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Supramolecular metal complex systems based on crown-substituted tetrapyrroles

A Yu Tsivadze

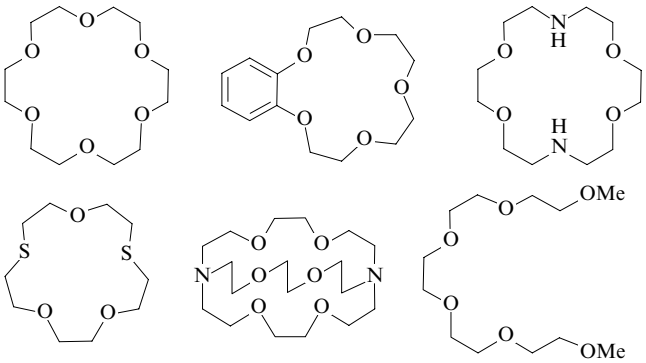
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Abstract. The characteristic features of the structures and properties of crown-substituted porphyrinates and phthalocyaninates are considered. Interactions of these compounds with alkali metal salts yield supramolecular ensembles. The factors determining the architecture of such ensembles are described. The bibliography includes 97 references.

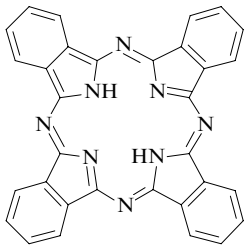
I. Introduction

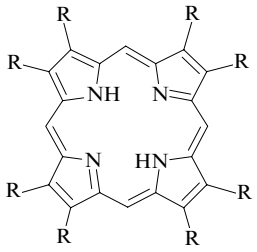
Over many years, the development of coordination chemistry was associated with a search for ligands able to form stable complexes with metal ions. It is polydentate chelate ligands that proved to be these ligands, among which macrocyclic compounds occupy a special place.[1–13] Such macrocyclic ligands as crown ethers, azacrown ethers and thiacrown ethers, cryptands, podands, phthalocyanines, porphyrins and other polyazacyclic compounds have received especially wide acceptance in coordination chemistry.



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Natural porphyrins and their synthetic analogues, *viz*., phthalocyanines, which are the most spectacular representatives of polyazacyclic compounds, are related to the class of conformationally rigid macrocyclic ligands. With metal ions in the oxidation state 2+, these ligands form intramolecular planar tetragonal complexes where two protons of the ligand are replaced by metal ions. Formally, the central metal ion in such complexes forms two typically covalent and two typically coordination bonds with the nitrogen atoms of the polyazacycle, which actually become equivalent as a result of complexation.

Metal complexes with crown ethers contain neither typically covalent, nor typically coordination metal—ligand bonds. Crown ethers form surprisingly stable complexes even with ions of alkali metals, which until recently were not considered as metals that form complexes.

In contrast to porphyrins and phthalocyanines, crown ethers represent conformationally flexible ligands. In the free state, the distribution of donor heteroatoms in crown compounds is random; however, after penetration of the cation into the cavity of the macrocycle the latter adopts a crown-shaped conformation. For example, 12-crown-4 (12-C-4) can exist in different conformations depending on the nature of the substituents, solvent, temperature and other factors (Fig. 1).

Flexible crown ligands are specifically adapted to the complexation conditions to yield various types of complexes (Fig. 2). Depending on the sizes of the cations and of the cavities of crown ethers, such complexes are divided into three main types, *viz*., complexes in which the size of a cation is comparable with that of the macrocyclic ligand cavity (complexes of the type **A** or **B**); complexes in which the size of a cation is smaller than that of the crown ligand cavity (compounds **C** or **D**) and complexes in which the size of a cation is larger than that of the macrocyclic ligand cavity (compounds **E** – **G**).

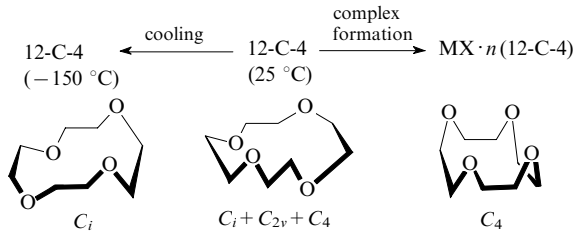


Figure 1. Conformations of 12-crown-4.

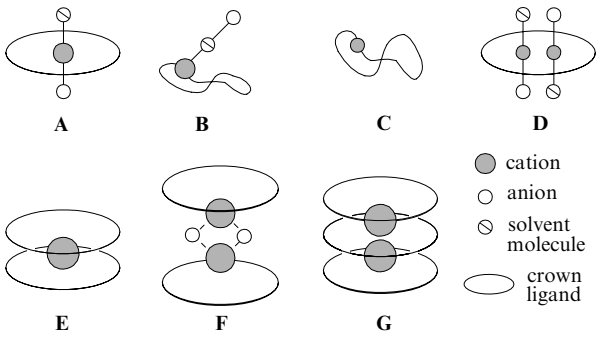


Figure 2. Various types of metal complexes with crown ligands (according to the Punia classification).
A, an encapsulated ion pair (the cation – anion pair remains to be a contact pair, M : L = 1 : 1); **B,** a partly encapsulated ion pair (the cation forms a solvent-separated pair with the anion, M : L = 1 : 1); **C,** enveloping encapsulation (M : L = 1 : 1); **D,** a compound with M : L = 2 : 1; **E,** a sandwich-like compound (M : L = 1 : 2); **F**, dimers linked by bridging ligands (M : L = 1 : 1); **G**, a triple-decker sandwich compound (M : L = 2 : 3).

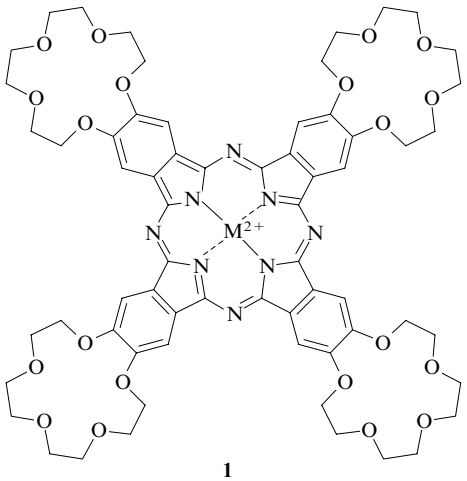
The progress in conformational analysis [6] and, particularly, in spectral conformational analysis † has made it possible to investigate, by the example of a vast (several hundreds) number of complexes, the conformational changes occurring in crown ligands under the influence of diverse factors (*e.g.*, peripheral substituents, metal that represents complexing agent, anions, solvent, *etc.*). This has led to elaboration of a fundamentally new conformational approach to modification of properties of macroheterocyclic compounds based on directed changes in the conformational equilibrium and hence in the complex-forming and ion-selective properties of the crown ligands. Thus an idea appeared to fix, with the help of peripheral substituents, those crown-ether conformations which are especially suitable for selective interactions with the target metal ion. Such a preorganisation of the ligand allows a purposeful choice of crown compounds that bind selectively specific cations.[1–13] At the same time, it should be remembered that rigid fixation of crown ethers deprives them of flexibility, which enables surprisingly effective adaptation to the existing conditions. Therefore, the choice of side substituents should be a reasonable compromise between the rigidity and flexibility of the ligands formed.‡

There are numerous examples of the violation of the Pedersen geometrical correspondence principle [2,3,6,12–15] according to which stable complexes are formed provided the size and shape of the macrocyclic ligand cavity match the size and shape of the complex-forming cation; these can be accounted for by the diversity of the conformational forms of the crown ethers. This principle is violated in those cases where the anion, solvent or intermolecular interactions force the ligand to adopt a conformation where the coordination with a cation (the size of which is larger or smaller than that expected based on the geometrical correspondence principle) is more favourable.

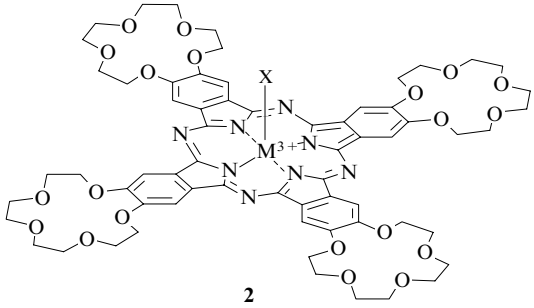
In this case, we deal with dimensional effects characteristic of nanochemistry and nanotechnology. For example, if the size of a metal cation exceeds that of the macrocyclic cavity to such an extent that the cation can by no means occupy the central position in the macrocycle, sandwich-like dimers and trimers (**E** and **G**) are formed; the metal cations in these aggregates are located between the neighbouring crown-ether molecules. The formation of such supramolecular aggregates ensures stability of the complex, but ordered architectures of the molecular ensembles.

The principles of the molecular stereodesign of crown compounds developed allow a purposeful search for highly selective extraction systems for isotope separation. In the choice of a particular system, it is important to know how a concrete crown extractant adapts to specific extraction and reextraction conditions by respective conformational changes. This approach has led to the development of a physicochemical basis of technological processes for the separation of lithium, magnesium, calcium, potassium and boron isotopes.[16]

It is known that porphyrins and phthalocyanines form stable metal complexes possessing unique electrophysical and optical properties;[17–19] however, poor solubility of such complexes in organic solvents and water prevents their wide utilisation. Many problems related to practical realisation of these unique properties of phthalocyaninates could be circumvented through the introduction of peripheral substituents. Some of these substituents ensured the required solubility on the complexes, while others conferred entirely new properties on them. Dimensional effects also play an important role. For example, metal ions with the sizes allowing them to occupy the central position in the macrocycle form monophthalocyaninates (compounds **1**, **2**), whereas bulkier ions (*e.g.,* rare-earth elements) form sandwich-like double- (compound **3**) and triple-decker complexes.



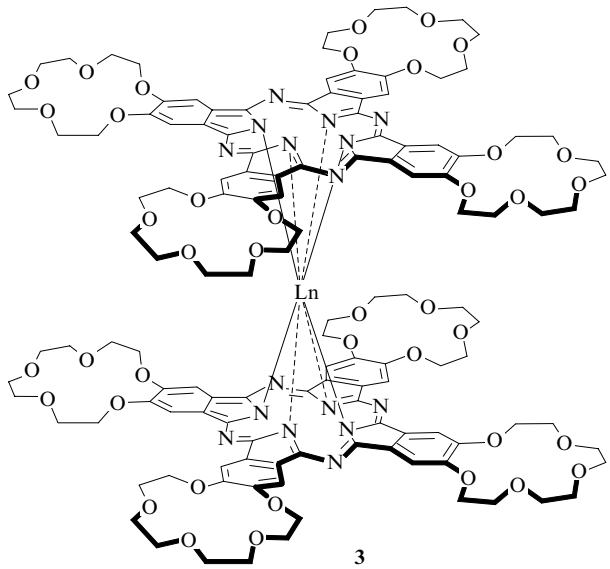
1



2

† Spectral conformational analysis combines oscillation spectroscopy, quantum-chemical calculations and theoretical analysis of normal molecular oscillations.

‡ In the case of porphyrins, nature itself has solved the problem through the selection of appropriate substituents.



3

It is noteworthy that peripheral substituents do not disturb the rigidity of the macrocycle, but influence the mutual arrangement of the phthalocyanine molecules, which, in turn, determines the type of $\pi-\pi$-interactions between the aromatic systems and the formation of supramolecular stacking or liquid crystalline systems. In this respect, crown-ether substituents differ favourably from all other substituents in their ability to provide the required solubility and ordering of complex supramolecular architectural ensembles and to confer novel properties on the phthalocyaninate complexes owing to the formation of additional ion conductivity side channels along with the central semiconducting channel.

A series of crown-substituted phthalocyanines have recently been synthesised which are readily soluble in the majority of solvents and do not form isomeric mixtures like unsubstituted phthalocyanines. Reactions of metal complexes of such tetracrown phthalocyanines with alkali metal salts yield heteronuclear supramolecular aggregates.[20–24] Proneness of crown substituents to form complexes with alkali metals and the tendency of phthalocyanines for stacking interactions of aromatic rings favour the formation of such aggregates.

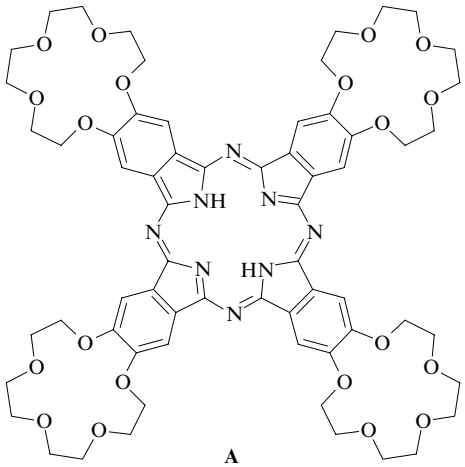
Although porphyrins and phthalocyanines belong to macrocyclic ligands, it was not until the discovery of crown ethers that the remarkable stability of the metal complexes of the former was associated with the macrocyclic effect. Nor did the elucidation of the mechanism of reversible binding of oxygen to hemoglobin lead to the introduction of the term 'supramolecular chemistry', although the non-linear cooperative effect observed thereupon was undoubtedly associated with the formation of supramolecular systems as follows from the sigmoidal shape of the titration curve. The necessity for the introduction of the term 'supramolecular chemistry' arose only in 1978 in the consideration of the unusual selectivity of the complexes formed by alkali metal cations and crown ethers.[1,4,5]

Supramolecular chemistry studies supramolecular systems formed as a result of noncovalent intermolecular interactions.[1–6] The main concepts of supramolecular chemistry are fixation (binding), recognition and coordination. The stability of alkali metal complexes with crown ligands is provided by the recognition of geometrically complementary species and the multiplicity of their interactions due to the increase in the interaction surface. A main goal of supramolecular chemistry is the design of ordered functional units having molecular sizes and that could receive, store, transmit and read information like chemical-and-biological 'machines'[§] responsible for skilful regulation of vital processes in nature.[1]

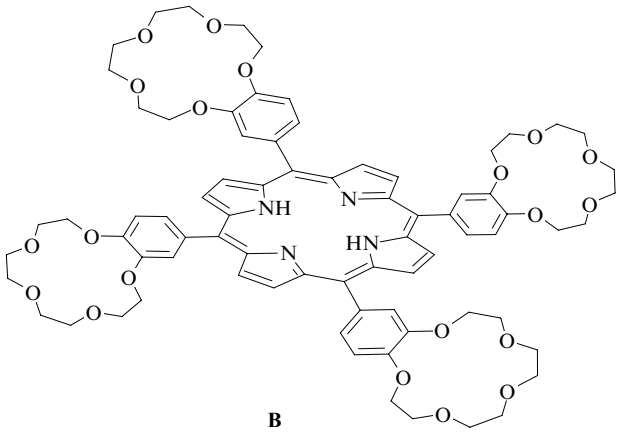
§ Photosynthesis performed by chlorophyll, one of the most typical representatives of natural porphyrins, is an example.

