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Outer-sphere association of calixarenes and other macrocyclic ligands with metal complexes as the basis for the design of molecular devices

A R Mustafina, V V Skripacheva, A I Konovalov

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Abstract. The regular features of the formation of outer-sphere associates of water-soluble calixarenes with metal complexes in solutions and their structure in the solid state are analysed. A comparison with analogous data for other outer-sphere macrocyclic ligands is carried out. Some physicochemical properties of the outer-sphere associates are considered in regards to their potential use for the development of new processes and materials. The bibliography includes 150 references.

I. Introduction

Recent rise of the chemists' interest in transition metal complexes is caused, *inter alia*, by the important role of these complexes in biological processes and their possible application in the design of molecular and nano-devices (conductors,[1] switches,[2] sensors [3] and molecular machines [4]). The transition metal ions are extremely important for living organisms.[5,6] It is essential that most of 'metals of life' are present in an organism as complexes, that can be divided according to their biological functions into transporters (ionophores), accumulators, activators of inert molecules and bio-catalysts.[7] The biochemical functioning of metal ions is related mainly to their outer-sphere coordination, which is also important in the design of switching systems based on transition metal complexes.[1,4] Weak noncovalent interactions are the driving forces of the formation of outer-sphere complexes [7] and therefore this is most efficient when a cooperative effect takes place. Such effect is especially pronounced in the case of many natural products (DNA molecules, natural ionophores, cyclodextrins) as well as artificial macrocycles. Calixarenes and their derivatives, which are receptors of various ions and molecules, belong to the latter class of compounds.[8,9] Calixarene complexes of ions and organic substrates are well documented. However, so far there are no reviews on calixarenes as outer-sphere ligands for metal complexes. The discussion of the chemistry of outer-sphere association of metal complexes with calixarene derivatives and comparison of these compounds with other similar natural and synthetic outer-sphere ligands, including macrocyclic ones, are the main objectives of the present review. The physicochemical properties of the resulting outer-sphere associates (super-complexes) and their potential application in advanced technological processes and design of new materials are also discussed.

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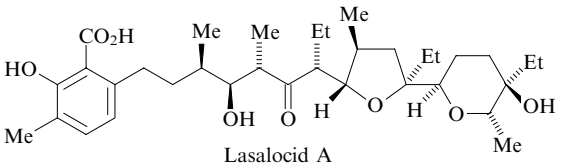
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II. The driving forces of outer-sphere association of transition metal complexes with various macrocycles, DNA and antibiotics

Many natural receptors, for example, DNA and antibiotics, are not macrocycles. However, their outer-sphere association with transition metal complexes follows the cooperative mechanism of 'host – guest' interactions. Numerous papers are devoted to complexation of DNA with transition metal complexes, many of them were discussed in a review.[10] The interest is caused by the use of coordinatively saturated transition metal complexes for studying the DNA structure. Coordinatively saturated Co^{III} and Ru^{II} octahedral complexes (mainly, polypyridyl complexes) are used for cleavage of DNA molecules and for their direct molecular and/or enantiomeric recognition.[10–12] It is known that charged phosphate fragments and hydrophobic grooves, formed by nitrogen-containing heterocycles, take part in binding of metal complex to the DNA molecule. Thus, in this case the electrostatic interactions, intermolecular hydrogen bonding and $\pi-\pi$-interactions between heterocycles representing the ligands of metal ion and DNA heterocycles are the main driving forces of outer-sphere complex formation.

Some natural antibiotics are also devoid of macrocyclic cavities, but, nevertheless, they possess receptor properties towards transition metal complexes due to the cooperative effect of intermolecular hydrogen bonds and electrostatic interactions in the crown ether-like conformation of their

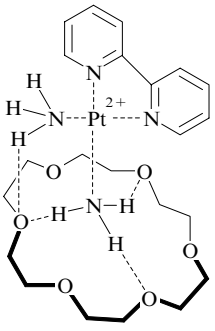
molecules. Among the natural ionophores, lasalocid A is the most popular receptor of transition metal complexes.[13,14]



Lasalocid A

It is known that lasalocid A is an anionic ionophore capable of effective (outer-sphere) binding of positively charged ammine and amine complexes of transition metals $[Ct^{n+}]$ ($[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_5Cl]^{2+}$, Δ- and Λ-$[Co(en)_3]^{3+}$, $[Pt(NH_3)_6]^{4+}$) to the complexes $[Ct^{n+}][LAS^-]_n$. The lasalocid anion $[LAS^-]$ in the latter surrounds the metal complex and adopts a cyclic pseudo-crown-ether conformation.[15–18]

Crown ethers represent a class of synthetic macrocyclic receptors modelling some intermolecular interactions ionophore–substrate.[19–22] The same forces are responsible for binding of metal complexes to crown ethers and ionophores, because the spatially pre-arranged ether oxygen atoms can be involved in both hydrogen bonding and electrostatic interactions. The efficiency of electrostatic interactions of metal complexes with crown ethers is lower than that with ionophores, which results in the increase in the contribution of hydrogen bonding to the total bonding energy. Therefore, the presence of acidic hydrogens in ligands that surround the metal complex is prerequisite for the efficient outer-sphere coordination of metal complexes by crown ethers. Particularly, in the process of formation of outer-sphere complexes of metal amine and ammine complexes with 18-crown-6 the hydrogen atoms of NH_3 or NH_2 ligands form hydrogen bonds with the oxygen atoms of the crown ether. Complex **1** is an example of such compounds.[23,24]

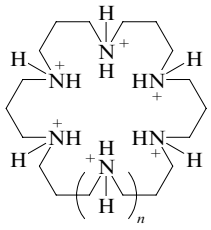


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A great number of complexes of crown ethers with transition metal aqua complexes and with metal complexes containing acetonitrile ligands are known. Acetonitrile CH-protons are sufficiently acidic to form hydrogen bonds with the ether oxygen atoms of the macrocycle.[24]

The structure modifications (*i.e.* introduction of various substituents) and enlargement of the crown-ether ring make possible π–π-interactions with ligands of metal complexes containing aromatic fragments.[25,26] Thus both NH_3 ligands take part in hydrogen bonding in the complex of dibenzo-18-crown-6 with $[Pt(bipy)(NH_3)_2]^{2+}$ (bipy is 2,2′-bipyridyl). The large and flexible crown-ether ring adopts a conformation favourable for the interactions of benzo-substituents with the bipy ligands in the inner coordination sphere of this platinum complex. The existence of these interactions was confirmed by X-ray crystallography and UV-spectroscopy (judging from the presence of charge transfer bands). The recognition of natural siderophore ferrioxamine B ($FeHDFB^+$) by dicyclohexano-18-crown-6 is based upon the ability of the crown-ether ring to bind a primary ammonium group.[20,27,28] However, lasalocid A binds $FeHDFB^+$ in a basic media more efficiently than benzo-18-crown-6 due to the possibility of ionisation and more flexible structure adjustable the structure of the 'guest' molecule. The charge neutralisation occuring simultaneously with hydrogen bonding with the deprotonated hydroxyl group and two ether oxygen atoms of the chain results in more efficient binding than that with the crown-ether oxygen atoms.[27,28]

In contrast to crown ethers possessing affinity to positively charged metal complexes, the polyaza-macrocycles in their protonated forms bind anionic complexes. For example, the macrocycles **2a**,**b** form outer-sphere associates (in the ratio 1 : 1) in water with transition metal anionic complexes $M(CN)_6^{4-}$, where M = Fe, Ru, Co.[29,30] In this case, the electrostatic interactions and hydrogen bonding are also the driving forces of formation of outer-sphere complex. The stability of such outer-sphere complexes being determined mainly by the number of protonated nitrogen atoms of the macrocyclic ligand rather than by the type of the metal in the complex anion.



2a,**b**

n = 1 (**a**), 2 (**b**).

Thus, crown ethers and polyazamacrocycles may be regarded as macrocycles that efficiently bind the charged metal complexes due to electrostatic interactions and hydrogen bonds while hydrophobic interactions in this case are much less important.

Cyclodextrins (CD) is a class of natural macrocycles with a hydrophobic cavity owing to which they form inclusion compounds with metal complexes,[31,32] while the presence of hydrophilic outer surface provides good solubility in water.

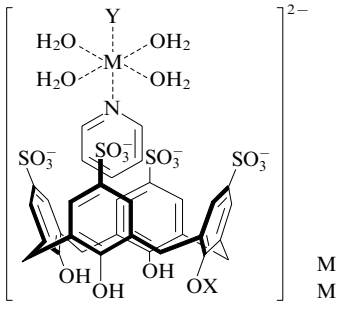
Cyclodextrins bind neutral and negatively charged species most efficiently, although many examples of the formation of inclusion complexes with positively charged metal complexes are documented.[32–36] For instance, β-CD binds the oxidised and reduced forms of ferrocenes as well as ferrocenecarboxylate with approximately the same stability constants (10^3–10^4) (Ref. 35). Stability of inclusion complexes is determined mainly by the match between the cavity diameter and the hydrophobic fragment size of a 'guest' molecule,[36–41] although intermolecular hydrogen bonds between a metal complex and hydroxyl groups of cyclodextrin may additionally stabilise the inclusion complexes.[42] The 1 : 1 adducts of β- and γ-cyclodextrins with ferrocene are described in Ref. 36, the orientation of ferrocene molecule in β-CD adduct is axial and in γ-CD adduct is equatorial.

