with carboxyl groups exhibit catalytic activity in many processes. Metal (Fe, Mn, Co) octacarboxyphthalocyanines catalyse oxidation of 2,4,6-trichlorophenol (TCP) to compounds of smaller environmental impact [15]. Co(II)PcOC deposited on titanium electrode exhibits bactericidal activity against *Escherichia coli* [16], while with the supply of oxygen and light it exhibits toxic action against fungus *Magnaporthe grisea* that causes diseases of rice [17].

Oxidation of compounds of R-SH type

Cobalt phthalocyanine and especially its substituted derivatives are ones of the most effective catalysts for oxidation of compounds with –SH group, e.g. thiols [2, 18, 19]. Complexes with sulfo groups are used as thiol oxidation catalysts (1) in desulphurization of petrochemical products (Merox process):

$$4H^+ + 4RS^- + O_2 \rightarrow 2RSSR + 2H_2O \tag{1}$$
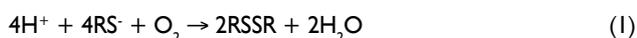
It is believed [18] that during oxidation of thiols to respective disulfides, the first reaction step involves formation of binary complexes thiolate – CoPcTS, which then react with oxygen resulting in ternary complexes:
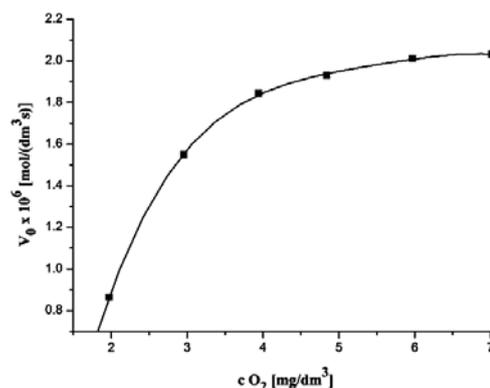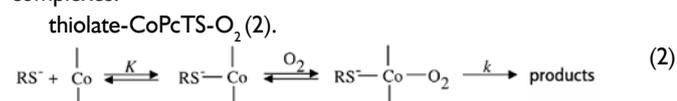
thiolate-CoPcTS-O$_2$ (2).

$$RS^- + \underset{|}{\overset{|}{Co}} \underset{K}{\rightleftarrows} RS^-\!\!-\!\!\underset{|}{\overset{|}{Co}} \overset{O_2}{\rightleftarrows} RS^-\!\!-\!\!\underset{|}{\overset{|}{Co}}\!\!-\!\!O_2 \xrightarrow{k} products \tag{2}$$

Fig. 6. Dependence of initial reaction rate of Cys oxidation on oxygen concentration, pH = 8.0; cCys = 0.02 mol/dm^3; cCoPcOC = 1·10^5 mol/dm^3

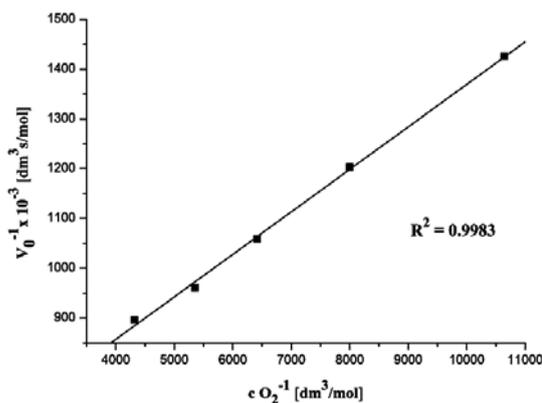**Fig. 7. Dependence of reciprocal of initial reaction rate of Cys oxidation on reciprocal of oxygen concentration, cCys = 0.02 mol/dm^3; cCoPcOC = 1·10^{-5} mol/dm^3, pH = 5.7**