The uniqueness and remarkable efficiency of chemical processes occurring in living organisms have always been a subject of admiration for chemists. The more mysteries of nature that are unravelled by chemists the more new enigmas and undisclosed mechanisms of control over various chemical processes in biological systems emerge. Recently, it has become evident that the unusual controllability and selectivity of vital processes cannot be explained in terms of covalent interactions. The ability to exert flexible control over chemical processes is one of the common features of biological and supramolecular processes realised at the molecular level. The ease of the control over chemical processes mediated by synthetic analogues of macrocyclic natural compounds is reached owing to their selectivity and extreme sensitivity to low-energy influences.

Synthesis of crown-substituted porphyrins and that of phthalocyanines are based on different approaches. This is due to differences in the modes of attachment of crown-ether substituents to porphyrins and phthalocyanines. Thus, crown-ether substituents are fused to phthalocyanines to form a fused tetracyclic system (structure **A**), while these are linked to porphyrins through a C—C bond between the carbon atoms of the benzene ring and the methine group (structure **B**) about which free rotation is possible. These differences are reflected in the supramolecular organisation of these systems.



A



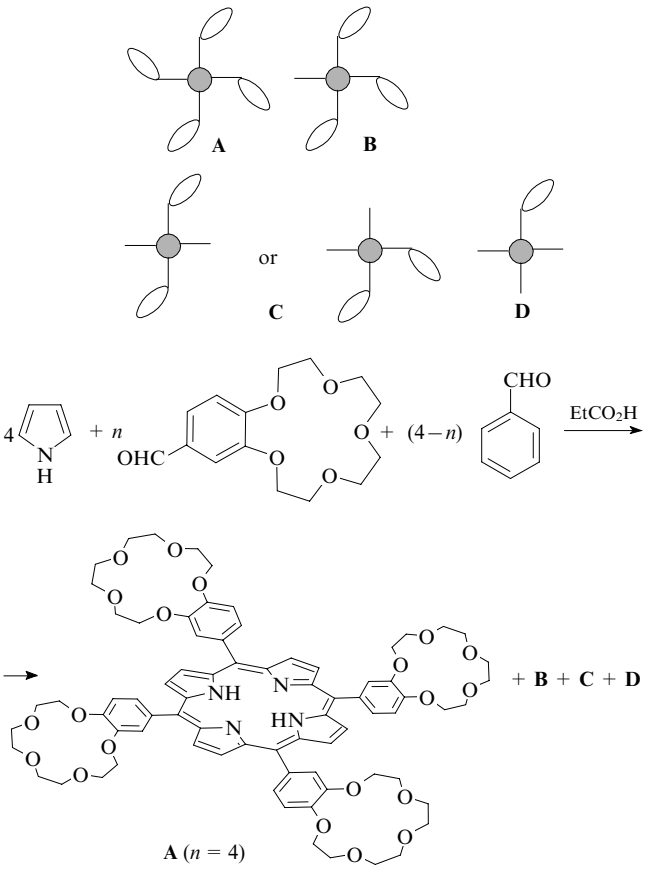
B

II. Crown-substituted porphyrins

Functionalised porphyrins present interest as models for the study of various biological processes, such as heme oxygenation, cytochrome activity and photosynthetic electron transport.[25–29] Thus it was tempting to use porphyrins containing macrocyclic substituents able to recognise cations for the study of sodium-potassium transport across biological membranes. The ionophoric behaviour of such substituted porphyrins can easily be

monitored by following fluorescence changes.¶ The methods for the synthesis of this class of model compounds depend on the nature and position of side substituents. Earlier, substituted pyrroles containing ester, amide or alkyl groups were used for the synthesis of substituted porphyrins;[30–32] however, compounds thus prepared did not possess ionophoric properties. The first attempt to synthesise crown-substituted porphyrins from 4′-formylbenzo-15-crown-5, pyrrole and benzaldehyde (Scheme 1) was undertaken in 1982 by Thanabal and Krishnan.[33] Depending on the ratio of the reactants, tetra- (**A**), tri- (**B**), di- (**C**) or mono-15-crown-5-substituted (**D**) porphyrins were obtained. If the porphyrin molecule is presented as a circle and 15-crown-5 as an ellipse, the resulting compounds will appear as shown in Scheme 1.

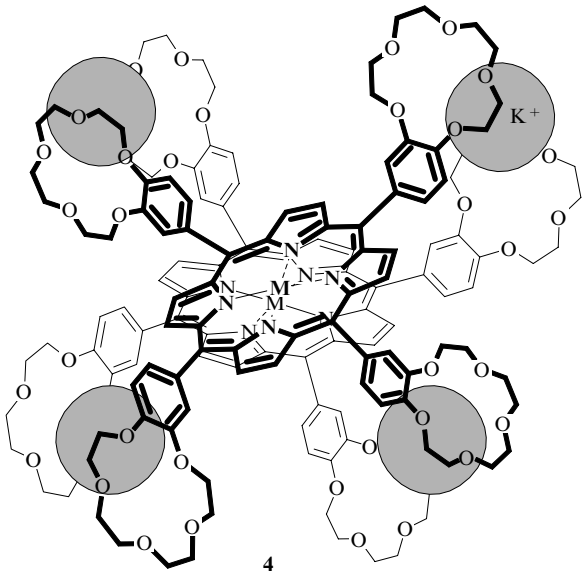
Scheme 1



$n = 1-4$.

Interactions of these crown-substituted porphyrins with metal salts (Co, Cu, Zn) yield chelate compounds. The addition of sodium, magnesium and calcium salts to solutions of tetra- and tricrown-substituted porphyrinates did not cause any changes in the electronic spectra of the complexes, whereas the addition of potassium, ammonium and barium salts resulted in a decrease in their intensities, changes in both Q-bands (broadening and shift by *ca.* 10 nm towards the long wavelength region) (a bathochromic shift) and Soret bands (a hypsochromic shift).†

Such changes can be attributed to specific complexation of crown-substituted porphyrins with these cations. The difference in the behaviour of these cations with respect to crown-substituted porphyrins is due to the formation of M : L = 1 : 1 complexes of benzo-15-crown-5 with sodium, magnesium and calcium cations, whereas potassium, ammonium and barium cations form sandwich complexes with the composition M : L = 1 : 2 (compound **4**). In the latter case, it is dimerisation of the macrocycles induced by a specific behaviour of potassium, ammonium and barium cations that causes changes in their electronic spectra.



M = 2H, Co, Zn, Cu.

The reaction of crown-substituted porphyrins (P) with potassium cations can schematically be presented as:

$$2P + 4K^+ \longrightarrow P_2(K^+)_4.$$

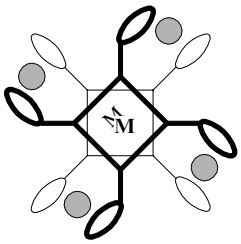
It was suggested [33] that the addition of potassium ions first induces the formation of the dimer P_2, which is followed by complexation, potassium cations filling all the unoccupied positions in the macrocyclic cavities of the peripheral crown-ether substituents. It should be noted that saturation is reached even at very low concentrations of potassium cations (10^{-5} mol litre^{-1}). The stability constant of the complex $P_2(K^+)_4$ is equal to 10^{23} litre^5 mol^{-5}, *i.e.*, it is by several orders of magnitude greater than the corresponding constants of the K^+ complexes with crown ethers.

It was found that the addition of even very small amounts of potassium ions (10^{-5} mol litre^{-1}) to a zinc complex with tetracrown porphyrin ($\sim 10^{-5}$ mol litre^{-1}) in the presence of an excess of sodium ions ($\sim 10^{-2}$ mol litre^{-1}) results in dimerisation as can be evidenced from the significant changes in the electronic absorption spectra of ZnTCP (TCP is tetracrown porphyrin) in ethanol. Such a selectivity of ZnTCP with respect to potassium cations enables its application for quantitation of low concentrations of potassium ions. No such selectivity is observed for ammonium and barium cations: the presence of even very small amounts of sodium ions leads to disaggregation of complexes $P_2(NH_4^+)_4$ and $P_2(Ba^{2+})_4$.

The addition of potassium ions to a CuTCP complex results in significant changes in the ESR spectra due to the formation of $(CuTCP)_2(K^+)_4$ complexes. ESR spectroscopic data suggest that copper ions occupy a position in the centre of the porphyrin ring cavity. The Cu–Cu distance in the dimer reaches ~ 4.20 Å, which is in favour of coaxial symmetry of the complex.[33] The porphyrin rings in the dimer $(CuTCP)_2(K^+)_4$ are turned by 45° relative to one another.

¶ The changes in the porphyrin fluorescence can be conjugated, *e.g*, to the inhibition of oxidative phosphorylation in respiratory mitochondrial systems.

† It is known that Q and Soret bands are extremely sensitive to structural changes.



X-Ray diffraction analysis of a potassium complex $K(B\text{-}15\text{-}C\text{-}5)_2I$ (B-15-C-5 is benzo-15-crown-5) revealed that the crown-ether ligands in this compound are at a distance of ~ 3.8 Å from one another and the plane passing through the oxygen atoms is parallel to the plane of the benzene ring.[34]

The formation of highly ordered systems is yet another specific feature of the tri- and disubstituted copper complexes $(CuTriCP)_2(K^+)_3$ and $(CuDCP)_2(K^+)_2$.[33] However, the Cu—Cu distance in these complexes is greater than that in the corresponding tetrasubstituted complex $(CuTCP)_2(K^+)_4$.

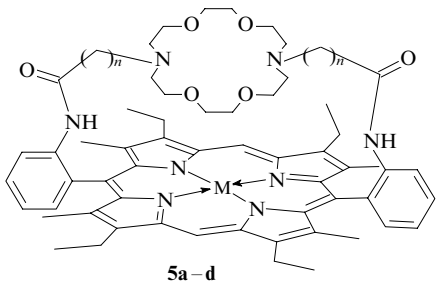
The addition of methanolic solutions of sodium, magnesium and calcium salts to solutions of free tetracrown porphyrin and its ZnTCP complex (5×10^{-5} mol litre^{-1}) in $CHCl_3$ does not bring about changes in their fluorescence spectra, while the addition of potassium salts induces significant changes due to dimerisation. (It is of note that the fluorescence spectra of the complexes appeared to be more sensitive to potassium ions than their absorption spectra). In the case of free tetracrown porphyrin, the dimerisation effect is insignificant.[33]

A detailed analysis of the ESR and optical spectra of a zinc complex with tetracrown porphyrin revealed [35] that the cavities of the porphyrin rings in the dimer are parallel and turned by 23° relative to one another.

Potassium, caesium, ammonium and barium cations induce the formation of porphyrin dimers in the case of vanadyl complexes, the dimerisation constant decreases on going from tetracrown-substituted vanadyl porphyrinate to tri- and disubstituted complexes. The constant of cation-induced dimerisation of vanadyl tetracrown porphyrinate decreases in the following order: $K^+ > Ba^{2+} > Cs^+ \approx NH_4^+$. According to data from ESR spectroscopy, the V—V distance in these dimeric complexes is equal to ~ 4.70 Å.

Magnesium, nickel and manganese(III) complexes with tetracrown porphyrin also yield dimers upon interaction with potassium salts.[36] An electrochemical analysis of redox properties of these metal complexes revealed that the oxidation of the porphyrin ring in dimers occurs at lower anodic potentials than in the corresponding monomers. The electronic absorption and emission spectra of the electrochemically oxidised and reduced states of these dimers were interpreted based on the changes in their electronic structures.[36] The ESR spectra of the oxidised dimeric radical show that the unpaired electron is localised on one of the porphyrin π-systems unlike chlorophyll molecules in bacterial photosynthetic systems.

Synthesis of dioxocyclam- and diaza-18-crown-6-substituted porphyrins (**5a**,**b**) and metal complexes based on them (**5c**,**d**) has been described.[37–39]



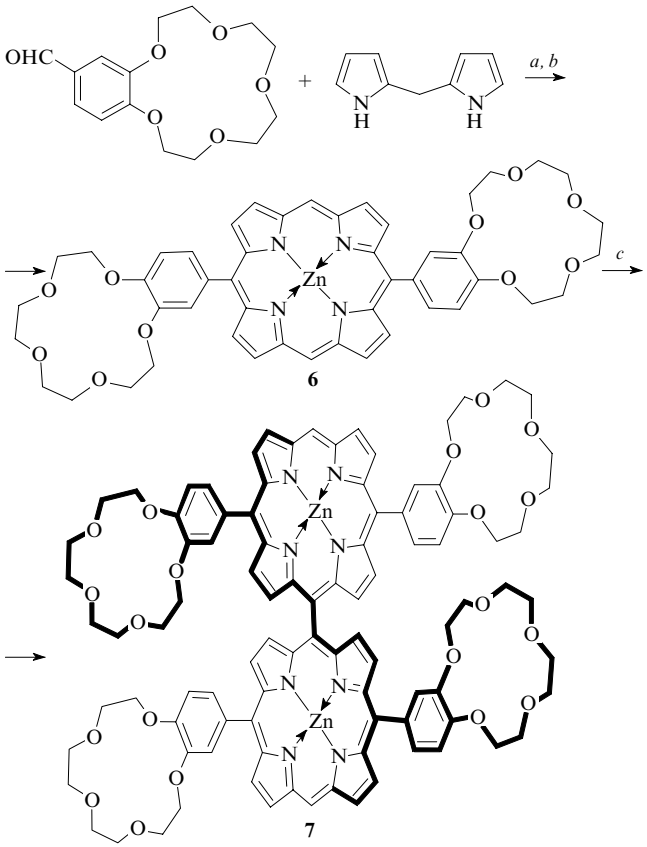
5a–d

5a: M = 2 H, n = 1;
5b: M = 2 H, n = 2;
5c: M = Zn(II), n = 1;
5d: M = Co(II), n = 2.

X-Ray diffraction analysis of compounds **5b** and **5c** [38] confirmed the presence in these compounds of a bridging diaza-18-crown-6 ligand binding two peripheral benzene rings attached to the porphyrin macrocycle. The cavity of diaza-18-crown-6 is coaxial with that of the macrocyclic ring of porphyrin (an analogous position of the rings was observed in a structurally similar 5,15-di(2-alkylamidophenyl)etioporphyrin complex with dioxocyclam [37]). Cobalt and zinc ions enter the cavity of the porphyrin ring. Electrochemical studies of these compounds revealed that cobalt complexes undergo oxidation in an atmosphere of nitrogen. In PhCN, the addition of oxygen is reversible, and irreversible in CH_2Cl_2. Oxidation of the cobalt complex in an atmosphere of carbon monoxide yields a compound in which the cobalt ion is linked to the carbonyl group.

A monomeric zinc complex with bis(benzo-15-crown-5)porphyrin was prepared starting from dipyrrolylmethane, 4′-formylbenzo-15-crown-5 and zinc acetate (Scheme 2).[40] Treatment of the complex **6** with $AgPF_6$ yielded a diporphyrin zinc complex **7** containing two covalently (*meso-meso*) linked porphyrin rings.

Scheme 2



a — $BF_3 \cdot OEt_2$, $CHCl_3$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone;
b — $Zn(OAc)_2 \cdot 2\,H_2O$, $CHCl_3$ – MeOH;
c — $AgPF_6$, $CHCl_3$ – MeOH – MeCN.

