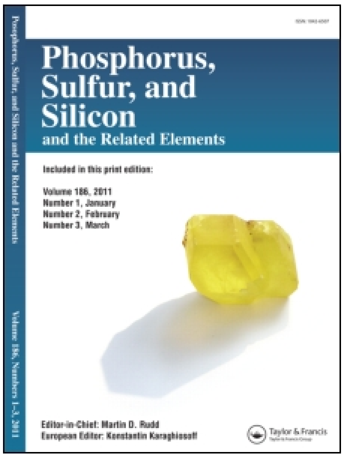

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Supramolecular Systems Based on Crownsubstituted Phthalocyaninates of Metals

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INTRODUCTION

The construction of functional materials from molecular building blocks as part of the field of supramolecular chemistry has gained increasing interest last time [1-2]. Supramolecular chemistry can be divided into two main and partly overlapping areas. One is the area of host-guest complementary molecules. The discovery of cation-binding crown ethers in the midle 1960's had a great impact on organic chemistry [3], since when a lot of receptors which can bind substrate molecules selectivity have been designed and synthesized. This binding, based on molecular recognition, can be followed by a chemical reaction, a transport process, or a detectable signal, i.e. a change in conformation or in electronic, ionic or optical properties. The second area in supramolecular chemistry concerns the formation of large molecular aggregates, in solution or in the solid state. The example of this type of compounds is phthalocyaninates of different metals.

Phthalocyanines (Pc) and its metal complexes (MPc) have been the focus of intensive investigation in the last few years because they exhibit properties which are interesting in material science [4-6]. Phthalocyanines owe their self-organizing abilities mainly to the strong attracting forces between their aromatic rings -also called π-π staking interactions. The overlap between the π-orbitals within a well organized stark of Pc molecules may result in interesting materials with conducting properties [7-9]. However, low solubility of unsubstituted Pc-complexes is a strong disadvantage for their application.

Crownphthalocyanines (Cr-Pc) combine the known properties of their crown- and phthalocyanine-ingredients with quite new features. Administration of crown-ethers into Pc-molecule increases their solubility both in organic solvents and in

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aqueous phase. Besides, Cr-Pc-molecules can form heteronuclear mixed M,M'-complexes which display the solubility, electrophysical and optical properties quite different from those that are typical for isolated Cr- or Pc-units [10-12]. The MCrPc form aggregates in polar solvents, which can be seen from the blue shifts of the absorption bands in the UV- VIS spectra. The addition of metal salts to solutions of these phthalocyanines also causes aggregation, due to complexation of the cations by the crown ether rings. Recently it was found that the electrical conductivities of these complexes were two to three orders of magnitude higher than in the case of the free host [12]. A positive co-operative binding effect was observed when alkaline metals was complexed with some MCrPc [11], and it has been suggested that this could be an important step in the realization of networks and molecular switches.

The goals of the our work are:

- to synthesize the new molecular compounds based on crown-substituted metallophthalocyanines, that should meet the following requirements:

- to act as sensors and selective detectors of ions;
- to have biological activity with amphiphility or aqueous solubility not less then 0.001 mol/l ;
- to form thin films with effective electrochromic, optical and conductivity properties.

- to investigate obtained compounds by electronic, IR, Raman, NMR spectroscopies and structurally characterize by X-ray method.
- to determine biological and photosensitive activity of metalcrownphthalocyaninates.
- to determine gas- and ion-selectivity, electrochromic and conductive properties of thin films of metalcrownphthalocyaninates.
- to investigate cation and solvent induced formation of highly organized columnar assembles of metalcrownphthalocyaninates.

SYNTHESIS

Transition-metal complexes with phthalocyanines are usially prepared by template synthesis in a high-boiling solvent or melt, e.g., from phthalonitrile in the presence of metal ions [5]. In our work we obtained tetra-15-crown-5-substituted phthalocyaninates of Lu, Yb (mono-, bis-, tris-) [13], unsymmetrical lutetium complexes, containing unsubstituted and tetra-15-crown-5-substituted phthalocyaninates [14] by the template synthesis in melt.

Co, Cu, Zn, Al tetracrownsubstituted phthalocyaninates (crown= 15-crown-5 and 18-crown-6) have been synthesized by template method in solution from dicyanobenzocrown and metal salts [15-17].

