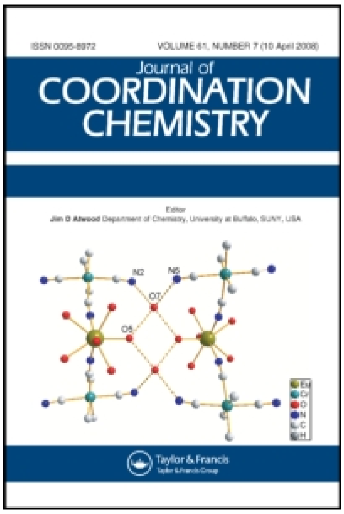

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SUPRAMOLECULAR SYSTEMS CONSTRUCTED FROM CROWNPHTHALOCYANINATES

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A review of coordination compounds of several metals (Co^{2+}, Ru^{2+}, Zn^{2+}, Al^{3+}, Y^{3+}, Ln^{3+} = La, Gd, Yb, Lu) with tetra-crown-substituted phthalocyanine H_2R_4Pc (R_4Pc^{2-} = [4,5,4′,5′,4″,5″,4‴,5‴-tetrakis(1,4,7,10,13-pentaoxotridecamethylen)phthalocyaninate-ion]) has been presented. The syntheses of compounds with a given tetra-azamacrocyclic ligand are described. The template method based on the crown-substituted phthalodinitrile is the optimum technique for preparation of Ru^{2+} monophthalocyaninate and sandwich complexes of Lu^{3+}. For other rare earth metals the new synthetic approach based on the application of the H_2R_4Pc ligand has been suggested. Some aspects of supramolecular chemistry including cation-induced aggregation in solutions have been discussed for the compounds of this class.

Keywords: Phthalocyaninates; Crown-ethers; Supramolecular chemistry; Cation-induced aggregation

INTRODUCTION

Supramolecular chemistry started with the investigation of selective bonding of cations of alkali metals by different natural and synthetic macrocyclic and macropolycyclic ligands [1].

Searching for new combinations on the basis of known structural fragments of molecular receptors is the important task, because, by changing some moieties that bind the molecules, one can control the receptor's ability to form specific complexes. This, in turn, allows the construction of composites possessing unique properties. Crownphthalocyaninates (Fig. 1), in which crown-ether substituents are an integral part of the phthalocyanine macrocycle, represent examples of such compounds. Having conformational flexibility, crown-ether substituents are available for selective capture of metal ions, facilitating the cation-induced organization of supramolecular assemblies. The presence of two channels – ionic (created by crown-ether side substituents) and electronic, which provide the transport in phthalocyanine piles, formed by the "stacking" interaction between macrocyclic aromatic rings – is typical for such

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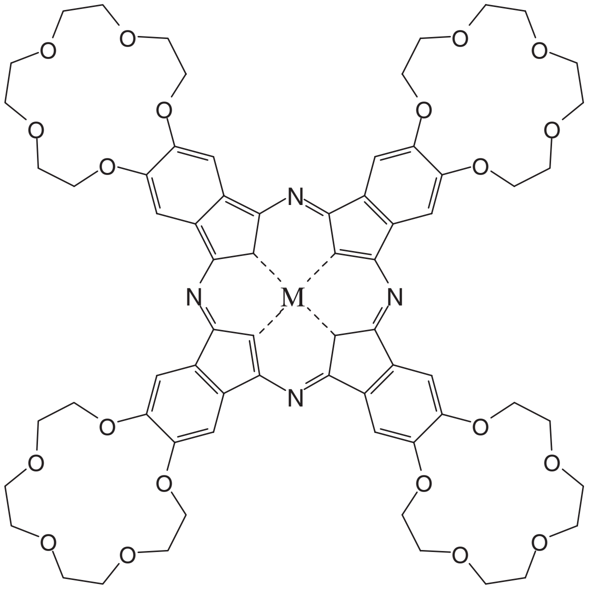

FIGURE 1 Crown-ether-substituted phthalocyaninates.

supramolecular structures. Because of these channels, crownphthalocyaninates possess unique electrophysical and optical properties, which permit development of supramolecular functional materials for modern ionic and molecular electronics [2].