The addition of sodium salts to the monomeric complex **6** in $CHCl_3 - CH_3CN$ (2 : 1) did not cause any changes in the electronic absorption spectra of the complex, whereas the addition of potassium ions caused a shift in the Soret band from 415 to 396 nm (with an isosbestic point at 404 nm) and a decrease in the fluorescence intensity. It was suggested [40] that these changes are due to the formation of a diporphyrin dimer similar to the dimers **4** described above. The changes in the NMR spectrum of the complex **6** following addition of cations K^+ provide additional evidence in favour of formation of a dimer of the type **4**. The addition of a potassium salt to the covalently linked dimeric zinc

complex **7** results in more complicated changes in the electronic absorption spectra.

In the absence of alkali metal ions, the Soret band in the electronic absorption spectrum of compound **7** appears as a doublet at 421 and 453 nm. The splitting of this band is attributed to an exciton interaction. Upon addition of a potassium salt to a solution of the complex **7**, the intensities of the bands at 421 and 453 nm first decrease, and when the concentration of potassium ions reaches 1.0×10^{-5} mol litre^{-1}, the Soret band is shifted towards 423 nm and its intensity increases. These changes are accompanied by an appearance of a shoulder with an isosbestic point at 408 nm on the high-energy side of the Soret band.‡

The fluorescence intensity of the dimer **7** also changes with the concentration of potassium ions. At first, potassium cations ($[K^+] \leqslant 1.0 \times 10^{-5}$ mol litre^{-1}) cause a decrease in the intensity of the fluorescence band; however, the fluorescence increases with increasing concentration of potassium ions. Similar changes in the electronic absorption and fluorescence spectra were observed upon addition of rubidium ions, but not in the case of caesium and sodium ions. These findings are in conflict with the data on the behaviour of the monomeric complex **6** under identical conditions. It may thus be assumed that the intermolecular interactions of the crown-ether fragments of the monomeric (**6**) and dimeric (**7**) zinc complexes with potassium ions have the same character, but the molecular ensembles formed by these complexes differ. Coaxial dimerisation of the monomeric zinc complex upon interaction with potassium ions (the formation of 'face-to-face' dimers) is probable, while self-complementary dimerisation of the covalently bound zinc complex is impossible and linear extended aggregation is more preferable (Fig. 3). The complex character of changes in the electronic absorption and luminescence spectra suggest a multistage equilibrium resulting in the formation of a linear ensemble. The decrease in the fluorescence intensity in the initial step points to the formation of a coaxial diporphyrin, while its subsequent increase may result from interactions of the crown-ether groups of the linear aggregates with alkali metal ions. The polymeric nature of the aggregates is confirmed by light scattering studies: the molecular weight of the aggregate may amount to 10^5, *i.e.,* the linear ensemble is made up of 50 aggregated molecules. It is suggested[40] that the methodology of the supramolecular organisation of porphyrins described above can successfully be used in the design of novel molecular architectural ensembles and new generations of highly efficient materials.

‡ The appearance of a shoulder on the high-energy side of the Soret band is interpreted as the formation of a stacking diporphyrin of the coaxial type (a 'face-to-face' dimer).[40]

III. Crown-substituted monophthalocyaninates

Unlike porphyrins, the pyrrole fragments of phthalocyanines (Pc) forming the macrocyclic cavity are linked by four nitrogen atoms of the azamethine groups. Although these four additional nitrogen atoms are not directly involved in the complexation due to remoteness from the cavity centre, they create quite different

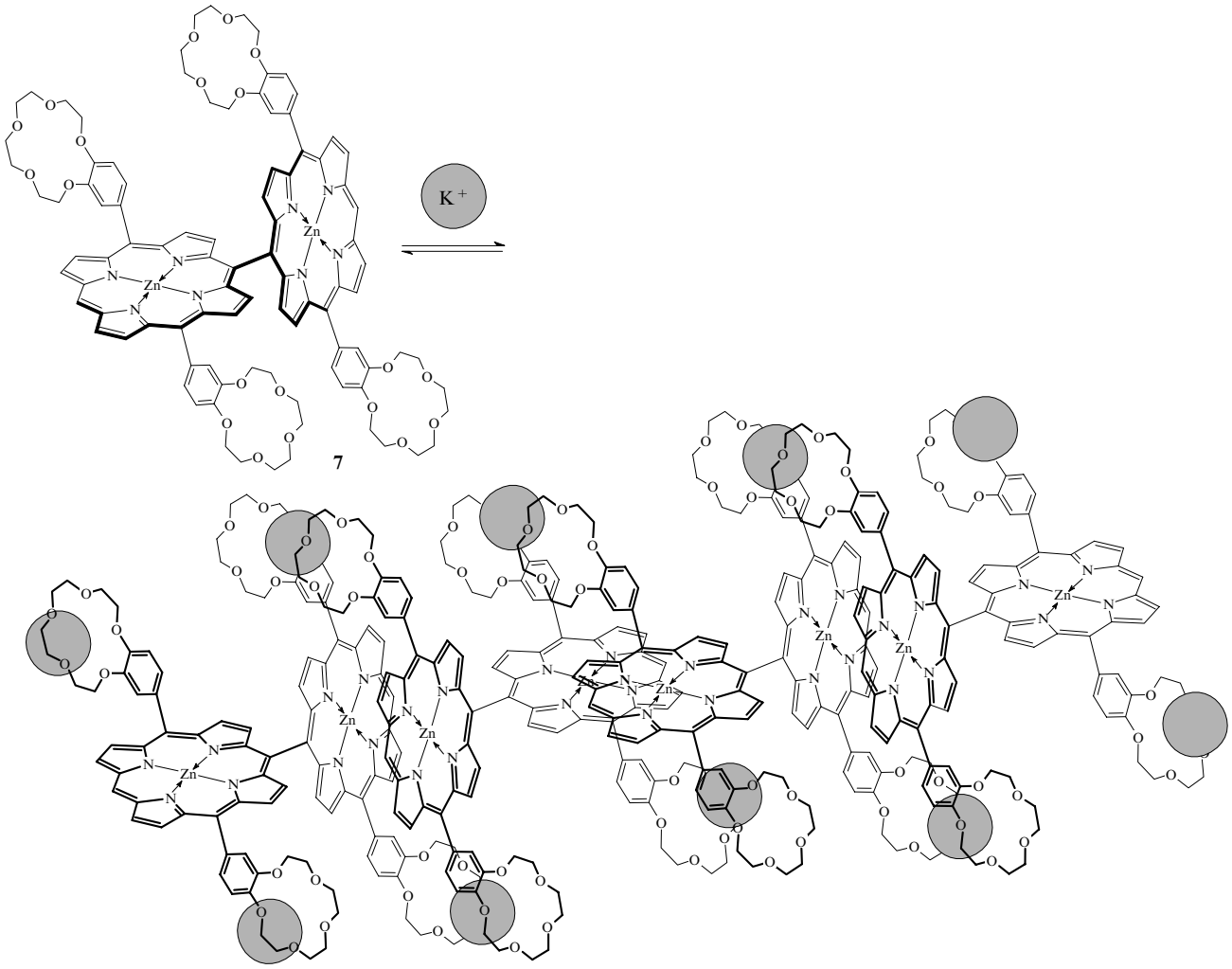


Figure 3. Supramolecular aggregation of dimeric zinc bis(benzo-15-crown-5)porphyrinates **7**.

conditions for the interaction with metal salts. Because of the peculiar electronic structure of the aromatic system, metal phthalocyanines manifest high chemical and thermal stability and possess unique optical, electrical and photochemical properties, which opens up new opportunities for their wide application as semiconductors, catalysts, sensors, pigments and biologically active compounds.

Phthalocyanines are conformationally rigid ligands; therefore, their complexation is accompanied by forced planar-tetragonal coordination of the central metal ion, which ensures high kinetic stability of the corresponding phthalocyaninates.

The first phthalocyanine complex (CuPc) was obtained by accident in 1927 during the synthesis of 1,2-dicyanobenzene from *o*-dibromobenzene and CuCN in pyridine at 200 °C (see Ref. 41). The nitrile-based and urea-based template syntheses of metallophthalocyanines were developed later. The former approach is based on the reaction of phthalonitrile with various metal salts.[42] At present, phthalocyanines are synthesised in different ways, but the template method is still the most popular.

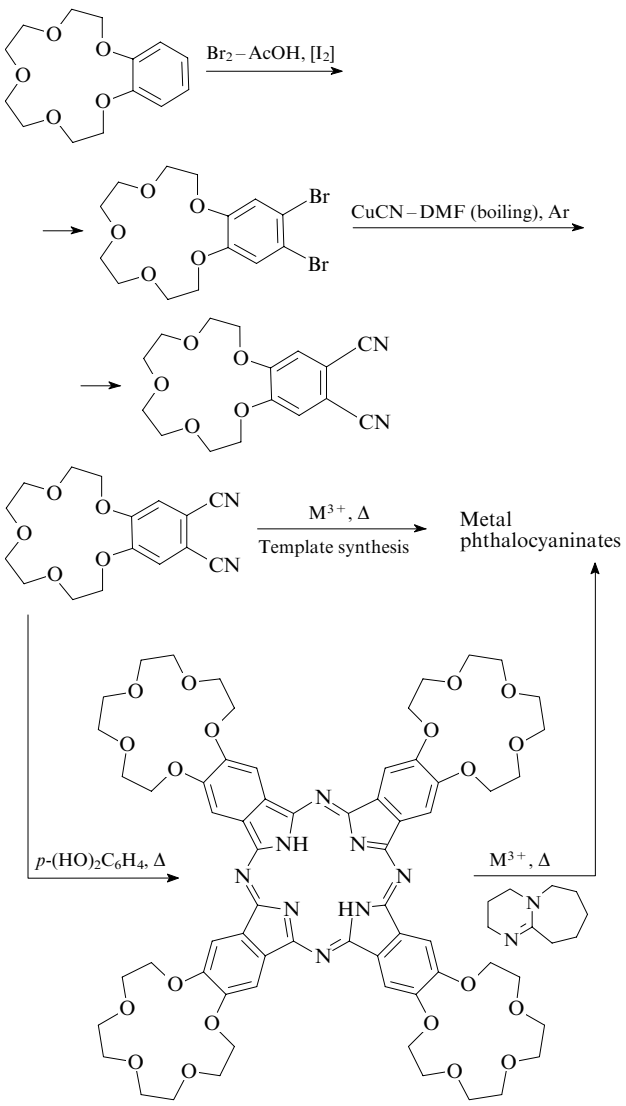
Metallophthalocyanines have limited application due to their poor solubility in organic solvents and water, which prevents the preparation of chemically pure substances and high-quality films based on them. Numerous substituted phthalocyanines have been synthesised in order to improve their solubility. Thus the introduction of bulky substituents (*e.g.*, *tert*-butyl, naphthyl or crown-ether substituents) into the benzene rings of the phthalocyanine molecule increases their solubility in organic solvents,[41,42] whereas sulfation of benzene rings increases the solubility of phthalocyanines in water.

The introduction of a crown-ether fragment into a phthalocyanine molecule as a substituent in the benzene ring of the isoindole fragment not only increases its solubility, but also favours the formation of heterometal complexes upon interaction of phthalocyaninates with alkali and alkaline earth metal salts. Syntheses of such complexes have been described.[20–24,43–46] Tetracrown-substituted phthalocyanines were prepared from benzo-15-crown-5, which was converted into dicyanobenzo-15-crown-5. The latter was used as a starting reagent in the nitrile template synthesis of tetracrown-substituted phthalocyanine (CR-Pc) (Scheme 3).

Interactions of dicyanobenzo-15-crown-5 with divalent metal salts yield chelate complexes M(CR-Pc) [M = Co(II), Ni(II), Zn(II), Cu(II), *etc*.]. With trivalent metals (M = Al), metal complexes are formed with extra ligands occupying an axial position. In contrast to the synthesis of crown-substituted porphyrins where mono-, di-, tri- and tetracrown-substituted derivatives are formed, in the case of phthalocyanines, tetracrown-substituted complexes are always formed as the reaction products. Data from various physicochemical methods have made it possible to postulate a symmetrical structure for the compounds formed. No direct evidence for such symmetry was available until recently due to a lack of X-ray data; however, a comparison of the vibrational spectra of tetracrown-substituted copper phthalocyaninate in a conformationally sensitive region of the IR and Raman spectra (600–1600 nm) (Fig. 4) revealed that these spectra did not coincide either in frequencies, or in relative intensities of the bands over the whole spectral region. This suggests that the IR and Raman spectra of this compound follow the alternative exclusion principle, *viz*., the frequencies that appear in the IR spectra are absent from the Raman spectra and *vice versa*. It is well known that these regularities are characteristic of highly symmetrical compounds.[6] Thus, the symmetrical structure of the above compound was deduced from its vibrational spectra.

An attempt to synthesise an aluminium complex with tetracrown phthalocyanine by the nitrile template method failed.[47] The interaction of aluminium chloride with dicyanobenzo-15-crown-5 (DCB15C5) in quinoline (the nitrile method) at 170 °C was accompanied by degradation of DCB15C5 and the complex was not formed. The yield of the corresponding Al(CR-Pc)(SO_4H) complex (**8**) synthesised from $Al_2(SO_4)_3$ and DCB15C5 in the melt

Scheme 3



was very low due to hydrolysis of the cyano groups. In order to exclude this undesirable effect, the reaction of $Al_2(SO_4)_3$ with DCB15C5 was carried out in urea as in the urea-based version of the template synthesis which is employed for the preparation of

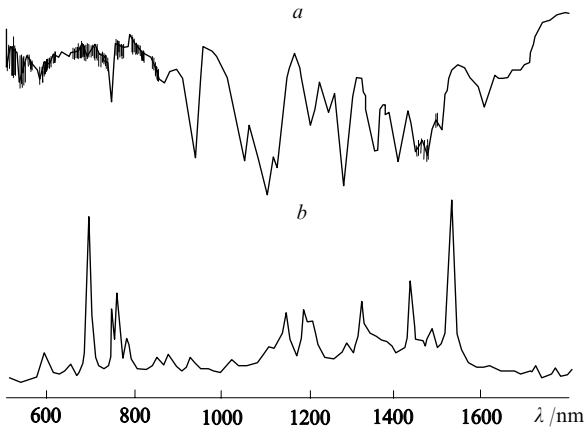
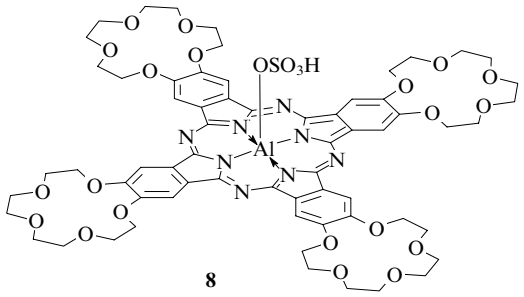


Figure 4. IR- (*a*) and Raman spectra (*b*) of copper tetra(15-crown-5)-phthalocyaninate.

phthalonitriles from phthalimide, phthalic acid or its derivatives and urea. Urea, which decomposes at 130 °C in the presence of a catalyst (ammonium molybdate) with evolution of ammonia, serves as an aminating reagent for the conversion of the phthalic acid derivative into phthalonitrile directly in the course of the synthesis.



