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Self-Association of Sulfo Derivatives of Cobalt Phthalocyaninates in the Presence of 1,4-Diazabicyclo[2.2.2]octane

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Abstract—Complex formation between water-soluble cobalt(II) phthalocyaninates and 1,4-diazabicyclo[2.2.2]-octane has been studied. The formation of the 1 : 1 molecular complex and the 2 : 1 sandwich-type dimers has been confirmed. The sandwich-type dimers and the *J*-aggregates involving the peripheral groups of the macrocycle are formed in ethanol medium. Stability constants of the molecular complexes have been determined, and the effect of size of the peripheral substituents on the dimeric structures stability has been elucidated.

Keywords: macrocycle, cobalt sulfophthalocyaninate, DABCO, molecular complex, dimer

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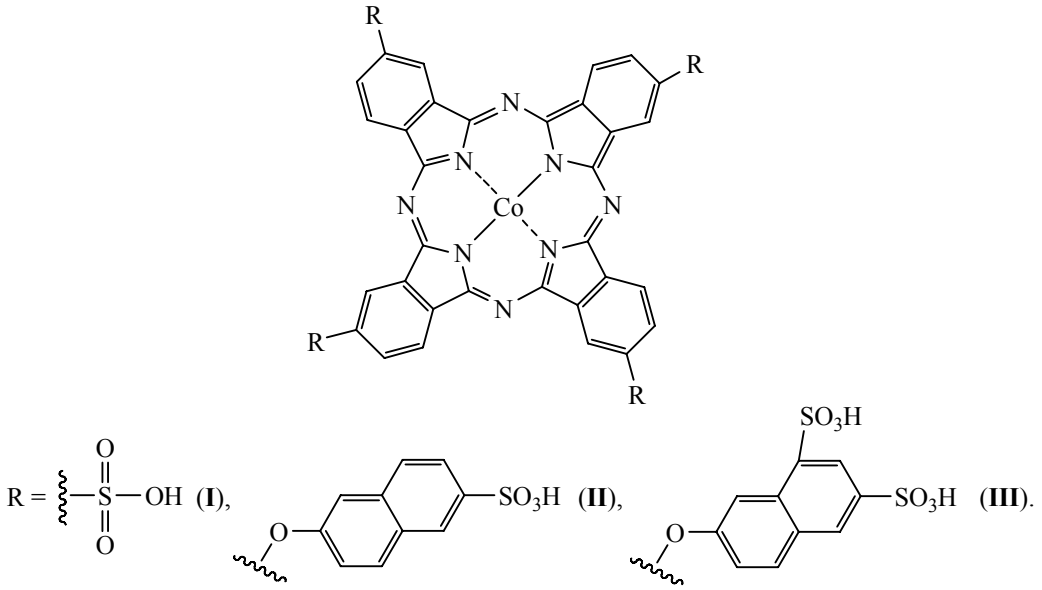
Metal complexes with substituted phthalocyanine have been widely applied as dyes [1, 2], catalysts [3–5], and medical and biological agents [6, 7]. Water-soluble derivatives of metal phthalocyaninates are of special importance for industrial and biomedical processes in aqueous medium [8–10].

Most of the utilitarian properties of metal phthalocyaninates are due to the possibility of coordination of additional ligands at the fifth and sixth coordination positions of the metal ion (the other four positions being occupied by the macrocycle donor atoms) [11]. Self-association of metal phthalocyaninates results in shielding of the metal cation, altering the coordination and catalytic properties of the complex [12]. The nature of peripheral substituents significantly affects the metal phthalocyaninates properties, including their association [13].

Phthalocyanines can form dimers as well as higher associates in aqueous media [14]. The association can occur via the π–σ-attraction and π–π-repulsion of the two conjugated π-electron macrocyclic systems; the π–π-associates (*H*-aggregates) are so formed, most often they are dimers [15]. The metal cation is not directly involved in the formation of *H*-aggregates. Another type of association, via the interaction of a phthalocyaninate molecule coordination site with heteroatoms of peripheral substituent of another macrocycle, results in the formation of *J*-aggregates [16]. The described processes are merely interactions between the macrocycle fragments, without coordination of additional ligands (other than the solvent molecules) by the metal ion.