The template reaction at high temperatures gives many by-products (phthalimide, resin-like compounds, protonated phthalocyanines, unreacted phthalonitrile, etc.), and the yield of the target product is small (5-10 %). That is why, a new method for synthesis of rare earth elements pthalocyaninates based on the protonated tetra-15-crown-5 substituted phthalocyanine and rare earth elements acetates (REE= Nd, Gd, Yb, Lu) have been developed. The synthesis was carried out in medium of a organic solvents with high boiling points (1,2- dichlorobenzene - 180°C, 1-chloronaphtalene - 260°C) in the presence of the strong organic bases - 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), 1,10-phenantroline (Phen). The catalyst of the formation of macrocycles (DBU) widely used in the synthesis of phthalocyanines is a strong deprotonating agents [18-19]. It has been found that the yield of mono- , diphthalocyaninates or club-sandwich complexes of REE depends on the boiling point of solvents. Another important condition for formation of phthalocianine complexes with REE is presence of DBU or Phen, which promote deprotonation of ligand. Monophthalocyanines are formed in refluxing 1,2-dichlorobenzene in presence of salts of Gd, Yb, and Lu. Sandwich and club-sandwich complexes are produced in refluxing 1-chloronaphtalene. At the same time in the case of Nd, the club-sandwich complexes have been obtained when synthesis was carried out in refluxing 1,2-dichlorobenzene. This fact could be explained due to large radius of Nd(III), that provides a larger distance between the two-charged ligand's ions and in turn promotes attenuation of the interionic repulsion and stabilizasion of sandwich complexes.

The regularities, which has been found, allow to carry out the direct synthesis of crownphthalocyaninates of REE with predicted structures.

STRUCTURES

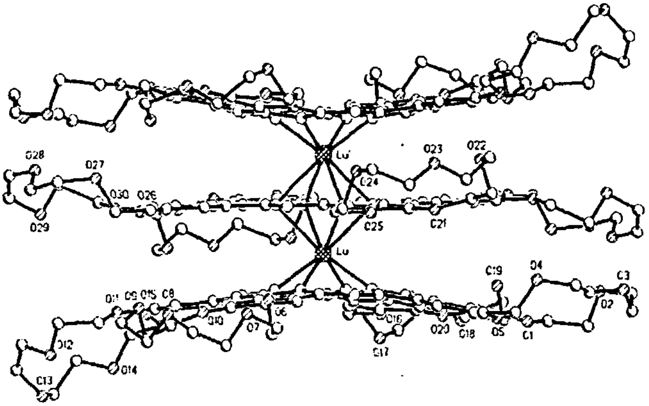
There are four molecular structures types of phthalocyaninates complexes depending on the valency and nature of central metal ion:

- Monophthalocyaninates (symmetry D_{4h}) in the case of metals(II);
- Monophthalocyaninates with extraligands (symmetry C_{4v}) in the case of metals(III);
- Bisphthalocyaninates (symmetry C_{4v}) in the case of metals(III), when the ionic radius ≥1.36 Å;
- Trisphthalocyaninates (symmetry C_{4v}) in the case of metals(III), when the ionic radius ≥1.36 Å;

The most reliable method of the structure determination of the compounds is the X-ray diffraction study. However, it is very dificult to obtain single crystals of the substituted phthalocyaninates. But, these compounds have bright colors (from green to blue), therefore, the absorption spectroscopy can be sucessfully used for their study. The electronic spectroscopy is, presently, the simplest method of identification of the colored forms of phthalocyaninates providing the greatest information volume. The introduction of crown ether into the aromatic rings of phthalocyanine does not change the character of their absorption spectra, but only leads to an small shift of absorption bands. Therefore, the known correlation between the structure and the parametres of the electronic spectra of nonsubstituted phthalocyanines allowed as to precisely identify the formation of a type of crownphthalocyaninates, sintesized in this work. IR, Raman and NMR spectroscopies are also used for structure investigations of our compounds. In our work we synthesized the compounds with following structures:

Central Metal	Structures types of
Cu, Co, Zn	MCr_4Pc, $MCr_4Pc \times nM_1X$, M_1= alkali metal, Cr=15-crown-5 & 18-crown-6
Al, Lu, Yb	$MCr_4Pc \times Y$, Y=extraligand, $MCr_4Pc \times nM_1X$, M_1= alkali or rare earth metal
Lu, Yb, Gd, Nd	$M(Cr_4Pc)_2$
Lu, Yb, Gd, Nd	$M_2(Cr_4Pc)_3$

In the first time, the single crystal of $Lu_2(CrPc)_3$ have been isolated and studied by X-ray analysis in our laboratory [20]. Prismatic dark blue crystals were obtained by slow crystallization in an NMR tube from a mixed solution of the composition DMSO-d_6: $CDCl_3$ = 2:1. The crystal consists of descrete centrosymmetric dilutetium triphthalocyaniunate molecules. The molecular structure of the complex in the crystal is shown in figure. The lutetium atoms are located between the planes of phthalocyanine ligands (R_4Pc^{2-}).