Cucurbit[*n*]urils and calix[*n*]arenes are the most intensively studied compounds among the synthetic macrocycles. They are widely used as molecular containers for metal complexes and the interest in these compounds increased significantly during the last decade.

The size of internal cavities of cucurbit[*n*]urils with $n = 6-8$ is close to the size of cavities of the molecules of α-, β and γ-CD, respectively.[43] However, in contrast to the cyclodextrins, the oxygen atoms of carbonyl groups in cucurbituril portals are more polarised. As a result, the contribution of electrostatic interactions to the total binding energy of the 'host – guest' system is higher than that of CDs and the adducts with positively charged ions are more stable.[44] The adducts with metal aqua complexes are the most thoroughly studied. They are efficiently bound to carbonyl portals of cucurbiturils and do not form inclusion complexes.[45–47] However, the inclusion complexes of cucurbiturils are also known. Particularly, such complexes are formed with a number of solvents and indicators.[48–50] The cucurbit[8]uril is more suitable for the formation of inclusion complexes with positively charged metal complexes than cucurbit[6]- and cucurbit[7]urils due to the larger size of the molecular cavity. It was shown [51–54] that outer-sphere association of cobalt, copper and nickel complexes with ethylenediamine and cyclam results in the formation of inclusion complexes of cucurbit[8]uril.

Calixarenes represent an important class of synthetic receptors, which may exhibit all above-mentioned types of intermolecular interactions.[8,9] Their spatial structure consists of clearly separated hydrophilic (rim) and hydrophobic (cavity) areas. Besides, the potential of rim modifications and cavity size variations for these molecules is higher than that for cyclodextrins and cucurbiturils.[8,9] The present review mainly discusses the water-soluble receptors obtained by the introduction of ionised groups into the calixarene matrix, because compounds of this particular class are most comprehensively studied as outer-sphere ligands for charged metal complexes.[55–59]

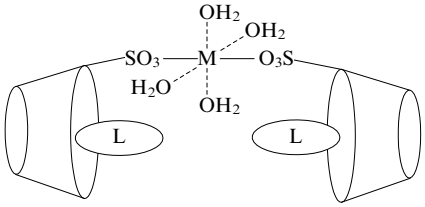
For the first time, the possibility of outer-sphere coordination of nickel and copper complexes $[Ni(H_2O)_5py]^{2+}$ and $[Cu(H_2O)_4py_2]^{2+}$ with *p*-sulfonatocalix[4]arene was shown by X-ray analysis.[55] The pyridine moiety of the metal complexes is located inside the cavity (structures **3a**,**b**).



M = Ni, X = Na, Y = H_2O (**a**);
M = Cu, X = H, Y = py (**b**).

3a,**b**

Later similar studies were performed for outer-sphere complexes of *p*-sulfonatocalix[4]arene with $[Ni(phen)_3]^{2+}$ (phen is 1,10-phenanthroline) and $[Co(diHOsar)]^{3+}$ [sar is 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane, diHOsar = 1,8-$(OH)_2$sar], and also its thia-analogue with $[Co(bipy)_3]^{3+}$ (Refs 56–59). The structure of the outer-sphere associate depends on the composition of the solution when the outer-sphere coordination of a labile complex takes place or when free metal ions and ligands are present in the solution alongside with the complex. For example, the above-discussed outer-sphere complexes are not formed in slightly acidic aqueous solutions containing cobalt(II) or nickel(II) salts, pyridine *N*-oxide and *p*-sulfonatocalix[5]arene. Aqua-ions $[Co(H_2O)_4]^{2+}$ or $[Ni(H_2O)_4]^{2+}$ coordinate sulfo groups of two different calixarene units forming a bridge between them.[60] The cavities contain pyridine *N*-oxide molecule (L) non-coordinated to the metal.



M = Co, Ni.

Depending on the type of the metal, the system sulfonatocalix[5]arene – lanthanide ion – pyridine *N*-oxide yields, alongside with the complexes of the described type, complexes in which the molecules of pyridine *N*-oxide are coordinated by the metal atoms and complexes of the type **3** where the ligand is located inside the cavity.[61] Thus, gadolinium forms complexes of the first type, while in Eu^{III}, Tb^{III} and Yb^{III} complexes, mixed inner- and outer-sphere coordination was observed. Hence, the presence of several binding centres (the cavity, substituents of the upper and lower rims) allows wide modification of a supra-molecular structure upon variation of the composition of a multi-component solution.[62] Cucurbiturils also form such ternary complexes in which an organic molecule is incorporated into a macrocyclic cavity and a metal ion is linked to the donor groups of the rim. Particularly, such complexes with sodium ions and some solvents were described for cucurbit[6]uril.[47]

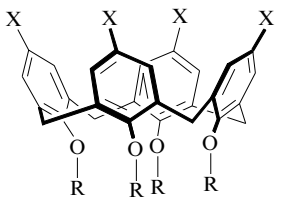
It should be noted that the efficiency of the discussed classes of compounds including the macrocycles as the outer-sphere ligands is determined by cooperative effect of electrostatic and hydrophobic interactions as well as by hydrogen bonding, while the relative contribution of interactions of each type depends on the structure of the outer-sphere ligand. The presence of hydrophobic cavities and hydrophilic rims is a common feature of cyclodextrins, cucurbiturils and calixarenes. For this reason, we will restrict our discussion to the comparative analysis of these macrocycles. However, alongside with the common features, there is also a number of important differences between these compounds. Thus, in contrast to cyclodextrins, cucurbiturils, due to the presence of polar portals, are able to form non-inclusion outer-sphere associates with metal aqua complexes and ternary complexes where the solvent molecules are located inside the cavity and the metal ions are bound by the carbonyl groups of portals. Of numerous calix[*n*]arenes, the water-soluble derivatives, particularly *p*-sulfonatocalix[*n*]arenes, are of special interest as outer-sphere ligands for metal complexes. Such macrocycles can form outer-sphere associates with the charged metal complexes as well as bind metal ions (through inter-sphere coordination by donor groups of upper and lower rims) and, simultaneously ligands (through inclusion to the calixarene cavity). Yet another characteristic of calixarene molecules is their conformational flexibility, which distinguishes them from rigid molecules of cyclodextrins and cucurbiturils. The mobility of aromatic rings of even the most conformationally restricted *p*-sulfonatocalix[4]arenes allows the adjustment of the 'host' cavity to the 'guest' structure. The results of quantum chemical calculations [63] show that the inclusion of hydrophobic 'guest' fragment into the cavity of *p*-sulfonatocalix[4]arene decreases the conformational mobility of the cavity-forming rings; the inclusion of aliphatic fragments stabilises the C_{4v} conformation of the complex, the inclusion of aromatic fragments results in the C_{2v} conformation.[63] In all the known cases, inclusion of ligand fragments of Cu^{II}, Co^{II}, Co^{III} and Ni^{II} complexes into the cavity of *p*-sulfonatocalix[4]arene and its thia-analogue stabilises the flattened cone conformation (C_{2v}).[56–59,64] X-Ray structural analysis of the crystals obtained from the solution of *p*-sulfonatothiacalix[4]arene and tris(bipyridyl) nickel revealed [64] a conformational transition of the 'host' molecule

from the cone conformation into the so-called partial cone conformation due to the inclusion complex formation. However, it should be noted that the crystal was grown in an autoclave under high temperature and pressure.

III. The thermodynamics of outer-sphere association of water-soluble calixarenes with charged complexes and organic ions in comparison with that of cyclodextrins and cucurbiturils

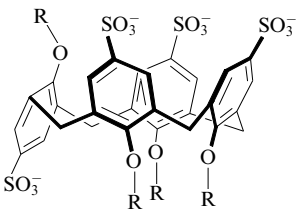
The data discussed in the previous Section provide a basis for the analysis of similarities and differences in the driving forces of the outer-sphere association of charged complex species with various macrocycles. As the number of papers on the thermodynamics of outer-sphere association of metal complexes with mentioned macrocycles in aqueous solutions is very limited, we compare the formation of complexes of calixarenes, cyclodextrins and cucurbiturils not only with metal complexes, but also with organic cations and neutral molecules. The main difference between cyclodextrins and water-soluble calixarenes is that the formation of cyclodextrin complexes with organic substrates is the entropy-favourable process, while the formation of complexes of water-soluble calix[4]resorcinarenes is entropy-unfavourable process.[65] In the case of cyclodextrins, the hydrophobic effect caused by water destructurisation due to the decrease in hydrophobic surface, is dominant and results in the entropy increase.[66] Meanwhile the multi-centred interactions of a guest molecule with the cyclodextrin cavity are usually not sufficiently effective to be a driving force of the formation of cyclodextrin complexes in aqueous solutions.[67] As it has already been mentioned, the presence of the polar portals in the cucurbituril molecules significantly increases the contribution of electrostatic interactions in comparison with that in the case of formation of cyclodextrin complexes. For instance, cucurbit[7]uril binds the methylviologen cation (MV^{2+}) more efficiently than β-CD of similar size due to the enthalpy contribution.[68] Cucurbit[7]uril is also more efficient in binding ferrocene and its alkylammonium derivatives: the corresponding binding constants of β-CD are in the range of 10^3-10^4 litre mol^{-1}, while for cucurbit[*n*]urils ($n = 7, 8$) the range is 10^9-10^{10} litre mol^{-1}. The value of the constant significantly increases (up to $10^{12}-10^{13}$ litre mol^{-1}) for ammonium derivatives of ferrocene.[69] However, the entropy contribution in the binding of cucurbit[7]uril with MV^{2+} cation is positive, while the entropy changes in the interactions with ferrocene and its ammonium derivative are negative.[35] Thus, the presence of polar portals in the cucurbit[7]uril molecules makes the enthalpy contribution in the interactions with positively charged metal complexes favourable. At the same time, the entropy changes depend on a number of factors, the most important being desolvation of the guest species, which in turn is determined by its structure.