The control of self-association of metal phthalocyaninates in aqueous solution allows preparation of supramolecular assemblies with the finely tuned properties. One of the approaches towards control of the equilibrium between monomer and dimer forms of metal phthalocyaninates in solution is the molecular complex formation with small organic ligands containing electron-donor atoms [17, 18]. For instance, reports on coordination interaction of Co, Ru, and Mn phthalocyaninates with monodentate ligands have been published [19–21]. Upon the molecular complex formation with nitrogen-containing molecules the central metal ion can successively coordinate up to two ligands (sometimes only a single ligand can be coordinated, depending on the complex geometry). The presence of the axial ligand prevents the formation

Scheme 1.



of H-associates. Of special interest is the report [19] discussing preparation and study of a series of ruthenium complexes with substituted phthalocyanines and their naphthyl derivatives. The mentioned complexes additionally contain one or two axial ligands (pyridine derivatives). It has been demonstrated that shielding of the coordination center stabilizes the monomer form of the macrocycle and affects its electrochemical and catalytic properties. However, the complex formation with exobidentate ligands is far more interesting in view of controlled formation of ordered phthalocyanine structures. A series of ligands containing two heteroatoms has been as well discussed in [19]; however, only unstable μ-dimers have been obtained in that work, likely due to the insuccessful choice of ligands.

Our previous studies [22–25] have shown that sulfonated derivatives of cobalt phthalocyaninate can form dimers via the π-stacking in aqueous medium; importantly, the introduction of naphthalene fragment to the peripheral substituent affects the associate stability but not its type. In the presence of pyridine in aqueous solutions of phthalocyanines, stable 1 : 1 molecular complexes are formed, preventing the macrocycles association. This work extends our studies on association behavior of water-soluble phthalocyanines in the solutions and the formation of their ordered structures. In particular, interaction of tetrasulfo- and octasulfo-substituted cobalt phthalocyaninates with 1,4-diazabicyclo[2.2.2]octane (DABCO) in water and in water–ethanol medium was studied using spectral methods. The object was chosen in view of unique electron absorption spectra of metal phthalocyaninates sensitive to the state of π-electron chromophore system of the macrocycle [11], allowing for differentiation of monomer and associated forms of phthalocyanine in the solution.

The following cobalt(II) complexes were studied: 3,10,17,24-tetrasulfophthalocyaninate (**I**), 3,10,17,24-tetrakis(6-sulfo-2-naphthyloxy)phthalocyaninate (**II**), and 3,10,17,24-tetrakis(6,8-disulfo-2-naphthyloxy)-phthalocyaninate (**III**) (Scheme 1).

We have earlier demonstrated that compounds **I**–**III** are soluble in alkaline aqueous media to form the corresponding salts existing predominantly in the form of dimeric *H*-aggregates at concentration range of 2×10^{-5}–2×10^{-4} mol/L [23]. Stability of the *H*-aggregates increases in the **III** < **II** < **I** series, pointing at the redistribution of the electron density in the macrocycle affected by the peripheral substituents.

The electron absorption spectrum of compound **I** aqueous solution was significantly changed in the course of its titration with DABCO solution (Fig. 1). In particular, the absorption band at 630 nm (assigned to the dimer) became weaker and suffered a red shift. Simultaneously, the absorption band at 670 nm (assigned to the monomer) became stronger, and was shifted towards longer wavelength by 8 nm. Those changes and the presence of isosbestic points in the

spectral series pointed at coordination of DABCO at the central metal ion and establishing of equilibrium (1) of dissociation compound **I** π–π-dimers.

$$(CoPc)_2 + DABCO \overset{K_e}{\rightleftarrows} CoPc{\cdot}DABCO + CoPc. \quad (1)$$

In Eq (1), $(CoPc)_2$ is the dimer form of a phthalocyaninate, CoPc is the corresponding monomer form, and CoPc·DABCO is the phthalocyaninate complex with DABCO.

The red shift of the *Q*-band was due to the change in the reaction site geometry: The coordination of DABCO resulted likely in pulling the metal cation out of the coordination plane. The redistribution of π-electron density in the macrocycle led to the prevalence of π–π-repulsion over π–σ-attraction, and the *H*-associate dissociated.

The stability constant of the molecular complex K_s = [CoPc·DABCO]/([CoPc]·[DABCO]) was calculated from the change in the absorbance of the solution at the *Q*-band range in the course of the titration with DABCO. Taking into account the material balance equation, the stability constant under conditions of large excess of DABCO with respect to the phthalocyanine could be represented as

$$K_s = (A_0 - A_c)/(A_0 - A_\infty)c^i_{DABCO},$$

with A_0, A_c, and A_∞ being the absorbance at the *Q*-band wavelength in the absence of DABCO, at DABCO concentration of c^i_{DABCO}, and at complete dissociation of the dimer, respectively.