8

It was found that the Al(CR-Pc)(SO_4H) complex is soluble in both organic solvents (*e.g.*, chloroform, acetone, pyridine, ethanol, dimethyl sulfoxide, *N*,*N*-dimethylformamide) and in water. The aqueous solution of this complex is stable in neutral and weakly acidic media. At pH > 7, complex **8** is hydrolysed into Al(CR-Pc)OH.

The synthesis of a zinc complex with a crown-substituted phthalocyanine by the nitrile template method is also difficult due to the necessity of prolonged heating of the reagents and relative instability of zinc phthalocyanine complexes.[48] Therefore, the direct method, *viz.*, the reaction of zinc acetate with H_2(CR-Pc), was used for the synthesis of the crown-substituted zinc monophthalocyaninate Zn(CR-Pc).[49] This reaction was carried out either in the presence of an excess of lithium hydroxide in a chloroform–ethanol mixture or in the presence of a stoichiometric amount of BuLi in dimethyl sulfoxide. In the latter case, the yield of the Zn(CR-Pc) complex reached 95%.

Similar problems were observed in the template synthesis of crown-substituted monophthalocyaninates of rare-earth elements (REE). Because of the large radii of lanthanide ions, it is much more difficult to prepare REE monophthalocyaninates than sandwich bisphthalocyaninates.[50–54] An analysis of known methods for the synthesis of crown-substituted REE monophthalocyaninates revealed [55] that the protonated ligand H_2(CR-Pc) is the most suitable starting material. However, reactions of REE acetates with H_2(CR-Pc) occur only in the presence of strong bases, *e.g.*, 1,10-phenanthroline (Phen) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[55] Boiling of lutetium acetate and H_2(CR-Pc) in dichlorobenzene in the presence of an excess of DBU gives crown-substituted lutetium monophthalocyaninate.

$$H_2(\text{CR-Pc}) + Lu(OAc)_3 \xrightarrow[\Delta]{\text{DBU, } o\text{-}Cl_2C_6H_4} Lu(\text{CR-Pc})(\text{DBU})OAc.$$

In the presence of 1,10-phenanthroline, the reaction proceeds in a similar way. In the compound Lu(CR-Pc)$(Phen)_2X$ formed, phenanthroline acts both as the base and the chelating ligand for lutetium ions. Both lutetium complexes possess sufficiently high solubilities in organic solvents of various polarity (*e.g.,* chloroform, dichloromethane, dimethyl sulfoxide, acetone) and in water (the concentration of a saturated aqueous solution of the DBU complex is 1.7×10^{-4} mol litre^{-1}).

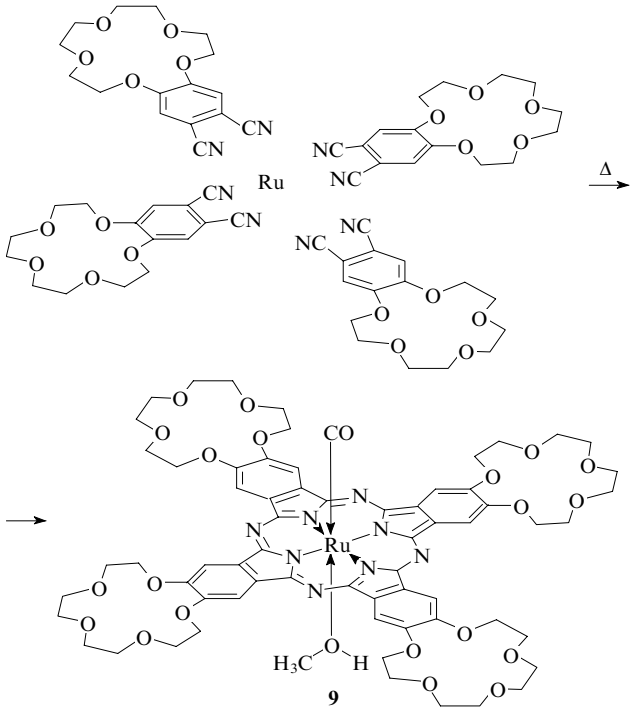
Until recently, data on the synthesis of crown-substituted phthalocyaninates of platinum metals were absent from the literature. At the same time, complexes of platinum metals with such ligands present substantial interest because of the great diversity of coordination properties of both the ligands and the central metal atoms. The synthesis of a complex of ruthenium(II) with tetra(15-crown-5)phthalocyanine has been described.[56]

The template synthesis is mainly used in the preparation of ruthenium complexes with unsubstituted phthalocyanine from phthalonitrile (or cyanobenzamide) and ruthenium trichloride is the main procedure.[57–60] The ruthenium(II) monophthalocyaninate 'PcRu' reacts with various ligands to give complexes with the composition $PcRuL_2$ (L = Py, DMF, DMSO, *etc.*).[60,61] This approach was also used in the synthesis of tetraalkyl-substituted ruthenium phthalocyaninates (yield 95%).[62]

There are still no unambiguous literature data on the structure of the 'PcRu' complex prepared by the template synthesis. Using LAXS and EXAFS methods, Ercolani and co-workers [60,63] have demonstrated that the 'PcRu' complex represents a dimer the length of the Ru–Ru bond in which is equal to 2.40 Å. The molecular formula of this complex can be written as $[(PcRu)_2]_6$. The Ru···Ru distance between the neighbouring dimers (4.30–4.40 Å) exceeds significantly that in the dimer. In the crystal structures of $[(Ru(Py)Pc)_2(\mu\text{-}C)]$ [64] and $(Bu^n_4N)[Ru(CN)(Py)Pc]$,[65] the ruthenium atoms deviate from the plane of the macrocycle by ~0.05 Å. The distance between the neighbouring pyrrole planes, $(Np)_4$,§ is 3.65 Å.[64,65]

The template method was also used for the synthesis of ruthenium tetra(15-crown-5)phthalocyaninate (Scheme 4).[56] It is of note that one complex, Ru(CR-Pc)(CO)CH_3OH (**9**), containing an axial carbonyl group is formed irrespective of the starting ruthenium compound, *viz.*, $RuCl_3 \cdot n H_2O$ or $Ru_3(CO)_{12}$. The formation of a Ru(CR-Pc)(CO)CH_3OH complex was expected in the case of $Ru_3(CO)_{12}$, the formation of a complex with the same composition from $RuCl_3$ was rather unexpected. However, considering that the attachment of CO to the Ru atom occurred in the template synthesis of unsubstituted ruthenium phthalocyanine complexes in an atmosphere of CO with ruthenium chloride as a starting reagent,[66] the formation of a complex of this composition can hardly be called unexpected.

Scheme 4



9

Ru = $RuCl_3 \cdot n H_2O$; $Ru_3(CO)_{12}$.

The IR spectra of two Ru(CR-Pc)(CO)CH_3OH complexes prepared from $RuCl_3$ (α-form) and $Ru_3(CO)_{12}$ (β-form) differ in the region around 1000–1300 cm^{-1} which contains characteristic bands corresponding to ν(COC) of the crown-ether groups. This suggests that crown-ether substituents in the α- and β-forms of Ru(CR-Pc)(CO)CH_3OH have different conformations.[56]

§ $(Np)_4$ is a plane passing through four nitrogen atoms of the pyrrole rings.

It can thus be concluded that Co, Ni, Zn and Cu cations in the oxidation state 2+ form chelate monophthalocyaninate complexes with crown-substituted phthalocyanines, whereas REE and aluminium cations in the oxidation state 3+ and ruthenium cations in the oxidation state 2+ form monophthalocyaninates with various axial ligands.

IV. Supramolecular aggregation of crown-substituted monophthalocyaninates

Crown-substituted metal monophthalocyaninates can form various supramolecular polymeric ensembles by noncovalent interactions. The stability of such ensembles in solution is determined by the multiplicity and dynamism of weak interactions of the $\pi-\pi$-stacking type.[67, 68] These interactions govern packaging of molecules into crystals and, correspondingly, such important characteristics of materials as electron transport. Modification of phthalocyanines by crown-ether substituents creates the necessary prerequisites for preparation of pillar-type structures with C_4, symmetry and high electroconductivity.

Crown-substituted phthalocyanines and their metal complexes form rigid stable coaxial dimers in the presence of alkali and alkaline earth metal ions for which the crown-ether fragments represent chelating ligands. The main prerequisite for the formation of such dimers is a large diameter of the cation which significantly exceeds that of the crown-ether ligand cavity. The formation of heteronuclear supramolecular dimers in the presence of potassium halides or acetate (KX) was studied [20–23, 43–46] using bivalent transition metal complexes (Cu, Ni, Co, Zn) as examples. These studies have demonstrated the possibility of formation of rigid coaxial dimers with the composition $2\,M(CR\text{-}Pc)\cdot 4\,K^+$ (M = Cu, Ni, Co, Zn). It was found also that the aggregation strongly depends on the nature of the solvent and the type of anion.

The electronic absorption spectra, which are highly sensitive to any changes in the complexes in the course of their aggregation, were selected as a tool for dimerisation studies. These spectra are very informative and demonstrate, in the most illustrative way, the characteristic changes in the structure of supramolecular aggregates under the influence of various factors.[20, 21]

In contrast to the aggregation of crown-substituted phthalocyanines, which occurs upon an increase in their concentration in solution and does not result in changes in their absorption spectra, the dimerisation induced by alkali metal cations has well-defined spectral manifestations. Thus it was found that the short-wavelength shift of the major absorption bands (*i.e.*, the Q-band and the Soret band) suggest the formation of rigid coaxial dimers in the system, the so-called H-dimers. The magnitude of the Q-band shifts depends on the distance between the interacting transient dipoles that appear as a result of an electron transfer in the phthalocyanine ligands.

The presence of a Q-band at 670 nm with a half-width of 500 cm^{-1} and a vibrational satellite at 610 nm and of a Soret band around ~ 350 nm with a shoulder in the short-wavelength region is characteristic of electronic absorption spectra of solutions of monophthalocyanines. Absorption around ~ 420 nm, which corresponds to the $n \rightarrow \pi^*$-transition due to the presence of crown-ether substituents, is represented by a broad low-intensity symmetrical band.

In addition to the aforementioned shifts of the major bands, interactions of alkali metal cations with crown-substituted metal phthalocyaninates are accompanied by broadening and a decrease in intensity of Q-bands. For example, the decrease in the intensity of the Q-band of $(15\text{-C-}5)_4$PcCu and $(18\text{-C-}6)_4$PcCu complexes depends on the concentration of the alkali metal salt: the corresponding dependence is linear and reaches a plateau at the stoichiometry 2 : 1 (four cations per two ligands) indicating the formation of the sandwich dimers **10** (Fig. 5).

If the diameter of the alkali metal cation (d_{M^+}) is larger than the size of the cavity of the crown-ether substituent (d_{CR}), highly

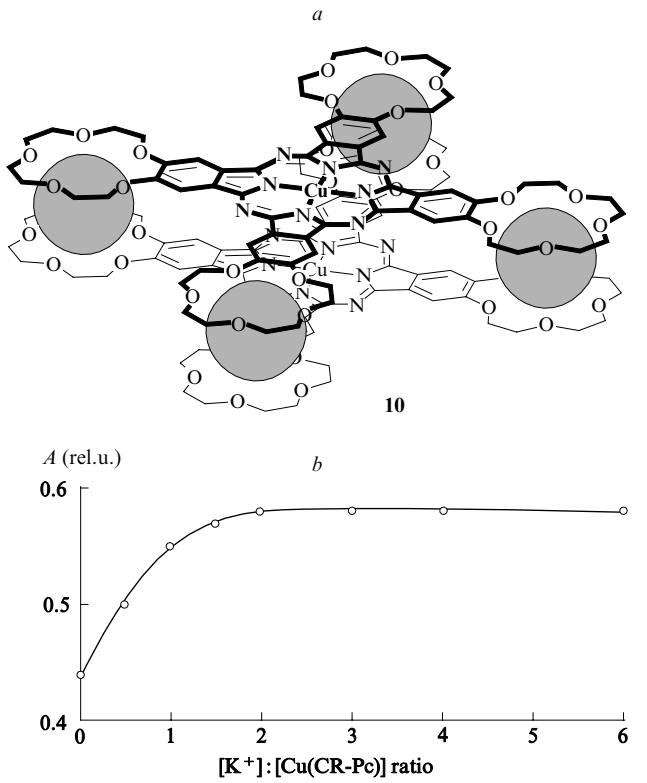


Figure 5. The structure of a sandwich-like supramolecular dimer $K_4[Cu(CR\text{-}Pc)]_2$ (**10**) (*a*) and a spectrophotometric titration curve of the Cu(CR-Pc) complex with potassium thiocyanate (*b*).

symmetrical sandwich complexes with the composition $4\,MX\cdot 2\,M(CR\text{-}Pc)$ are formed, while for $d_{M^+} < d_{CR}$, monophthalocyanine complexes $4\,MX\cdot M(CR\text{-}Pc)$ are formed.

Studies of formation of Co(CR-Pc) complexes with sodium and potassium thiocyanates (Scheme 5) (d_{K^+} = 2.66 Å; d_{Na^+} = 1.94 Å; d_{CR} = 1.7–2.2 Å) by the molar ratio method revealed [69] that the increase in the $[M^+]$: [Co(CR-Pc)] ratio results in changes in the electronic absorption spectra typical of phthalocyanine aggregation, *viz.*, a significant decrease in the intensity of Q-bands up to $[M^+]$: [Co(CR-Pc)] = 2 (nearly twofold for KSCN and threefold for NaSCN) with a simultaneous broadening of the Q-bands characteristic of complex formation and an appearance of an additional absorption band around 626 nm (for M = K) or 737 nm (for M = Na) (Fig. 6). Further increase in the metal : ligand ratio leads to precipitation.

