Calixarene complexes with soft metal ions

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Abstract

In this review calixarene complexes with copper, silver, gold, zinc, cadmium and mercury ions are described, showing their properties and application possibilities. In some cases also resorcinarene and pyrogallolarene metal complexes are presented. The attention is paid to species interesting in the search of artificial enzymes.

Keywords: Calixarene, complex, guest, metal ion, pyrogallolarene, resorcinarene

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Introduction

Calixarenes, along with related compounds, *i.e.* resorcinarenes and pyrogallolarenes are metacyclophanes intensively studied due to their interesting properties; they may serve as receptors of ionic and neutral species[1-3] and as building blocks of structures of supramolecular chemistry, for example as components of cavitands[4-6] , capsules[4,7,8] and nanotubes.[9,10]

A great number of works dealing with calixarenes is a reflection of an increasing research in view of usefulness of these species, *e.g.* in the molecular recognition,[11] separation procedures[12-14] and as mimics of biological processes.[15] Growing attention is paid today to calixarene complexes with metal ions; numerous calixarene complexes with alkali,[16,17] alkaline earth[12,18] and transition metal[19,20] ions are now a topic of an intense study. This rapidly developing area is investigated from the theoretical and practical viewpoint due to possible applications of such complexes as catalysts[21,22] as well as in the search for artificial enzymes,[23] and in the design of sensors for determination of trace amounts of metal ions,[24-26] especially in the aspect of the environment protection.[27] One should point out the works on calixarene complexes with cesium[28,29] as well as with lanthanides [30,31] and actinides [31,32] are aimed at management of nuclear waste materials.

The present review is connected with our former papers concerning calixarene dime-ric[33] as well as trimeric and hexameric[34] capsules, cavitands,[35-37] inclusion complexes of calixarenes,[38] heterocalixarenes,[39] resorcinarenes,[40] and calixpyrroles,[41] and is a continuation of papers on calixarene complexes with transition metal ions.[42,43] The references cited in the latter both articles describe research results in this field of chemistry; the area of our present paper covers more recent works. Since the amount of reports dealing with metal complexes of calixarenes is enormous, the selected examples of calixarene complexes with soft metal ions – copper, silver, gold, zinc, cadmium and mercury are described. The references are cited mainly of works that appeared during 2005-2007.

1. Calixarene complexes with copper ions

It is known that Cu^{2+} ion plays an important role in biological systems, however it is also a significant environmental pollutant; the detection and determination of this ion receives today growing attention. [44] Many reports deal with calixarene copper complexes.[45-50]

In investigation of calixarenes **1**-**3** bearing β-ketoimine groups, it was shown that these functions enable their complexation with transition metal ions. Calixarenes **1**-**3** exist in a cone conformation in solution; with Cu^{2+}, Ag^{+} and Hg^{2+} ions they yield the 1:1 complexes.[51] In the solid state "a polymeric linear chain" is formed as a result of intermolecular interactions between β-ketoimine groups.

The water-soluble calixarene **4**, in which the 2,2'-bipyridine units show both hydrophilic and chelating properties, forms complexes with Cu^{+} and Cu^{2+} ions. The aqueous solution of **4** treated with $[Cu(MeCN)_4]PF_6$ affords the 1:1 complex $\mathbf{Cu^{+}\cdot 4}$.[52] It should be pointed out that $\mathbf{Cu^{+}\cdot 4}$ is very stable, even in the presence of bovine serum albumin and is promising for use in biological media.

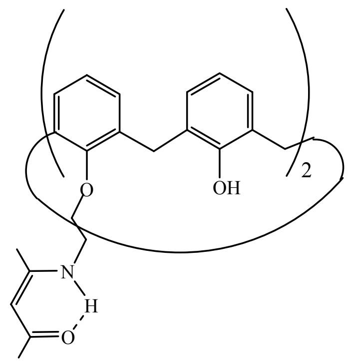
The complexation properties of calixarenes **5** and **6** toward Cu^{2+} and Zn^{2+} ions have been investigated. [53] The binding of **5** with metal ion M^{2+} (Cu^{2+} or Zn^{2+}) is a two-step process, the first step involves the complexation of metal ions with imine functions affording **7** and the second one concerns the binding of two ether oxygen atoms of the pendants to give **8**.

It was found that the spacer imine groups of **5** that are in conjugation with the anthryl units are responsible for fluorescence quenching when the metal ion is absent. In free **5** the imine group conjugated with the anthryl unit makes the system rigid; the lone electron pair is delocalized on the π-cloud of the anthracene unit. Due to this rigidity a favorable orbital overlap between the imine nitrogen atom and the π-orbital of anthracene exists, resulting in photoinduced electron transfer (PET) from imine nitrogen atom to the photoexcited anthryl unit. The presence of the conjugated imine moiety in **5** is responsible for the fluorescence quenching of the anthryl unit, since the photoinduced electron transfer (PET) from nitrogen atom of the imine group to the anthryl π-cloud exists.

The binding of the metal ion with imine groups destroys the effect of the lone pairs of nitrogen atoms which had caused the conjugation; therefore the PET is prevented and the fluorescence intensity increases. This fluorescence enhancement is stronger in **5** than in **6** where no imine moiety is present. It was found that **5** acts as a chemosensor for Cu^{2+}; since the increase in the fluorescence intensity for Cu^{2+} is higher than for Zn^{2+}, these both ions can be differentiated.

The chiral amphiphilic resorcinarene **9** containing four L-proline (Pro) moieties at the wide rim and four undecyl groups at the narrow rim has been synthesized. The molecules of **9** may self-assemble at the air-water interface as stable Langmuir monolayers. In the investigation of the effect of various cations on the stability of Langmuir monolayers it was found that their stability is highly increased in the presence of Cu^{2+} ions, while in the presence of Cd^{2+}, Co^{2+} and Ni^{2+} ions only slight stabilization occurs.[54]

The supramolecular complex **Cu^{2+}·9** shows enantioselective recognition properties towards phenylalanine (Phe), with a stronger affinity for D-Phe than for L-Phe. The recognition process occurs *via* the formation of a ternary complex **Cu^{2+}·9·D-Phe**. In this complex the Cu^{2+} ion is chelated by two carboxylato oxygen atoms and by two nitrogen atoms of Pro and Phe, forming a planar square. [54] The above results are promising for the use of macrocyclic receptors of the type of **9** as active layers in the design of enantioselective sensors.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N
H
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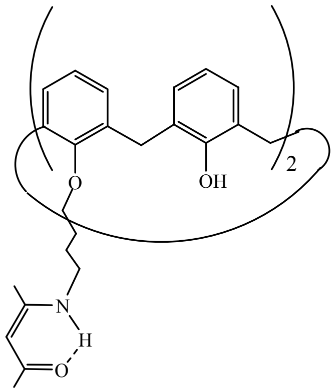
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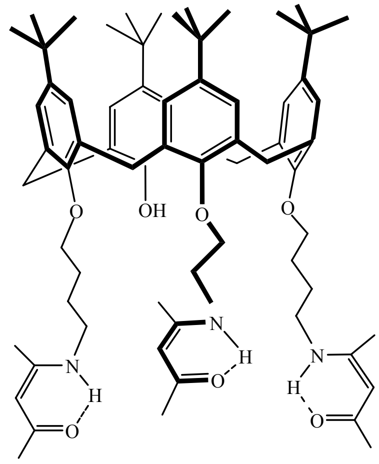
2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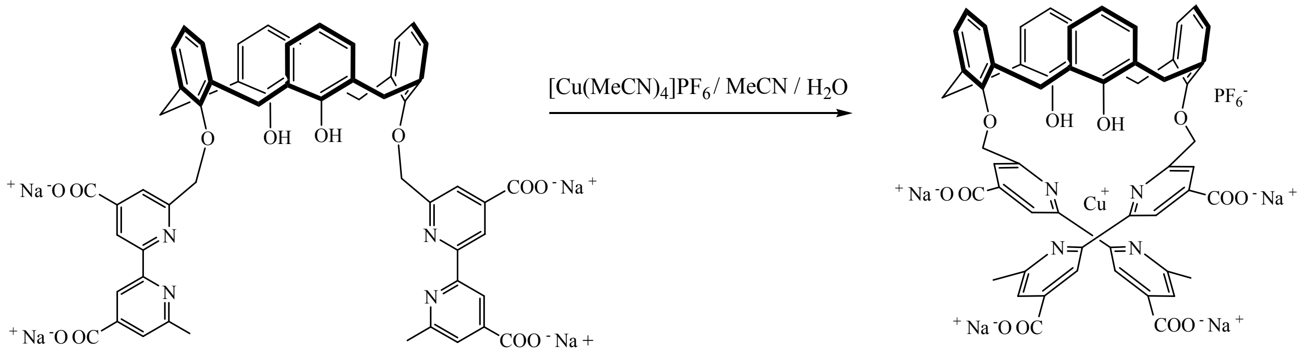
3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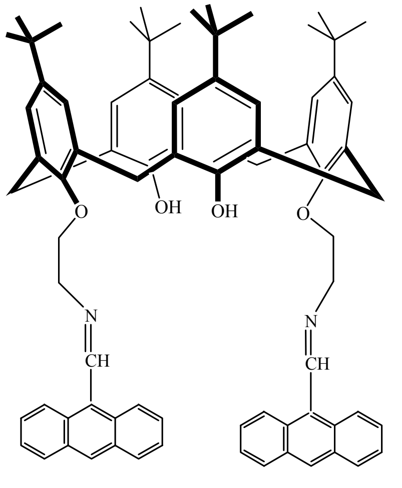
OH
OH
O
+ Na -O OC
N
N
+ Na -O OC
COO - Na +
N
N
COO - Na +
[Cu(MeCN)$_4$]PF$_6$ / MeCN / H$_2$O
PF$_6^-$
O
OH
OH
O
+ Na -O OC
N
Cu$^+$
N
COO - Na +
N
N
+ Na -O OC
COO - Na +

4

Cu$^+$ • 4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OH
OH
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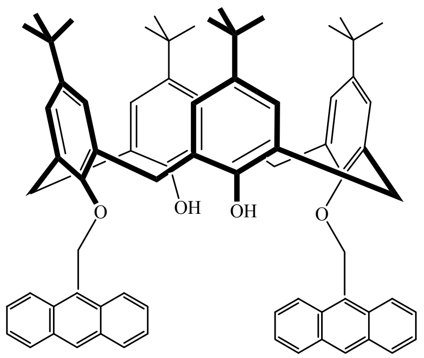
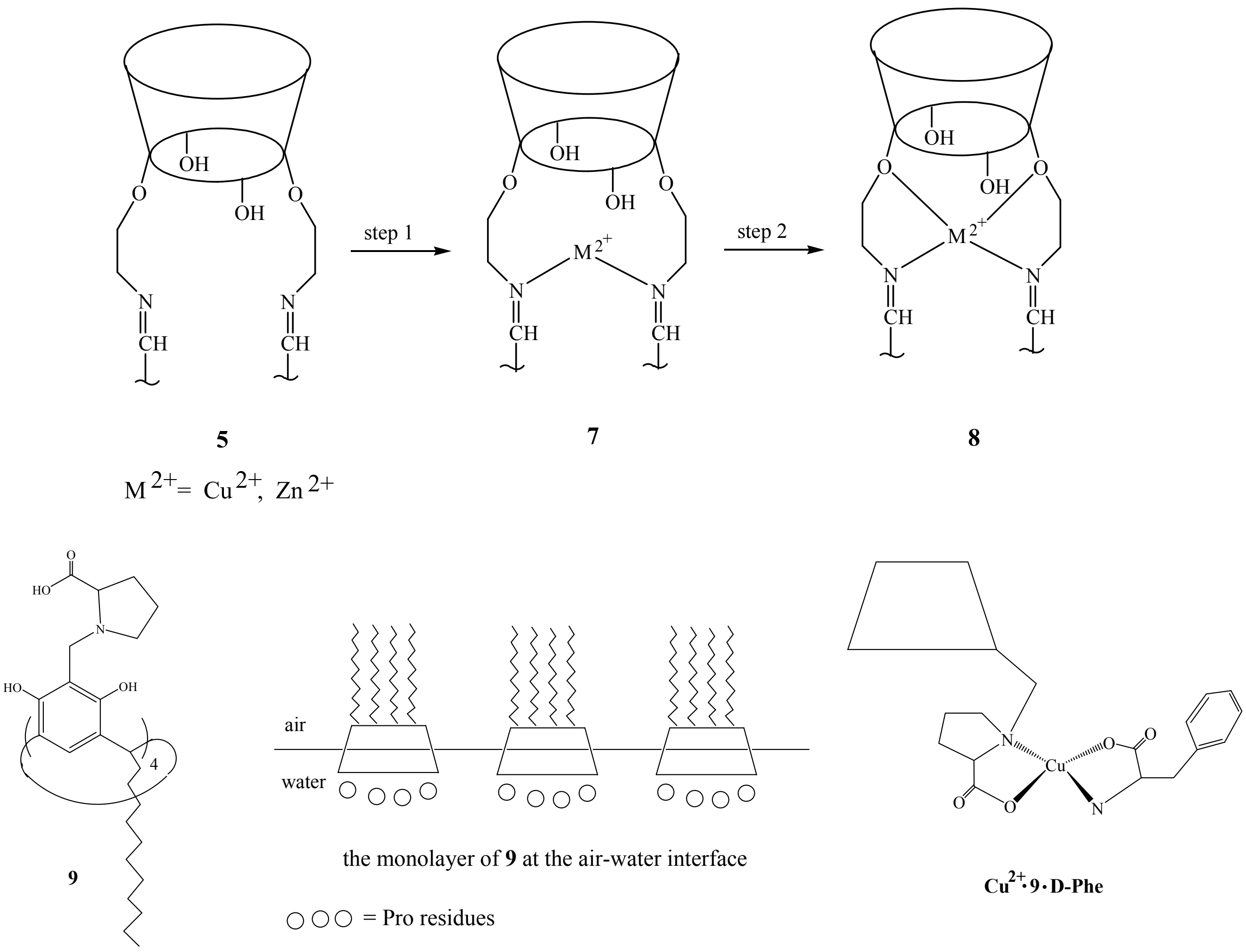
N
CH
N
CH

5


O
OH
OH
O

6



Scheme 1

The complexation of calixazacrowns **10a-c** and their homologues **11a**,**b** with Cu^{2+} was studied. It was found that Cu^{2+} forms with **10a** the 1:1 complex *i.e.* **Cu^{2+}·10a**, and with **11a** the 2:1 complex, *i.e.* **$(Cu^{2+})_2$ ·11a**; compounds **10a** and **11a** are promising for the design of fluorescent chemosensors for Cu^{2+} ion. [44] It should be mentioned that **10a** may form in the solid state channels for small molecules, *e.g.* methanol.