Tetra-crown-substituted phthalocyaninates $M(R_4Pc)$ ($M = 2H^+$, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}) have been described by several research groups [3–8]. Studies of the interaction of cobalt tetra-15-crown-5-phthalocyaninate with sodium and potassium thiocyanates [9], have shown unusual sodium–potassium selectivity. Now we have developed methods for the synthesis of metal tetra-crownphthalocyaninates, in which the side substitutents are: 15-crown-5 (M = Al(III) [10], Ru(II) [11], Zn(II) [12], Lu(III) [13–15], Yb(III) [15], Gd(III) [15], La(III) [16], Y(III) [17] or 18-crown-6 (M = 2H, Cu, Zn [18]). Also we have prepared the asymmetric double-decker lutetium phthalocyaninate, containing unsubstituted and tetra-15-crown-5-substituted phthalocyanine rings [19].

We have studied the influence of various factors (the nature of the receptor and the substrate, the polarity of the solvent), which can effect generation of aggregates with different architecture, on the processes of formation of supramolecular assemblies for a series of crown-substituted phthalocyanines.

As a result, we recognize patterns for cation-induced organization of supramolecular assemblies based on metal crownphthalocyaninates.

EXPERIMENTAL

Compounds were identified using time-of-flight mass spectrometry with matrix-assisted laser desorption ionization (Reflex-III mass spectrometer, Bruker Daltonics). The UV-Vis spectra were obtained with a Varian Cary-100 spectrometer. The IR spectra of samples were recorded on a Nicolet Nexus spectrometer. Diamagnetic complexes were characterized by PMR spectroscopy (Bruker WM-500 and Bruker AC-200 instruments). The radical nature of double-decker complexes was confirmed by EPR spectra; the signal (singlet with $g = 2.0031$) in the EPR spectra of solutions of corresponding compounds in chloroform indicates the presence of an unpaired electron in the molecule $[(R_4Pc^{2-})M^{3+}(R_4Pc^{-\bullet})]^0$. EPR spectra were obtained with an SE-X-2542 Radiopan instrument at room temperature. The electronic absorption spectrum in near-IR is recorded on a Specord NIR-61 spectrometer, Carl Zeiss, Jena. The bands near 900 nm and at 1400–1600 nm in the electronic spectra of double-decker complexes also confirm the radical nature of these complexes. These bands are ascribed to an exchange donor–acceptor interaction between dianion Pc^{2-} and monoanion Pc^{-}.

RESULTS AND DISCUSSION

Synthesis

The supramolecular synthesis divides into two steps: (1) the synthesis of the molecular components (building blocks) by the formation of strong, kinetically non-labile, covalent bonds; and (2) the generation of supramolecular particles by the spontaneous association of these components in predetermined ways, involving relatively weak and kinetically labile non-covalent interactions.

Synthesis of Crownphthalocyaninates – Building Blocks

The synthesis of crown-substituted single-, double- and triple-decker phthalocyaninates of composition $(M^{n+} : Pc^{2-})$ 1 : 1, 1 : 2, 2 : 3 has been performed. Co, Cu, Zn, Al, Ru and Lu complexes with tetra-crownphthalocyanine (crown = 15-crown-5 and 18-crown-6) were obtained using the previously developed method of template designing of crownphthalocyaninates on the matrix of a metal cation, based on precursors (dicyanobenzo-15-crown-5 and dicyanobenzo-18-crown-6) in a melt or in a solution of high-boiling solvents [4, 10, 11, 13, 18]. However, in order to increase the efficiency of the synthesis we have developed a new technique of direct production of metal crownphthalocyaninates from a protonated ligand and a metal salt [14–17]. This procedure was demonstrated by the crownphthalocyaninates of rare earth metals (Lu, Yb, Gd, La, Y).