The interaction of sodium thiocyanate with Co(CR-Pc) occurs in two steps.[69] Initially, an increase in the $[Na^+]$: [Co(CR-Pc)]

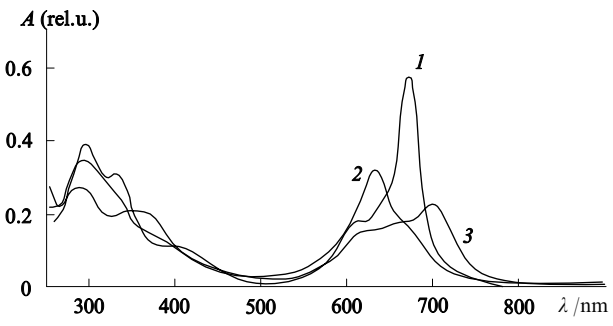
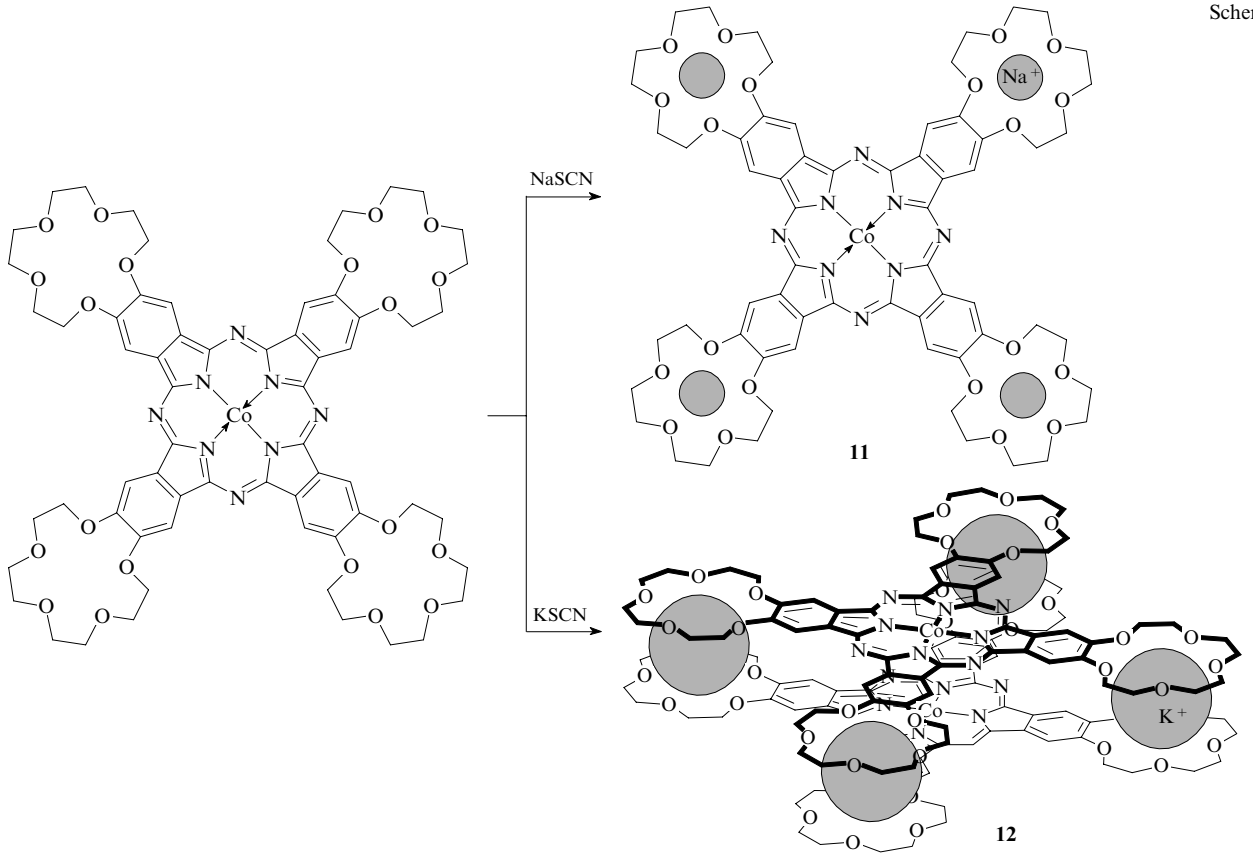


Figure 6. Electronic absorption spectra of Co(CR-Pc) (curve *1*) and its complexes with potassium (curve *2*) and sodium ions (curve *3*) in a chloroform – ethanol mixture (80 : 20, by volume).

Scheme 5



ratio from 0 to 2 results in a decrease in absorption intensity at 668 nm and an increase at 629 nm. Then in the interval of $[Na^+]:[Co(CR\text{-}Pc)]$ ratios from 2 to 4, the intensity of absorption at 629 nm decreases with a simultaneous increase in the absorption intensity around 700 nm, which suggests the formation of a complex with the composition $4\,NaSCN\cdot Co(CR\text{-}Pc)$ (**11**) (see Fig. 6). At a metal : ligand ratio of 4, the complex is precipitated as a solid phase. The complex with the composition $4\,NaSCN\cdot Co(CR\text{-}Pc)$ is characterised by $\lambda_{max} = 737$ nm and $\varepsilon = 2.90\times10^4$ litre mol^{-1} cm^{-1}, whereas the corresponding parameters for the complex with the composition $4\,KSCN\cdot 2\,Co(CR\text{-}Pc)$ (**12**) established by the molar ratio method are $\lambda_{max} = 626$ nm and $\lambda = 4.28\times10^4$ litre mol^{-1} cm^{-1}. The difference between the λ_{max} equal to 111 nm is sufficient for simultaneous detection of sodium and potassium ions in a solution using the Co(CR-Pc) complex (Figs 6–8). Other known crown-containing phthalocyaninates do not manifest such specific sodium–potassium selectivity.

The form of crown-containing phthalocyaninates present in a solution often plays a crucial role as regards their practical applications. Thus successful application of crown-containing phthalocyaninates as photosensitisers in the photodynamic therapy of malignant tumours requires that these were present in the monomeric form. Contrariwise, the synthesis of liquid crystals demands that soluble crown-containing phthalocyaninates formed the so-called stacks characteristic of unsubstituted phthalocyaninates.[70]

Similar sodium–potassium selectivity was observed for Co(CR-Pc) solutions in chloroform,[69] since the Co(CR-Pc) complex is poorly soluble in water. In order to detect sodium and potassium ions in biological systems with the help of the Co(CR-Pc) complex, it seemed important to characterise the behaviour of the complex in solvents of different polarity and their mixtures with the aim to search for an optimum system where the Co(CR-Pc) complex existed in the monomeric form and manifested sodium–potassium selectivity. It was shown[71] that in a chloroform–ethanol mixture containing $\leqslant 20$ vol.% ethanol

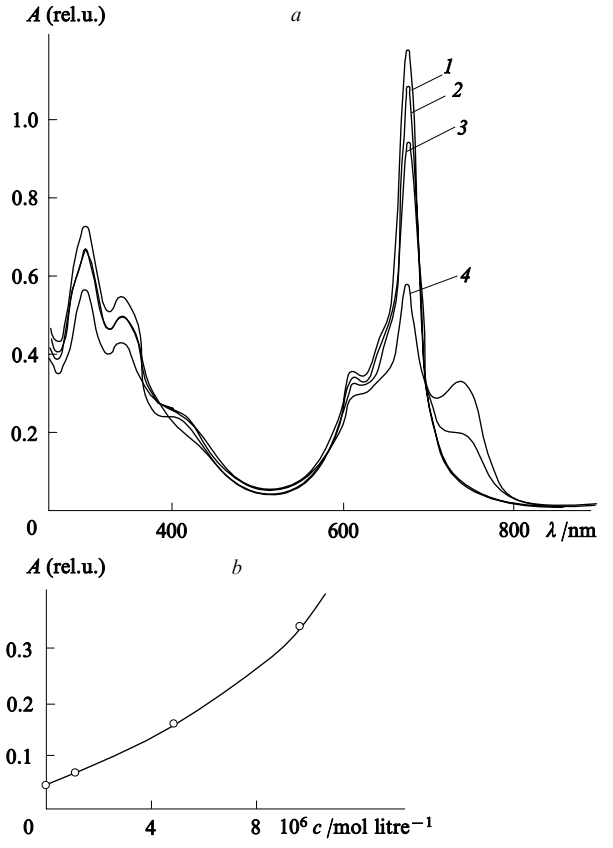


Figure 7. Absorption spectra (*a*) and the calibration curve (*b*) of the $n\,NaSCN\cdot Co(CR\text{-}Pc)$ complex ($n = 0-4$). Concentrations of the Na^+ cations /mol litre^{-1}: (*1*) 0, (*2*) 1×10^{-6}, (*3*) 5×10^{-6}, (*4*) 1×10^{-5} ($\lambda_{max} = 737$ nm).[72]

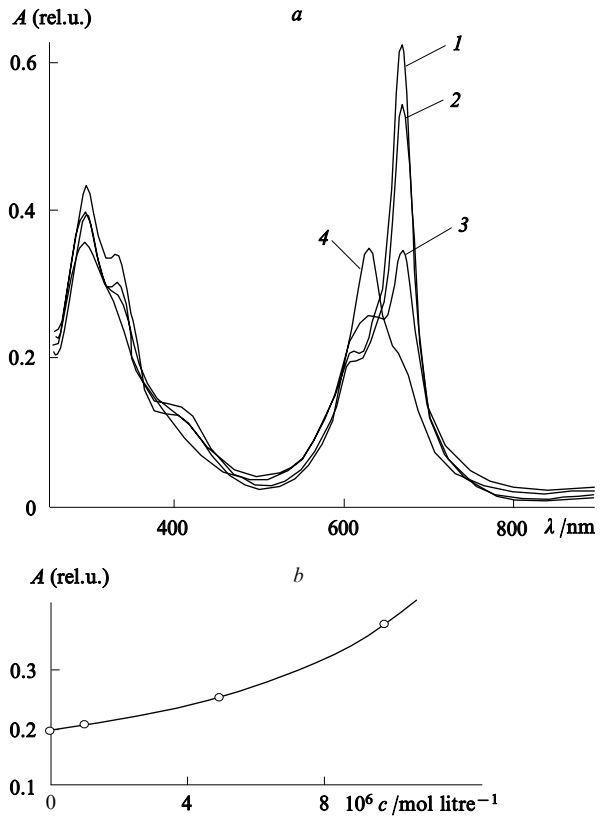


Figure 8. Absorption spectra (*a*) and the calibration curve (*b*) of the nKSCN·Co(CR-Pc) complex ($n = 0-2$). Concentration of the K^+ cations, mol litre^{-1}: (*1*) 0, (*2*) 1×10^{-6}, (*3*) 5×10^{-6}, (*4*) 1×10^{-5} (λ_{max} = 626 nm).[72]

the Co(CR-Pc) complex existed almost completely in the monomeric state. This makes it possible to rule out the effect of the solvent on the interaction of this complex with alkali metal ions. A chloroform–water mixture can be used for the study of biological fluids. However, it cannot be used as a model system because of the limited solubility of water in chloroform.

The kinetics of formation of heteronuclear complexes of Co(CR-Pc) with sodium and potassium cations in a chloroform–ethanol–water mixture was studied in order to apply the effect of differently directed shifts of the Q-band in the absorption spectrum of this compound under the influence of sodium and potassium salts for analytical purposes.[72]

The time dependence of the optical density of the absorption band of Co(CR-Pc) at 626 nm in the presence of an equimolar amount of KSCN suggests that the Co(CR-Pc) complex with potassium is formed at a sufficiently high rate (the equilibrium is reached within 3–5 min). A similar time dependence of the optical density of the absorption band at 737 nm upon addition of NaSCN suggests that the complexation with sodium ions proceeds at a much lower rate than with potassium ions and is complete only after 20–30 min. As a consequence, Co(CR-Pc) complexes with K^+ and Na^+ are formed at different rates, presumably due to differences in their structures, *viz.*, the 'sandwich' complex **12** with K^+ is formed from the starting compounds practically instantaneously, while the formation of the planar sodium complex **11** proceeds through the formation of an intermediate complex with a stoichiometric composition 2M·L. A comparison of the spectral data suggests that both complexes are characterised by a strong dependence of the optical density on the concentration of the metal ions, which enables their application for quantitative determination of Na^+ and K^+ present in a solution simultaneously (Figs 7 and 8).[72]

It is of note that the sodium–potassium selectivity of the Co(CR-Pc) complex is observed only in the case of sodium and potassium thiocyanates and is not manifested in the presence of anions other than NCS^- (*e.g.*, Cl^-, Br^-, I^-, AcO^-). Presumably, ambident thiocyanate ions play a crucial role in the complexation of Co(CR-Pc) with K^+ and Na^+ cations. If sodium ions were located in the centre of the crown-ether cavity, as it normally occurs, to form monomeric complexes, no changes in their electronic spectra would have been observed. In all probability, thiocyanate ions favour the rearrangement of the supramolecular aggregates based on heteronuclear (Co,Na)-monomeric complexes due to the formation of the Co–SCN bonds.

Interactions of alkali metal cations with crown-containing phthalocyaninates of trivalent metal ions with axial ligands occur differently. Thus the Al(CR-Pc)(SO_4H) complex in chloroform interacts with K^+ ions, which is confirmed by a decrease in the intensity of the Q-band; however, the dimer is not formed as can be evidenced from the absence of the corresponding absorption band.[47] This suggests that in contrast to the bivalent metal chelate complexes M(CR-Pc) (M = Cu, Co, Zn, *etc.*), the Al(CR-Pc)(SO_4H) complex does not form 'sandwich' molecules. Apparently, a coordinated extra ligand (SO_4H^-) prevents this process. Even such polar solvents as MeOH and EtOH are incapable to induce the dimerisation of the complex **8**. The electronic absorption spectra indicate that the aluminium complex in chloroform is aggregated to a larger extent than that in the $CHCl_3$–EtOH mixture. Nevertheless, the absorption spectra of the complex **8** depend on the nature of the solvent (Fig. 9).

The aggregation of Al(CR-Pc)(SO_4H) molecules strongly depends on the type of the anion; the corresponding electronic absorption spectra provide an illustrative example (Fig. 10).

As can be seen from Fig. 10, no changes in the Q-band at ~ 691 nm occur upon the interaction of Al(CR-Pc)(SO_4H) with sodium chloride despite the appearance of low-intensity bands at ~ 657 nm characteristic of dimers. The interactions of the complex **8** with sodium bromide and sodium iodide result in the disappearance of the band at ~ 691 nm and an appearance of less intense bands characteristic of aggregated forms around ~ 652 and ~648 nm. However, more significant spectral changes manifested in the appearance of a narrow intense band at ~ 639 nm are observed in the interaction of Al(CR-Pc)(SO_4H) with sodium fluoride: the band intensity is comparable to that at ~ 691 nm. It may thus be concluded that in this case we deal with

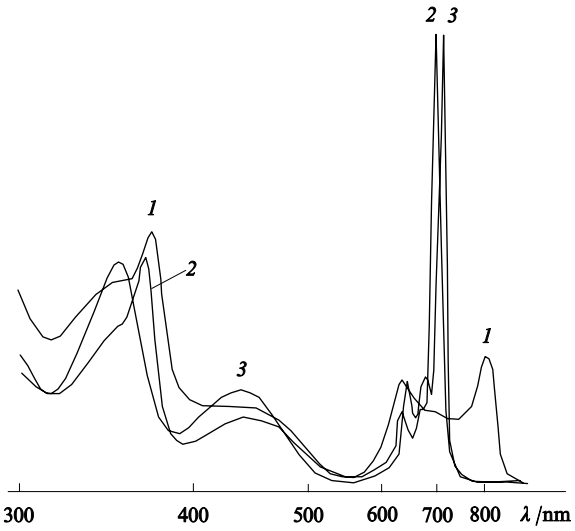


Figure 9. Electronic absorption spectrum of Al(CR-Pc)(SO_4H) in different solvents.
(*1*) Water, (*2*) dimethyl sulfoxide, (*3*) chloroform.