The presence of the ionised groups at the rims of water-soluble calix[*n*]arenes and calix[4]resorcinarenes significantly increases the contribution of electrostatic interactions to the total energy of formation of a 'host–guest' complex.[66] Such conclusion, for example, was made on the basis of a study of complexation properties of calixarenes **4a–c** and calixarene **4d**, which adopts a partial cone conformation.[70–72] In particular, it was found that the efficiency of binding of tetramethylammonium cations by calixarene **4b** is an order of magnitude higher than that by calixarene **4c**. A comparison of the complexation ability of calixarenes with amino acids leads to the conclusion that the presence of sulfonate groups in the upper rim of calixarene is necessary for the binding of amino acids.[70] It should be noted that the binding constant of organic ions also depends on the conformational rigidity of sulfonate groups at the rim of the cyclophane receptor. For example, the binding constant of tetramethylammonium decreases by two orders of magnitude upon transition from calix[4]arene **4a** (Ref. 71) with fixed sulfonate groups in the upper rim of the molecule to sulfonatomethylcalix[4]resorcinarene (**5**)[73] with conformationally mobile sulfonate groups.[70–73]



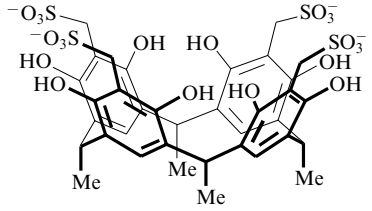
4a–c

R = H, X = SO_3^- (**a**);
R = CH_2CO_2H: X = SO_3^- (**b**), H (**c**).



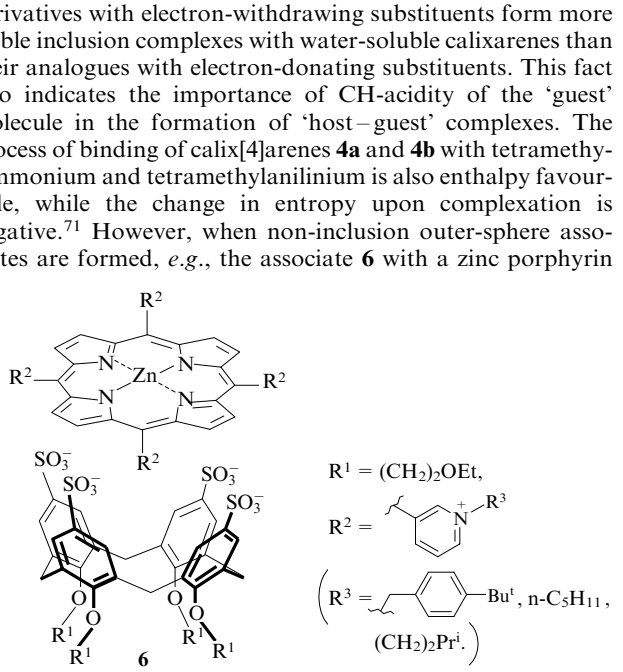
4d

R = CH_2CO_2H.



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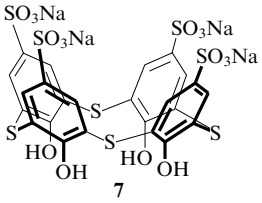
However, the contribution of the electrostatic interactions to the total energy of formation of inclusion complexes of water-soluble calixarenes and resorcinarenes is considerable, but not decisive. In particular, the analysis of ^1H NMR spectra and thermodynamic characteristics of inclusion complexes of water-soluble sulfonatocalix[4]resorcinarene with a number of organic molecules and ions[66] reveals that the complexation constant of a non-charged substrate with calixarene is determined mainly by the efficiency of interactions of CH-fragments of the guest molecule with the π-donor cavity of the host molecule. It was shown that the formation of inclusion complexes of water-soluble calix[4]resorcinarenes is an enthalpy-favourable process because CH–π-interactions make a significant contribution to the formation energy. As a result, the higher the CH-acidity of the substrate molecule and the higher the π-donor character of the calixarene cavity, the more efficient the binding.[66] Later[74] it was shown that benzene derivatives with electron-withdrawing substituents form more stable inclusion complexes with water-soluble calixarenes than their analogues with electron-donating substituents. This fact also indicates the importance of CH-acidity of the 'guest' molecule in the formation of 'host–guest' complexes. The process of binding of calix[4]arenes **4a** and **4b** with tetramethylammonium and tetramethylanilinium is also enthalpy favourable, while the change in entropy upon complexation is negative.[71] However, when non-inclusion outer-sphere associates are formed, *e.g.*, the associate **6** with a zinc porphyrin



6

complex, the multi-centred interactions between charged rim and the guest molecule require their substantial desolvation. Probably, this is the reason for the positive entropy change in this process.[75]

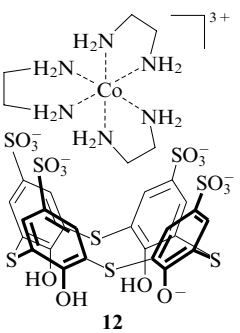
p-Sulfonatothiacalix[4]arene (**7**) is an analogue of *p*-sulfonatocalix[4]arene in which the methylene bridges are replaced by sulfur atoms.[76]



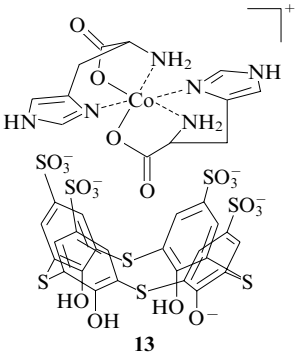
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It was suggested[77] that thiacalix[4]arene exceeds classical calixarene in its ability to form inclusion complexes due to the larger size of the cavity. However, the later results[78–80] do not support this suggestion. In particular, a comparison of the values of ΔG, ΔH and ΔS of formation of pyridinium complexes with both receptors revealed that the binding with thiacalix[4]arene is less efficient due to smaller enthalpy contribution.[79] This was accounted for by the lesser π-donor character of thiacalixarene hydrophobic cavity in comparison with that of classic calixarene, which results in less efficient CH – π-interactions. Hence, thiacalixarene is more selective towards the aromatic fragment of toluene, while calixarene itself binds the methyl group and the aromatic ring with the same probability.[74]

As already mentioned before, the thermodynamic characteristics of inclusion complexes of water-soluble calixarenes with metal complexes are little studied. However, it is natural to assume that the driving forces of the formation of such outer-sphere associates are also electrostatic interactions with the rim and CH – π-interactions with the hydrophobic cavity. The stability and the structure of outer-sphere associates of complexes $[Co(en)_3]^{3+}$(**8**), $[Co(en)_2ox]^{+}$(**9**), $[Co(L\text{-}His)_2]^{+}$ (**10**), $[Co(bipy)_3]^{3+}$(**11**) (en is ethylenediamine, ox is oxalate, L-His is L-histidine) with *p*-sulfonatothiacalix[4]arene and sulfonatomethylcalix[4]resorcinarene (for example, associate **12**) were studied.[81] It was shown that, similarly to the binding of organic cations, the larger the charge of the complex and the more compact its ligands, the higher the stability of outer-sphere associates. For both receptors, the association constant of compound **8** is the highest and the values of the constants decrease in the series **8** > **11** > **10** > **9**. Thus, the substitution of the oxalate anion for one of the en ligands as well as enlargement of the chelate ring on going from en to bipy results in the decrease in the calixarene complexation constant. Moreover, it was shown that the outer-sphere associate **13** containing cation **10** is not an inclusion complex and is formed as a result of multi-centred electrostatic interactions with the rim of the calixarene molecule.



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Thus, the following conclusions may be drawn from the analysis of thermodynamic parameters of complexes of cyclodextrins, cucurbiturils and calixarenes with organic and metal-containing substrates:

1. Binding of substrates to cyclodextrins is usually the entropy-favourable process due to a hydrophobic effect, while the 'host – guest' interactions are not efficient enough for a favourable enthalpy contribution. The presence of polar portals in cucurbiturils and charge of rims in calixarenes increases their affinity towards positively charged metal complexes due to more favourable (in comparison with cyclodextrins) enthalpy contribution in the total interaction energy. The enthalpy contribution increases on going from cucurbiturils to water-soluble calixarenes. However, the favourable enthalpy contribution in the formation of 'host – guest' complexes of water-soluble calixarenes is the result of not only significant contribution of electrostatic interactions with charged groups of the rim but also of CH – π interactions with the calixarene cavity.