The covalent radii of rare earth elements make them larger than the inner cavity of a phthalocyanine. Therefore, along with monophthalocyaninates, rare earth elements also form complexes with a sandwich structure: double-decker neutral monoradical complexes and binuclear trisphthalocyaninates with isoelectronic doubly charged macrocyclic ligands. The classic method of template condensation in the melt of phthalonitrile, which is used because of its technological simplicity, has two main drawbacks: it is impossible to control the process and it is difficult to separate the products. In addition, the yield of metal complexes depends on the nature of the matrix Ln^{3+} cation. For example, during production of sandwich complexes at high temperatures the demetallization of Gd^{3+} monophthalocyaninate occurs (the charge density of the Gd^{3+} cation is less than that of the Lu^{3+} cation), which may act as a matrix for the synthesis of the next macrocycle with formation of a sandwich complex. As a result, the yield of double- and triple-decker gadolinium phthalocyaninates is small in the template synthesis, and reproducibility is poor.

We have found that the macrocyclic effect, the shielding of reacting centers by the π-electron system of a ligand, prevents direct substitution of isoindol protons for metal cations. Therefore we used strong organic bases 1,8-diazobicyclo[5,4,0]undecene-7 (DBU) and 1,10-phenanthroline (Phen) as deprotonating nucleophilic agents. This allowed us to synthesize both types of sandwich complexes of crown-substituted gadolinium, ytterbium and lutetium phthalocyaninates. The solvent is also very important in direct synthesis. Use of various solvents for the synthesis allowed regulation of the yield of specific products. To obtain gadolinium, ytterbium and lutetium monophthalocyaninates, the synthesis should be conducted in *o*-dichlorobenzene (boiling point 180°C). Refluxing in 1-chloronaphthalene (boiling point 260°C) results in formation of double- and triple-decker compounds of these metals. In the case of lanthanum, sandwich-type double-decker phthalocyaninates were prepared even in *o*-dichlorobenzene. This can be explained in terms of ionic radii. Because the lanthanum ionic radius is larger than that of gadolinium, ytterbium or lutetium, the distance between phthalocyanine ligands is increased, resulting in stabilization of the sandwich structure of the complex of lanthanum with phthalocyanine. These studies revealed some peculiarities of complexation of lanthanides with $H_2(R_4Pc)$ on going from lanthanum to lutetium. With the aim of studying the dependence of the properties of the obtained compounds on the nature of the metal, the synthesis has also been used to make yttrium crownphthalocyaninates [17], whose chemical properties are similar to the properties of lanthanides. Yttrium forms both monophthalocyaninates and sandwich complexes because its ionic radius is close to that of lanthanides in the middle of the row.

Previously, discussions on the structure of crownphthalocyaninates were based on comparative analysis of their absorption spectra with the absorption spectra of unsubstituted analogues. Since phthalocyanines have bright colors, absorption spectroscopy is suitable and informative for their analysis. However, owing to the lack of X-ray data on crownphthalocyaninates, determination of their structures could not be performed unambiguously. Crystals of the lutetium complex with tetra-15-crown-5-phthalocyanine (metal–ligand ratio of 2 : 3) were isolated, and for the first time the structure of the triple-decker complex (see Fig. 2), containing three substituted phthalocyanine ligands was established [20]. This structure was the first one determined for crown-substituted phthalocyaninates, providing the first X-ray evidence for the molecular structure of the metal complexes with crownphthalocyanine ligands. The crystal is constructed from individual centrosymmetrical molecules, consisting of three mutually parallel tetra-15-crown-5-phthalocyanine ligands and two ions of Lu(III). The central ligand is turned by 43.7° relative to external ligands. The mean interplanar spacing is 2.923 Å. The lutetium ions are localized between ligands with distorted square antiprism geometry. The four lutetium–nitrogen bonds, including the isoindol nitrogen atoms of external phthalocyanine ligands (mean bond length 2.305 Å), are shorter than the corresponding distances to the inner ligand (mean value 2.560 Å). The intramolecular lutetium–lutetium distance is 3.406 Å. The shortest intermolecular distance between the adjacent phthalocyanine planes is 10.443 Å.