The stability constant of the complex between compound **I** and DABCO in water calculated from the experimental data is given in Table 1.

Equilibrium (1) was completely shifted towards the products formation at the **I** : DABCO molar ratio of 1 : 100. Further addition of DABCO was expected to favor the free phthalocyanine transformation into the molecular complex; that would be reflected in enhancement of the *Q*-band and degeneration of the absorption band of the dimer. However, the dimer band degeneration was not observed experimentally; instead, a new band appeared at 605 nm. Accounting for the available reference data [26, 27], we suggested that the monomer form of phthalocyanine accumulated in sufficient amount could interact with the molecular complex to form the sandwich-type associates (Fig. 2):

$$CoPc{\cdot}DABCO + CoPc \rightleftarrows CoPc{\cdot}DABCO{\cdot}CoPc. \quad (2)$$

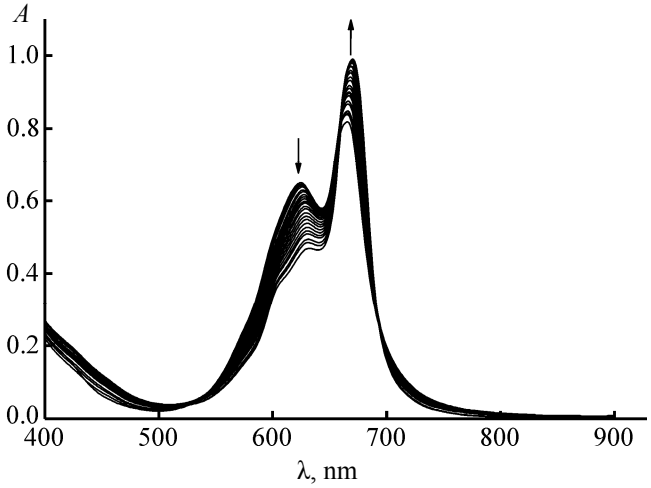


Fig. 1. Variation of electron absorption spectrum of compound **I** aqueous solution ($c = 4 \times 10^{-5}$ mol/L) during titration with DABCO solution ($n = 0–2 \times 10^{-3}$ mol).

The introduction of naphthyl fragments at the peripheral substituents significantly weakened the sulfo groups influence on the central metal ion. In turn, this altered the associative and coordination properties of the phthalocyaninates **II** and **III** as compared to those of compound **I**. For example, Fig. 3 illustrates the changes in electron absorption spectra of aqueous solution of complex **II** in the course of its titration with DABCO solution.

In the presence of DABCO the absorption band of compound **II** dimer was significantly enhanced and shifted towards longer wavelength by 30 nm, the band of the monomer form at 665–670 nm [23] being absent. The spectral changes were essentially the same in the case of compound **III**. Stability constants of the molecular complexes of compounds **II** and **III** with DABCO calculated as described above are given in Table 1. The collected data show stronger association of phthalocyanines **II** and **III** as compared to compound **I**; that was only possible owing to the formation of the sandwich-type aggregates. The stability of the sandwich-type aggregates of the studied compounds

Table 1. Stability constants of the 1 : 1 molecular complexes of compounds **I**–**III** with DABCO in water and in ethanol

Solvent	K_s, L/mol		
	I	**II**	**III**
Water	13000±100	8500±100	6700±100
Ethanol	280±20	No complex formed	

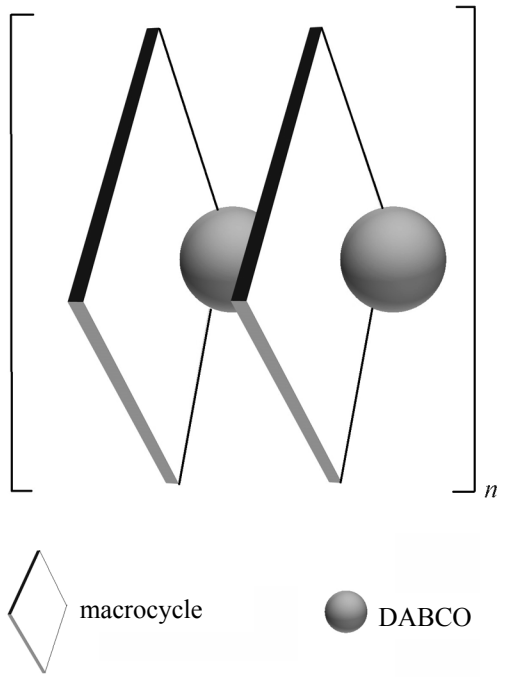


Fig. 2. Scheme of the sandwich-type associate.