Chiral calix[5]arenes ***(R)*-12** and ***(S)*-12** have been synthesized. It was observed that they selectively bind Cu^{2+} over other (Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) ions. [55]

The complexes [**Cu^{2+}·*(R)*-12**] and [**Cu^{2+}·*(S)*-12**] may be used as binary hosts to recognize carbohydrates. The fluorescent titration results have shown that they selectively recognize D-(+)gluconic acid δ-lactone over other carbohydrates, such as D-(+)xylose, D-(-)ribose, 2-deoxy-D-ribose, D-(-)arabinose and D-(+)glucose.

Calix[6]arenes **13** and **14** react with bis(bromomethyl)-1,10-phenanthroline to give bridged calix[6]arenes **15** and **16**, respectively.[56-58] Compound **16** is chiral. It should be noted that in the crystal of **16** the arene rings adopt an *udiudi* (*u= up; d=down; i= in*) conformation, although in the starting **14** *all-up* conformation predominates. This observation indicates that during the bridging process leading from **14** to **16**, two arene rings invert from an *up* to a *down* orientation. Reaction of **15** with chiral reagents, *e.g.* camphor sulfonyl chloride **17** affords chiral calix[6]arene derivative **18**.

The presence of the phenanthroline bridge in **15**, **16** and **18** enables the chelation of Cu^+ ions; the formed complexes were tested as ligands for copper ion in the Cu(I) catalyzed cyclopropanation of styrene and indene with ethyl diazoacetate **19**. [59] It was found that chiral **16** and **18** alter the stereoselectivities of the cyclopropanations of styrene towards *cis* and indene towards *endo* products, *i.e.* in the same direction as in the case of nonmodified **15**.

In biological systems the coordination properties of the metal ion are controlled by proteins. In order to mimic such biological coordination, ligands basing on calix[6]arenes functionalized at the narrow rim by nitrogen arms were designed. In these ligands the aza-donors secure the first coordination sphere with one open binding site directed toward the center of calixarene cavity. The calixarene narrow rim defines the second coordination sphere, whereas the aromatic units of the calixarene act as a hydrophobic funnel selecting and driving the guest molecule to the metal center.[60]

The complexation of Cu^+ and Cu^{2+} ions by tris(pyridine)calix[6]arene **20** has been studied. [61,62] It was observed that **Cu^+·20** upon addition of MeCN affords complex **Cu^+·20·MeCN** in which Cu^+ ion has the tetrahedral (T_d) geometry and is coordinated by three pyridine nitrogen atoms and by nitrogen atom of MeCN ligand situated inside the cavity.

However, in **Cu^{2+}·20·MeCN**, the Cu^{2+} ion has the square-based pyramidal geometry (SBP); in the complex one nitrogen arm is in the apical site, and the water molecule is situated outside the cavity.

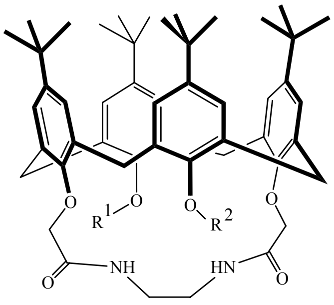
In both complexes, *i.e.* **Cu^+·20·MeCN** and **Cu^{2+}·20·MeCN**, as well as in the transition state **A** the CH-π interactions between the phenyl units of the cavity and the methyl group of MeCN exist. The MeCN unit plays in these complexes an important role since it controls the coordination of Cu^+ and Cu^{2+} ions by combination of the Cu/N (nitrile) bond and second sphere interactions; the presence of MeCN is necessary to maintain the architecture of complexes. The existing host-guest interaction generates a supramolecular stress resulting in a driving force pulling the Cu^+ or Cu^{2+} ions inside the calixarene cavity. The above Cu^+/Cu^{2+} systems are of interest in the study of biomimetic processes of proteins.

It was established that calix[6]arene capped at the narrow rim by a tmpa unit (where tmpa = [tris(2-methylpyridyl)amine]), *i.e.* **21** upon treatment with Cu^{2+} ions and the guest G affords funnel complexes.[63,64]

The reaction of **21** with $Cu(ClO_4)_2(H_2O)_6$ and guests G (G= MeCN, DMF) yields the Cu^{2+} complexes **$[Cu^{2+}·21·G)]^{2+}$** *i.e.* **22**; when instead of G the anion X^- (X^- = OH^-, Cl^-, F^-, N_3^-) is used, the Cu^+ complexes **$[Cu^+·21·X]^+$**, *i.e.* **23** are formed. Complexes **23** may also be obtained by reacting **22** with anions X^-. The Cu^{2+} complexes **22** are very stable; the 5-coordinate Cu^{2+} ion is strongly bound to the tmpa cap in a trigonal bipyramidal (TBP) geometry; they show high affinity for neutral guests that sterically fit into the calix cavity. These properties are similar to those of funnel Cu^{2+} complexes based on calix[6]tris(imidazole) **24** and on calix[6]tren **25** (where tren = tris(2-aminoethyl)amine).

An important difference however exists, resulting from the fact that the second coordination sphere provided by a narrow rim in **22** forms a different electronic environment than in the case of **24** and **25**. In **24** and **25** the oxygen atoms connecting phenyl moieties with imidazole units (in **24**) or with nitrogen atoms (in **25**) are directed inwards. In the case of complexes **22**, however, the structure is rigid due to the presence of tmpa, therefore the oxygen atoms connecting phenyl moieties with pyridyl units are directed outwards, *i.e.* towards the bulk.

In this way the dipolar inversion of the second coordination sphere responsible for anion binding occurs. As a result, the Cu^{2+} ion in **22** is able to bind a large variety of anions, while in the case of **24** and **25** [65-68] the anion binding in the cavity is strongly disfavored because of charge-dipole repulsion at the narrow rim. The above complexes are highly biologically relevant to mononuclear active sites of metalloenzymes. [63]



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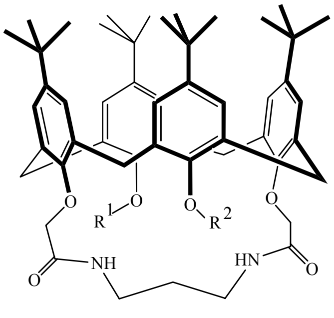

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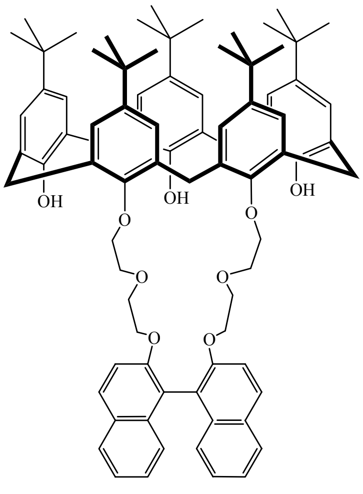
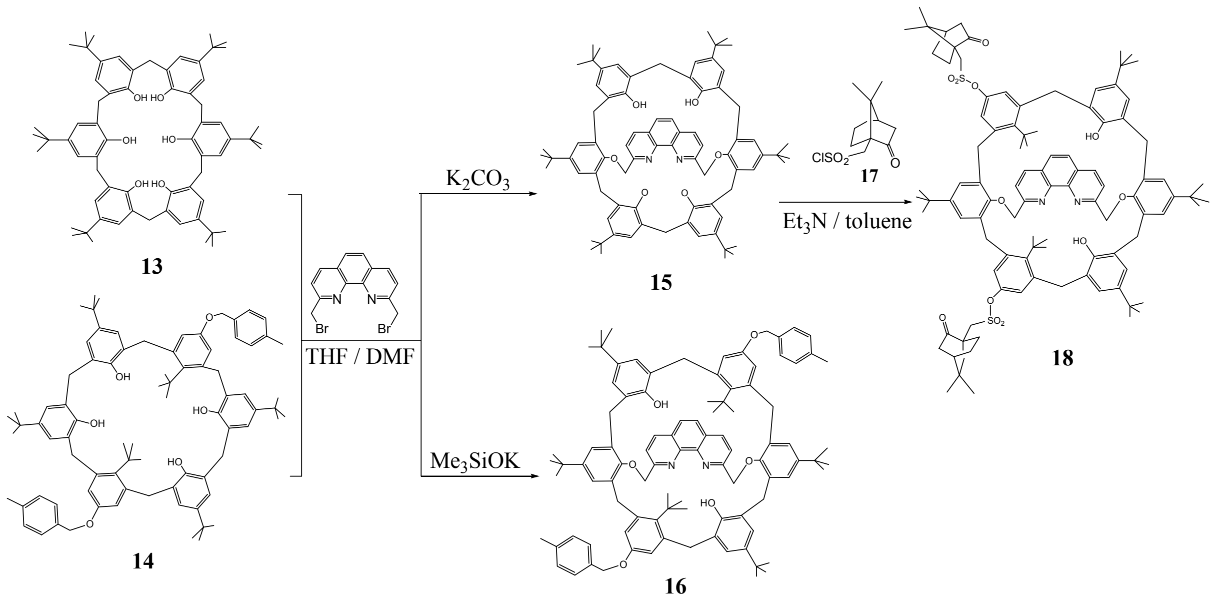
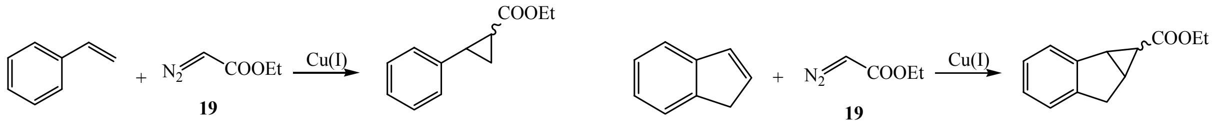


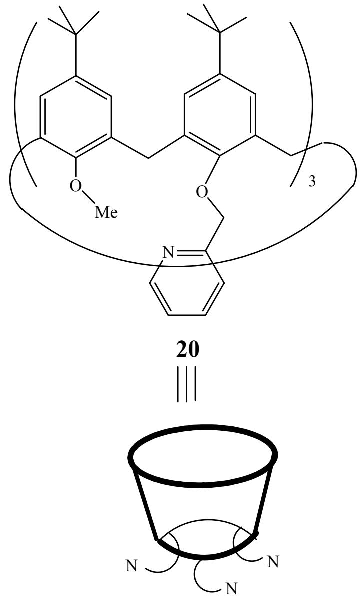
12

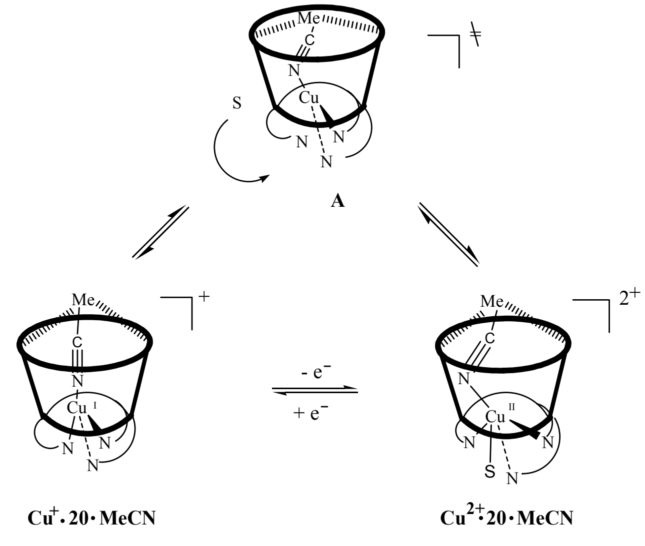
		R^1	R^2
10	**a**	H	H
	b	H	CH_2COOMe
	c	CH_2COOMe	CH_2COOMe

		R^1	R^2
11	**a**	H	H
	b	CH_2COOMe	CH_2COOMe

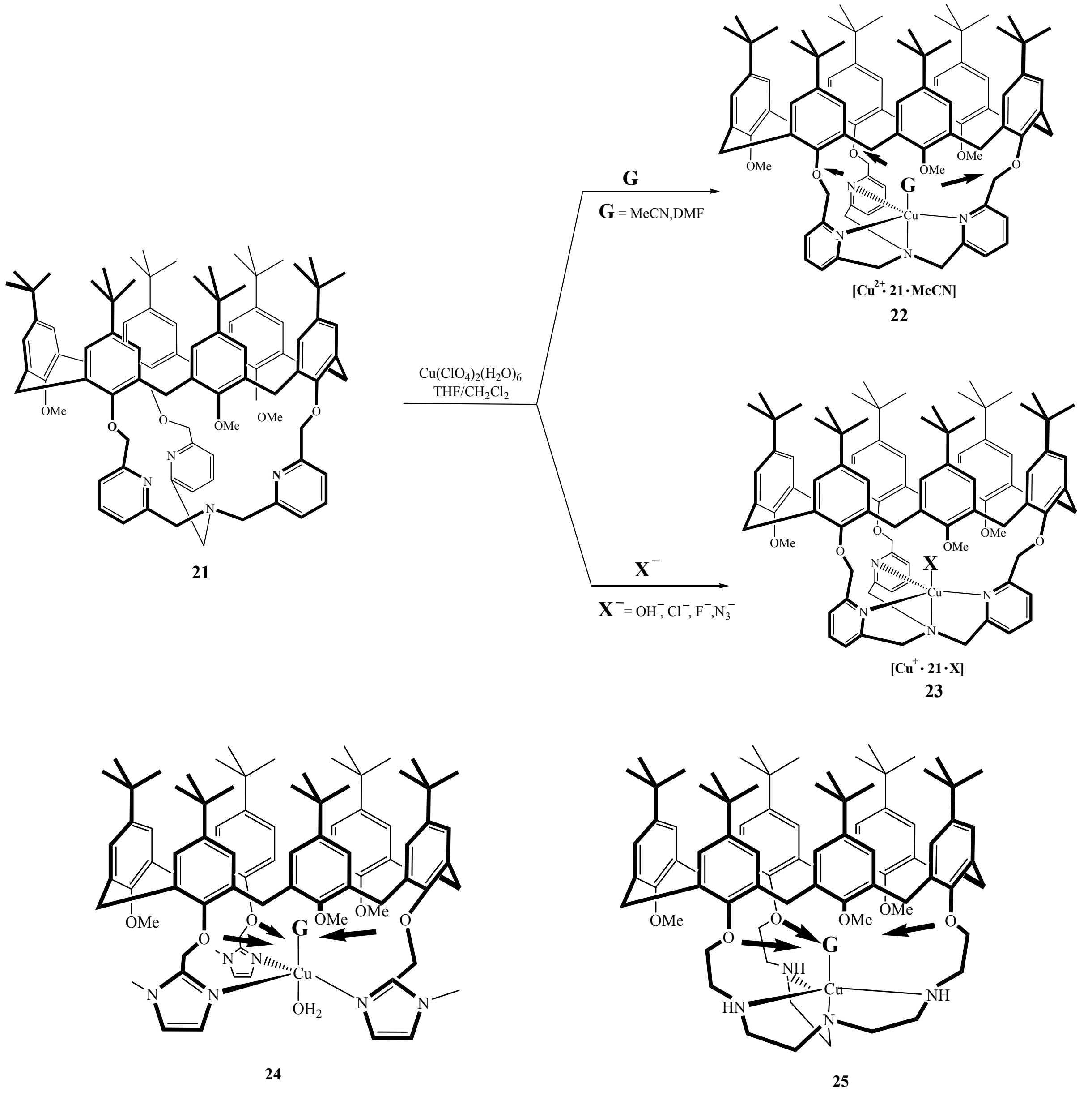








ııııııı = CH-π interaction
S = solvent (H_2O)



Scheme 2

2. Calixarene complexes with silver ions

In the study of calixarene complexes with silver ions [69-73] it was found that calixarenes **26** and **27** containing sulfur atoms as soft binding site may be used as cation sensors for ion-selective electrodes. In order to investigate the influence of neighboring halogen atoms on cation selectivity, the fluorosubstituted (*i.e.* **28**, **29**) and dichlorosubstituted (*i.e.* **30**-**32**) analogues of **26**, **27** were studied.[74] The ion-selective electrodes based on **26**-**32** as neutral ionophores have been prepared, and their selectivity coefficients for Ag^+ were examined against alkali metal, alkaline earth metal, lead, and some transition metal ions using the fixed interference method (FIM). It was found that they have high Ag^+ selectivity over Na^+, K^+, NH_4^+, Ca^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} interfering ions, except for Hg^{2+}.