Synthesis of Supramolecular Assemblies

The second step is direct supramolecular synthesis of assemblies with complex architectures. This process can be induced by increasing the concentration of a complex in solution, by changing the polarity of a solvent or by interaction of a complex with

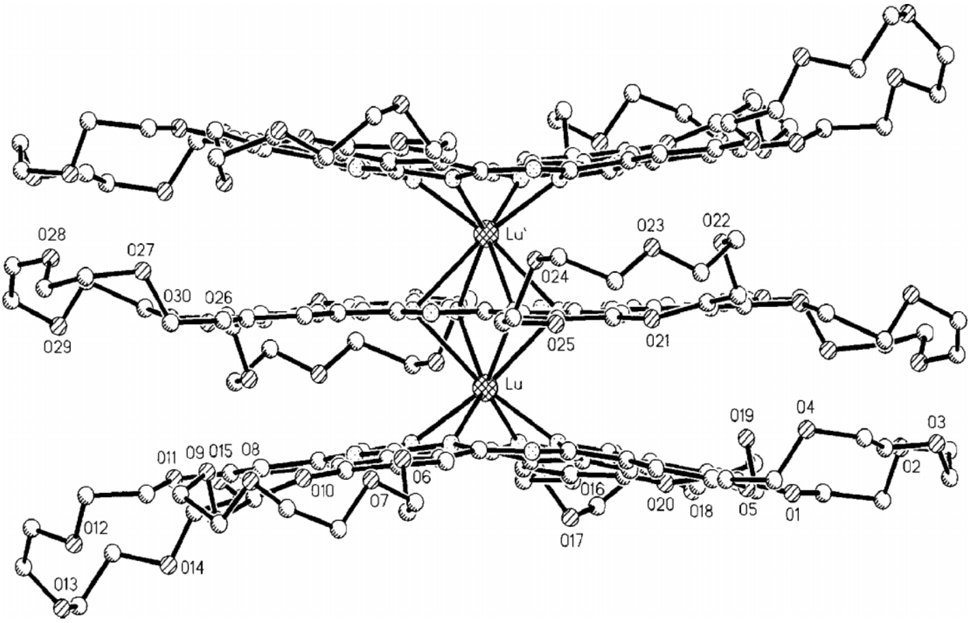

FIGURE 2 Side view of the $Lu_2(R_4Pc)_3$ molecule showing the triple-decker structure of the sandwich complex and the numbering of crystallographically independent oxygen atoms.

ions of alkaline, alkaline earth and rare earth metals. Complete understanding of the system requires investigation of the organization of the structure of inner bonds. One of the most efficient approaches is examination of intermolecular interactions of crown-substituted phthalocyaninates in solution using UV-Vis spectroscopy. Spectral investigation of "host–guest" complexation is based on the chromophoric properties of phthalocyanine. The interactions between phthalocyanine molecules are explained on the basis of spectral data; in this case the energetically delocalized states called excitons are considered. Splitting of the electronic levels of an excited state (Davydov splitting) resulting from the exciton interaction is determined by the mutual orientation of the transition interacting dipoles and the number of interacting molecules. For example, when the dipole moments of the molecules are parallel to each other, the hypsochromic shift of the Q and Cope bands occurs in the electronic absorption spectrum of phthalocyanine. Such aggregates with cofacial configuration are denoted the H-aggregates (Fig. 3). If the transition dipoles are in line, a bathochromic shift of the Q-band occurs in the spectrum. In this case, higher aggregates of the edge-to-edge type (J-aggregates), which cause a significant bathochromic shift with an intense narrow-band, are formed. J-aggregates ordering three-dimensional structures (Fig. 4) possess unique properties of photoluminescence and non-linear optics.

Synthesis of Cofacial Dimers Formation of heteronuclear supramolecular dimers was studied for several crown-substituted phthalocyaninates of bivalent transition metals [4–9, 21, 22]. Crown-substituted phthalocyanines and their metal complexes form rigid, stable cofacial dimers in the presence of ions of alkali and alkaline earth metals for which the crown-ether fragments represent chelating ligands. The key condition of dimer formation is that the diameter of the cation is more than that of the cavity