2. The hydrophobic effect is mainly responsible for the entropy change in the formation of 'host – guest' complexes of cyclodextrins. The entropy change in the cases of cucurbiturils and calixarenes is caused primarily by the guest molecule desolvation and therefore depends on the structure of the molecule as well as on the structure of the 'host – guest' complex.

3. In contrast to cyclodextrins and cucurbiturils, water-soluble calix[4]arenes form outer-sphere associates, where the charged metal complex only covers the charged rim and its ligands are not inserted into the macrocyclic cavity. Obviously, the efficiency of multi-centred electrostatic interactions with the ionised groups of the calixarene rim is responsible for the formation of such complexes of water-soluble calixarenes.

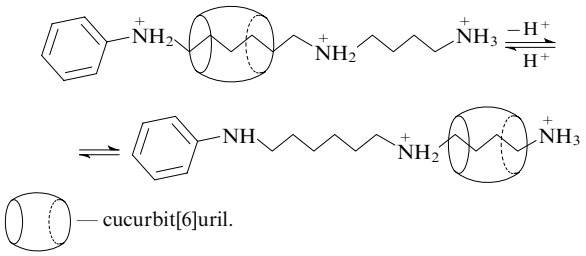
IV. Design of switchable systems on the basis of outer-sphere coordination of charged metal complexes and macrocycles

There is a growing interest in recent years in supramolecular systems in which an external action causes re-orientation of their fragments (components) and/or changes in their physicochemical properties as potential building blocks in the design of the so-called molecular devices and machines.[82–84] In the present chapter, we discuss the possibility of changing the structure of outer-sphere associates of charged metal complexes and water-soluble macrocycles by varying pH and the electrochemical potential.

1. pH-Switchable systems

Obviously, the presence of ionisable groups in the macrocycle and/or in the guest molecule is a prerequisite for pH-switchable outer-sphere coordination of a metal complex to a macrocycle. Cucurbiturils are devoid of such groups and deprotonation of the hydroxyl groups of cyclodextrins is observed only under strongly basic conditions.[44] For that reason, the design of pH-switchable systems with these macrocycles is based on the processes of protonation – deprotonation of the guest species. For instance, it was shown[85] that the binding constants of novocaine with β-cyclodextrin in acidic and neutral media are almost identical in spite of the different degrees of protonation of novocaine (singly and doubly-charged cation, respectively). Only in the basic media, when a neutral form of novocaine is formed, was the fivefold increase in the binding constant was observed. Obviously, cucurbiturils with their additional sources of electrostatic interactions 'host – guest' (the polar portals) are more promising as potential pH-switchable systems than cyclodextrins. The system polyamine – cucurbit[6]uril is one of the first examples of pH-controllable translocation.[86] pH-In-

duced translocation in this system is caused by different basicity of the nitrogen containing fragments at the opposite ends of the guest molecule.



The protonation of amino groups also drives the polyrotaxane-based molecular machines.[87,88]

The carbonyl portals of cucurbiturils may be protonated in highly acidic media;[44] however, low basicity of the carbonyl groups seriously hinders the application of this process as the source of pH-induced translocation. As it has been mentioned above, the presence of ionised groups at the rim of water-soluble calixarenes results in much stronger dependence of the formation constant of a host–guest complex on the charge of the guest molecule, than in the case of cucurbiturils. However, there were no observations of threading of oxyethyl or polyrotaxane chains through the cavity in the case of water-soluble calix[4]arenes. It was shown[89] by ^{1}H NMR study in benzene that triphenylureidocalix[6]arene may form pseudorotaxanes due to the large size and conformational lability of the cavity. However, cyclodextrins and cucurbiturils are more widely used in the design of such molecular machines.

Yet another interesting feature of *p*-sulfonatocalix[4]arenes and their thia-analogues, namely the high acidity of their hydroxyl groups,[90] should be noted. It is caused by the presence of strong circular intramolecular hydrogen bonds between the phenolic OH-groups at the lower rim of the calixarene cavity. This in turn makes it possible to control the π-donor character of the cavity[91] or the charge at the upper rim[73] of calixarenes by pH-induced deprotonation of hydroxyl groups. Alteration of the orientation of non-symmetrical organic cations inside calixarene cavity is one of interesting consequences of the pH dependence of water-soluble calixarene complexation. One of the first examples of pH-regulated relative orientation of a nonsymmetrical 'guest' (trimethylanilinium cation, TMA) and 'host' (*p*-sulfonatocalix[4]arene) was described.[91,92] The formation of inclusion complex in a wide range of pH values was proved on the basis of ^{1}H and ^{13}C NMR spectroscopic data. The calixarene cavity contains mainly the aromatic fragment of TMA at high acidity (pD 0.4), while under neutral conditions (pD 7.3) trimethylammonium group and aromatic moiety are non-specifically bound by the 'host' molecule.

The differences in the binding modes may be caused,[91] by changes in the electron-donating properties of an aromatic π-system due to dissociation of hydroxyl groups in the neutral media. The available data[71] show that ditopic TMA is bound selectively through its aromatic fragment to all host molecules having fixed cone conformation and sulfonate groups at the upper rim (compounds **4a**,**b**,**d**). At the same time, calixarene **4c** recognises only polar alkylammonium group of TMA. Calixarene **4d**, which adopts a partial cone conformation binds TMA non-selectively like conformationally much more flexible receptor **4a**. Thus, the selectivity of inclusion of more hydrophobic (aromatic) or of more charged (trimethylammonium) fragments is determined by the efficiency of both electrostatic interactions at the rim and CH–π interactions with the calixarene cavity.

In the study of complexation of ditopic *N*-methylpyridinium cation with sulfonatomethylcalix[4]resorcinarene it was found[73] that in neutral and slightly acidic media the aromatic fragment is included into the resorcinarene cavity, while deprotonation of calix[4]resorcinarene hydroxyl groups predominantly results in inclusion of the *N*-methyl group into the cavity.

The use of a ditopic guest becomes even more interesting when there is a possibility of comparing the complexation that proceeds under kinetic or thermodynamic control (Fig. 1). Under kinetic conditions, in a multicomponent supramolecular system containing cucurbit[6]uril (CB[6]U), cucurbit[7]uril (CB[7]U), symmetrical cyclohexane-1,4-diammonium cation (**14**) and ditopic adamantyl(alkyl)ammonium ion (Alk = Bu^n, n-C_6H_{13}, n-C_8H_{17}) (**15**), cation **14** is included into the cavity of cucurbit[7]uril and the alkyl chain of cation **15**, into the cavity of cucurbit[6]uril.[93] In equilibrium, the symmetrical cation **14** is included predominantly into the cavity of cucurbit[6]uril and the adamantyl fragment of ditopic cation **15**, into the cavity of cucurbit[7]uril.

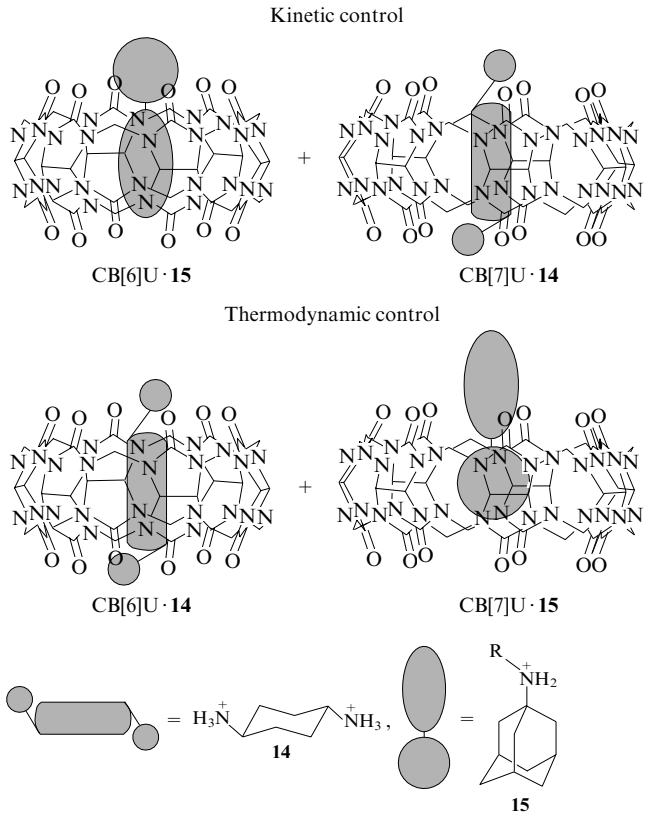
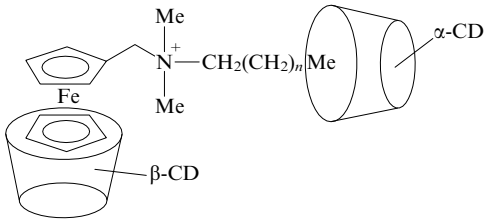
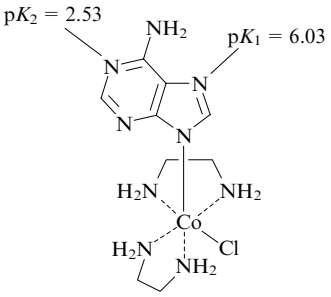


Figure 1. Kinetically and thermodynamically controlled complex formation of cucurbit[*n*]urils (n = 6, 7) with symmetrical cyclohexanediammonium cation and ditopic adamantyl(alkyl)ammonium cation.