Calixarenes **28-32** contain sulfur atoms as a soft binding site and neighboring halogen atoms as assistant donors taking part in complexation of silver ions. The ^{1}H NMR analysis has shown that **29** exists as several conformers in solution, and the ^{19}F NMR spectra of **Ag^+ ·29** revealed that the fluorine atoms participate in complexation of silver ion.

Calixarenes **33-36** bearing allyl groups and calixarenes **37a**,**b** containing benzothiazole units have been investigated in view of their affinity towards Ag^+ ion; among them **34**, **37a** and **37b** were used for construction of Ag^+ ion-selective electrodes. [75,76] It was observed that **37b** coordinates Ag^+ more strongly than **37a** .

It was observed that calixarenes **38a-c** form 1:1 inclusion complexes with Ag^+; their stability constants, determined by the ESI-MS (electrospray-ionization mass spectrometry) method decrease in the order **38b**>**38a**>**38c**.[72]

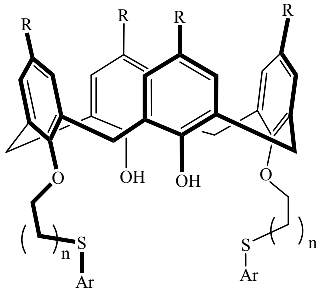
The complexation of calixarene **39** with Ag^+ was investigated.[77-79] Although calixarene **39** has low solubility, the amines can solubilize it *via* acid-base host-guest chemistry, resulting in the abstraction of a single proton from **39** by the amine. Majority of inclusion complexes of **39** are formed in solution by van der Waals interactions of a guest with hydrophobic cavity of **39**, leading to 1:1 or 2:1 host-guest systems. [80] In the solid state, however, the symmetry of the calixarene is disrupted, therefore simple 1:1 or 2:1 host-guest complexes are not formed.

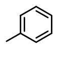
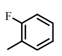
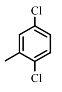
It was observed that the solution of **39** and $AgNO_3$ in ethylenediamine **40** after evaporation of excess solvent affords crystals of the clathrate **$[Ag^+ \cdot 39 \cdot (40)_3]$**, *i.e.* **41**. In **41** one molecule of **39** interacts with three ethylenediamine **40** molecules coordinating one Ag^+ ion. The calixarene **39** serves as a counterion, a single proton being abstracted from one of its phenol groups by the excess ethylenediamine left behind as solvent. In **41** one bidentate-chelating molecule of **40** is situated within the calixarene (*endo*), whereas two singly coordinated molecules of **40** reside outside the calixarene cavity (*exo*); the four-coordinate Ag^+ ion has a distorted tetrahedral geometry.[77]

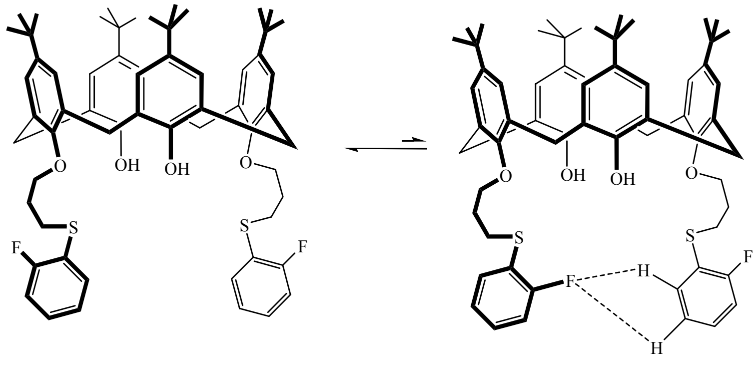
The clathrate **41** is further stabilized through a network of hydrogen bonds. The *endo* coordinated amine units interact with the phenolic hydroxyl groups of calixarene **39**. The free amino groups of the two *exo* molecules of **40** form weak hydrogen bonds with free amino groups of the adjacent molecules of **41**. Due to the above hydrogen bonds, the distortion of the capped structural motif takes place.

It was observed that upon deamination occurring by heating the sample **41**, its color changes from white to yellow and then to brown, indicating the reduction of the Ag^+ ion and formation of nanocrystalline clusters consisting of **39** and metallic silver.

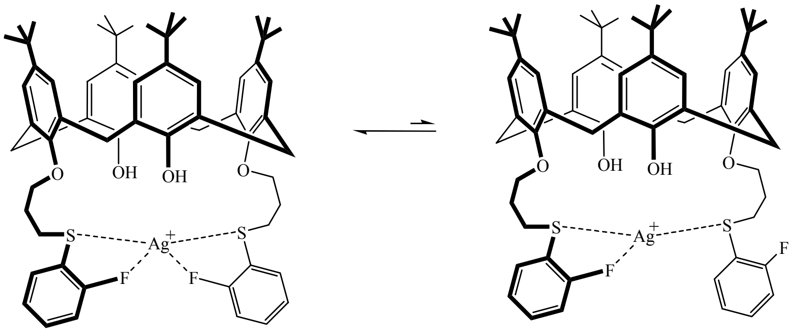
The oligophenylene-substituted calix[4]crowns **42a-d** form complexes with Ag^+ ion. [81] The binding of crown ether moiety with Ag^+ ion is weak, therefore the reversible disassembling of the complex in the presence of KI is possible. It should be pointed out that despite weakness, this interaction is useful in the design of supramolecular structures.



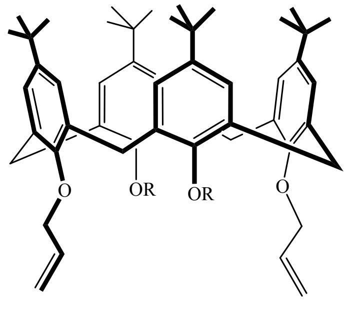
	n	R	Ar
26	1	H	
27	1	*t*-Bu	
28	1	H	
29	2	*t*-Bu	
30	1	H	
31	1	*t*-Bu	
32	2	*t*-Bu	



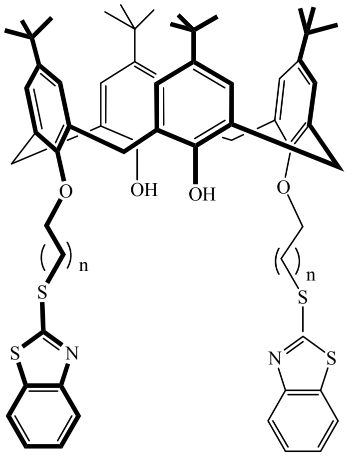
conformational equilibrium of **29**



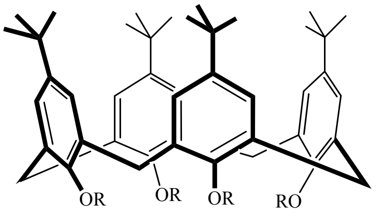
conformational equilibrium of $\mathbf{Ag^{+}\cdot 29}$



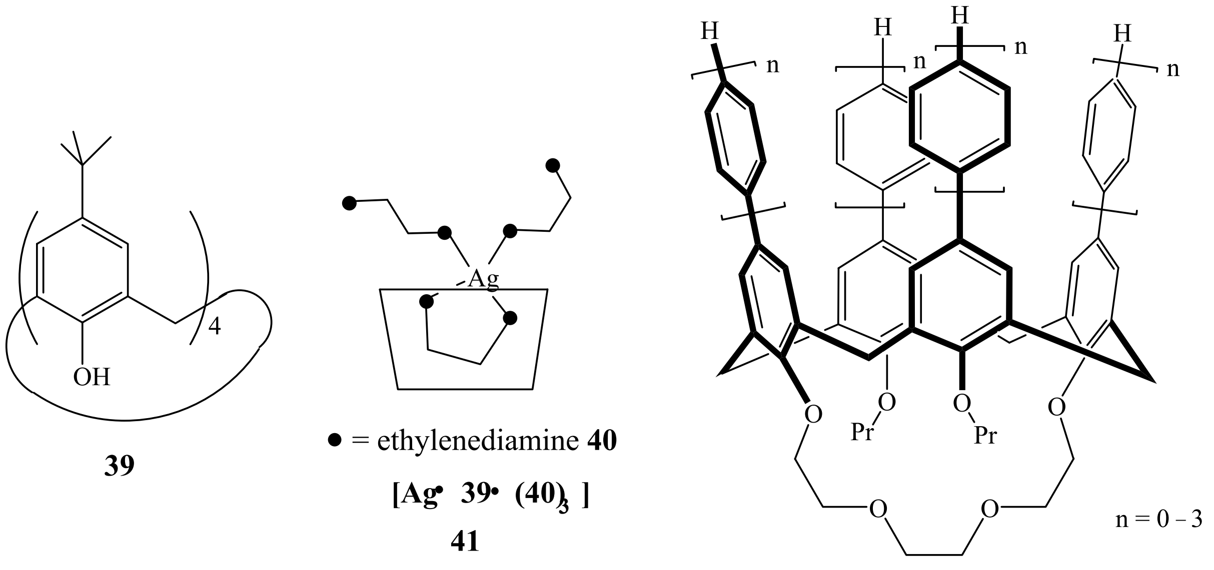
	R
33	H
34	allyl
35	CH_2Ph
36	Bu



37	n
a	1
b	2



38	R
a	$-(CH_2)_2CH_3$
b	$-CH_2CH=CH_2$
c	$-(CH_2)_6CH=CH_2$



39

● = ethylenediamine **40**

[Ag• 39• (40)$_3$]

41

	n
a	0
b	1
c	2
d	3

42

Scheme 3

3. Calixarene complexes with gold ions

In the study of calixarene gold complexes[49,82] it was observed that the compound **43** containing four two-coordinate linear gold halide units exists as an equilibrium between two boat conformers **43a** and **43b** which undergo an easy conformational exchange[83-85] in solution. In order to synthesize resorcinarene digold complexes the disilver complexes **44a-c** were treated with [AuCl(SMe$_2$)]. The reactions occur with the precipitation of silver chloride, and as products the resorcinarene digold complexes **45a-c** are formed.[83]

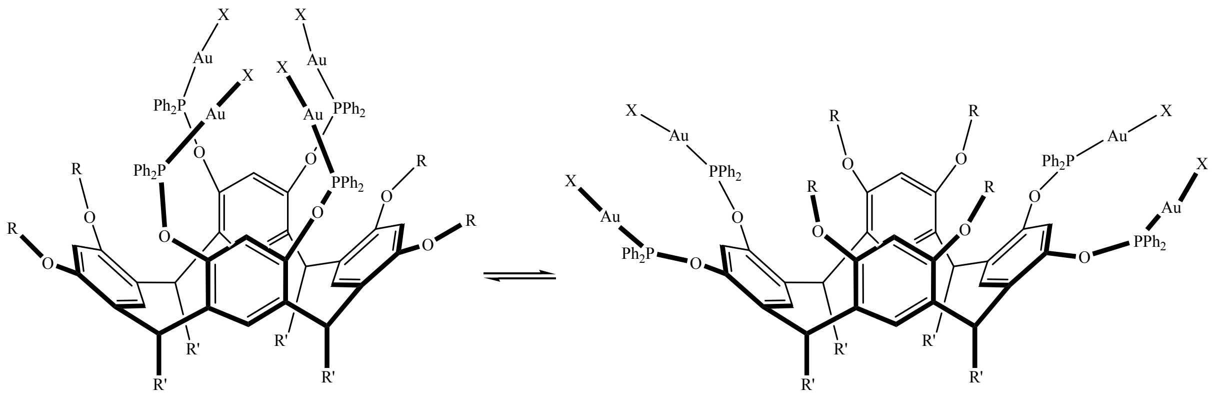
It was found that the reaction of resorcinarene **46** with [AuCl(SMe$_2$)] yields polymeric complex [**46**$_4${AuCl}$_2$·[**46**$_4$Au$_2$][AuCl$_2$]$_2$, *i.e.* **47**, consisting of two different species: the dicationic component **A** and the neutral component **B**. In the dicationic component **A** the gold(I) centers have linear S-Au-S coordination, with chelation of each gold(I) center by two sulfur atoms of the thiophosphinate groups. The anions of **47** are [AuCl$_2$]$^-$.Thus the dicationic component is analogous to the dications in disilver and digold (I) complexes **44** and **45**. The neutral component **B** has two linear S-Au-Cl units, one at each end of the molecule of **47**; two sulfur atoms are noncoordinated. In both components the resorcinarene molecule has a boat conformation in which the thiophosphinate-derivatized arene rings are in the flattened position, and the acylated rings stand upright. [83]

It should be pointed out that the complex **47** has an unusual polymeric structure in the solid state in which molecules **A** and **B** are linked *via* Au···Au interactions at each end; in this way two intermolecular aurophilic bonds are formed. The presence of these aurophilic attractions between the chelated S-Au-S gold centers and the linear S-Au-Cl gold centers results in an infinite, alternating pattern of the two different components **A** and **B**, which create this polymeric structure. The solid-state structure of the complex **47** contains both the chelate form in **A** and the terminal ligand form in **B**.

The reaction of calixarene **48** with four equivalents of [AuCl(THT)] (where THT = tetrahydrothiophene)] affords the tetragold complex **49**. [86] In the study of stepwise titration of **48** with AuCl(THT) it has been shown that the first complexation step affords a mononuclear species **50,** existing in equilibrium with the assembly **51**. The NMR study indicates the dynamic behavior of **50**; its all four phosphorus atoms are involved in coordination. The chloro-gold units jump from one phosphorus atom to another; it should be pointed out that both intermolecular and intramolecular jumps are possible. Molecular mechanics calculations have shown the tetrahedral geometry of gold centers.