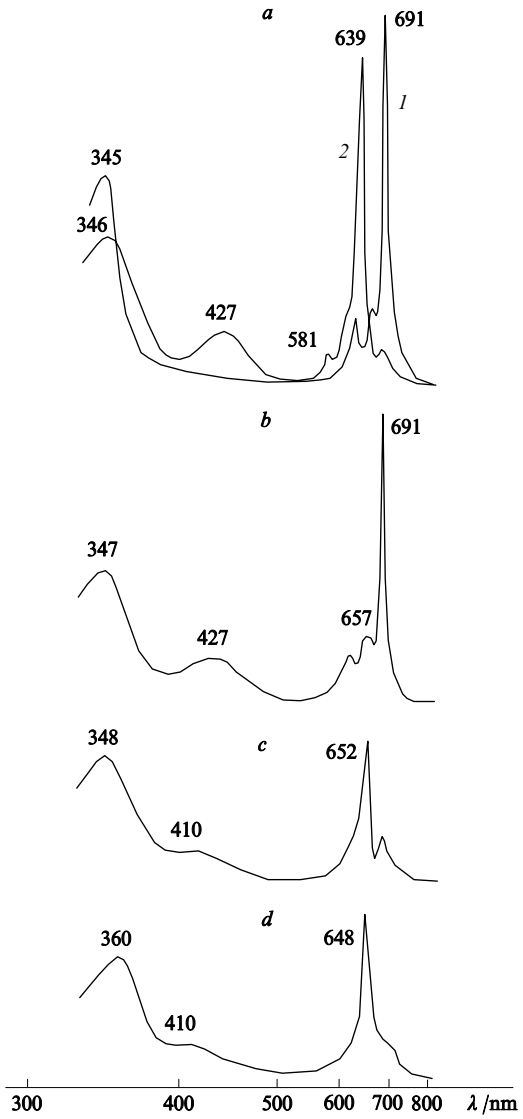


Figure 10. Electronic absorption spectra of Al(CR-Pc)(SO_4H) complexes with NaX where X = F (*a*), Cl (*b*), Br (*c*), I (*d*), in $CHCl_3$.
The concentration of the Al(CR-Pc)(SO_4H) complex in chloroform is 2.5×10^{-6} mol litre^{-1}.
(*1*) Al(CR-Pc)(SO_4H), (*2*) Al(CR-Pc)(SO_4H)$\cdot 4\,Na^+$.

the formation of highly ordered supramolecular ensembles which involve fluoride bridges.

Supramolecular aggregation occurs upon dissolution of Al(CR-Pc)(SO_4H) in water as can be evidenced from significant changes in the electronic absorption (see Fig. 9) and luminescence spectra (Fig. 11). Lowering of the intensity of the luminescence band of complex **8** in water limits its application in the photodynamic therapy of cancer despite its easy solubility in water and normally high quantum yields of luminescence of aluminium phthalocyaninates.

The photodynamic activity of crown-containing phthalocyaninates is manifested in those cases where they are present in aqueous solutions as monomers.[73] However, the majority of crown-containing phthalocyaninates form aggregates in water due to dispersion interactions between aromatic systems.[74] If the charge of the central metal ion is three, a charge-compensating ligand is required for partial separation of the macrocycles, which favours the existence of crown-containing phthalocyaninates in water as monomers.

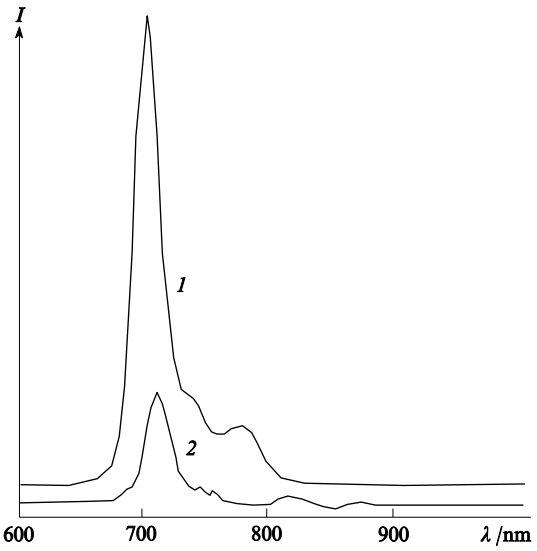


Figure 11. Luminescence spectra of Al(CR-Pc)(SO_4H) solutions in chloroform (λ_{max} = 696 nm) (*1*) and water (λ_{max} = 705 nm) (*2*).

It has been shown[75] that depending on the mutual arrangement of macrocyclic π-aromatic systems in the aggregates their electronic spectra exhibit a short- or a long-wavelength shift of the absorption band in the visible region of the spectrum relative to its position in the corresponding spectrum of the monomer. Aggregates of the first type usually contain a small number of molecules with strong π-interactions between each other. These include, in particular, coaxial dimers also referred to as H-aggregates. In the second type of aggregates termed as J-aggregates, the molecules are strongly displaced relative each other. Here, another type of interaction between electronic π-systems of the molecules results in a long-wavelength shift with a simultaneous narrowing of the absorption band.[75] These changes in the electronic absorption spectra are observed only in aggregates consisting of 4–9 monomers. The mutual arrangement of molecules in such aggregates differs from that in J-dimers which are spectrally indistinguishable from monomers.[75]

A compound with the composition Lu[(15-C-5)$_4$Pc](OAc)$_2\cdot$ 2 Phen, the phenanthroline molecules in which play the role of chelating ligands, has been synthesised[55,76] in order to obtain phthalocyaninates which normally do not form aggregates in aqueous solutions (as is required of preparations used in the photodynamic therapy of cancer). It was suggested[76] that such axial chelate ligands prevent the aggregation. Indeed, this compound was found to exist in aqueous solutions (pH 5.5) in the monomeric state.

Since physiological solutions contain sodium and potassium salts, it is important to elucidate the behaviour of this compound in aqueous solutions containing NaCl and KCl. It was found that NaCl does not induce any aggregation of the Lu(CR-Pc)(OAc)$\cdot$ 2 Phen complex. When the latter is used in the concentration 2×10^{-5} mol litre^{-1} and NaCl is used in the concentrations < 2.0 mol litre^{-1}, no significant changes are observed in the Lu(CR-Pc)(OAc)$\cdot$ 2 Phen complex within the pH range 3.5–9.0 and J-aggregates are formed only upon alkaline hydrolysis.

The interaction of the lutetium complex with potassium chloride in aqueous solutions is accompanied by the formation of H-dimers, however, only if the electrolyte is used in a large excess.

The interaction of the Lu(CR-Pc)(OAc)$\cdot 2\,H_2O$ complex with sodium and potassium acetates was studied using spectrophotometry and ^{1}H NMR spectroscopy.[77] It was found that potassium ions favour the formation of 2[Lu(CR-Pc)(OAc)$\cdot 2\,H_2O$]$\cdot 4\,K^+$ dimers in a $CHCl_3$ – DMSO mixture. It was thus assumed that the

complex represents a coaxial dimer of the 'guest – host' type and has an eclipsed conformation.

The interaction of the ruthenium complex **9** containing CO and CH_3OH molecules as axial ligands with sodium and potassium thiocyanates presents substantial interest. The cation-induced supramolecular aggregation of this complex was studied by electronic absorption spectroscopy (Fig. 12).[78] An analysis of changes in the absorption intensity of the Q-band of the complex **9** *vs.* the $[M^+]:[\mathbf{9}] = n$ ratio revealed that the interactions of the complex **9** with K^+, Rb^+ and Cs^+ thiocyanates yield supramolecular aggregates of the composition $n\mathbf{9}\cdot 2n$MNCS in the form of 'brickwork' (Fig. 13).

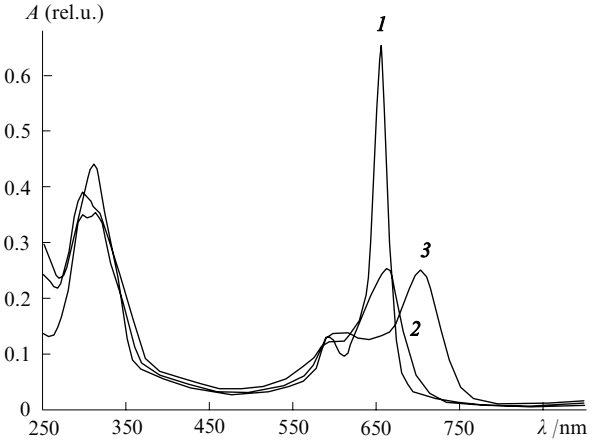


Figure 12. Electronic absorption spectra of (CR-Pc)Ru(CO)(CH_3OH) (**9**) and its complexes with KSCN and NaSCN in $CHCl_3$.
(*1*) **9**, (*2*) **9** + 2 KSCN, (*3*) **9** + 2 NaSCN (after 8 days).

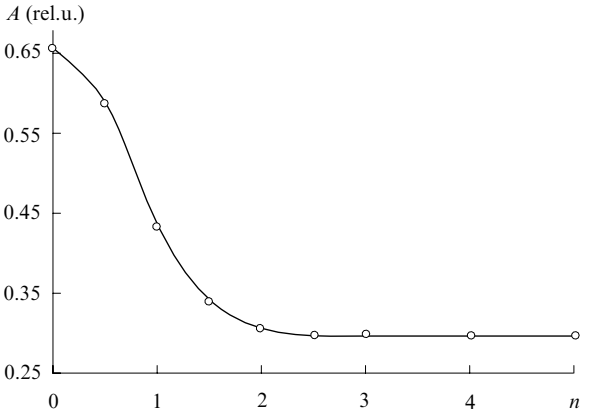


Figure 13. Dependence of the intensity of the absorption Q-band in the electronic absorption spectra of complex **9** in $CHCl_3$ on n ($n = [KSCN]:[\mathbf{9}]$). Similar dependencies are also observed for Rb^+ and Cs^+.

The interaction of the complex **9** with NaSCN is more complicated. In contrast to the cations K^+, Rb^+ and Cs^+, the diameter of the Na^+ cation coincides with the size of the cavity of 15-crown-5, which favours the encapsulation of Na^+ into the crown ether.[6] At the initial moment of time, the interaction of the complex **9** with NaSCN causes a bathochromic shift of the Q-band from 655 to 679 nm, which is followed by more complex reaction kinetics: after 30 min, the Q-band is shifted to 690 nm, after 2 days, to 698 nm, after 4 days, to 701 nm and after 8 days, to 704 nm (see Fig. 12, curve *3*). Such a complex kinetic behaviour and a simultaneous strong shift of the absorption Q-band can be attributed to the formation of a coordination bond between the thiocyanate ions, sodium cations present in the cavities of the crown ethers and ruthenium(II) ions. This can occur upon substitution of the thiocyanate ion for an axially coordinated methanol molecule.

Elucidation of structural specificities of supramolecular aggregates formed upon interaction of the ruthenium complex with sodium thiocyanate required the use of data from vibrational spectra, since it is well known that vibrational frequencies change considerably depending on the mode of coordination of the NCS groups.[79] The NCS^- group can coordinate a metal through a nitrogen or a sulfur atom as well as through a bridging structure. The type of coordination depends on the nature of the metal. The type of bonding of the NCS group in metal complexes is determined on the basis of empirical criteria.[80] Thus the stretching vibration frequencies ν(CN) in N-bonded complexes lie around 2070 cm^{-1} and are lower than those in S-bonded complexes (around 2100 cm^{-1}). The vibration frequencies ν(CN) in the bridged $M-NCS-M'$ complexes lie above 2100 cm^{-1}. The ν(CN) values for thiocyanate alkali metal complexes with crown ethers are usually lower than those for thiocyanate complexes with transition metals.[10, 11, 79] The IR spectra of ruthenium complexes before and after interaction with potassium and sodium thiocyanates are shown in Figs 14 and 15, respectively.

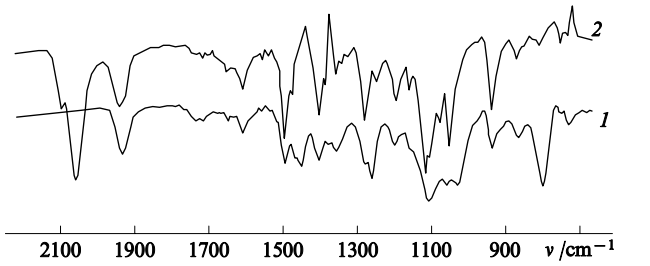


Figure 14. IR spectra of Ru(CR-Pc)(CO)(CH_3OH) (*1*) and its complex with KSCN (*2*).

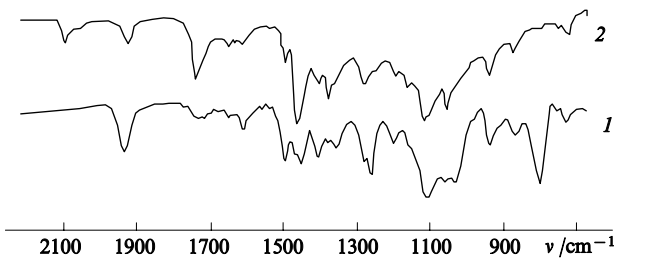


Figure 15. IR spectra of Ru(CR-Pc)(CO)(CH_3OH) (*1*) and its complex with NaSCN (*2*).

The IR spectra of ruthenium crown-containing phthalocyaninates contain all the bands characteristic of metal complexes with crown-containing phthalocyanines. The most intense bands lie around 900 – 1300 cm^{-1}, *i.e.*, in the region where complex stretching-deformation vibrations of the CO, CC and HCH fragments of the crown ether are manifested. It is in this region that the conformational changes associated with the complexation of crown ethers with alkali metals are displayed.[6]

Analysis of the IR spectra of ruthenium phthalocyaninate **9** and its complexes with KSCN and NaSCN allows certain conclusions to be drawn concerning the effect of complexation of alkali metals with crown-substituted ruthenium(II) phthalocyaninate on the conformational state of the crown-ether substituent. The IR spectra of alkali metal complexes with Ru(CR-Pc)(CO).(CH_3OH) in the conformation-sensitive region (900 –

1400 cm^{-1}) differ essentially from the IR spectrum of the original complex, which points to conformational rearrangements in the crown ethers.

Analysis of changes in the IR spectra around 2000–2150 cm^{-1} points also to a strong effect of the nature of the substrate anion on the architecture of the supramolecular ensembles formed. The IR spectrum of the Ru(CR-Pc)(CO)(CH_3OH) complex with potassium thiocyanate contains a stretching vibration band [ν(CN)] at 2060 cm^{-1} (see Fig. 14), which suggests that the NCS group represents an outer-sphere ligand [6, 79] which is not involved in the formation of a supramolecular aggregate. The IR spectrum of the Ru(CR-Pc)(CO)(CH_3OH) complex with sodium thiocyanate contains two stretching vibration bands [ν(CN)] at 2097 cm^{-1} and 2060 cm^{-1} (Fig. 16), which points to coordination of sodium ion with the nitrogen atom of the NCS group. At the same time, the increase in the vibration frequency [ν(CN)] of complex **9** with NaCNS is so significant in comparison with the vibration frequency of the free NCS^- ion and sodium thiocyanate complexes with benzocrown ethers that it may lead to coordination of the sulfur atoms by the ruthenium atom resulting in the formation of bridged complexes.[6, 79] The changes in the IR spectrum of complex **9** with NaSCN (by analogy with the electronic absorption spectra) occurring during several days testify to further rearrangements of the architecture of the aggregate associated with coordination of the NCS group by the ruthenium atom of the macrocycle. This is confirmed by changes in the relative intensities of the absorption bands at 2097 and 2060 cm^{-1}. The band at 2060 cm^{-1} in the IR spectrum of the completely formed supramolecular aggregate is transformed into a shoulder, while the band at 2097 cm^{-1} is transformed into the major band (Fig. 16). This suggests that the NCS^- anion makes the most weighty contribution to the formation of a supramolecular ensemble in the interaction of the Ru(CR-Pc)(CO)(CH_3OH) complex with the NaSCN anion. The hypothetical structures of the supramolecular ensembles formed upon interaction of ruthenium complexes **9** with potassium (*a*) and sodium thiocyanate (*b*), respectively, are shown in Fig. 17.