The results of studies on catalytic activity of di-, tetra- and octacarboxyphthalocyanines in homogeneous aerobic oxidation of 2-thioethanol were presented in [19]. The activity depended on metal type (iron and cobalt complexes proved to be most active), number of carboxyl groups and association causing reduction of number of active sites. Zinc and aluminium polymeric phthalocyanines with peripheral carboxyl groups catalyse photochemical oxidation of Na$_2$S and Na$_2$S$_2$O$_3$ [20]. Paper [21] presents results of research on catalytic activity of copper, zinc and cobalt octacarboxyphthalocyanine in electrochemical oxidation o 2-thioethanol, *L*-cysteine and 1,4-dithio-2,3-butanediol, while [22] shows preliminary results of research on impact of MPcOC (Fe, Co, Cu) on aerobic oxidation of selected sulphur compounds in buffered solutions. The further section of the article presents results of studies on catalytic activity of CoPcOC in aerobic homogenoues oxidation of *L*-cysteine (Cys). This amino acid is commonly studied as a model substrate allowing to compare catalytic activity of different phthalocyanines in oxidation of R-SH type compounds. The Authors found strong effect of pH of solution on reaction rate of oxidation of this compound. The higher the pH, the faster the reaction, what was measured by decrease of oxygen concentration in solution. It is believed that oxidation mechanism of *L*-cysteine to cystine follows the general chemical equation proposed for thiols [2,18,19]. The rate of studied reaction is affected by CoPcOC association and dissociation of the substrate (its presence in molecular or ionic form RS$^-$). The analysis of UV-Vis spectra leads to conclusions that in solutions of pH = 4 cobalt octacarboxyphthalocyanine is present to a large degree in associated form, hence it shows virtually none catalytic activity. However, as pH increases, concentration of monomeric form increases as well due to the degradation of associates, what in turn is related to increasing number of catalytic sites. UV-Vis spectra for pH>5.5 buffered solutions exhibit monomer band at $\lambda_{max} \approx$ 680 nm.

Curves of dependence of initial reaction rate (V_0) on oxygen concentration allow to conclude that *L*-cysteine oxidation by CoPcOC can be seen as enzyme-like catalysis. Figure 6 presents such curve for solutions of pH=8.0. Initially, with the increase of oxygen concentration, initial reaction rate grows significantly, but at oxygen concentration equal to approx. 5 mg/dm^3 there is clear change in course of the curve. Further increase of concentration does not result in significant increase of reaction rate.

Kinetics of oxidation process of *L*-cysteine in the presence of CoPcOC might be then described using Michaelis-Menten theory. Reaction kinetic parameters might be determined from Lineweaver–Burk equation (3):

$$\frac{1}{V_0} = \frac{1}{V_{max}} + \frac{K_A}{V_{max}}\frac{1}{[O_2]_0} \qquad (3)$$

where: V_0-initial reaction rate, V_{max}-maximum rate, K_A-Michaelis constant.

Plots of reciprocal of initial reaction rate ($1/V_0$) vs. reciprocal of oxygen concentration ($1/cO_2$) are linear. Figure 7 presents such plot for solutions of pH=5.7. For CoPcOC-catalysed oxidation reaction of *L*-cysteine at 25 °C in solutions of pH=8.0 Michaelis constant K_A was determined to be of order of 10^{-6} mol/dm^3. This value indicate high catalytic activity of CoPcOC in oxidation of this substrate.

Summary

Metal octacarboxylphthalocyanines might be obtained by many methods. The choice of suitable one depends mostly on the character of metal. Complexes of some metals exhibit high chemical and thermal stability, e.g. copper, cobalt and nickel, while others, e.g. zinc or manganese, are relatively unstable. It is particularly important to maintain anaerobic conditions and suitable temperature during base hydrolysis of octacyanine or imide derivatives to respective octacarboxyphthalocyanines. In case of some syntheses by-products may form, e.g. polyphthalocyanines.

Properties of octacarboxyphthalocyanines are strongly dependent on association. It causes among other fluorescence quenching of aqueous solutions of ZnPcOC and decrease of catalytic activity of CoPcOC in homogeneous oxidation of *L*-cysteine. Obtained results indicate enzyme-like character of catalytic activity of CoPcOC in oxidation of this amino acid.

Octacarboxyphthalocyanine association can be limited by appropriate choice of pH of the solutions and by addition of suitable cationic surfactants. Tetraalkylammonium cations cause disassociation of CuPcOC and stabilization of ionized, monomeric form of this phthalocyanine.

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