The binding of the second gold unit is more difficult than in the case of the first one. The addition of the second AuCl(THT) molecule leads to the dinuclear gold complex **52** existing in an equilibrium with the assembly **53**. The X-ray structure of **53** shows that the linking gold atoms having near-trigonal geometry. The addition of the third AuCl(THT) molecule results in formation of labile complex **54**, which upon reaction with the fourth AuCl(THT) molecule yields **49**.

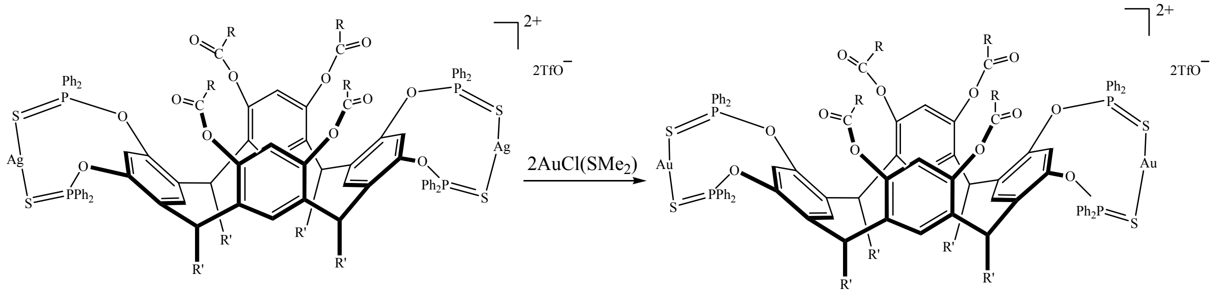
In the investigation of vacuum deposition of metal-containing organic compounds [87-89] it was observed that the incorporation of coordinated metal atoms has a stabilizing effect. [90-92] The scanning tunneling microscopy (STM) results indicate that the stability of a large organic compound sublimated onto a Au (111) surface under ultrahigh vacuum conditions may be considerably enhanced by coordinating it to gold atoms prior to deposition. For this purpose gold-functionalized calix[4]arene **55** containing two arms derived from melamine units and terminating by triphenylphosphine groups has been synthesized.



R = alkyl
R' = CH_2CH_2Ph
X = halide

43a

43b

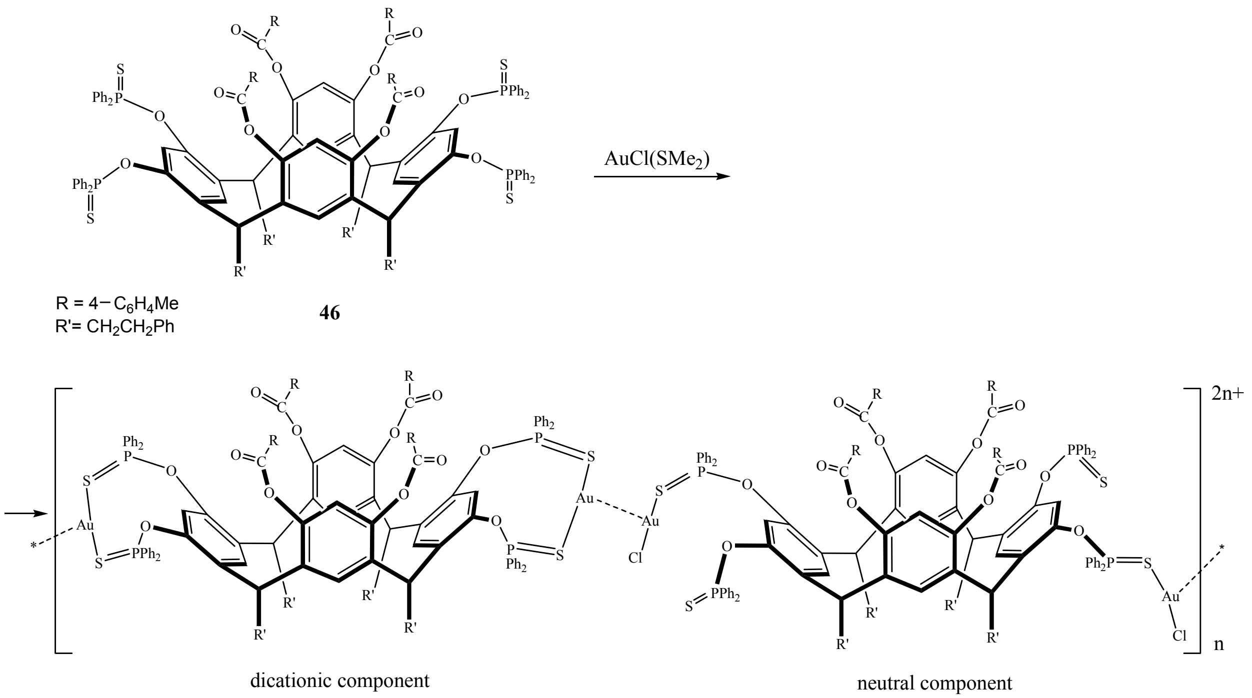


	R
44	**a** $4-C_6H_4Me$ **b** $2-C_4H_3S$ **c** $O-CH_2CCH$

R' = CH_2CH_2Ph

	R
45	**a** $4-C_6H_4Me$ **b** $2-C_4H_3S$ **c** $O-CH_2CCH$

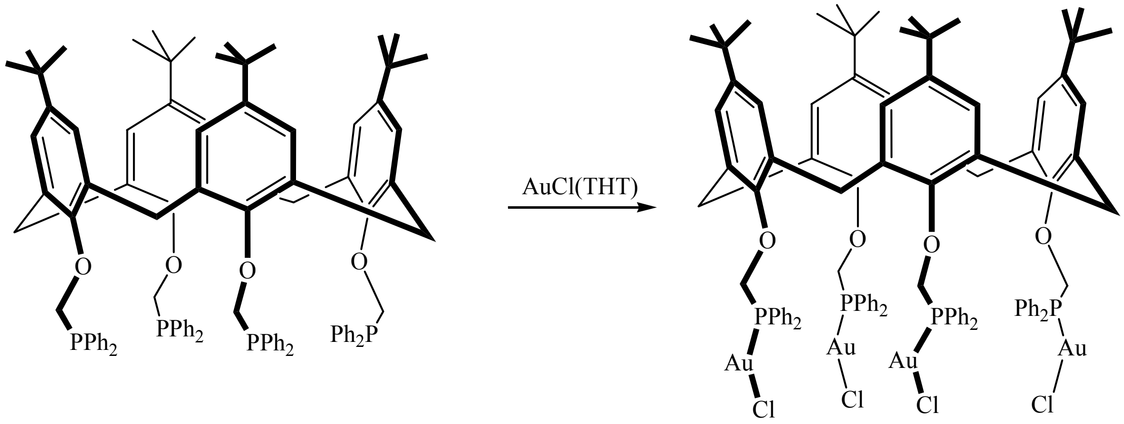
R' = CH_2CH_2Ph



R = 4−C_6H_4Me
R'= CH_2CH_2Ph

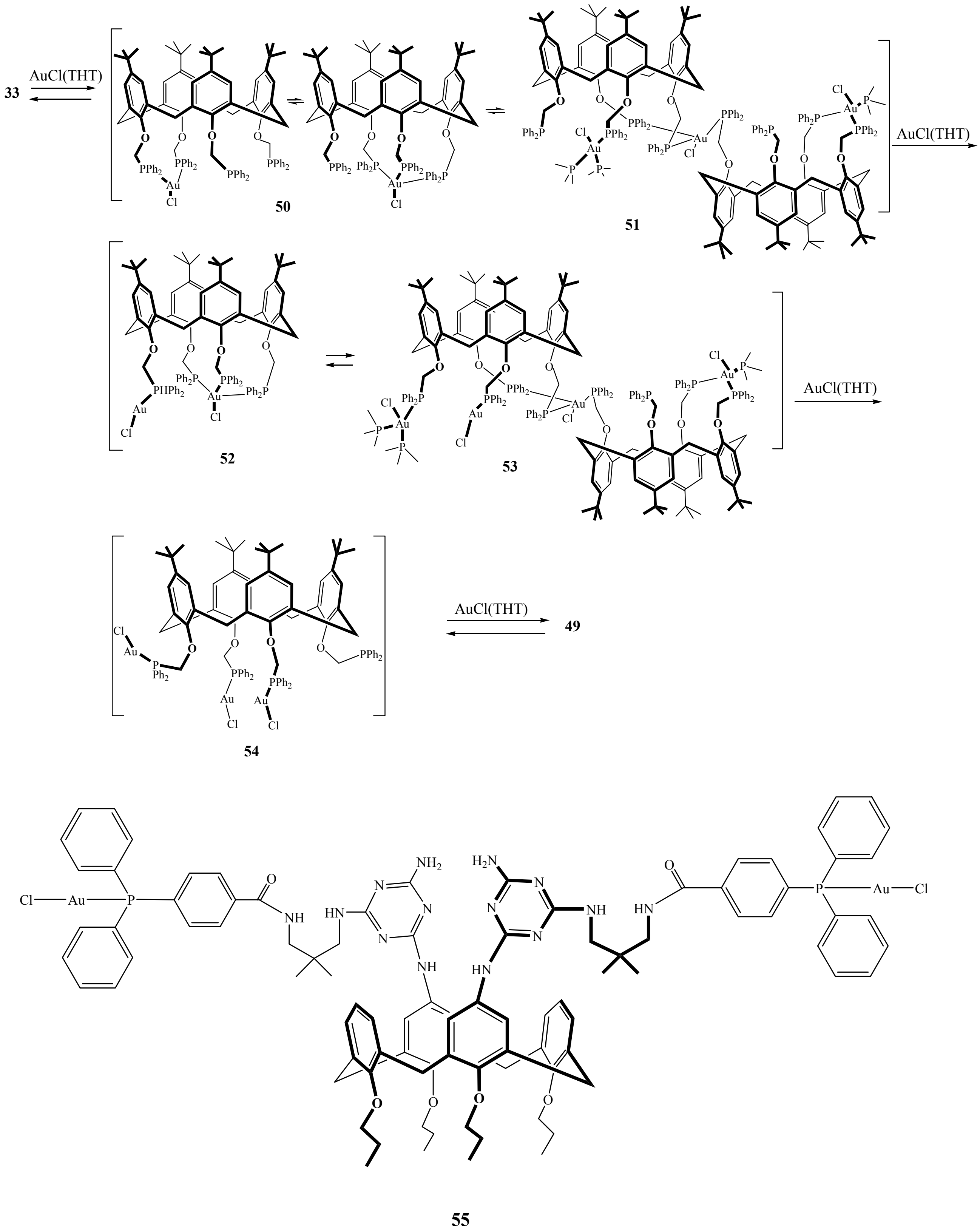
46

A **47** **B**



48 **49**

THT = tetrahydrothiophene



Scheme 4

4. Calixarene complexes with zinc ions

Zinc is widely used in fine chemicals and paint industries, as well as in electroplating; zinc is also present in high protein foods. Excess of Zn^{2+} ions is toxic for humans, therefore methods for zinc monitoring are of importance.[93] Calixarene zinc complexes are intensively studied; [49, 78, 94-96] some examples will be shown below.

Investigations of complexing properties of calix[4]arene **56** towards cations and anions have shown that different moieties of the pendant arms serve as active sites for complexation, therefore **56** may be considered as a ditopic receptor. Calixarene **56** forms with Zn^{2+} ion the complex **Zn^{2+}·56**; in this process the hydroxyl and carbonyl groups of the pendant arms at the narrow rim of **56** function as active sites for interaction.[97,98]

It was established that 4-*t*-butylcalix[4]arene **39** may be used as a Zn (II) selective potentiometric sensor.[93] Poly(vinyl chloride) based membranes containing **39** show a very good selectivity for Zn^{2+} over other mono-, bi- and trivalent cations; one should point out their fast response and good reproducibility. The sensor may be used as an indicator ionoselective electrode in the potentiometric titration of Zn^{2+} against EDTA [27,28] (EDTA = ethylenediaminetetraacetic acid) and for estimation of zinc ions in industrial waste waters.

It is known that macrocyclic host molecules are promising models for enzymes. When transition metals are coordinated in proximity to the hydrophobic cavities of receptors, the macrocycles function as metalloenzymes. [99] Metalloenzyme models acting in aqueous solution have been designed by employing self-assembly of the *p*-sulfonatocalix[4]arene **57** (used as a macrocyclic host able to bind cationic guests), bicyclic azoalkanes **58-60** [100,101] serving as guests, and Zn^{2+} as a metal ion. [102] In this model the metal-guest bond formation is host-assisted, *i.e.* is templated by the host. In the soformed ternary complex consisting of **57**, the guest and the metal ion, the guest is held by hydrophobic interactions with the host, while the metal ion is held by Coulombic attraction of negative charges situated at the wide rim of **57**. If the guest is a weak ligand, the host can assist, *i.e.* can template the formation of a metal-guest bond. The guest used should be large enough to maximize hydrophobic interactions, and sufficienty small to enable the docking of cations to the wide rim of calixarene **57**. The guest should contain functional groups to allow metal-guest interactions.

Bicyclic azoalkanes **58-60** have been chosen as guests. Among them, **58** is the most convenient guest, since its binding constant with **57** is the highest, and its small and spherical shape enables the binding of metal ions. [103] The formation of the complex **57·58** and the subsequent binding of metal ion may be controlled by optical spectroscopy, since **58** shows strong fluorescence in water, as well as the near UV absorption.

When **57** is added to an aqueous solution of **58**, the 1: 1 complex is formed. The subsequent addition of Zn^{2+} results in the formation of a ternary complex **Zn^{2+}·57·58**, in which the azo group of **58** serves as a monodentate ligand. This behavior, *i.e.* that the host brings **58** and Zn^{2+} together is similar to the function of enzyme bringing together the substrate and the catalytic center. The formation of the ternary complex **Zn^{2+}·57·58** is an example of a cooperative binding.[102] It is known that **58** shows in water a high fluorescence, which is quenched upon complexation with **57**. When Zn^{2+} ions (which do not quench the fluorescence of free **58**) are added, the fluorescence of **58** is further decreased, indicating the formation of the ternary complex.

It should be noted that **59** and **60** do not form similar ternary complexes, in the case of **59** due to steric hindrance and in the case of **60** due to charge repulsion between Zn^{2+} cations and the positive ammonium group of **60**. In these both cases of **59** and **60** the release of the guest occurs, due to the competitive binding of **59** or **60** and Zn with **57**. [102] These observations indicate the high selectivity of **57**, since it forms ternary complex only with **58** and not with **59** or **60**, although the structural differences of **59** and **60** as compared to **58** are slight.

