

## Information

### Supramolecular metal complex systems based on crown-substituted tetrapyrrole compounds\*

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Characteristic features of the structure and properties of crown-substituted metal porphyrinates and phthalocyaninates are considered. The reactions of crown-substituted metal porphyrinates and phthalocyaninates with alkali metal salts afford complex heteronuclear supramolecular architectural ensembles, whose ordering determines their optical and electrophysical properties. The structure of supramolecular ensembles depends also on the cation size of both alkali and transition metals. The reactions of alkali metal salts with sandwich double-decker complexes formed by rare-earth metals with crown-substituted phthalocyanines show a nonlinear cooperative effect depending on the size of the alkali metal cation, whereas no such effect was found for lanthanide mono-phthalocyaninates and triple-decker complexes.

Crown-substituted porphyrins (CrPr) are synthesized by the reactions of 4'-formylbenzo-15-crown-5 with pyrrole and benzaldehyde in propionic acid. Depending on the concentration ratio of the reactants, this gives tetra-15-crown-5-, tri-15-crown-5-, di-15-crown-5-, or mono-

15-crown-5-substituted porphyrins. When they react with metal salts (Co, Cu, and Zn), chelates of this metals with crown-substituted porphyrins are formed.

The reactions of sodium, magnesium, and calcium salts with crown-substituted porphyrins and complexes based on them in solutions give monomeric heteronuclear metal complexes. In the case of potassium, ammonium, and barium, dimerization of macrocycles is induced by the specific behavior of these cations.

Unlike porphyrins, in phthalocyanines, the four nitrogen atoms of the macrocyclic cavity are connected to four nitrogen atoms of the azomethine groups. Although they are not directly involved in complexation due to the remoteness from the cavity center, they still create absolutely new conditions for the reactions with metal salts. Owing to the specific atomic and electronic structure of the aromatic system, metal phthalocyanines exhibit high chemical and thermal stabilities, unique optical, electrical, and photochemical properties, which stimulate their extensive practical use as semiconductors, catalysts, sensors, pigments, and biologically active compounds.

The reactions of dicyanobenzo-15-crown-5 with divalent metal salts ( $M = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{etc.}$ ) result in the chelates MCrPc, whereas trivalent metals ( $M = \text{Al}^{\text{III}}$ ) give metal complexes with extra ligands in

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which the axial position is occupied by an acid residue or a neutral ligand. The reactions with lanthanide salts afford crown-substituted monophthalocyaninates or double- and triple-decker phthalocyaninates. However, the template method provides the synthesis of only a limited range of compounds in a low yield. Therefore, a direct synthesis by the reaction of the ligand with lanthanide salts in the presence of strong bases has been developed. Unlike porphyrins, in the case of phthalocyanines, tetracrown-substituted phthalocyanines are formed as the reaction products.

Crown-substituted metal monophthalocyaninates can form various supramolecular polymeric ensembles through noncovalent interactions. The stability of these ensembles in solution is due to cooperative effect of the multiplicity and the dynamics of weak interactions such as  $\pi$ - $\pi$ -stacking. These interactions also control the molecular packing in the crystals and, hence, the properties of materials, for example, electron transport. The modification of phthalocyanines by crown-ether substituents creates conditions for the formation of stacked columns with  $C_4$  symmetry, which exhibit high electrical conductivity.

The pattern of interaction of crown-substituted monophthalocyaninates differs noticeably from that observed for similar double- and triple-decker complexes of lanthanides.

The reactions of crown-substituted d-element monophthalocyaninates with alkali metal salts give monomeric or dimeric heteronuclear complexes, depending on the size of the alkali metal cation. If the alkali metal cation fits into the crown ether cavity, monomeric heteronuclear complexes are formed. In the case of larger cations (potassium cations for 15-crown-5, rubidium cations for 18-crown-6, *etc.*), supramolecular heteronuclear dimers are produced. In most cases, as for crown-substituted porphyrins, the anions have no influence on the supramolecular organization. The exception is provided by aluminum complexes in reactions with sodium halides and cobalt and ruthenium complexes in the reactions with sodium and potassium thiocyanates.

The reactions of tetracrown-substituted cobalt and ruthenium monophthalocyaninates show optical sodium—potassium selectivity, which is manifested as shifts of the Q-band in different directions, in particular, to longer wavelengths for sodium thiocyanate ( $\alpha_{\max} = 737$  nm) and to shorter wavelengths for potassium thiocyanate ( $\alpha_{\max} = 626$  nm). This great difference (110 nm) in the electronic spectra can be used to develop ion selective optodes or for selective photometric determination of sodium and potassium. Potassium ions form supramolecular dimers without being linked to the thiocyanate ions. Unlike this, in the case of sodium ion, the thiocyanate ions form bridges between the sodium ions (through

the nitrogen atom of the NCS group) and cobalt or ruthenium ions (through the sulfur atom of the NCS group). This gives rise to supramolecular ensembles of a specific architecture (aggregation according to the brickwork pattern is possible).

Unlike monophthalocyanines, in the case of double- and triple-decker complexes, the crown phthalocyanine ligands are separated by lanthanide ions, which prevent the penetration of the alkali metal cations between the neighboring phthalocyanine fragments. Meanwhile, alkali metal cations can be bound above and below the sandwich dimer, at least, in double-decker complexes. The insertion of the first cation between two ligands is somewhat hampered compared to that of the second and subsequent cations, as conditions for the insertion have already been created by preorganization. Thus, positive cooperative effect is observed. The curve of spectrophotometric titration shows a typical linear pattern. In the case of interaction of rubidium ions with lutetium tetra-18-crown-6-bisphthalocyaninate, the curve of spectrophotometric titration has a sigmoidal shape similar to that observed in the interaction of hemoglobin with dioxygen. In this case, a nonlinear cooperative effect is involved, resulting in the formation of giant ordered supramolecular oligomers containing about 260  $\text{Lu}(\text{CRPc})_2$  building blocks. This nonlinear cooperative effect is unusual for triple-decker complexes or monophthalocyaninates. For one-electron-reduced form of the lanthanum complex, the nonlinear cooperative effect is also observed for potassium cations in the reaction with tetra-15-crown-5-substituted phthalocyanine. Unlike the radical form of the complex, which showed different behaviors toward potassium and rubidium nitrate, the one-electron-reduced form of the lanthanum complex is organized into host—guest supramolecular structures according to the same mode for potassium, rubidium, and cesium thiocyanates with a nonlinear cooperative effect in all cases. On passing to other potassium salts (acetate or bromide), no anion effect is involved. Hence, the reduced form of the double-decker lanthanide crown phthalocyaninates functions as a group sensor for alkali metal cations ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ).

Thus, depending on the size of the alkali metal cations and other factors, aggregation produces ordered supramolecular structures as columns and tubes, which enable one-dimensional transport of electrons, energy, and ions. The conductivity of these columns and nanotubes depends appreciably on the ordering of giant supramolecular architectural ensembles. These properties may provide impetus for a new series of intensive research aimed at the development and production of functional materials of a new generation and development of ionic and molecular electronics.