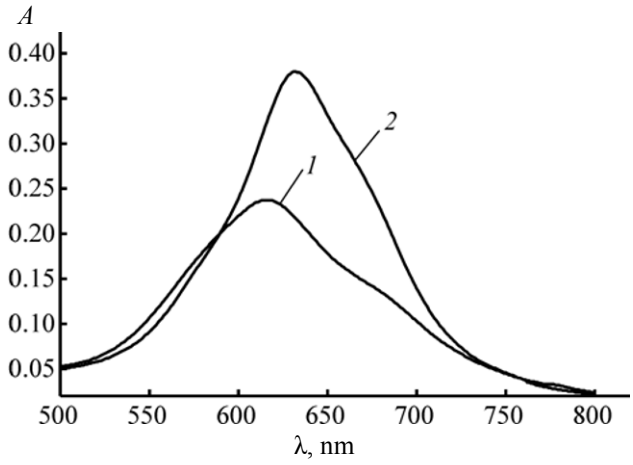


Fig. 3. Change of electron absorption spectrum of compound **II** aqueous solution due to interaction with DABCO: (*1*) initial solution of compound **II** ($c = 5.7 \times 10^{-5}$ mol/L) and (*2*) the same solution in the presence of DABCO ($n = 2 \times 10^{-2}$ mol).

followed the series reversed with respect to that of the *H*-aggregates stability. That was attributed to the stronger macrocycle–ligand interactions as compared to the π–π-interaction of two macrocycles. The larger substituents induced likely an additional interaction at the macrocycle periphery (hydrogen bonding) stabilizing the associate.

Stability constants of the sandwich-type aggregates (β) were determined from the absorbance data recorded at two wavelengths [28–31] using the following equation:

$$\beta = [\text{CoPc·DABCO·CoPc}]/[\text{CoPc·DABCO}][\text{CoPc}] = \Delta A_{i,\lambda 1}\Delta A_{0,\lambda 2}/[\text{CoPc·DABCO}]\Delta A_{0,\lambda 1}\Delta A_{i,\lambda 2},$$

with λ_1 being wavelength of the absorbance maximum of the initial solution, λ_2 being that in the presence of DABCO, [CoPc·DABCO] being equilibrium concentration of the molecular complex, $\Delta A_{0,\lambda 1}$ and $\Delta A_{0,\lambda 2}$ being the maximal change of the absorbance at the corresponding wavelength, $\Delta A_{i,\lambda 1}$ and $\Delta A_{i,\lambda 2}$ being those at the current DABCO concentration. Accuracy of β determination was better than ±7%.

Efficiency of the formation of the sandwich-type associates could be improved due to specific solvating properties of the solvent. In order to confirm this, we studied DABCO coordination with compounds **I**–**III** in ethanol solutions. We have earlier demonstrated that compound **I** in ethanol exists mainly in the monomer form due to the axial coordination of the solvent [32]. The ligand exchange was fairly smooth in the case of that macrocycle, and the addition of DABCO led to the formation of the 1 : 1 molecular complex.

The titration of alcoholic solution of compound **I** with DABCO was accompanied by enhancement of the *Q*-band at 670 nm, the band being simultaneously narrowed. The shape of integral titration curve was typical of the molecular complex formation (Fig. 4).

The complex composition was determined by the Bent–French method [33] from the slope of the log $[(A_0 - A_c)/(A_c - A_\infty)]$ plotted as a function of log [DABCO]. The formed complex was relatively unstable (K_s = 280±8 L/mol), likely due to the formation of the DABCO molecular associates via the donor-acceptor interaction with the solvent [34]. Just the low complex stability favored the formation of the more stable *J*-associated metal phthalocyanines.