The above results show possibility of two modes of binding, *i.e.* cooperative and competitive binding. The cooperative binding occurs when steric and electrostatic factors are favorable and when the geometry allows the formation of the metal-guest bond. The binding constant of **57·58** increases fourfold by addition of Zn^{2+}; this observation indicates a positive cooperativity of the binding, *i.e.* the synergistic effect. This increase of binding constant of **57·58** in the presence of metal ion, resulting from metal-guest interaction is promising in sensor design.

UV spectral analysis has revealed that at pH 2 the guest **58** in **57** is protonated to give the complex **58·57·H**$^+$. Upon addition of Zn^{2+} ions, the complex **Zn**$^{2+}$**·57·58** is formed. That means that in this particular case, Zn^{2+} ions do not destabilize the complex of **56** with a cationic guest, *i.e.* the release of **58** does not occur as it took place in the case of **60**, but the guest is deprotonated by Zn^{2+} which forms the metal-guest bond. This behavior resembles function of Zn^{2+} ions in hydrolytic metalloenzymes, where Zn^{2+} ions deprotonate ligands by formation of metal-ligand bonds. [102,104]

Calix[6]arenes may be used as hydrophobic hosts, their large cavity enables inclusion of a variety of organic guests. Since calix[6]arenes are very flexible, in order to obtain a cavity able to include a guest they must be restricted in a cone conformation. [68]

In order to design biomimetic receptors, the system **61** mimicking metalloenzyme active sites by binding metal center incorporated inside a calix[6]arene cavity with a neutral guest has been developed. This system is based on calix[6]arene bearing three imidazole arms and contains the Zn^{2+} ion. [105] The imidazole arms are mimicking the histidine residues of the protein. The Zn^{2+} ion is coordinated in a tetrahedral geometry. Such funnel complex, increasing Lewis acid character of metal ion in the hydrophobic neutral environment is highly sensitive to different guests (G) of an electron donor character, *e.g.* RNH_2 , ROH, $RCONH_2$, RCN, RCOOH; their encapsulation leads to **61**. The hydrophobic pocket is a selective molecular funnel for neutral species. This system **61** is similar to **24**, *i.e.* to copper funnel complex based on calix[6]arene bearing three imidazole arms and Cu^{2+} ion, containing the guest molecule G.

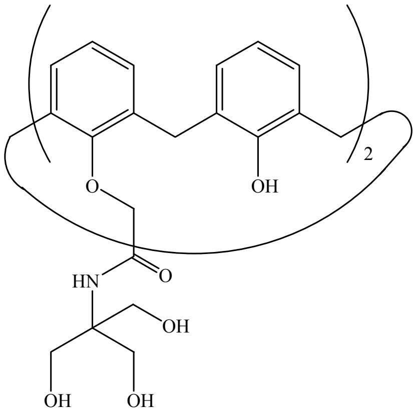
In the study of biomimetic zinc funnel complexes basing on calix[6]arene, it was observed that calix[6]arenes **62a·H** and **62b·H** bearing two imidazole arms and one phenol arm may form three types of complexes with Zn^{2+} ion, namely dicationic, monocationic and neutral ones. [106]

(1) It was found that **62a·H** reacts with $Zn(H_2O)_6(ClO_4)_2$ in THF to give the dicationic complex [Zn(**62a·H**)(H_2O)]$(ClO_4)_2$, *i.e.* **A** in which Zn^{2+} is coordinated to three nitrogen atoms, to the linking OH group and to H_2O molecule. One should mention that in the case of **62b·H** the formation of a dicationic complex similar to **A** was not observed. When the $CDCl_3$ solution of **A** was treated with a small neutral guest G, *e.g.,* ROH, RCN, $RCONH_2$ (ethanol, acetonitrile, propionitrile, acetamide), the exchange of H_2O for G molecule took place, affording the dicationic complex [Zn(**62a·H**)(G)]$(ClO_4)_2$.

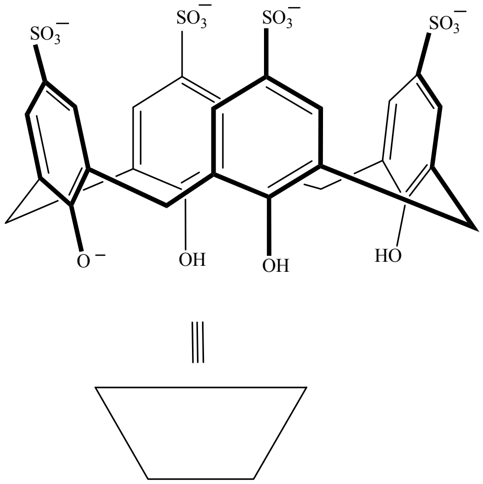
(2) The reaction of **62a·H** and **62b·H** with $Zn(H_2O)_6(ClO_4)_2$ in MeOH in the presence of triethylamine leads to monocationic complexes [Zn(**62·H**)](ClO_4), *i.e.***B** in which the linking OH group underwent deprotonation to oxygen atom. This complex also binds a guest, although with a lower affinity than the dicationic complex **A**; as a result [Zn(**62·H**)(G)](ClO_4) is formed. The exchange rate of guest increases in the order [Zn(**62a·H**)(G)]$^{2+}$ < [Zn(**62b**)(G)]$^{+}$ < [Zn(**62a**)(G)]$^{+}$, *i.e.* following the increase of the donor ability of the calixarene-based coordination core; the stronger is the Zn Lewis acidity, the stronger is the Zn-guest bond and the slower is the exchange rate.

(3) The reaction of **62a·H** and **62b·H** with $Zn(H_2O)_6(ClO_4)_2$ in MeOH in the presence of an anion (X^- = OH^-, Cl^-, N_3^-, $PhCOO^-$) affords neutral complexes [Zn(**62**)X], *i.e* **C** in which the anion X^- coordinates Zn^{2+} from the outside of the cavity. In these complexes calixarene has a partial cone conformation with one imidazole arm released by the metal center. The other imidazole arm, still bound to the metal center, undergoes self-inclusion into the calixarene cavity and fills it. Therefore the formed complex [Zn(**62**)X] is unable to endo-bind guests. Thus the coordination of two anions (ArO^- and X^-) decreases the Lewis acidity of zinc to a point that the metal center does not bind a fifth donor, *i.e.* the complex [Zn(**62**)X] cannot include guests into its cavity. The zinc affinity for a guest decreases in the order: dicationic **A** > monocationic **B** > neutral **C**, which does not bind guests at all.

It should be pointed out that the above complexes behave as acid-base switch for guest binding to give *ON – OFF* system. The dicationic form having the strongest Lewis acidic Zn center represents the *ON* state; it includes the small guest G. Deprotonation of the phenol group weakens the Zn-G bond; the formed monocationic complex either remains in an *ON* state or releases G to give the *OFF* state. Further addition of a base leads to the full *OFF* state, *i.e.* the formation of the neutral complex, with the self-inclusion of the imidazole substituent. The process is reversible, addition of an acid to the neutral complex drives back the equilibria to the *ON* state. Some features of the above systems are similar to behavior of Zn-peptidases of the astacin and serralysin families, in which the active Zn(II) site is coordinated to three histidine residues. [106]



56



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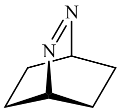
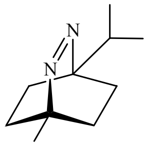


58



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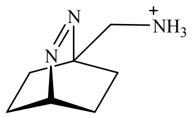
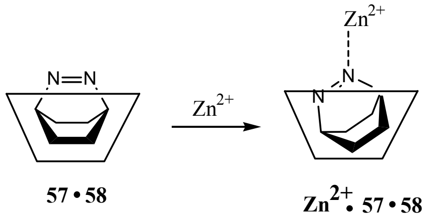
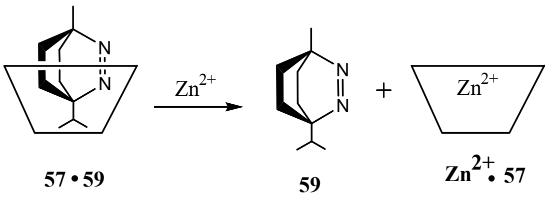


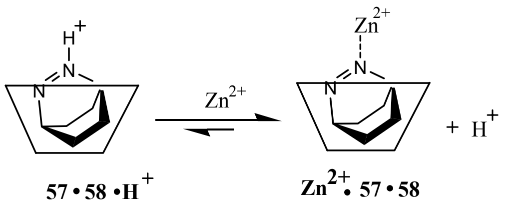
60

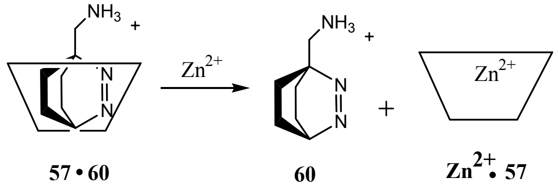


cooperative binding

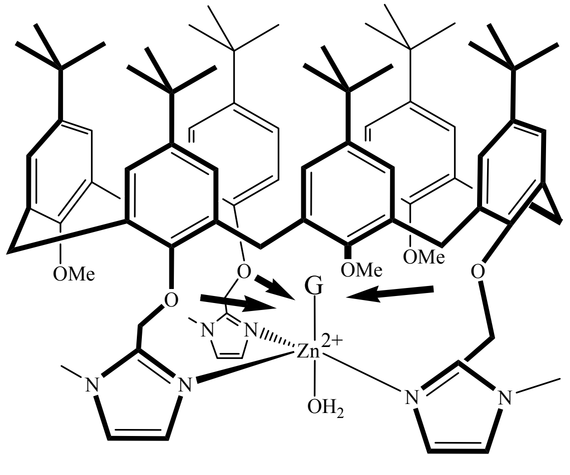


competitive binding

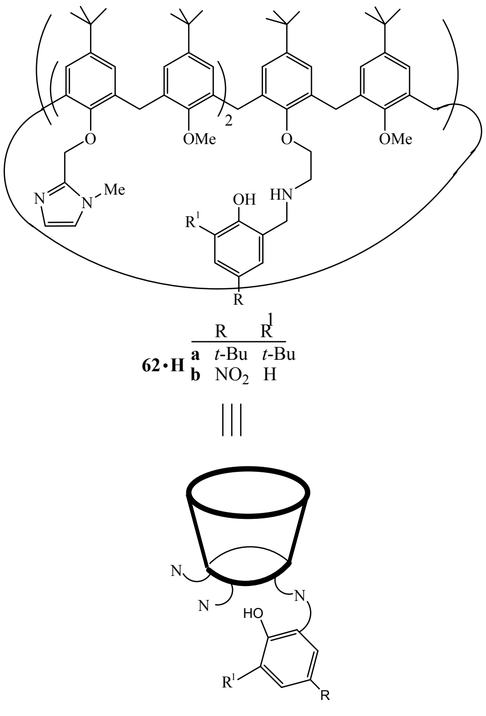


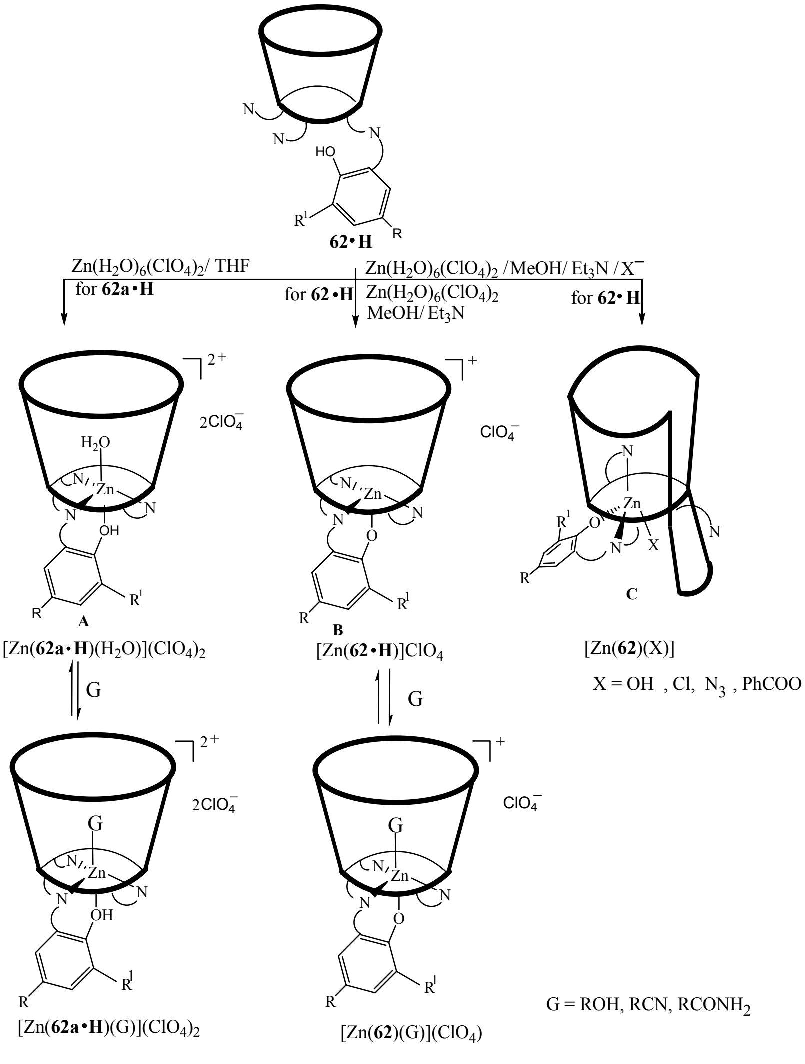


competitive binding


OMe
O
O
G
OMe
OMe
O
N
N
Zn2+
N
N
OH2
N
N

61


O
OMe
2
O
OMe
N
N
Me
OH
HN
R1
R
R R1
62•H
a t-Bu t-Bu
b NO2 H
N
N
HO
N
R1
R


N
N
N
HO
R1
R
62•H
Zn(H2O)6(ClO4)2/ THF
for 62a•H
Zn(H2O)6(ClO4)2 /MeOH/ Et3N /X−
for 62•H
Zn(H2O)6(ClO4)2
MeOH/ Et3N
for 62•H
2+
2ClO4−
H2O
N
Zn
N
N
OH
R
R1
A
[Zn(62a•H)(H2O)](ClO4)2
+
ClO4−
N
Zn
N
N
O
R
R1
B
[Zn(62•H)]ClO4
N
Zn
R1
O
N
X
N
R
C
[Zn(62)(X)]
X = OH , Cl, N3 , PhCOO
G
G
2+
2ClO4−
G
N
Zn
N
N
OH
R
R1
[Zn(62a•H)(G)](ClO4)2
+
ClO4−
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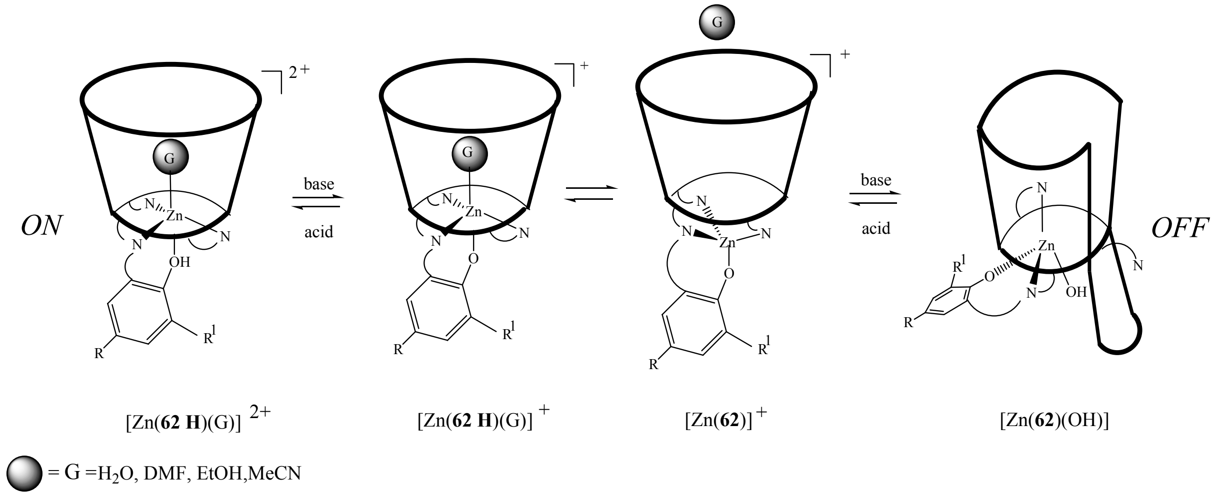
R
R1
[Zn(62)(G)](ClO4)
G = ROH, RCN, RCONH2