Two owter phthalocyanine rings have identical orientation with respect to the inner ring. The inner ring is turned by 43.7° relative to the outer tetraaza macrocycles, such that a coordination polyhedron of the lutetium ion is a distorted square antiprism. It have been proved that the "blue" form of phthalocyanine has a triple-decker structure. ***It is important to note that this is the first crystal structure for crownphthalocyaninates as well as other substituted phthalocyanines.***

CATION AND SOLVENT INDUCED AGGREGATION OF CROWN-PHTHALOCYANINATES OF METALS

Electronic absorption spectroscopy is useful technique to study aggregation in solution. As is known [21], depending on the mutual arrangment of macrocyclic π-aromatic systems in aggregates, a spectral band in the visible region undergoes either a blue or a red shift relative to the absorption band of the monomer. The aggregates of the first type contain, as a rule, a small number of neighboring strongly interacting molecules; there are, specifically, cofacial dimers, also referred to as H-aggregates. In the aggregates of the second type, named J-aggregates, molecules are considerably shifted with respect to one another, and another type of dipole-dipole interaction between their π-systems lead to a red shift of the absorption band. These changes in electronic absorption spectra are observed for aggregates comprising 4-9 monomers: since the mutual arrangement of molecules in these aggregates differs from that in J-dimers, which are spectrally indiscernible from monomers [21]. Aggregation of tetracrown-substituted metal phthalocyaninates in organic media has been studied [10,11, 22-27]. In chloroform they form heteronuclear complexes with alkali metal cations. The complex composition is dictated by the metal-to-phthalocyanine ratio and relative sizes of the cation and the macrocyclic cavity. We observed a Na/K optical selectivity of cobalt tetra-15-crown-5-phthalocyaninate ($CoCr_4Pc$). Sandwich dimers are formed, when the metal ion is potassium and the ratio potassium: $CoCr_4Pc=2:1$. The latter give rise to the Q-absorption band at 620-640 nm. In the system, containing sodium ions at the ratio of 2:1, monomer combine to form dimers, which latter with an increase in $[Na^+]$, transform into the $CoCr_4Pc \times 4NaX$ complex ($\lambda max=710$ nm). The difference of Q-absorption band maximums (80 nm) is quite sufficient to determine that potassium and sodium ions simultaneously occur in solution. It has been found, that the determination of potassium ions at a tenfold exess of sodium ions, and the determination of sodium ions, at a fivefolds excess of potassium ions. This fact can be used for development of sensors and selectively detectors of alkali iones.

AGENTS FOR PHOTODYNAMIC DIAGNOSTIC AND THERAPY OF CANCER.

Metal complexes with phthalocyanines are widely used as sensitizers in photodynamic diagnostics and therapy of cancer (PDT) [27]. Diamagnetic Zn(II), Al(III) and Ga(III) complexes with phthalocyanines are promising second-generation compounds in the PDT because of their strong absorption in the red region of electronic spectrum [28, 29]. Studying a number of metallocomplexes with phthalocyanine has shown that their photosensitizing properties depend on the substituent nature [30]. Therefore, a search for new hydrophilic and lipophilic agents for use in PDT is a rather urgent problem. The main requirements for sensitizers are a constant composition, strong absorption in the red and near-IR regions of the spectrum, the optimum ratio between the values of the fluorescence quantum yield and the quantum yield of singlet oxygen, low toxicity, selectivity of accumulation in tumors, solubility in water, and monomer presence in aqueous solutions. The procedure of preparation of compounds with photodynamic activity must be easy. The compounds considered in this work meet the above requirements in many respects. Some crownsubstituted phthalocyaninates of metals $Lu(Cr_4Pc)_2$, $Yb(Cr_4Pc)_2$, non-symmetrical $(Pc)Lu(Cr_4Pc)$, complexes with extraligands - $LuCr_4Pc{\times}OAc{\times}DBU$ and $LuR_4Pc{\times}OAc{\times}2Phen$ that have absorption from 670 mn to 686 nm were offered as potential photosensitizers. Investigation of their physico-chemical, spectral and photophysical characteristics, cytotoxicity, biodistribution and pharmacokinetic was carried out.

All compounds are provide good solubility in water and biological liquids, but complexes with extraligands have the best solubility in water. Therefore, we studied the luminescence spectra of $LuCr_4Pc{\times}OAc{\times}DBU$ and $LuR_4Pc{\times}OAc{\times}2Phen$ in aqueous solutions. The luminescence spectra of $LuR_4Pc{\times}OAc{\times}2Phen$ and $LuR_4Pc{\times}OAc{\times}DBU$ in water are characterized by a strong band at 700 nm, a poorly pronounced shoulder at 730-740 nm, and a weak band at 760-770 nm. For a concentrated solution of $LuR_4Pc{\times}OAc{\times}2Phen$ ($c=1.7\times10^{-4}$ mol/l) a shift of the first band of luminescence to the long-wave region to 707 nm is observed. A low quantum yield in these systems should be noted. The one of requirements for sensitizers is monomer presence in aqueous solutions. By the way of introduction of phenantroline molecules as extraligand to phtalocyaninate we can obtained compounds, that have monomer structures in water [26]. At the same time selectivity of accumulation in tumors is increase.

The obtained data allow us to consider the complexes of tetracrown-substituted lutetium phthalocianinate with the extraligands as candidates for photodynamic diagnostics and therapy of cancer.

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