Indeed, the complex between compound **I** and DABCO was twice more stable than that of compound **I** with ethanol [32], resulting in the substitution with DABCO of ethanol molecule from the inner coordination sphere of compound **I**. The stability of the complex between compound **I** and DABCO in aqueous solution was by an order of magnitude higher,

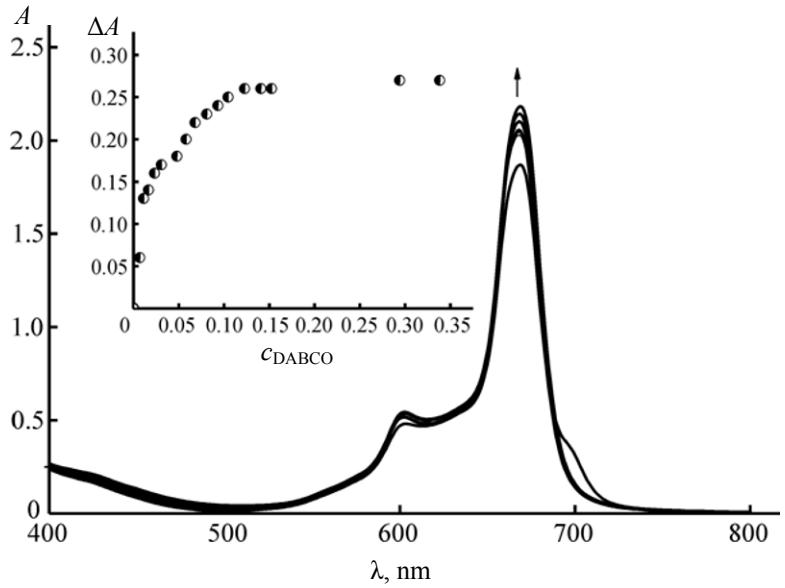


Fig. 4. Variation of electron absorption spectrum of compound **I** ethanolic solution (c = 5.4 × 10^{-5} mol/L) during titration with DABCO solution.

reflecting the effect of solvation on the complex formation and dimerization. At the **I** : DABCO molar ratio of 72 : 1 in ethanol medium, the *Q*-band in the electron absorption spectrum was weakened [$\Delta A(\lambda_{max})$ = 0.592], and the isosbestic point was shifted. Those changes were attributed to the coordination of the second metal phthalocyaninate molecule and the formation of the **I**·DABCO·**I** sandwich-type dimers; thermodynamic constant of the second macrocycle binding was 50±4 L/mol.

Compounds **II** and **III** were insoluble in anhydrous ethanol, therefore their complexes formation was studied in binary water–ethanol mixtures. The sufficiently high solubility of the complexes was attained at the ethanol:water volume ratio of 7 : 1; the macrocycles were not associated under these conditions. The complexes self-association yielding the H-dimers was observed with the increasing water fraction in the solvent: both compounds were significantly associated in the 1 : 1 water–ethanol mixture at the concentration of ~10^{-5} mol/L. The electron absorption spectrum of compound **II** solution contained a broad band at 625 nm (assigned to the dimer form), whereas an absorption maximum at 620 nm and a shoulder at 650 nm (the latter being the *Q*-band) were observed in the case of compound **III**. The bands assigned to the dimer form were progressively weakened at the dilution the complexes solutions from 9 × 10^{-5} to 9 × 10^{-6} mol/L, the ratio of the *Q*-band and the dimer band intensities showing no increase. The solutions absorbance at the dimer band wavelength followed the Beer's law up to the complex concentration of 10^{-4} (**II**) and 10^{-3} (**III**) mol/L.

The two-fold increase in the molar absorptivity of the *H*-aggregates in the ethanol solution as compared to those in the aqueous solution (Table 2) pointed at the higher solvation ability of the water–ethanol mixture towards the studied macrocycles attributed to specific interactions. On top of that, the effect of the peripheral substituent size was evident: compounds **II** and **III** containing the larger (and, hence, farther from the macrocycle) peripheral groups were dimerized in aqueous ethanol even in the dilute solution, whereas compound **I** existed in the monomer form. That could be explained by the intermolecular interactions at the periphery of the phthalocyaninate molecule, including the possibility of coordination of the side groups of the macrocycle with cobalt ion of the other molecule (*J*-aggregation) [16].

The spectral changes observed in the course of titration of the water-ethanol solution of compound **II** with DABCO pointed at the association enhancement via the formation of the sandwich-type dimers (Table 2), whereas the formation of the molecular complex was not detected.