It is natural to suggest that the switchable complex formation may be based upon ditopic metal complexes, for instance, alkyldimethyl(ferrocenylmethyl)ammonium. It was shown[94] that the ferrocene fragment of this complex, in accordance with its size, is bound most efficiently to the cavity of β-CD, while the alkyl fragment, of α-CD. Thus, this ditopic 'guest' and α- and β-cyclodextrins are the basis for the construction of a multicomponent supramolecular system.



The mutual arrangement of guest and host molecules in the supramolecular complex formed can be changed by varying pH and hence, the charges on various parts of a metal complex. Adeninato-chloro-bis(ethylenediamine)cobalt(III) (**16**) has been chosen as a non-symmetrical guest. This complex undergoes two-stage protonation at the basic nitrogen atoms of adenine heterocycle in neutral and slightly acidic media.



$[Co(en)_2(Ad)Cl]^+$ (**16**)

Data from ^1H NMR spectroscopy show that the protonation of the adenine moiety of complex **16** upon decrease in pH from 9 to 6 results in structural changes of outer-sphere associate between *p*-sulfonatothiacalix[4]arene (ST[4]A) and cobalt complex (the structures **17a–c**) (Fig. 2) and in significant increase in its stability constant.[95] The decrease in pH brings about protonation of both the metal complex and the phenolate rim of *p*-sulfonatothiacalix[4]arene from hexa- to penta-anion. As mentioned above, the increase in π-donor character of the calixarene cavity induced by deprotonation of the phenolic groups results in more efficient CH–π interactions. Therefore, in this case the neutralisation of the adenine fragment due to its protonation rather than the decrease in the π-donor character of the receptor cavity due to the protonation of the phenolate groups is the decisive factor that determines the 'host–guest' binding constant and the orientation of metal complex relative the macrocycle cavity.

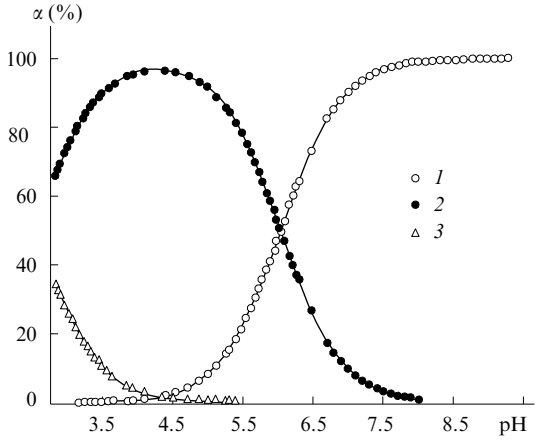
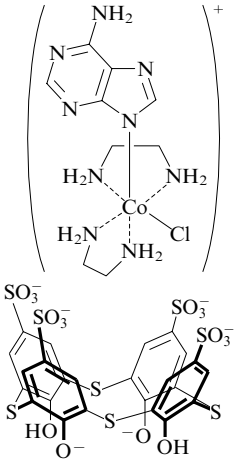
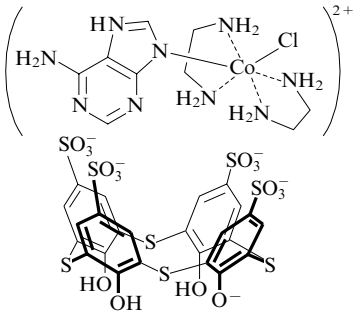


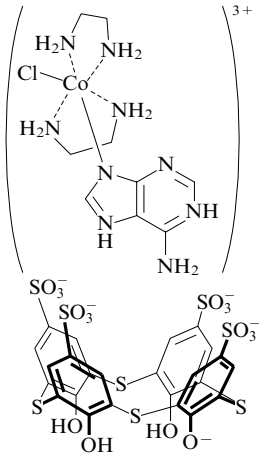
Figure 2. Percentage (α) of the adeninatochlorobis(ethylenediamine)-cobalt(III) forms with different degrees of protonation as a function of pH. (*1*) Form **17a**, (*2*) form **17b**, (*3*) form **17c**.



$[Co(en)_2(Ad)Cl]^+ \cdot ST[4]A$ (**17a**)



$[Co(en)_2(HAd)Cl]^{2+} \cdot ST[4]A$ (**17b**)



$[Co(en)_2(H_2Ad)Cl]^{3+} \cdot ST[4]A$ (**17c**)

Thus, the presence of ionised and/or ionisable groups at both rims of calix[*n*]arenes is responsible for more efficient pH control of the complexation than in the case of cucurbiturils and cyclodextrins. However, the ability of the calixarene cavity to be 'threaded' by aliphatic and oxyethylene chains is much poorer than that of cyclodextrins and calixarenes, therefore the water-soluble calixarene-based molecular devices and machines should be designed differently.

2. Redox-switchable systems

The electrochemical properties of the inclusion complexes are crucial for the construction of redox-switchable systems. It is known that the redox potential of a redox-active species depends on the character of the solvent and the counter-ions. Naturally the outer-sphere association with macrocycles also should result in the modification of electrochemical properties. In other words, if the outer-sphere environment of a redox-active complex stabilises its reduced or oxidised form, the shift in the electrochemical potential of the pair is observed. Therefore, the larger the difference between the constants of outer-sphere association of macrocycle with reduced and oxidised forms of a metal complex, the larger the shift of the potential. As mentioned above, β-cyclodextrin binds the reduced form of ferrocene more efficiently, which results in a significant shift of potential of the pair Fe^{III}/Fe^{II} into the anode region.[33]

The opposite shift should be expected for macrocycles that contain polar or ionised groups and therefore form more stable outer-sphere associates with charged metal complexes. Indeed,

the outer-sphere association with *p*-sulfonatocalix[6]arene results in the cathodic shift of the redox potentials of Fe^{II} (ferrocene) and Co^{III} (cobaltocene) complexes due to stabilisation of oxidised forms with highest positive charge.[96,97] Outer-sphere interaction of cobalt tris(bipyridyl) with sulfonate derivatives of thiacalix[4]arene and calix[4]resorcinarene [57] brings about analogous stabilisation of the oxidised form of the complex.

It is natural to expect that cucurbiturils should exhibit properties intermediate between these two extreme cases (sulfocalixarenes and cyclodextrins). Indeed, the inclusion of metal complexes and organic cations into the cavities of cucurbiturils may result in both the anodic and cathodic shifts of the reductive potential of a guest depending on the structure of the latter. Particularly, significant negative (cathodic) shift of the reductive potential of methylviologen (MV^{2+}/MV^{+} and MV^{+}/MV^{0}) inserted into the cavity of cucurbit[8]uril indicates that the inclusion complex of the oxidised (charged) form of methylviologen is more stable than that of the reduced form.[68] However, the inclusion of copper cyclamate [54] and ferrocene [69] into the cucurbituril cavity causes a positive (anodic) shift of the potential of the pairs Cu^{2+}/Cu^{+} and Fe^{3+}/Fe^{2+}. Probably, relative stabilisation of the reduced form in this case indicates a dominant hydrophobic contribution to the energy of host–guest binding. Thus, the cucurbiturils can stabilise preferably both oxidised and reduced forms of a guest molecule. Large cavity of cucurbit[8]uril may include two molecules of a partially reduced form MV^{+}, which results in a redox-controlled stoichiometry of the complexation, because the oxidised form MV^{2+} produces a 1 : 1 complex.[98] Yet another very important difference between the electrochemical properties of inclusion complexes of cyclodextrins and cucurbiturils should be emphasised, namely, the different mechanism of redox processes. In the case of cucurbit[*n*]urils ($n = 7, 8$), the direct electron transfer to methylviologen or from cucurbit[*n*]uril-bound ferrocene takes place, which follows from the fact that the voltammograms recorded at the various scan rates are identical and that the difference in the reduction and oxidation potentials remains the same within the limits of reversibility.[68,69] At the same time the oxidation or reduction of cyclodextrin inclusion complexes takes place only upon their dissociation. This results in different cyclic voltammograms recorded at the different scan rates [93,99] as well as in the increase in the difference of the reduction and oxidation potentials up to 70–80 mV, which is beyond the reversibility limits.