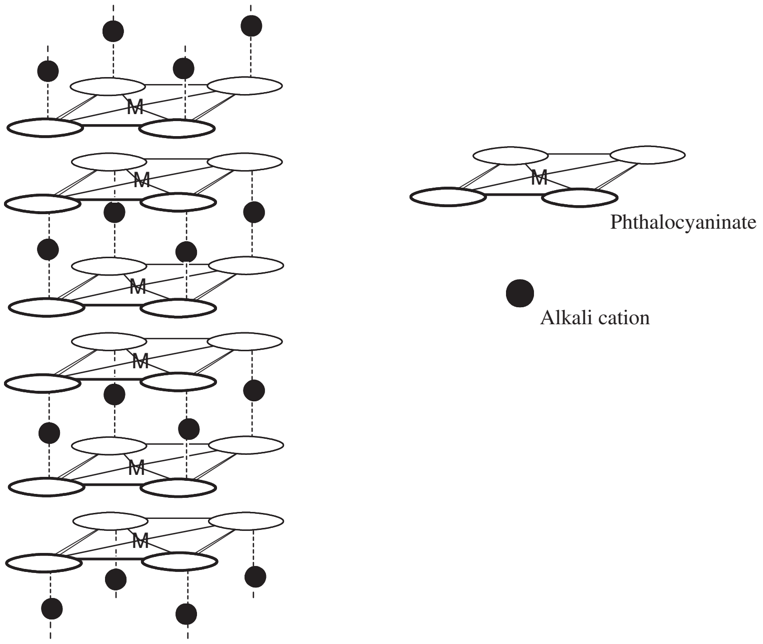

FIGURE 3 Schematic representation of the cofacial aggregates.

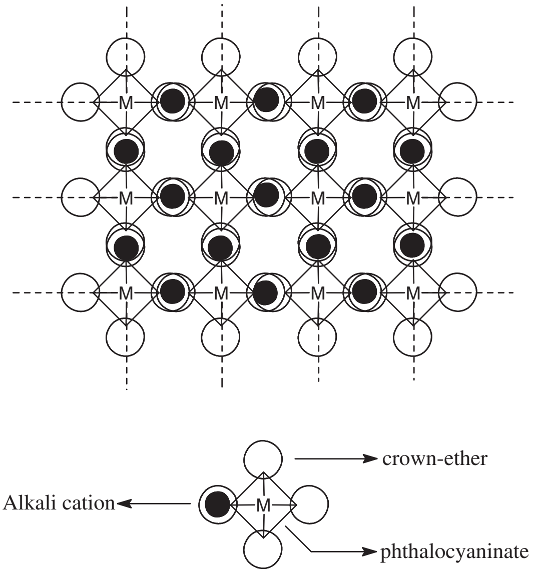

FIGURE 4 Schematic representation of the edge-to-edge network aggregates.

of a crown-ether ligand. Rigid cofacial dimers of composition $2MR_4Pc \times 4K^+$ ($M = Cu^{2+}$, Co^{2+}, Zn^{2+}; R_4Pc^{2-} = tetra-15-crown-5-phthalocyaninate ion) are formed. These results differ from those obtained for supramolecular aggregates of porphyrines containing 15-crown-5 in meso-positions [23]. Because of less rigid binding, the crown-ethers in a macrocycle are more labile, and the formation of dimers takes place between porphyrin molecules, turned by 45° to each other. Cofacial dimers of crownphthalocyanines are perfectly eclipsed and will be more interesting in the ion-electronic studies. In the case of asymmetric double-decker lutetium phthalocyaninate containing unsubstituted and tetra-15-crown-5-substituted phthalocyanine rings, the cofacial dimer of composition $2[Lu(R_4Pc)Pc] \times 4K^+$ is also formed [24].

Interaction of $Al(R_4Pc)SO_4H \times 2H_2O$ with potassium and sodium halides was studied in organic solvents [25]. The composition of the heteronuclear complexes obtained depends on the nature of the solvent. In chloroform sandwich complexes of composition $4MX \times 2Al(R_4Pc)SO_4H \times 2H_2O$ ($M = K^+$, Na^+; $X = Cl^-$, Br^-, I^-) are formed. In $CHCl_3 : MeOH = 7 : 3$ (v/v) complexes with composition $4Na^+X \times Al(R_4Pc)SO_4H \times 2H_2O$ ($X = Br^-$, I^-) are produced. The effect of the anion on the stability of these complexes was analyzed for sodium cations showing that the stability of sandwich structures decreases from I^- to Cl^- with increasing rigidity of the anion.