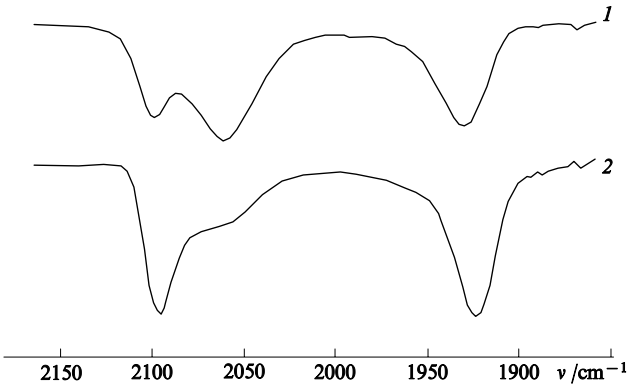


Figure 16. IR spectra of the Ru(CR-Pc)(CO)(CH_3OH) complex with NaSCN around 1900–2150 cm^{-1} recorded after 30 min (*1*) and 8 days (*2*).

V. Sandwich-like double- and triple-decker crown-substituted phthalocyaninates

The size of lanthanide cations exceeds the diameter of the phthalocyanine ligand cavity; therefore, their interactions yield predominantly sandwich-like structures (the so-called double- and triple-decker complexes). Depending on synthetic conditions, differently coloured ('green' and 'blue') forms of REE diphthalocyaninates are formed.

Until recently, the architectures of 'green' and 'blue' forms of diphthalocyaninates were open to discussion. Based on the ESR data for the 'green' form of the diphthalocyaninates $LnPc_2$, the structure of the radical paramagnetic complex was postulated as the most probable.[51–54, 81–83] The 'blue' form was often associated with the protonated diamagnetic structure $HLnPc_2$.[51, 81] Based on data from X-ray diffraction spectroscopy and ESR, it was proposed [84] that the central metal atom is in the oxidation state 4+. According to other authors,[52–54] intramolecular electron transfer is possible in the 'green' form as a result of which the degree of oxidation of the central metal atom changes from Ln^{3+} to Ln^{4+} and a 'blue' form is formed instead.

For the first time, diphthalocyaninates of REE were prepared by fusion of metal acetates with phthalonitrile.[51] Later, it was found [52–54] that this reaction occurs in several steps and depends on the nature of the central metal atom. Monophthalocyanine is formed in the first step of the synthesis of *tert*-butyl-substituted diphthalocyaninates of REE, it is further converted into a 'green' and then into a 'blue' form.

The synthesis of tetra(15-crown-5)-substituted lutetium diphthalocyaninate Lu(CR-Pc)$_2$ was carried out by boiling dicyanobenzo-15-crown-5 as a starting reagent in hexanol for 20 h.[85] A simpler and more convenient method for the template synthesis of a sandwich green form of Lu(CR-Pc)$_2$ has been proposed which consists in the fusion of lutetium acetate with dicyanobenzo-15-crown-5 in a sealed evacuated tube. [86] The optimum conditions for the synthesis of the 'green' and 'blue' forms of crown-substituted lutetium diphthalocyaninates were established by varying the

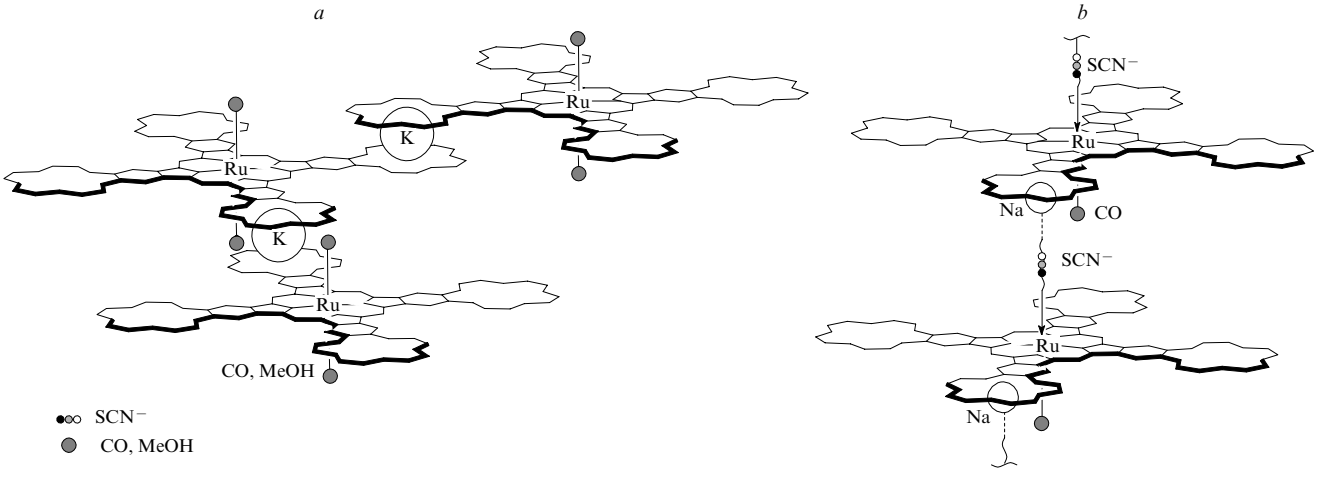
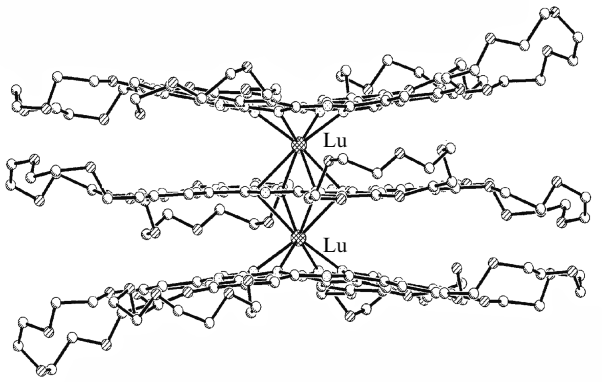


Figure 17. Tentative structures of the supramolecular ensembles based on the Ru(CR-Pc)(CO)(CH_3OH) complexes with KSCN (*a*) and NaSCN (*b*).

temperature (200 – 290 °C), molar ratios of the reagents (from 1 : 1 to 1 : 8) and reaction time (from 30 min to 5 h).

For a long time, the data on X-day diffraction analysis of crown-substituted metal phthalocyaninates were absent due to significant difficulties in growing of single crystals of this class of compounds. Recently, the molecular crystal structure of the 'blue' form of the $Lu_2(CR\text{-}Pc)_3$ complex (**13**) was established using X-ray diffraction spectroscopy.[87] Prismatic dark-blue crystals were obtained by slow crystallisation of complex **13** from a mixed solvent ($DMSO - CHCl_3$, 2 : 1). This compound was found to have a triple-decker structure (Fig. 18).



13

Figure 18. Structure of the triple-decker complex $Lu_2(CR\text{-}Pc)_3$.

The lutetium atoms in compound **13** are localised between the planes of the phthalocyanine ligands. Two outer phthalocyanine rings have similar orientations with respect to the internal ring which is turned by 43.7° relative to these rings.

The neighbouring macrocycles are not equidistant from the lutetium ion; the distances between the lutetium atoms and the planes of the outer phthalocyanine ligands passing through the donor atoms of the pyrrole ring nitrogens are equal to 1.218 Å, while the corresponding distances from the central ligand are much greater (1.703 Å). This fact agrees with a significant increase in the metal – bridging ligand distance characteristic of all presently known triple-decker molecules with tetrapyrrole macrocyclic ligands.[88,89] The lutetium atom in the double-decker molecule of $LuPc_2$ occupies a practically symmetrical position: for the average metal – ligand distance equal to 1.34 Å, the difference in the distances does not exceed 0.01 Å.[90].

The coordination polyhedron of the lutetium ion represents a distorted tetragonal antiprism. The Lu – Lu distance is 3.406 Å. The Ln – Ln distances in structurally similar Ce_2P_3 (see Ref. 88) and Nd_2Pc_2P[89] complexes (P is porphyrin) exceed the sum of the corresponding lanthanide atomic radii by 0.1 and 0.06 Å, respectively.[91]

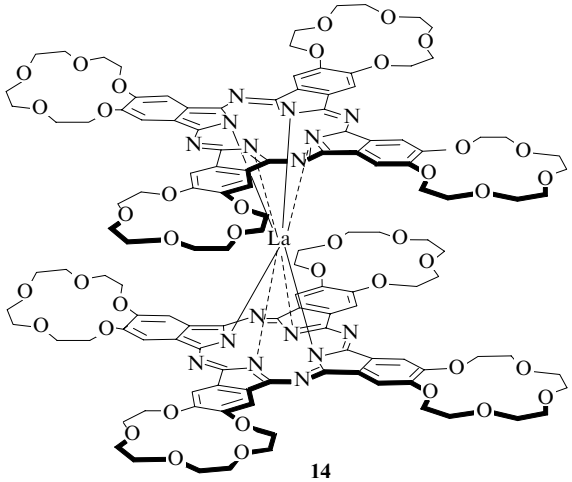
The intramolecular interplanar distance between two neighbouring ligands is 2.923 Å [in $LuPc_2$, the ligands are even closer to one another (2.69 Å)[90]], *i.e.*, the distance between them is less than the van der Waals distance (3.34 Å) between two aromatic systems. Minimisation of the non-bonding interactions is achieved due to a turn of the central macroligand relative to the outer ligands. The atoms in the crown-ether rings protrude above the plane passing through the nitrogen atoms of the pyrrole rings to a greater extent than other atoms constituting the phthalocyanine backbone.

Compound **13** is the first example of a substituted phthalocyanine complex with the established crystal structure.

Double-decker phthalocyaninates of REE are neutral compounds, which represent stable free radicals $[Pc^{2-}M^{3+}Pc^{-\bullet}]^0$. They undergo reversible redox conversions:

$$\underset{\text{Blue form (anionic)}}{[Pc^{2-}M^{3+}Pc^{2-}]^-} \underset{e}{\overset{-e}{\rightleftharpoons}} \underset{\text{Green form (neutral)}}{[Pc^{2-}M^{3+}Pc^{-\bullet}]^0} \underset{e}{\overset{-e}{\rightleftharpoons}} \underset{\text{Red form (cationic)}}{[Pc^{-\bullet}M^{3+}Pc^{-\bullet}]^+}.$$

The data on double- and triple-decker crown-substituted phthalocyaninates of REE are mainly available for lutetium complexes. Other authors describe the synthesis of double- and triple-decker ytterbium and gadolinium complexes with tetra(15-crown-5)phthalocyanine.[92] $Yb(CR\text{-}Pc)_2$ [but not $Yb_2(CR\text{-}Pc)_3$], $Gd_2(CR\text{-}Pc)_3$ or $Gd(CR\text{-}Pc)_2$ could be prepared by template synthesis,[92] but the yields of the target products were extremely low. Direct interaction of the protonated ligand $H_2(CR\text{-}Pc)$ with ytterbium and gadolinium acetates in the presence of a strong base (DBU) yields the same complexes, *viz.*, $M(CR\text{-}Pc)_2$ and $M_2(CR\text{-}Pc)_3$ [M = Gd, Yb, CR-Pc = (15-C-5)$_4$Pc]. This approach affords sufficiently high yields and a high degree of purity and was also used in the synthesis of the lanthanum complex **14**.[93]



14

$$H_2(CR\text{-}Pc) \xrightarrow{a \text{ or } b} [La(CR\text{-}Pc)_2]^- + [La(CR\text{-}Pc)_2]^0$$

a — $H_2(CR\text{-}Pc) : [La(OAc)_3 \cdot 1.5\,H_2O] : DBU = 1 : 10 : 200$, boiling *o*-dichlorobenzene (b.p. 180 °C), 3 h;
b — $H_2(CR\text{-}Pc) : [La(OAc)_3 \cdot 1.5\,H_2O] : DBU = 1 : 1.5 : 10$, boiling 1-chloronaphthalene (b.p. 250 °C), 2 h.

However, the reaction products represented a radical-neutral form $[(CR\text{-}Pc)^{2-}La^{3+}(CR\text{-}Pc)^{-\bullet}]^0$ and a single-electron-reduced form $[La^{3+}(CR\text{-}Pc)_2^{2-}]^-$; DBU, which is commonly used as a deprotonating reagent in organic synthesis, stabilises the reduced form of crown-substituted lanthanum diphthalocyaninate.

This is the first reaction where a single-electron-reduced form of diphthalocyaninate is prepared in the course of synthesis. The neutral form of the $M(CR\text{-}Pc)_2$ complex represents a stable free radical. Its stability in the case of the terminal elements of the lanthanide series can be attributed to delocalisation of the unpaired electron over two phthalocyanine ligands. In complex **14,** the delocalisation of the electron is much more difficult, since the phthalocyanine rings in this compound are at a much greater distance from one another than, *e.g.*, in the stable complex $[(CR\text{-}Pc)^{2-}Lu^{3+}(CR\text{-}Pc)^{-\bullet}]^0$. For this reason, the electronic state of the two ligands in the $La(CR\text{-}Pc)_2$ complex is levelled off giving rise to the anionic form $[La(CR\text{-}Pc)_2]^-$.

The reaction of $H_2(CR\text{-}Pc)$ with Gd, Yb and Lu acetates in boiling *o*-dichlorobenzene yields the corresponding monophthalocyaninates, whereas boiling of these reagents in chloronaphthalene yields double- and triple-decker complexes. Sandwich-like double-decker lanthanum complexes are formed even upon boiling in *o*-dichlorobenzene. This can be explained by the fact that the larger radius of La (1.061 Å) in comparison with Gd (0.938 Å), Yb (0.858 Å) and Lu (0.848 Å) results in an increase in the

distance between the phthalocyanine ligands, which in turn stabilises the sandwich-like structure of the phthalocyaninate due to the weakening of $\pi-\pi$-interactions.

VI. Supramolecular systems based on double- and triple-decker crown-substituted phthalocyaninates

As mentioned above, crown-substituted metal monophthalocyaninates interact with bulky alkali metal cations to form supramolecular dimers as a result of binding of alkali metal cations to the crown-ether fragments of the neighbouring ligands. The crown-containing phthalocyanine ligands in double- and triple-decker complexes are separated by REE ions which prevent the penetration of alkali metal cations between two neighbouring phthalocyanine fragments of the sandwich complex. However, alkali metals can coordinate with the 'top' and 'bottom' crown-substituted phthalocyanine ligands of the sandwich-like dimers to give pillar-like structures (Scheme 6).