Scheme 5

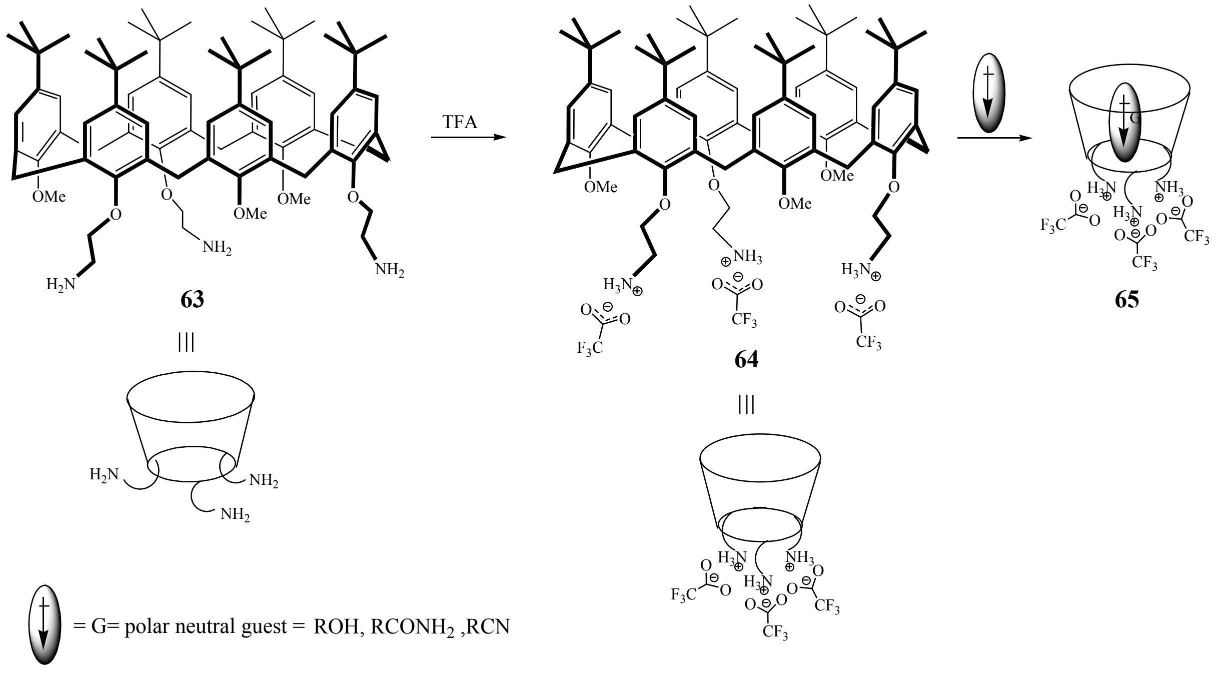
Complexing properties of calix[6]arene **63**, bearing three primary alkylamino arms have been studied. [105] It was found that **63** can be structured by strong acids, *e.g.* TFA to give a polarized receptor **64**. Upon this protonation of **63** leading to **64** the three ammonium groups of **63** become sealed together by the counter-anions. Calixarene **64** , having a hydrophobic π-basic cavity terminating in a tricationic protic site, shows a strong affinity for polar neutral guests G such as alcohols, amides, ureas or nitriles; their encapsulation yields complexes **65**. [107-110] This behavior is due to the self-assembly of the ion-paired platform, closing the narrow rim of the cavity and freezing the calixarene cone conformation, as well as stabilizing the neutral guests *via* hydrogen bonding and charge-dipole interactions.

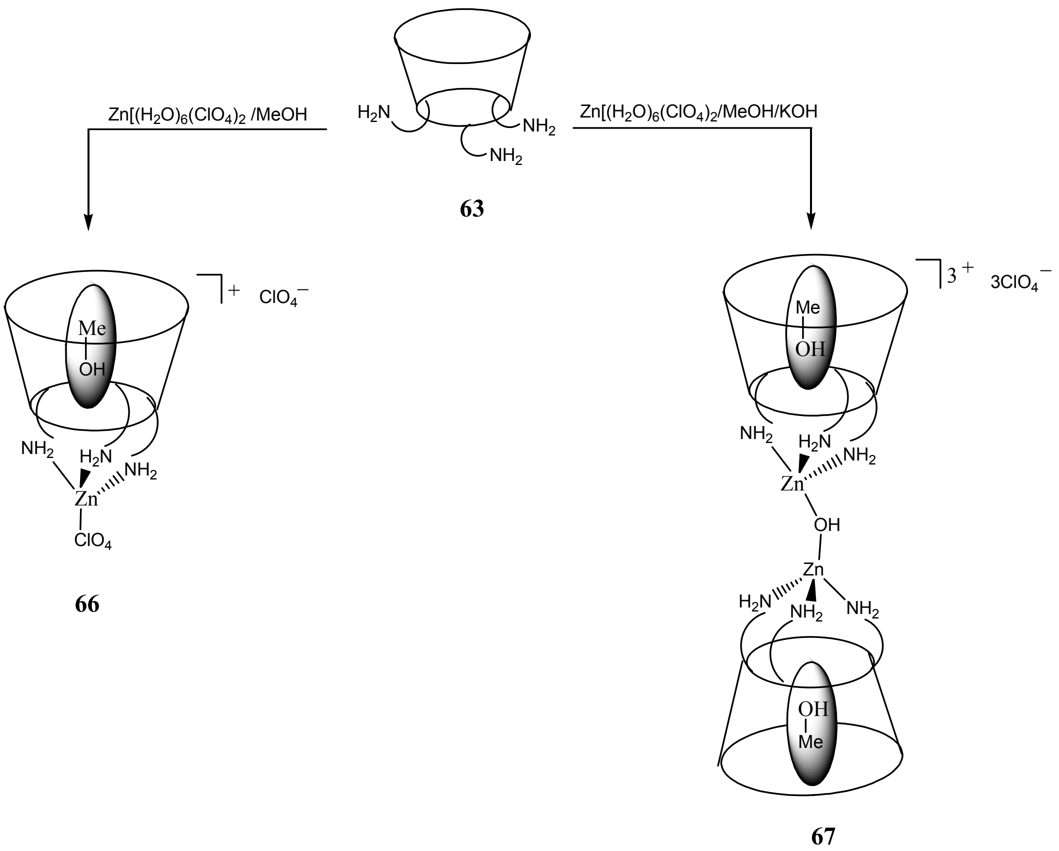
The reaction of **63** with $Zn(H_2O)_6(ClO_4)_2$ in MeOH affords mononuclear complex **66**, whereas reaction with $Zn(H_2O)_6(ClO_4)_2$ in MeOH in the presence of KOH leads to the dinuclear μ-hydroxo complex **67**.

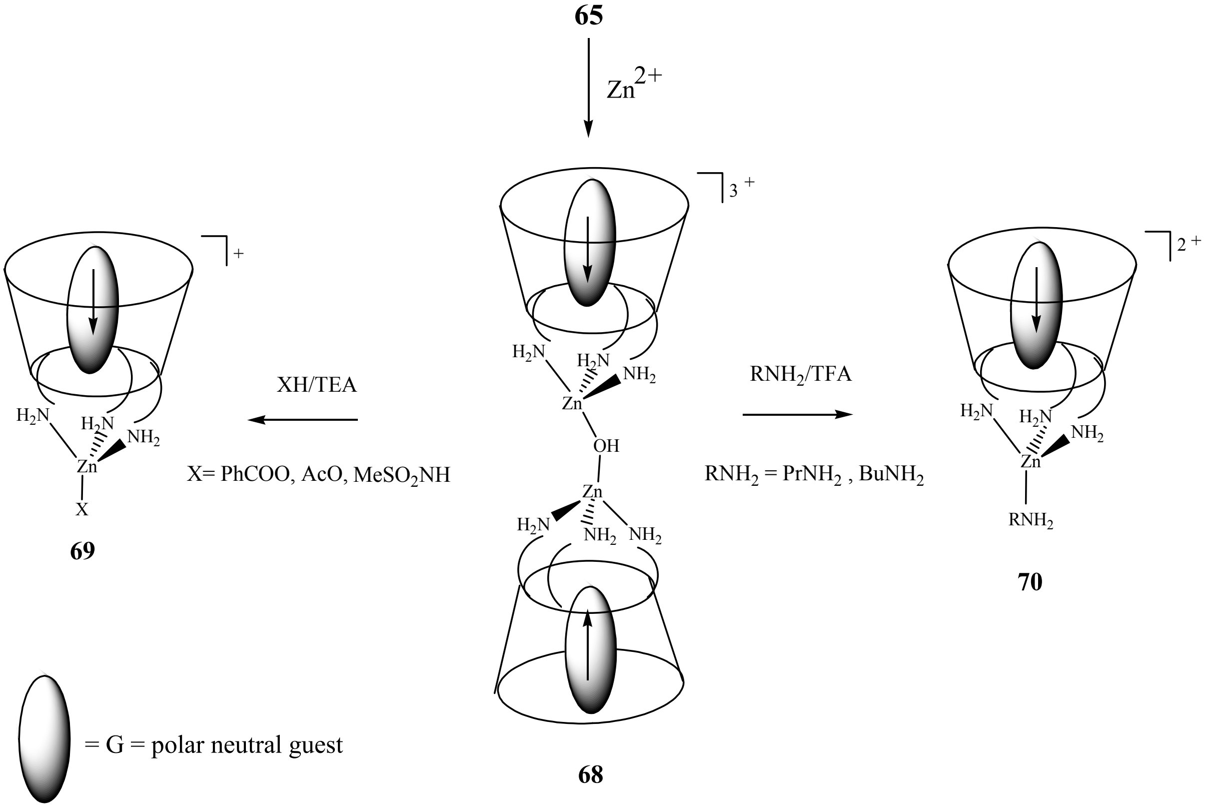
It was found that **65** forms with Zn^{2+} ion the dinuclear complex **68.** Treatment of **68** with a carboxylic acid or a sulfonamide, *i.e.* XH (X = PhCOO, AcO, $MeSO_2NH$) and TEA (TEA = triethanoloamine) affords complex **69**, while treatment of **68** with alkylamine and strong acid, *e.g.* RNH_2/TFA leads to complex **70**. It is of importance that the asymmetry of an enantiopure amino ligand is transmitted to the calixarene core, in this way the asymmetry of the external ligands is sensed by the guest. Complexes **69** and **70** contain the tetrahedral Zn^+ ion bound to three amino arms and to an exogenous ligand (X or RNH_2) protruding outside the cavity. As a result, the metal ion structures the calixarene core, constraining it in a cone conformation suitable for guest inclusion. The formed calixarene cone acts as a polarized receptor; its host properties can be allosterically tuned by the environment *via* the binding of external ligands to Zn^{2+} ion. In the case of the electron rich external ligand, the receptor is less polarized, and highly sensitive to the hydrogen bonding ability of the guest, however in the case of less electron rich external ligand, the receptor becomes more polarized, and more sensitive to the dipole moment of the guest, *i.e.* the binding of dipolar molecules is more efficient. These properties are different than those of funnel Zn complexes, *e.g.* **61**, in which the coordination link of Zn^{2+} with the guest plays a dominant role. The above observations are of interest in the search for artificial enzymes. [105]

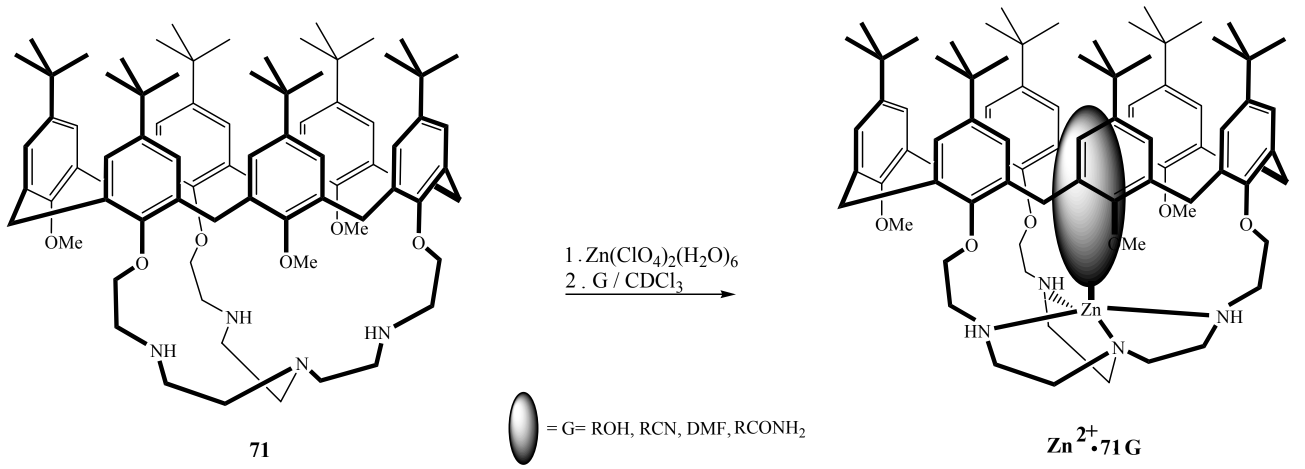
In calix[6]tren **71** the cone conformation is restricted by presence of the tren cap. The calix[6]tren **71** is an effective receptor with the cavity consisting of highly π-basic aromatic walls; the grid-like nitrogenous cap is also highly basic. The host properties of **71** can be tuned by the environment, more or less basic or by presence of metal ions. As a result, **71** may include cationic species such as metal ions or ammoniums as well as various neutral molecules. The reaction of **71** with $[Zn(ClO_4)_2(H_2O)_6$ and the guest G yields the complex Zn^{2+}·**71**·G. [104]

Complexes Zn^{2+}·**71**· G, where the guest G = ROH, RCN, DMF or $RCONH_2$ are highly resistant; the addition of AcOH, MeI, Et_3N or a strong base such as NBu_4OH does not result in deprotonation of the guest or decoordination of Zn^{2+}. This high robustness is due to both a strong chelate effect of the tren cap and a cavity-controlled access to the metal center.