The addition of DABCO to the solution of compound **III** in the 1 : 3 (v/v) water–ethanol mixture resulted in more complicated spectral changes (Fig. 5) corresponding to the transition of the chromophore

Table 2. Molar absorptivity (ε) of H-aggregates and stability constants (β) of sandwich-type complexes in different media

Macrocycle	ε, L mol^{-1} cm^{-1}		β(CoPc–DABCO–CoPc) × 10^{-3}, L/mol	
	water[a]	ethanol–water (v/v ratio)	water	ethanol–water (v/v ratio)
I	15200±50	exists in monomeric form (1 : 0)	8±1	38±1 (1 : 0)
II	4800±50	10500±100 (1 : 1)	52±2	24±1 (1 : 1)
III	800±20	1100±50 (1 : 3)	77±4	12±1 (1 : 3)

[a] Data from [23].

between its equilibrated forms. The *Q*-band of compound **III** was initially weakened in the course of the titration, and then (after attaining the **III** : DABCO equimolar ratio) it grew stronger and was shifted to longer wavelength by 10 nm. The absorption band of the macrocycle dimer form was simultaneously narrowed and weakened. At the **III** : DABCO molar ratio of 1 : 50, the aggregation was enhanced, and the compound precipitated.

The observations commented above pointed at the enhanced dimerization of compound **III** in aqueous ethanol medium as compared with the aqueous solution. The addition of DABCO to the solution induced the transformation of monomer form of compound **III** into the associate reflected in weakening of the *Q*-band. At further titration one of the dimer types (likely, the H-dimer) was converted into other associates with the non-interacting conjugated π-electron systems of the macrocycles (likely, the *J*-associates were formed via the interaction of the cobalt ion and the peripheral substituent of the other macrocycle), reflected in the *Q*-band shift. Such associates could not be formed in the case of compounds **I** and **II** because of their peripheral substituents structure. The DABCO contributed to the transformations of compound **III** by the formation of the intermediate molecular complex, moving off the π-electron system of the interacting macrocycles.

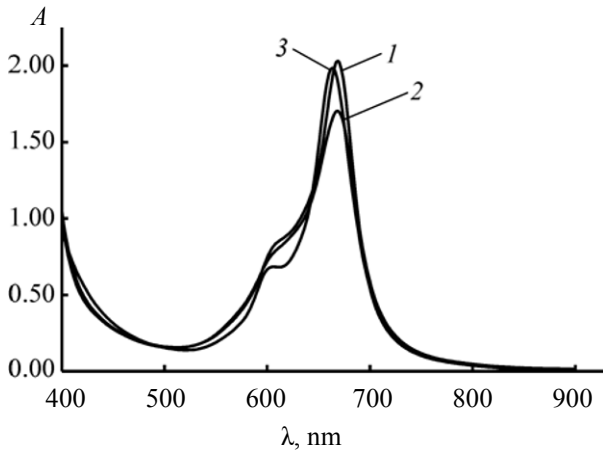


Fig. 5. Change of electron absorption spectrum during titration of compound **III** solution in the binary water–ethanol solvent (1 : 3, v/v) with DABCO solution: (*1*) initial solution of compound **III**, (*2*) $n_{\mathbf{III}} : n_{DABCO} = 1 : 1$, and (*3*) $n_{\mathbf{III}} : n_{DABCO} = 1 : 10$.

The stability of the dimeric structures formed by compounds **I**–**III** in ethanol was inversed as compared to the data for aqueous solutions (Table 2); this was attributed to the different solvating ability of the medium towards the peripheral functional groups. Furthermore, the competition between ethanol and DABCO for coordination with cobalt cation and/or the equilibrium between the sandwich-type dimers and the *J*-aggregates could contribute to the association state of the studied compounds in the presence of ethanol.

To conclude, coordination of DABCO at the studied macrocycles in the aqueous solutions resulted in the formation of the stable 1 : 1 molecular complexes capable of transformation into the sandwich-type dimers. In the water–ethanol mixture the compounds behavior was different. Compound **I** gave the 1 : 1 molecular complexes, but less stable than in the absence of ethanol. Compounds **II** and **III** formed the sandwich-type dimers instead of the 1 : 1 complexes. At higher DABCO concentration the compound **III** dimer was converted into the precipitating *J*-aggregate. The associates stability was in line with the size of the peripheral substituent in the macrocycle.

EXPERIMENTAL

Ethanol was purified as described in [35]. Cobalt(II) tetrasulfophthalocyaninate (99.8%) and 1,4-diazabicyclo[2.2.2]octane (99.8%) (both from Sigma–

Aldrich) were used as received. Synthesis, purification, and identification of the phthalocyaninates were performed as described in [36].

Electron absorption spectra were recorded using a Unico 2800 spectrophotometer in quartz cells with the optical path of 10 mm at 298.15 K.

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