The complexes of 15-crown-5-substituted diphthalocyaninates of REE with alkali metal salts are more stable than the benzo-15-crown-5 itself.[45, 94, 95] The authors point to a positive cooperative effect in the reaction of crown-substituted lutetium diphthalocyaninates with alkali metal cations. This can be explained by the fact that the insertion of the first cation between the two ligands is more difficult in comparison with the insertion of the second and subsequent cations due to prearrangement of the structure. The nature of these positive non-linear cooperative interactions has been studied in detail. The curves of spectrophotometric titration of transition-metal monophthalocyaninates by alkali and alkaline earth metal salts have a common linear shape, whereas the titration curve of octa(18-crown-6)-substituted lutetium diphthalocyaninate by rubidium salts is sigmoidal and resembles that observed in the interaction of hemoglobin with molecular oxygen. This suggests that in this case we deal with a non-linear cooperative effect which is not typical of triple-decker complexes and monophthalocyaninates. Based on the results of light scattering studies, a mechanism for the formation of supramolecular oligomers containing up to 260 building blocks of the $Lu(CR\text{-}Pc)_2$ complex with KSCN has been proposed.[45] Such supramolecular aggregates have pillar-like and tubular shapes where one-dimensional transport of electrons and ions is possible (Fig. 19). It was suggested that these structures can be used in ionic and molecular electronics as well as in the design of new generations of functional materials.[45, 94, 95]

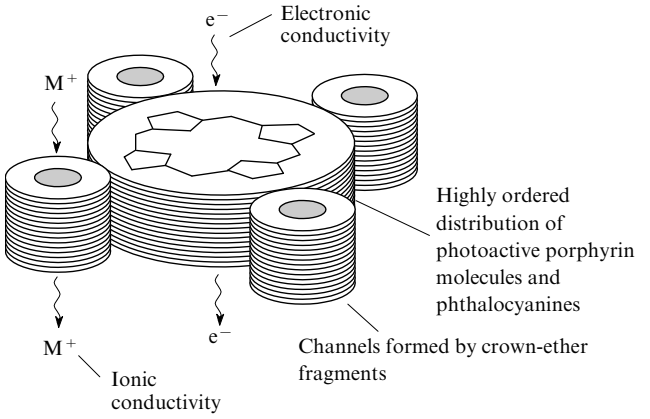
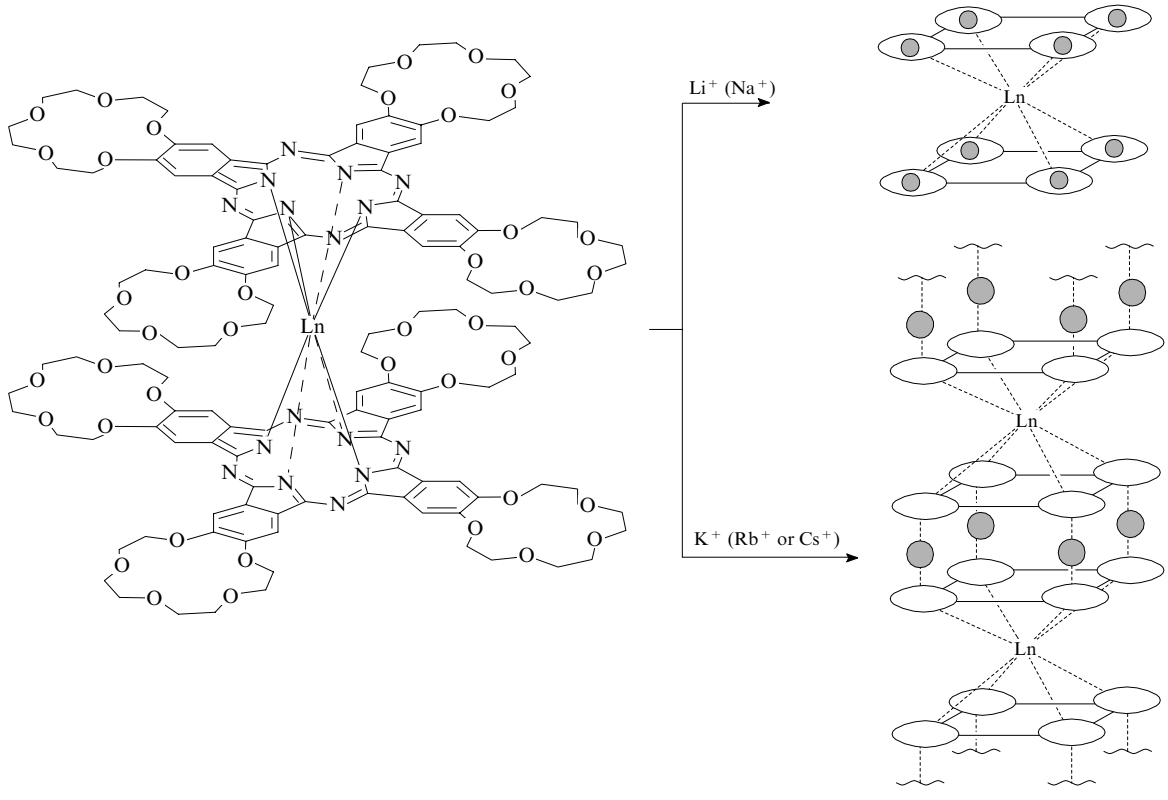


Figure 19. A schematic representation of an ordered supramolecular ensemble based on metal crown phthalocyaninates.

The supramolecular assembly of single-electron-reduced forms of octa(15-crown-5)diphthalocyaninates of the REE series $[Ln(CR\text{-}Pc)_2]^-$ (Ln = Y, Gd, Yb, Lu) has been studied.[96] It was found that the single-electron-reduced form is generated upon dissolution of the radical form in the presence of DBU or by titration of the radical form with DBU in chloroform. The addition of K^+, Rb^+ or Cs^+ thiocyanates to a solution of $[Ln(CR\text{-}Pc)_2]^-$ induces similar spectral changes manifested in a bathochromic shift with a simultaneous decrease in the half-width

Scheme 6



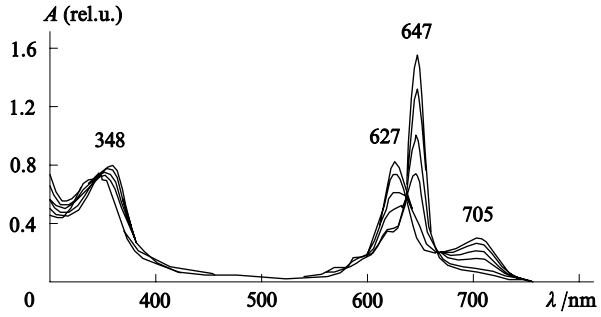


Figure 20. Changes in the electronic absorption spectra of the $[Lu(CR\text{-}Pc)_2]^-$ complex ($c = 6.0 \times 10^{-6}$ mol litre^{-1}) with potassium cations as a function of K^+ concentration.
The concentration of KSCN varied from 0 to 4.8×10^{-5} mol litre^{-1}.

of the Q_1-band (Fig. 20). The splitting of the band of the reduced form also disappears. Analysis of the electronic absorption spectra and spectrophotometric titration curves of the $[Ln(CR\text{-}Pc)_2]^-$ complexes by alkali metal thiocyanates prompted a conclusion about the formation of polymeric coaxial supramolecular aggregates $[(Ln(CR\text{-}Pc)_2)\cdot 4\,MSCN]_n$ ($n > 20$). The radical form of the complex $Lu(CR\text{-}Pc)_2$ interacts differently with potassium and rubidium picrates, whereas the single-electron-reduced form of the complex is arranged into supramolecular 'host–guest' structures on interaction with K^+, Rb^+ and Cs thiocyanates in the same manner. Non-linear cooperative effects are manifested in all the three cases (Fig. 21). No such effect of the anion on the assembly was observed for other potassium salts (acetate, bromide).

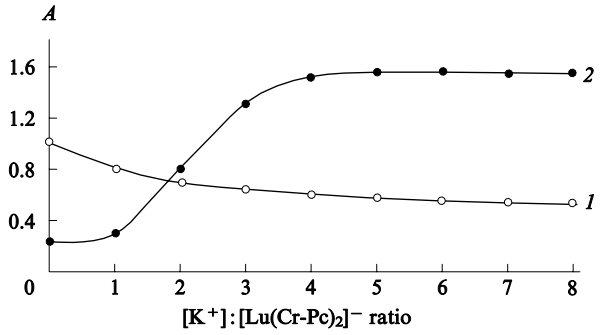


Figure 21. Spectrophotometric titration curves of the $[Lu(CR\text{-}Pc)_2]^-$ complex with potassium cations. The optical densities of the bands at 627 (*1*) and 647 nm (*2*) are given at various $[K^+]:[Lu(CR\text{-}Pc)_2]^-$ ratios. The sigmoidal shape of the titration curve points to a non-linear cooperative effect of the complex formation.

It was shown that interactions of $[La(CR\text{-}Pc)_2]^-$ with cations K^+, Rb^+ and Cs^+ are also accompanied by a non-linear positive cooperative effect (Fig. 22) and yield highly ordered polymeric aggregates.[97] The reduced form of sandwich double-decker crown phthalocyaninates of REE were shown to represent a common sensor for the cations K^+, Rb^+ and Cs^+.

VII. Conclusion

Attachment of crown-ether fragments to porphyrins and phthalocyanines not only improves the inherent properties of crown ethers, porphyrins and phthalocyanines, but also confers novel properties on them. Thus the selectivity of crown-substituted porphyrins and phthalocyanines with respect to alkali metal ions and the stability of the corresponding complexes markedly

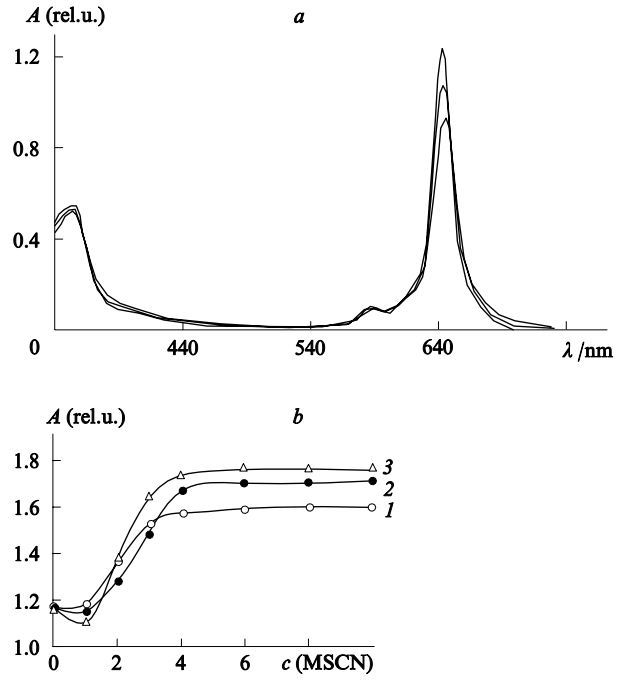


Figure 22. Electronic absorption spectra of the $[La(CR\text{-}Pc)_2]^-$ complex with potassium thiocyanate at different concentrations of K^+ (*a*) and spectrophotometric titration curves (*b*) of the $[La(CR\text{-}Pc)_2]^-$ complex with potassium (*1*), rubidium (*2*) and caesium thiocyanates (*3*).

exceeds the corresponding parameters of crown ethers and their complexes. The solubilities of crown-substituted porphyrins and phthalocyanines are also higher than those of unsubstituted compounds. Some representatives of this class are soluble even in water and thus acquire amphiphilic properties. The ability of crown-substituted porphyrins and phthalocyanines to form heteronuclear supramolecular architectural ensembles upon interaction with alkali metal salts is their characteristic feature.

Crown-ether fragments are linked to porphyrins and phthalocyanines in different fashions. Benzocrown-ether fragments are attached to porphyrins by a C–C bond to produce flexible structures, whereas bonding of crown-ether fragments to phthalocyanines is rigid. In contrast to crown-containing phthalocyanines, porphyrins form tetracrown-substituted analogues along with mono-, di- and tricrown-substituted derivatives. Crown-substituted porphyrins and phthalocyanines differ also in the type of supramolecular heteronuclear architectural ensembles formed upon their interaction with alkali metal salts.

Interactions of potassium, ammonium and barium salts with tetra- and tricrown-substituted porphyrins and metal complexes based on them result in the formation of supramolecular dimers (interactions with sodium, magnesium and calcium salts occur by a different mechanism).

Treatment of the monomeric zinc–bis(benzo-15-crown-5)-porphyrin complex with $AgPF_6$ yields a dimer in which two porphyrin rings are linked by a covalent *meso-meso* bond. Although intermolecular contacts between the neighbouring crown-ether fragments in the monomeric and dimeric zinc complexes interacting with potassium ions are similar, the supramolecular architectural ensembles formed differ from one another. Coaxial ('face-to-face') dimerisation of monomeric zinc complexes is possible upon interaction with potassium ions, whereas linear extended aggregation is more preferable for covalently bonded dimeric zinc complexes.

The nature of the central metal atom in porphyrinates strongly affects the structure of the complexes formed upon their interaction with alkali metal salts. According to the ESR data, the porphyrin rings in the dimeric potassium complex with copper

tetracrown monoporphyrinate are turned by 45° relative to one another, whereas in an analogous zinc complex they are turned by 23°.

The mode of interaction of alkali metal salts with crown-substituted monophthalocyaninates of d-elements differs significantly from that with analogous double- and triple-decker complexes of REE. In the former case, monomeric or dimeric heteronuclear complexes are formed depending on the size of the alkali metal cations; in the latter case, oligomeric supramolecular ensembles are formed.

The stucture of the complexes formed also depends on the nature of the anion. For example, the reaction of the Al(CR-Pc)(SO_4H) complex with sodium chloride is not accompanied by changes in the electronic spectra of the complex, which points to the formation of monomeric heteronuclear complexes. On the other hand, interactions with sodium bromide and iodide afford dimers and the interaction with sodium fluoride yields polymeric supramolecular aggregates.

The optical sodium–potassium selectivity observed in reactions of tetracrown-substituted cobalt monophthalocyaninates with potassium and sodium thiocyanates is manifested in an oppositely directed shift of the Q-band: towards the long-wavelength region (λ_{max} = 737 nm) in the case of sodium thiocyanate and towards the short-wavelength region (λ_{max} = 626 nm) in the case of potassium thiocyanate. The difference in the Q-band shift in the case of a ruthenium complex with tetra(15-crown-5)phthalocyanine is 75 nm. Such a great difference enables the use of this effect for selective photometric measurements of sodium and potassium ions.

The ordered supramolecular aggregates formed upon interaction of sandwich-like phthalocyanine complexes of REE with alkali metals have pillar-like and tubular shapes, where one-dimensional transport of electrons, energy and ions is possible. The electric conductivity of these pillar-like and 'nanotubular' structures strongly depends on the orderliness of the giant supramolecular architectural ensembles formed. It is believed that such ensembles can be used as a starting material in the design of new generations of functional materials for ionic and molecular electronics.

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