We have synthesized for the first time amphiphilic complexes with an extra ligand, $LuR_4Pc \times OAc \times DBU$ and $LuR_4Pc \times OAc \times 2Phen$, which dissolve both in organic solvents and in water [14]. There is no aggregation of the complexes in aqueous solution since the extra ligand creates steric restrictions for the intermolecular interaction. Potassium ions induce aggregation of macromolecules resulting in formation of supramolecular cofacial H-dimers [26]. Unlike low-polarity media ($CHCl_3$), dimerization in water takes place with large excess of an electrolyte with respect to these lutetium complexes. The interaction of $LuR_4Pc \times OAc$ with potassium and sodium acetates in $CHCl_3$–DMSO was studied using spectrophotometric analysis and PMR [27]. Interaction with potassium ions leads to formation of "host–guest" cofacial dimers; sodium ions do not generate such dimers.

Previously it has been shown that the cobalt complex with tetra-15-crown-5-phthalocyanine $Co(R_4Pc)$ has sodium–potassium selectivity such that the interaction of this complex with sodium and potassium thiocyanates in chloroform causes a significant shift of the Q-band (in different directions) in the absorption spectrum of the complex [4, 9]. This fact was explained in terms of the creation of complexes of different composition. For potassium the highly symmetric cofacial dimer of composition $K^+ : Co(R_4Pc) = 2 : 1$ is formed; in the case of sodium a flat complex of composition $Na^+ : Co(R_4Pc) = 4 : 1$ is produced. However, for sodium ions the interaction time is 30 min, during which the electronic absorption spectrum of the solution changes gradually, accompanied by the bathochromic shift of the Q-band of the resulting aggregate. One can assume that formation of the supramolecular aggregate induced by sodium cations has two steps. In the first step, a flat complex of composition $4NaSCN \times Co(R_4Pc)$ is formed. The second step includes participation of thiocyanate ions in complexation with cobalt ions of adjacent molecules along an axial coordinate. As a result, aggregates of "edge-to-edge" type are formed. If the thiocyanate ions are replaced by Cl^-, ClO_4^- or CH_3COO^- ions, the selectivity is not reproduced, serving as indirect evidence of our assumptions.

The sodium–potassium selectivity of cobalt crownphthalocyaninate can be used in medicine for determination of sodium and potassium ions in biological liquids [28]. However, for this analysis the use of solutions of substances in pure chloroform has no prospects in medicine. Therefore, in order to choose the optimum system possessing sodium–potassium selectivity, it is necessary to study the behavior of $Co(R_4Pc)$ complex in solvents with different polarity and in their mixtures [presumably the $Co(R_4Pc)$ complex should be in the monomeric state]. To solve this problem, the electronic absorption spectra of the Co(R_4Pc) complex have been studied in the mixtures chloroform–S (S = CH_3OH, C_2H_5OH, H_2O). In a chloroform–ethanol mixture (20% v/v) the complex is monomeric [29].

We have conducted a spectrophotometric investigation of the influence of ruthenium(II) tetra-15-crown-5-phthalocyaninate (R_4Pc)Ru(CO)(CH_3OH) on the cation-induced organization of supramolecular assemblies. The addition of KSCN in methanol to a solution of (R_4Pc)Ru(CO)(CH_3OH) in chloroform causes a bathochromic shift of the Q-band by 11 nm, which is not typical for cofacial aggregation. A network model was proposed for the structure of the assembly formed. The network consists of [Ru(CRPc)(CO)(MeOH)] molecules, which are retained by K^+ ions. The axially coordinated CO and MeOH molecules prevent formation of assemblies with a cofacial structure. The interaction with Na^+ ions is complex, probably proceeding by a scheme similar to that for the Co(R_4Pc) complex.

The effect of potassium and sodium thiocyanates on the triple-decker lutetium phthalocyaninate $Lu_2(R_4Pc)_3$ was studied in $CHCl_3$ solution [30]. Based on spectrophotometric titration data, formation of a sandwich dimer of composition $2[Lu_2(R_4Pc)_3] \times 4KSCN$ was observed. Sodium thiocyanate does not induce formation of permolecular sandwich structures, because it has no influence on the spectrum of the triple-decker complex.