Zn[(H2O)6(ClO4)2 /MeOH
Zn[(H2O)6(ClO4)2/MeOH/KOH
H2N
NH2
NH2
63
Me
OH
+ ClO4−
NH2
H2N
NH2
Zn
ClO4
66
3+ 3ClO4−
Me
OH
NH2
H2N
NH2
Zn
OH
Zn
H2N
NH2
NH2
OH
Me
67


65
Zn2+
3+
H2N
H2N
NH2
Zn
OH
Zn
H2N
NH2
NH2
68
XH/TEA
X= PhCOO, AcO, MeSO2NH
+
H2N
H2N
NH2
Zn
X
69
RNH2/TFA
RNH2 = PrNH2 , BuNH2
2+
H2N
H2N
NH2
Zn
RNH2
70
= G = polar neutral guest



71

Zn^{2+}•71 G

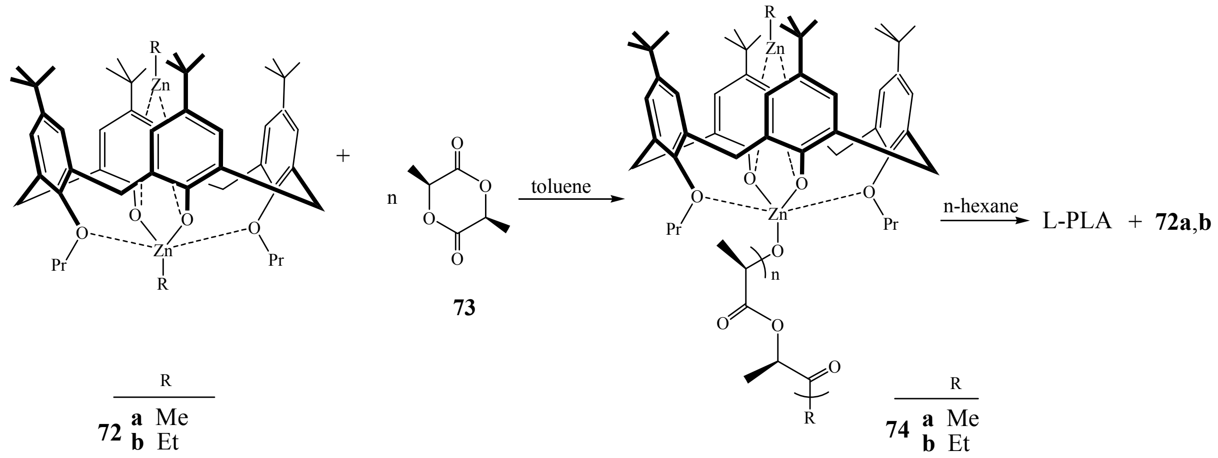
Scheme 6

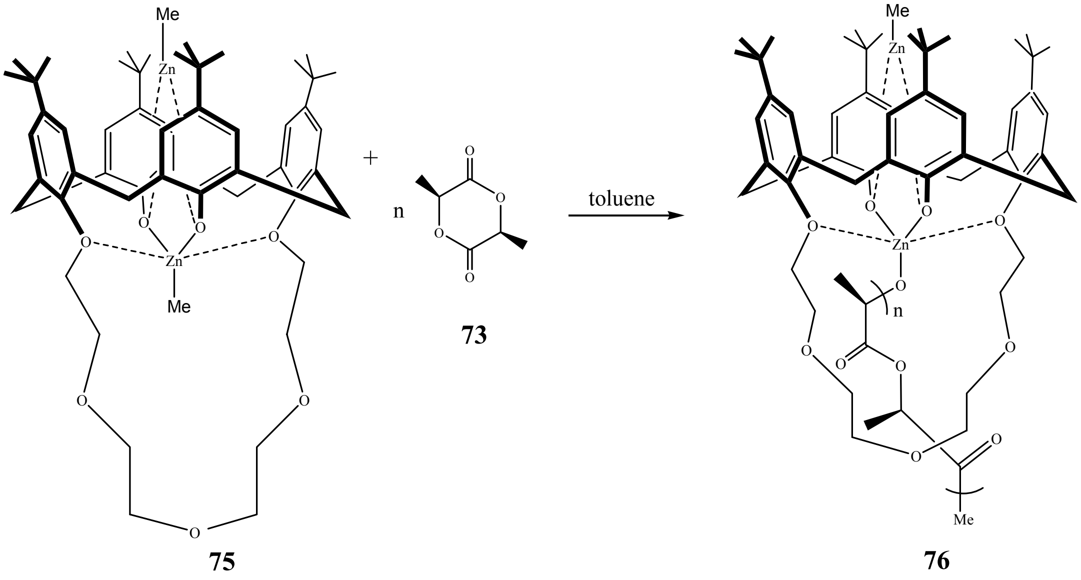
Bimetallic zinc complexes are of interest in catalytic processes involving asymmetric organic syntheses and enzymatic reactions. Bimetallic zinc complexes usually act as catalysts in organic and enzymatic processes by a tandem participation of both zinc atoms. The catalytic activity of calixarenes containing two zinc centres in close proximity to each other, has been studied. [111] For this purpose bimetallic zinc complex **72a** was used as a catalyst of the ring-opening polymerization of L-lactide **73**. The reaction leads to complex **74a** which by precipitation with *n*-hexane affords poly(lactic acid) PLA and free **72a**. In this process PLA with high molecular weight and a low degree of polydispersity is obtained; it was observed that the catalytic activity of **72b** is higher than that of **72a**. It should be pointed out that PLA is a polymer promising for its biocompatible and biodegradable properties.

It was established that the catalytic activity of **72** depends only on the external alkyl zinc group serving as an initiator, and is independent on the alkyl zinc group situated inside the calixarene cavity; this zinc atom, immersed in the calixarene cavity does not participate in catalysis. The above results are an example of the single-site catalytic mechanism of a bimetallic zinc calixarene complex. [111,112] It should be noted that the calixcrown bimetallic zinc complex **75** also catalyzes ring-opening polymerization of L-lactide to give the complex **76**; this process is a confirmation of the zinc single-site catalytic mechanism.

The reaction of the bimetallic zinc complex **77** with $B(C_6F_5)_3$ in benzene, followed by the addition of a bidentate ligand L, such as bipyridine or phenanthroline affords bimetallic complexes **78**, whereas upon treatment with wet trifluoroborane etherate the monometallic complex **79** is formed. [113,114]

The single-crystal X-ray analysis of **79**, obtained from the toluene solution, shows that Zn^{2+} is situated at the centre of an octahedron, with four calixarene oxygen atoms in the equatorial plane. Two water molecules are localized at axial positions, one of them being immersed in the calixarene cavity.


R
Zn
O
O
O
O
Zn
R
Pr
Pr
+
n
O
O
O
O
73
toluene
R
Zn
O
O
O
O
Zn
O
n
O
O
O
O
R
Pr
Pr
n-hexane
L-PLA + 72a,b
R
72 a Me
b Et
R
74 a Me
b Et


Me
Zn
O
O
O
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Zn
Me
O
O
O
75
+
n
O
O
O
O
73
toluene
Me
Zn
O
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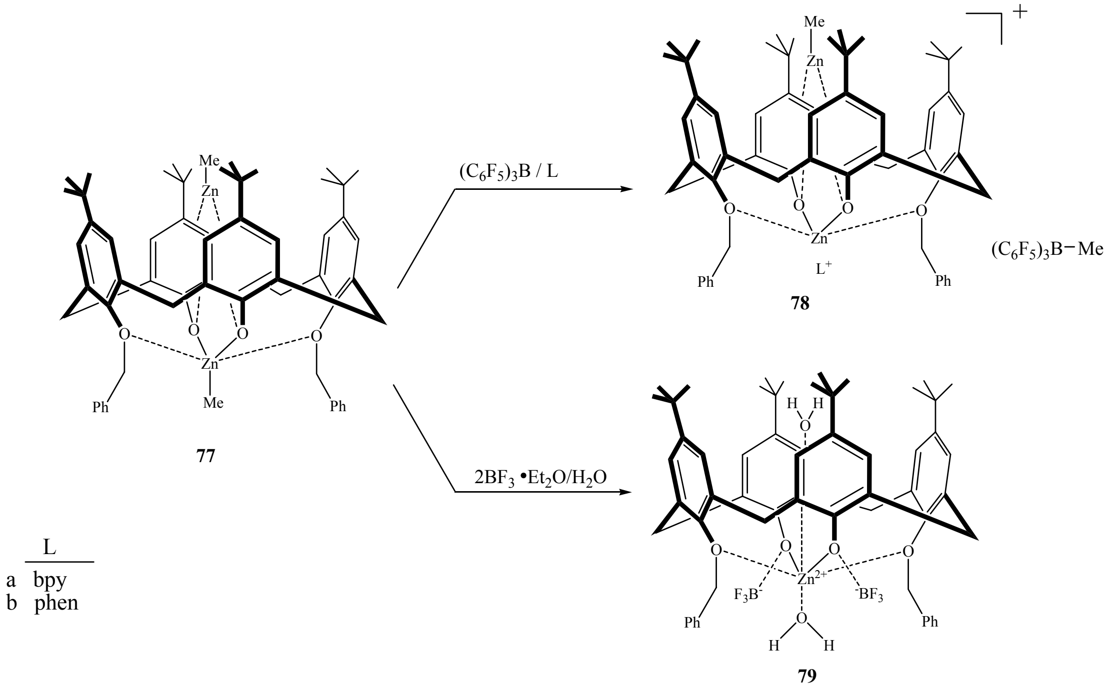
O
Zn
O
n
O
O
O
O
O
O
O
Me
76



Scheme 7

5. Calixarene complexes with cadmium ions

Cadmium is used in industry, *e.g.* in the production of pigments and anticorrosive coatings, alloys and batteries; due to the presence in natural waters, its determination with the use of simple, disposable devices is necessary. Cadmium is toxic to plants and humans, its toxicity involves the strong affinity to thiol groups, displacing the biologically important zinc. [115] Examples of works dealing with calixarene cadmium complexes [49] are described below.

In the study of calix[5]arenes, [116-119] the complexing properties of calix[5]arene **80b** with metal ions have been determined. The complexation of calix[5]arene **80b** with Cd^{2+} and Hg^{2+} ions was investigated by conductometric titrations in methanol and in acetonitrile; it was found that 1:1 complexes are formed, the binding constant of Hg^{2+} complex being higher than that of the Cd^{2+} complex. [120] It is noteworthy that analogous tetrameric calix[4]arene **80a** shows more efficient binding ability than **80b** towards Cd^{2+} and Hg^{2+} ions. [120]

In the search for cadmium sensors it was found that calixarenes **81** and **82** may serve for modification of screen-printed carbon electrodes for complexation of Cd^{2+} traces at open circuit. [115] It should be noted that **82** has higher configurational stability than **81**, since **82** contains *t*-butyl substituents at the wide rim, and ethylthio substituents at the narrow rim, therefore **82** has greater propensity to the cone conformation. Since **81** does not bear these groups, it may move through the four possible conformations, *i.e.* cone, partial cone, 1,2- and 1,3-alternate.

The screen-printed carbon electrodes modified with **81** and **82** are able to accumulate Cd^{2+} ions; the better results have been obtained in the case of **82**. It should be noted that the screen-printed sensor modified with **82** may be used for the trace determination of Cd^{2+} in environmental water samples. [115]

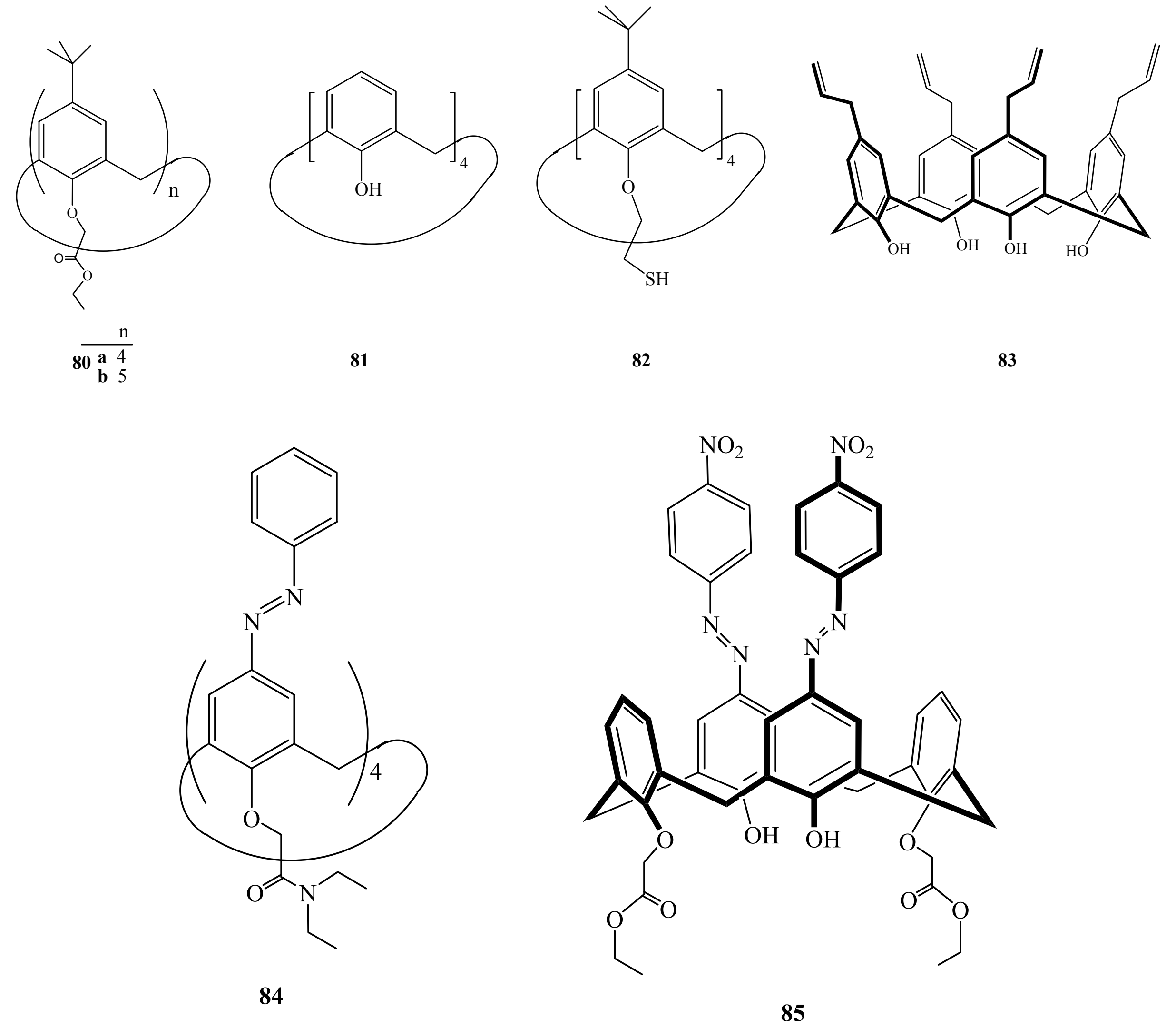
It was found that calixarene **83**, bearing four allyl groups includes Cd^{2+} and Tl^{+} ions. [121] This behavior served for building of glassy carbon electrode coated with Langmuir-Blodgett (LB) film of **83**, able to simultaneous determination of traces of Cd^{2+} and Tl^{+} in environmental water; indium does not respond to the above LB film electrode.