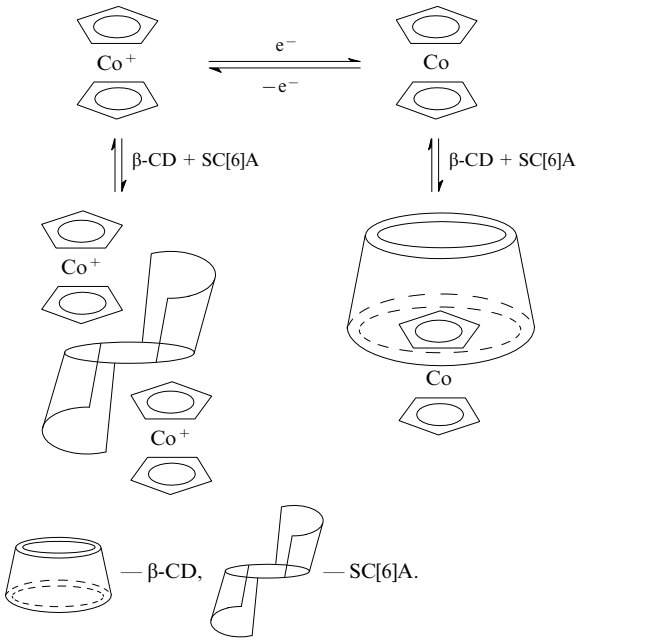


Figure 3. A scheme of the complexation of oxidised and reduced forms of cobaltocene with sulfonatocalix[6]arene (SC[6]A) and β-cyclodextrin, respectively.

The combination of a redox-active metal complex and various macrocycles is of interest for the design of switchable systems. For example, the design of a molecular machine was based on the predominant inclusion of the oxidised form of cobaltocene into the cavity of sulfocalix[6]arene and of the reduced form, into the cyclodextrin cavity (Fig. 3).[97]

V. Outer-sphere association of metal complexes with macrocycles as a method of modifying physicochemical properties of a supramolecular system

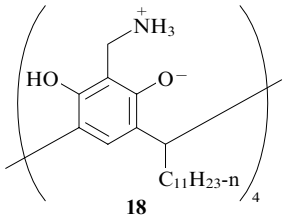
It was shown in the previous Section that it is possible to control the process of inclusion of a metal complex into the cavity of the macrocycles under consideration by an external action (variation of pH or electrochemical potential). The dependence of thermodynamic parameters of the complexation on the charge and structure of the metal complex is the basis for such control. Inclusion of metal complexes into macrocycles also results in changes of their electrochemical properties, which depend on the character of the macrocycle. Therefore, these macrocycles can be regarded as molecular containers, immersion of metal complexes into these containers modifies the physicochemical properties of the complexes. The modification of physicochemical properties of metal complexes induced by their outer-sphere association with macrocycles is discussed in the present Section.

1. Solubility modification

There are hydrophilic and lipophilic areas in molecules of all macrocycles under consideration, which enables modifying the solubility of metal complexes by formation of the corresponding outer-sphere associates. For instance, cyclodextrins and water-soluble calixarenes increase the solubility of water-insoluble species due to their inclusion into the hydrophobic cavity, while the hydrophilic outer surface of the molecule or the hydrophilic rim make the associate formed water-soluble. For this reason the cyclodextrins are used successfully for the transportation of lipophilic metal-containing catalysts into the aqueous phase.[41] In the case of calixarenes, the outer-sphere association with charged metal complexes results in significant decrease in solubility mainly due to neutralisation of the macrocycle rim charge. On the contrary the formation of inclusion complexes of cucurbiturils with charged bis-chelate complexes of transition metals causes the increase in water solubility, while the macrocycle itself is soluble only in highly acidic aqueous media. Binding of charged metal complexes to the macrocycles possessing lipophilic outer surface and hydrophilic inner cavity (antibiotics,[14] crown ethers,[100] calixarenes with hydrophobic substituents [101]), makes them lipophilic. It should be noted that the selectivity of metal ion–calixarene binding at the chloroform–water interface differs significantly from that in a one-phase system.[102] It is caused by the increase in the contribution of solvation and dissolvation energy to free energy of extraction. Similar effect is observed in the extraction of a series of charged copper and cobalt complexes by calix[4]resorcinarene derivatives from aqueous solutions into the chloroform layer.[101] Identically measured degrees of extraction of various metal complexes by calix[4]resorcinarene derivatives do not correlate with the corresponding binding constants measured in water–alcohol media. The presence of

ionisable groups, for example, hydroxyl groups in calix[4]resorcinarenes and lasalocid, determines the pH-dependence of extraction and transport of the corresponding metal complexes through the chloroform membrane.[20, 101] We are not going to discuss this area in the present review as there is a number of other reviews on this subject (see, for example, Refs 102 and 103).

The case of calixarene functionalisation is a clear advantage over other macrocycles as it makes possible introduction of substituents required for the efficient binding of the ion to be extracted and the corresponding counter-ion as well as of groups ensuring the required lipophilicity of the extractant or the carrier.[103] For example, the effective transfer of charged metal complexes was achieved by the introduction of aminomethyl and alkyl (particularly, n-$C_{11}H_{23}$) groups in to the calix[4]resorcinarene matrix.[101] Macrocycle **18** exists in a zwitter-ionic form due to intramolecular proton transfer from hydroxyl to aminomethyl group and its transportability depends on the presence of both anionic (phenolate) and cationic (ammonium) groups.



18

At the same time, the cyclodextrins increase the water solubility of lipophilic metal complexes more effectively than calixarenes and cucurbiturils.[41] Probably, the reason is that cucurbiturils are less water-soluble than cyclodextrins while the cavity of calixarenes, in contrast to that of cyclodextrins, is not proper for deep embedding of a guest molecule.

2. Modification of spectral properties of metal complexes

a. NMR spectroscopy

It is known that the inclusion of a fragment of a guest molecule into the receptor cavity results in changes in chemical shifts of its protons in the ^{1}H NMR spectra.[104] These changes depend on the mutual arrangement of the guest protons in the host cavity and on the structure of the macrocycle. Taking into account the π-donor properties of the calixarene cavity, it is natural to assume that inclusion of a fragment of the inner sphere of the metal complex into the cavity will result in more substantial upfield shift of proton signals than in the case of cyclodextrins or cucurbiturils. From a comparison of single-crystal X-ray data for inclusion complexes of various macrocycles it is possible to conclude that metal complexes are embedded deeper in the cavities of cucurbiturils[51–53] and cyclodextrins[39] than in the cavities of water-soluble calixarenes.[55–59] However, the changes in the chemical shifts in ^{1}H NMR spectra are comparable with, or even less than, those in the case of calixarenes.[35, 41, 51, 57] It should be noted that the calixarene cavity shielding effect provides additional possibilities for studying the structure of host–guest complexes due to more pronounced dependence of the chemical shifts of the guest protons on the position of the molecule in the cavity of the host.[104–106]

The rate of exchange between free and macrocycle-bound guests is yet another important characteristic of the complexation process. The rate of such exchange for cucurbiturils and cyclodextrins depends on the nature of the guest. Particularly, the slow exchange rate was found for the complex of cucurbit[7]uril with methylviologen ($\sim 10^2$ s^{-1}),[68] while the rate of exchange in the complexes of β-CD with ferrocenecarboxylate, cobaltocene and reduced forms of methylviologen is equal to $\sim 10^4$ s^{-1}. Fast (on the NMR time scale) exchange is typical of inclusion complexes of water-soluble calixarenes with organic cations and charged metal complexes.[66, 71, 81] However, the exchange slows down significantly upon encapsulation of a guest molecule between two calixarene molecules.[107–109]

Thus, the NMR spectra of the 'guest' and the 'host' change upon complexation with all three macrocycles. The shielding effect, which causes the upfield shift of signals of protons of the guest molecule is most pronounced for cucurbiturils (due to the presence of polar portals) and calix[4]arenes (due to the presence of ionised groups at the rim of the molecule and of the π-donating cavity).

b. Electronic absorption spectroscopy

Analysis of the changes in the spectra of metal complexes induced by interactions with macrocycles should be preceded by the analysis of similar changes in indicators because the spectral properties of molecules and ions of the indicators are extremely sensitive to the changes in the micro-environment polarity due to the presence of chromophore groups and an extended π-system. It is for this reason that many indicators are successfully used as probes in the studies of structural and thermodynamic parameters of micellar pseudophases in aqueous solutions.[110] Thus the most long-wave absorption bands of some indicators (acridine red, acridine orange, pyronin) exhibit red shift in the formation of inclusion complexes with cyclodextrins and blue shift when placed into the cavity of sulfonated calix[6]arenes in aqueous solutions.[111] Using the known dependence of the shift of absorption bands of the indicator on the polarity of the solvent,[110] one can conclude that the polarity of micro-environment decreases upon inclusion into the cyclodextrin cavity and increases in the cavities of water-soluble calixarenes.[111] This difference reveals significant dissimilarity between the cavities of these macrocycles. Unfortunately, the low solubility of cucurbiturils in neutral aqueous solutions prevents their comparison with their associates under analogous conditions. A comparison of the inclusion complex formation of β-CD and cucurbituril with a series of indicators in water–formic acid media[48] showed that the presence of carbonyl portals affects the 'host–guest' binding constant, but the changes in spectral characteristics of the indicator molecules upon inclusion into the cucurbituril cavity is analogous to those in the case of cyclodextrin.