Synthesis of Aggregates (oligomers) ($n > 2$) The nonlinear processes for formation of oligomeric supramolecular assemblies, induced by K^+, Rb^+ and Cs^+, were studied using spectrophotometric analysis as for neutral-radical double-decker lutetium complexes with tetra-15-crown-5- and tetra-18-crown-6-phthalocyanines [2, 31]. Based on the titration data and the fact that complexation with picrates of alkali metals on both sides of a sandwich is possible for sandwich complexes, the supramolecular oligomers containing 20 molecules of building-blocks $Lu(R_4Pc)_2$ are assumed to be produced. Depending on the cation size, a positive nonlinear cooperative effect is observed, accompanied by formation of supramolecular aggregates in the form of "columns" and "tubes" in which one-dimensional transport of electrons and ions can occur. The development of ionic and molecular electronics by creation of a new generation of functional materials is predicted on the basis of these data [2].

Investigation of supramolecular assembly processes has been performed for the one-electron reduced form of octa-15-crown-5-bisphthalocyaninates of rare earth metals $[Ln(R_4Pc)_2]^-$ (Ln = Y, Gd, Yb, Lu) [30]. A one-electron reduced form is produced on dissolving the radical form in DBU, or by titration of its solution in chloroform using DBU. The addition of K^+, Rb^+ or Cs^+ thiocyanates to solutions of the reduced form of crownphthalocyaninates of rare earth metals, obtained in this way leads to the same spectral changes, consisting of the bathochromic shift of the Q_1-band with simultaneous decrease of the half-width of this band. The splitting of the Q-band of the reduced form disappears. Analysis of the spectrophotometric data together with the spectral study conducted by the scheme

$$(Ln(R_4Pc)_2)^{0\bullet} + MSCN \rightarrow [(Ln(R_4Pc)_2)^{0\bullet} \times 4MSCN]_n + DBU$$

allowed us to draw conclusions about the formation of polymeric cofacial supramolecular structures ($n > 20$) [30]. In contrast to the radical form of the complex, for which differences in interaction with potassium and rubidium picrates occur, the one-electron reduced form is organized in supramolecular structures of the ''host–guest'' type by the mechanism involving K^+, Rb^+, Cs^+ thiocyanates. Nonlinear cooperative effects are observed in all three cases. It was found that for other potassium salts (acetate, bromide) there is no anion effect. Therefore, the reduced form of the sandwich double-decker crownphthalocyaninates of rare earth metals is the group sensor on cations of alkali metals (K^+, Rb^+, Cs^+).

CONCLUSIONS

It was established that if the matrix is a transition metal or Lu^{3+} ion, the template method for synthesis of crown-substituted phthalocyanines could be applied. The lutetium cation has the highest charge density of all the rare earth metals, and therefore forms the strongest coordination bonds. This is responsible for the high degree of cyclotetramerization of phthalodinitrile and the high yield of target metal complexes. If the template matrix is less effective, the method of direct synthesis from H_2R_4Pc is better. The main feature of this method is that substitution of acidic protons by metal cations takes place through interaction with nitrogen-containing bases. The influence of the nature of a metalcomplexing agent and the temperature of the synthesis on the composition of the obtained compounds was shown. The structure of the triple-decker sandwich complex of rare earth metals with a substituted phthalocyanine ligand has been confirmed for the first time using X-ray analysis of $Lu_2(R_4Pc)_3$.

The regularities of the supramolecular organization of the metal complexes obtained with crownphthalocyanine ligands were established in solution in the presence of cations of alkali metals. The factors affecting the composition and the structure of supramolecular systems were revealed.

It was shown that during the interaction of $Al(R_4Pc)HSO_4$, $Lu(R_4Pc)OAcAX$ ($X = DBU$, Phen), $Co(R_4Pc)$ or $Lu_2(R_4Pc)_3$ with cations of diameter greater than that of the crown-ether ligand cavity cofacial H-dimers are formed.

The $Ru(R_4Pc)(CO)(MeOH)$ complex, which has axial ligands, aggregates with the formation of a network supramolecular structure.

DBU acts as a chemical reducing agent for one-electron reduction of monoradical diphthalocyaninates of Lu, Yb, Gd and Y. The reduced forms of double-decker phthalocyaninates of rare earth metals obtained with DBU have supramolecular polymer stacks, due to sandwich complexation between crown-ether substituents and K^+, Rb^+ or Cs^+ cations.

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