The spectral properties of the transition metal complexes also may change as a result of outer-sphere association with macrocycles. It is known that outer-sphere coordination with crown ethers does not alter significantly the spectra of ruthenium amino and diimino complexes,[112, 113] while the formation of intermolecular hydrogen bonds between hexacyano complexes of the transition metals and protonated polyazamacrocycles results in the shift of the charge transfer band metal–ligand or ligand–metal.[114] Similar spectral changes were observed for ruthenium(II) and cobalt(III) tris(bipyridyl) complexes and were caused by intermolecular π–π-interactions with DNA.[11, 12] Obviously, not merely the presence, but also some preorganisation of the aromatic fragments is required for the stacking interactions in the outer-sphere binding of metal tris(bipyridyl) complexes to macrocycles. For example, the inclusion of a bipyridyl fragment of tris(bipyridyl)cobalt(III) into the cavities of water-soluble calixarenes (sulfonatomethylcalix[4]resorcinarene and *p*-sulfonatothiacalix[4]arene) virtually does not affect the charge-transfer ligand–metal bands.[57] It should be noted that the contribution of stacking interactions increases as the conformation mobility of calixarenes increases with the enlargement of macrocycles on going from sulfonatocalix[4]arene to sulfonatocalix[*n*]arenes (n = 6, 8).[115] The hypsochromic shift of the metall–ligand charge-transfer band observed upon inclusion of tris(bipyridyl)ruthenium(II)

into the cavity of *p*-sulfonatocalix[8]arene may also be explained by the contribution of stacking-interactions.[116]

The inclusion complex of cucurbit[8]uril with *trans*-dichlorobis(ethylendiamine)cobalt(III) is an example of a complex in which both chelate rings are significantly distorted upon inclusion in the cavity of cucurbit[8]uril.[51] Particularly, one of the chelate rings contracts with the 0.06 Å shortening of the Co–N bonds while the second one expands and the corresponding bonds became 0.05 Å longer. Naturally, such a change in the geometry of the coordination polyhedron results in the variation of the ligand field and is confirmed by the corresponding spectral changes (by shifts and differences in the intensities of the bands of d–d-transitions).

It should be emphasised that the inclusion of Co^{III} bis- and tris(diethyldiamine) complexes into the cavity of water-soluble calixarenes does not affect the spectra in the region of d–d-transitions. This fact is in agreement with the abovementioned conformational mobility of the calixarene cavity, which adjusts itself to the guest molecule during inclusion complex formation.

Octahedral metal trischelates may exist as two chiral isomers (Δ and Λ),[117] and spectropolarimetric properties of metal tris(ethylenediamine) complexes are a sensitive instrument for studying conformation of their flexible chelate rings. The conformation of chelate rings in $[Co(en)_3]^{3+}$ in aqueous solution is a superposition of two limiting conformations: *lel* and *ob*. The C–C bond in the former is almost parallel and in the latter, orthogonal to the tris-chelate three-fold axis[81] (Fig. 4). It is known that electrostatic interaction and two- or three-centred intermolecular hydrogen bond are the driving forces of outer-sphere coordination of $[Co(en)_3]^{3+}$ to cyclic and acyclic polyanions.[118, 119] As a result, the ethylenediamine chelate ring is distorted towards *lel*-conformation in which the NH-protons are the most accessible for the formation of intermolecular hydrogen bond. This, in turn, causes some changes in the CD spectrum of the complex corresponding to the increasing contribution of the *lel*-conformation (Fig. 5).[120] Interestingly, the outer-sphere association of $[Co(en)_3]^{3+}$ complex with DNA results in changes in the CD spectrum similar to those in the case of association with such simple polyanions as tartrates, in spite of a much more complicated type of interactions.[10, 121] Outer-sphere interaction with sulfonate derivatives of thiacalixarene and calix[4]resorcinarene results in the opposite effect, *i.e.* in the increase in the main rotational component and in the decrease in the additional component in the CD spectra. This suggests the *lel* → *ob* inversion of the chelate ring. As mentioned above, the CH–π interactions are the main driving force of interactions of hydrocarbon fragments with the hydrophobic cavity of cyclophanes.[65] Therefore, it is logical to assume that these interactions with the cavities of water-soluble receptors are responsible for the *lel* → *ob* inversion of the chelate ring as the *ob* conformation provides the best accessibility of CH-protons for the interactions with hydrophobic cavity.

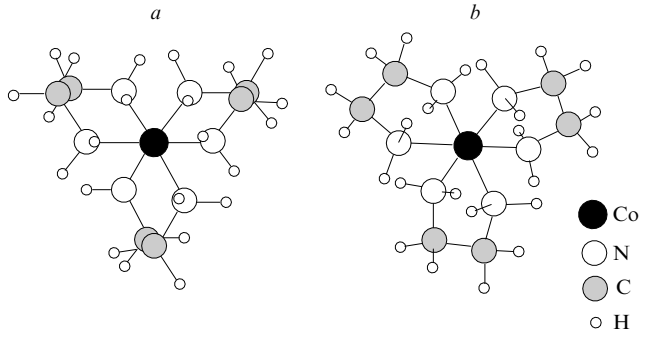


Figure 4. Limiting *lel*- (*a*) and *ob*-conformations (*b*) of ethylenediamine chelate rings in the complex $[Co(en)_3]^{3+}$.

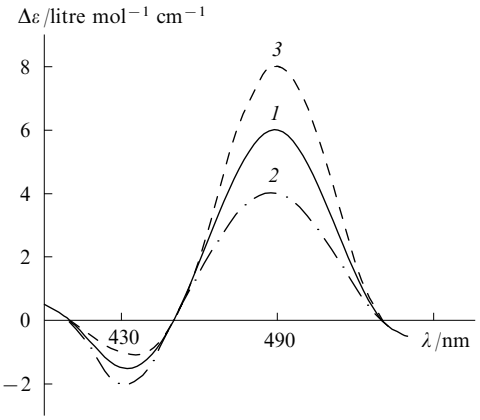


Figure 5. CD spectra of the complex $[Co(en)_3]^{3+}$ without (*1*) and with outer-sphere coordination with tartrate ions (*2*) and *p*-sulfonatothiacalix[4]arene (*3*).

Thus, the chiroptical properties of metal complexes are important for structural as well as chiral recognition and separation of macrocycles. Taking into account successful application of optical and chiroptical properties of cobalt and ruthenium trischelates for DNA recognition, application of chiral trischelates might be potentially useful for the synthesis of enanthiomerically pure chiral synthetic macrocycles, such as oxazine derivatives of calix[4]resorcinearenes.[122]

In conclusion of this Section, it should be noted that the spectral changes of the complexes reflect the types of interactions that emerge during the outer-sphere coordination of the complexes with various macrocycles. Particularly, the inclusion of complexes into rigid cavities of cyclodextrin and cucurbituril results in considerable distortion of the ligand environment of metal ion which, in turn, leads to more significant change in the spectral properties than in the case of non-rigid calixarenes. At the same time, the inclusion of a guest molecule into the calixarene cavity changes its spectral properties in a completely different way. CH–π interactions are typical of the most conformationally rigid *p*-sulfonatocalix[4]arene and its thia-analogue. These interactions cause distortion of the conformation of ethylendiamine chelate ring inside the cavity. The molecule of *p*-sulfonatocalix[8]arene better adjusts itself to the structure of included fragment due to higher conformational mobility. This makes possible, for example, the intermolecular π–π interactions between aromatic fragments of the ligand and one of the aromatic fragments of the 'host'molecule. These interactions cause the shift of metal–ligand or ligand–metal charge-transfer bands.[119]

c. Luminescent properties

Yet another practically important consequence of the inclusion of a complex into macrocyclic cavity is the change in its luminescent properties. Particularly, a significant increase in the quantum yield of luminescence and the change in the lifetime of the excited state of a lanthanide ion was observed upon inclusion of one of the ligands of the complexes $Ln(NTA)_3 \cdot H_2O$ [Ln = Eu, Gd; NTA is 1-(2-naphthoyl)-3,3,3-trifluoroacetone] into the cyclodextrin cavity.[123, 124] The alteration of photophysical properties of Ru^{II} polypyridyls upon their inclusion into the cavities of cyclodextrins[125, 126] and into DNA grooves[127, 128] is thoroughly studied. The increase in luminescence due to restricted deactivation of the emitting transition of Ru^{II} complex by water and oxygen

molecules was observed in both cases. The increase in intensity of luminescence was observed also upon addition of equimolar amount of *p*-sulfonatocalix[8]arene to the solution of tris(bipyridyl) ruthenium(II) in water.[116] At the same time, the intensity of fluorescence of an outer-sphere associate of tris(bipyridyl) ruthenium(II) with *p*-sulfonatocalix[4]arene in methanol is considerably lower than that of the free complex. Slight (5 nm) batochromic shift of the band in the emission spectrum of this associate was also observed.[129] These effects are presumably caused by interaction of *p*-sulfonatocalix[4]arene (counter-ion) with the dipole of tris(bipyridyl) ruthenium(II) in the excited state and possibly by photoinduced electron transfer as well. However, the possible influence of sulfonatocalix[4]arene on the photoinduced de-chelation caused by thermal transition from the emitting triplet level of bipyridyl to excited d-sublevels [130, 131] was not taken into account. In turn, the photophysical properties of tris(bipyridyl) ruthenium(II) in aqueous solution are determined to a large extent by the efficiency of photoinduced de-chelation.[131] Unfortunately, so far the number of similar papers on the changes in luminescent properties upon inclusion of complexes into the cucurbituril cavity is small.

3. Modification of reactivity and magnetic properties of metal complexes, stabilisation of unstable forms of complexes

It was already mentioned in Section II that the equilibrium of a complexation of a metal ion with ligands can be shifted upon formation of an outer-sphere associate with a macrocycle. It is very difficult to prove the existence of such stabilisation in solutions, which explains the scarcity of such studies. However, the X-ray studies of associates obtained from aqueous solutions of labile complexes under conditions of equilibrium between the metal ions, ligands and their complexes, show that the stabilisation of such complexes is possible by virtue of outer-sphere association with water-soluble derivatives of calix[*n*]arenes and calix[4]resorcinarenes.[55, 59, 132] The structure of the complex in a crystal grown from a multicomponent solution is determined by stabilisation effects at both the molecular level (the host–guest interaction with the macrocycle) and the supramolecular level (the crystal packing effects). The selectivity of formation of inclusion complexes of cucurbit[8]uril with respect to the *trans*-isomer of bis(ethylenediamine)cobalt(III) in comparison with the *cis*-isomer is a striking example of the first type of stabilisation effects.[51] Interestingly, the inclusion of the *trans*-isomer into the cavity of a macrocycle increases its thermal stability and inhibits its isomerisation into more thermodynamically stable *cis*-isomer in solutions..

As it has been mentioned in Section V.2.b, the inclusion of a molecule into the cavity of a macrocycle may result in changes in its spectra due to conformational and structural distortions of the chelate rings. The reactivity of the species inside the macrocycle cavity is also changed as a result of the change in the transition state energy upon inclusion complex formation. For example, the formation of a complex of the indicator Phenol Blue with sulfonatocalix[*n*]arenes ($n = 4, 6, 8$) inhibits its deamination in alkaline solutions.[133] Similarly, the inclusion of this indicator into the cavity of cucurbituril substantially inhibits its decomposition to *p*-benzoquinone and diamine in acidic media.[50]

The kinetic parameters of redox reactions and the reactions of ligand exchange are the quantitative characteristics of the reactivity of transition metal complexes. There is a number of papers on the catalysis and inhibition of redox reactions, particularly on the changes in the rate of outer-sphere metal-to-metal electron transfer upon outer-sphere binding of one of the transition metal complexes to cyclodextrins, micellar pseudophase, polyazamacrocycles, DNA and polypeptides.[134–141] The analysis of literature shows that there are two main factors determining the effect of outer-sphere association on the redox properties of a complex. The first one is a change in the interaction constant between metal complexes acting as reducing and oxidising agents. If a macrocycle is a counter-ion for one of these complexes, the outer-sphere association decreases the charge of the metal complex. If the oxidising and reducing agents bear opposite charges, inhibition of the redox process upon outer-sphere association of one of the reagents with a macrocycle may be related to the decrease in the constant of ion pair formation between the reactants. On the contrary, if the oxidising and reducing agents bear the same charge, the outer-sphere binding of one of the complexes with the macrocycle may result in more efficient interaction. For instance, it is possible to accelerate the reactions of hexacyanocobaltate and hexacyanoferrate with iodide ion upon outer-sphere association with a protonated polyazamacrocyle.[114] Neutralisation of negative charges of the complexes $[Co(CN)_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ results in more efficient reaction with iodide ion.

The second factor is the change in electrochemical potential or re-organisation energy. According to the Marcus–Hush theory, this may result in the change in a metal-to-metal electron transfer rate constant. The effect of *p*-sulfonatothiocalix[4]arene on the rate of outer-sphere electron transfer in the system $Fe^{II}-Co^{III}$ where the positively charged Co^{III} complex is included in the cavity of *p*-sulfonatothiocalix[4]arene and negatively charged Fe^{II} complex is not, was studied [142] for the complexes $[Co(en)_3]^{3+}$, $[Co(en)_2ox]^{+}$, $[Co(bipy)_3]^{3+}$, $[Co(L\text{-}His)_2]^{+}$ and $[Fe(CN)_6]^{4-}$. Kinetic data for the systems of *p*-sulfonatothiacalix[4]arene $-Fe^{II}-Co^{III}$ and for the corresponding binary systems indicate that the outer-sphere association with *p*-sulfonatothiacalix[4]arene results in the decrease in the formation constant of ion pair $Fe^{II}-Co^{III}$. This effect is particularly pronounced for the complex $[Co(en)_2ox]^{+}$ because the inclusion of ethylenediamine chelate ring into the cavity leads to the conformation in which negatively charged oxalate ring is located outside the cavity. This ring prevents the formation of the ion pair with hexacyanoferrate, while the outer-sphere association of *p*-sulfonatothiacalix[4]arene with $[Co(bipy)_3]^{3+}$ slightly decreases the association constant with hexacyanoferrate. It was noted in Chapter IV that outer-sphere association of tris(bipyridyl) cobalt(II) with *p*-sulfonatothiacalix[4]arene causes the shift of the reduction potential of the Co^{III}/Co^{II} pair due to stabilisation of the oxidised form.[57] Irreversible decomposition of other Co^{III} complexes studied upon their reduction prevents obtaining similar data for them. However, it is likely that this effect should be observed for all Co^{III} complexes. According to the Marcus–Hush theory[143, 144] the cathode shift of potential for the pair Co^{III}/Co^{II} should cause the decrease in the $Fe^{II}-Co^{III}$ electron transfer constant on going from the binary system $Fe^{II}-Co^{III}$ to the ternary system $Fe^{II}-Co^{III}-p$-sulfonatothiacalix[4]arene. However, the values of the electron transfer constants in ternary systems calculated on the basis of experimental data are either close to, or even higher than, those in the binary systems. Therefore, other factors, for instance, the re-organisation energy, affect the value of the electron transfer constant on going from the binary to the ternary system. Interestingly, the increase in the rate constant is observed only in those complexes ($[Co(en)_3]^{3+}$, $[Co(en)_2ox]^{+}$) where the inclusion of a complex into *p*-sulfonatothiacalix[4]arene cavity results in the distortion of the chelate ring conformation. In conclusion, it should be emphasised that the mechanism of this unusual effect of calixarene on the electron transfer rate is unclear and requires further investigation.

The transition metal complexes are very interesting also due to their magnetic properties. It is known that the spin state of the transition metal complexes and accordingly their mag-

netic properties are determined mainly by the character of ligands in the first coordination sphere. However, there are several interesting examples of the influence of crystal lattice [144] and phase transition [145, 146] on the spin state of Co^{II} and Fe^{II} complexes, respectively. One can assume that the distortions of the ligand environment due to inclusion of a metal complex into the macrocycle cavity may also cause admixture of the excited spin state of the complex to the ground state. This should result in a change in the spin state and accordingly of the spin transition temperature (high-spin – low-spin or *vice versa*). It is known, for example, that the increase in pressure destabilises the high-spin state and relatively stabilises the low-spin state of tris(ethylenediamine) cobalt(II), because the Co – N bond is longer in the high-spin state of Co^{II} than in the low-spin state.[147] It is of note that the internal pressure in a zeolite cavity exerts a similar effect of destabilisation of the high-spin state of tris(bipyridyl)cobalt(II).[148–150] One can expect that similar effects will also be observed upon inclusion of metal complexes into cavities of macrocycles, but so far there are no such reports in literature.

VI. Conclusion

The formation of outer-sphere associates of the transition metal complexes with cyclodextrins, cucurbiturils and water-soluble calixarenes has much in common with the formation of the inclusion complexes with organic substrates, which serves as the basis for the development of new recognition methods. At the same time, the inclusion of transition metal complexes into the cavities of macrocycles is most perspective for the modification of their physicochemical properties and for the design of switchable systems as fragments of molecular devices and machines. The analysis of structural and thermodynamic parameters of outer-sphere associates of transition metal complexes with abovementioned macrocycles points to the following properties of water-soluble calix[*n*]arenes that make them unique as molecular containers for metal complexes.

1. π-Donor character of the calix[*n*]arene cavity determines both the type of 'host – guest' interactions (CH – π, π – π) and the polarity of microenvironment of a species included into the cavity or its fragment.

2. Due to conformational mobility of the cavity, calix[*n*]arenes adjust themselves to the structure of the guest molecule so that the type of the host – guest interactions depends on the value of *n*.

3. Polyfunctionality of calixarenes, in particular, the presence of substituents at the upper and lower rims and of the hydrophobic cavity as an additional binding centre, provides a great variety of complexes that are formed in a multicomponent system 'metal ion – ligand – calixarene'.

4. The predominant contribution of electrostatic interactions into the total Gibbs energy of the complexation of water-soluble calixarenes results in more pronounced dependence of the complexation on pH and on the electrochemical potential.

Thus, the accumulated data show that outer-sphere associates of water-soluble calixarenes with complexes of transition metals are a promising basis for the construction of supramolecular systems the properties of which can be switched by external action.

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