The method involves chelation of metal ions from solution on the surface of glassy carbon electrode coated with **83**, reduction of the accumulated metal ions and electrochemical stripping of the reductive material back into solution. The electrode can be used to simultaneous determination of Cd^{2+} and Tl^{+} . This process is explained by hard soft acid and base (HSAB) principle, Cd^{2+} and Tl^{+} ions being soft acids, and allyl group and benzene ring being soft bases. It should be pointed out that the above electrode is environment friendly since it replaces current mercure electrode in environmental analysis.

The chromogenic calixarene **84** containing four azo groups may serve for detection of Cd^{2+} and Cu^{2+} ions, for this purpose the optical fiber sensor based on **84** has been built. [122] The detection of the above ions involves the covering of the optical fiber core by a transparent polymer containing a complexing agent; its absorption properties are modified in the presence of the considered ions. The trapping of the ion in the polymeric cladding, *i.e.* in the cavities of the chelating molecules induces a variation of the light power transmitted along the fiber.

The detection of metal ions by optical fiber is advantageous as compared to that performed by use of electrochemical techniques, since the probe is miniaturized and no effects of the ionic strength nor of the medium conductivity occur. The method is simple, the detection is done *in situ*, at ambient temperature and under atmospheric pressure; only source of light, optical fiber and detector are required. [122]

Complexing properties of chromogenic calixarene **85**, bearing two azo moieties towards Cd^{2+} ion has been studied by UV/Vis spectroscopy. The formation of the complex occurs in polar solvents like acetonitrile, acetone, methanol and DMF, but not in less polar solvents like $CHCl_3$ or THF. The most suitable solvent showed to be acetonitrile, ensuring efficient complexation without formation of aggregates. The obtained complexes have 1:1 stoichiometry. [123]



Scheme 8

6. Calixarene complexes with mercury ions

Mercury is a toxic metal dangerous for human health, its contamination is widespread in the environment. Mercury pollution arises from gold mining and combustion of fossil fuels, as well as from volcanic emissions. A growing attention is paid today to the detection of mercuric ion in the environment and in biological samples.[124] Calixarene complexes with mercury ions are a topic of numerous works. [71,125,126]

It was observed that thiohexyl oligophenylene substituted calixarenes **86a**,**b** form 1:1 complexes with Hg^{2+} and with Ag^{+} ions. The association constants were estimated by use of fluorescent titrations in $CHCl_3$/MeOH, this value for Hg^{2+}·**86a** being higher than that for

Hg^{2+}·**86b**. [127] The ^1H NMR spectroscopy results show that Hg^{2+} or Ag^+ ion is cooperatively bound by the two opposite sulfur atoms of **86a** leading to conformationally stable pinched cone structure. It is noteworthy that the binding affinities of **86a**,**b** toward Hg^{2+} and Ag^{2+} ions are stronger than those of the corresponding monomeric units due to the cooperation effect of the proximate fluoroionophores.

In the study of complexing properties of calixarenes bearing two dansyl groups it was observed that **87** is sensitive towards Hg^{2+} ions and exhibits high selectivity. Having in view these properties of **87**, its analogue **88**, showing an additional grafting ability on the silica surface was designed.

In order to build an optical sensor device, calixarene **88** was grafted on SBA-15 mesoporous silica and the fluorescence properties of the obtained material **88·SBA-15** have been investigated. [128] The detection limit is determined by a strong quenching of fluorescence upon the Hg^{2+} complexation. It was established that **88·SBA-15** reversibly detects Hg^{2+} ions in water and does not interfere with K^+, Ca^{2+}, Zn^{2+} and Cd^{2+} ions; it should be pointed out that the response is rapid.

It was found that the complexing ability of calixarene **89** toward metal cations is higher in MeCN than in DMF and MeOH. In MeCN **89** recognizes Hg^{2+} over Li^+, Na^+, Ag^+, Ca^{2+}, Cu^{2+} and Pb^{2+} ions, while in DMF and in MeOH **89** interacts only with Hg^{2+} and Ag^+. In all cases the 1:1 complexes are formed. [129]

The study of the strength of complexation of **89** with Hg^{2+} and Ag^+ in dependence of solvent has shown that for **89** and Hg^{2+} the strength of complexation decreases in the order MeCN > DMF > MeOH while for **89** and Ag^+ this sequence is MeOH > DMF > MeCN. Due to the inclusion of MeCN in the hydrophobic cavity of **89**, the hydrophilic cavity of the resulting complex **89**·MeCN becomes more receptive to include metal cations than the cavity of free **89**; this behavior results from the allosteric effect. [129]

One should mention that in MeCN **89** does not include Cd^{2+} ion, while **80a** does; this behavior is explained by the fact that the cavity of **80a** is larger than that of **89** due to higher electrostatic repulsion of pendant arms of **80a** resulting from the presence of four carbonyl groups, therefore the cavity of **80a** is more open and, as a result, more able to receive Cd^{2+} ion than the cavity of **89**. [129]

The complexation of calixarenes **89** and **90** toward Hg^{2+} and Ag^+ ions in a series of solvents have been investigated. The obtained thermodynamic data were used to assess the effect of solvation of these compounds on their complexing properties. [98,130]

Solubilities and derived Gibbs energies of solutions of **89** and **90** in various solvents have been reported. Solvation of **89** and **90** in one medium relative to another was analyzed from their standard transfer Gibbs energies using acetonitrile as the reference solvent. The standard solution enthalpies were determined for mercury and silver salts in acetonitrile, methanol and DMF. These data have been used to derive their transfer enthalpies from one medium to another.

It was found that the extent of complexation of **89** and **90** with metal cations in different media is not only controlled by the solvation changes of the free cation in various solvents, but also is controlled by the solvation of the ligand and of the metal-ion complex in these solvents. The selectivity of **90** for Hg^{2+} relative to Ag^+ in MeCN is reversed in MeOH and lost in DMF.

Solubility data were used to calculate the standard Gibbs energies of solution. For **89** the strength of solvation decreases in the order: *n*-BuOH > DMF > EtOH > MeCN > PC > MeOH. For **90** this sequence is as follows: *n*-BuOH > DMF > MeCN > EtOH > PC > MeOH (PC = propylene carbonate).It was found that the solvation of **89** is higher than that of **90**. [130]

In the study of calixarenes bearing arylazo and allyl groups at the wide rim, forming complexes with transition metal ions it was found that **91** – **93** show metal-chelating properties. Calixarenes **91a**-**93b** are very good chromogenic ionophores, especially for Hg^{2+}; the complexation of Hg^{2+} by **91b**-**93b** in methanol/chloroform is visible to the naked eye. [131,132] The narrow rim modification of **91b,c** affords chromoionophores **94b**,**c** which may also be used in metal ion detection. [131] One should mention that synthesized in the reported work compounds **92-94** are colored (**92a**, **93a** orange; **92b**, **93b**, **94b** yellow and **92c**, **94c** red).

The stoichiometry of complexes of all above calixarenes with metal ions was shown to be 1:1. Calixarene **91b** forms with Hg^{2+} the complex Hg^{2+}·**91b**. The binding strength of the investigated calixarenes toward Hg^{2+} decreases in the order **91b** > **91a** > **93b** > **92b** > **93a** ~ **92a** > **94b** >> **91c**. The selectivity of **91b** toward cations decreases in the order $Hg^{2+} > Cu^{2+} > Cr^{3+} > Ni^{2+}$.

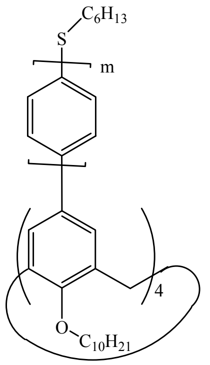
Calixarenes **95-98** are yellow; they form 1: 1 complexes with Hg^{2+} ion, this process being connected with color changes. The association constants of investigated receptors with Hg^{2+} decrease in the order **95**>**96**>**97a**>**98a**. [133] The *p*-allyl and *p*-methoxyphenylazo groups take part in the recognition of Hg^{2+} ion; calixarene **95**, containing three *p*-methoxyphenylazo groups binds Hg^{2+} stronger than **96** containing two *p*-methoxyphenylazo groups, as it is seen in the association constant of **95** higher than that of **96**. Calixarenes **95** and **96** have one and two allyl groups, respectively, whereas **97a** and **98a** have one and two thioacetoxypropyl groups, respectively, therefore the binding of Hg^{2+} ion by **95** and **96** is stronger than in the case of **96a** and **98a**. The possible binding modes for **Hg^{2+}·95** and **Hg^{2+}·96** have been proposed.

Among numerous techniques for Hg^{2+} screening, the fluorescent chemosensors are receiving recently a considerable attention due to their selectivity and simple construction. [134-137] Fluorescent chemosensors are mainly based on photoinduced electron transfer (PET), metal-ligand charge transfer (MLCT), intramolecular charge transfer (ICT), [138,139] excimer/exciplex formation,[140,141] imine isomerisation [142] and fluorescence resonance energy transfer (FRET). [143,144]

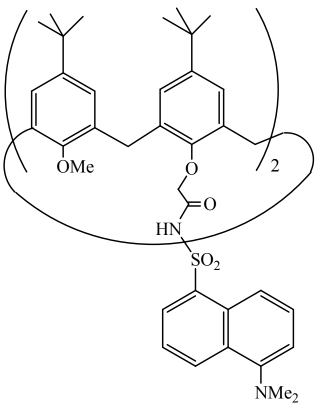
It should be pointed out that FRET is today of a great interest for possibility of its use in optical therapy and in cell physiology, as well as in a selective sensing toward molecular or ionic species. [145] FRET is an excited-state energy interaction between two fluorophores in which an excited energy donor transfers energy to an energy acceptor without photoemission. Many chemosensors are based on a FRET signal mechanism. [143,144]

In the study of calixarenes acting as chemosensors towards cations and anions, a calixarene-based chemosensor **99** which functions as Hg^{2+}-induced FRET from the pyrenyl excimer (energy donor) to rhodamine unit (energy acceptor) was reported.[124,146,147] Chemosensor **99** is a *N*-tripodal species consisting of two calixarene units, each bearing one pyrenyl group and a rhodamine B unit in a spirolactam form. The pyrenyl groups of neighboring calixarene units are planar, involving a π-π stacking interaction between them. The calixarene units of **99** are flexible, this fact can easily lead to the excimer emission. The excimer emission of pyrenyl and the fluorescence absorption of ring-opened rhodamine have a spectral overlap enabling the functionality of **99** as a FRET chemosensor if the pyrenyl unit is excited.

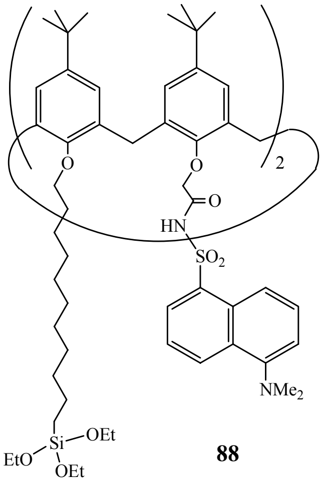
Addition of Hg^{2+} ion to the MeCN solution of **99** leads to the ring opening of the rhodamine spirolactam moieties with a FRET−*ON* signal mechanism and the energy transfer from pyrenyl excimer (energy donor) to rhodamine (energy acceptor). It is noteworthy that in the absence of Hg^{2+} ion, the energy transfer is impossible due to the spirolactam structure of the rhodamine unit (FRET−*OFF)*. Addition of Hg^{2+} to the solution of **99** results in the formation of the 1:1 complex **Hg^{2+}·99** and in a considerably enhanced fluorescence emission (FRET−*ON*). [124]



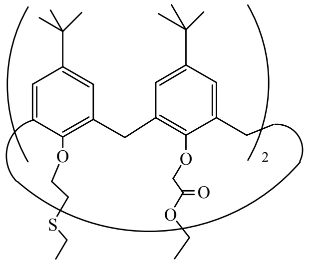
	m
86 a	2
b	3



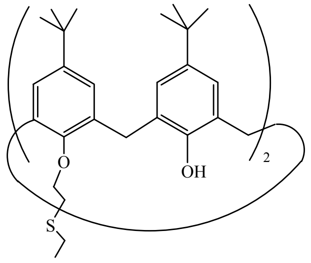
87



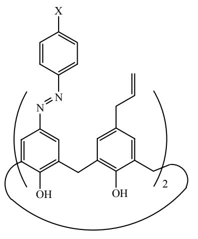
88



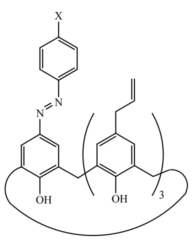
89



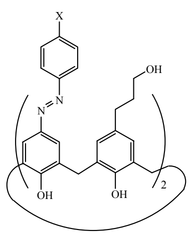
90



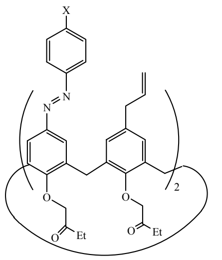
		X
91	**a**	H
	b	OMe
	c	NO_2



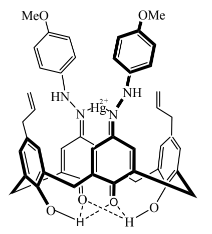
		X
92	**a**	H
	b	OMe
	c	NO_2



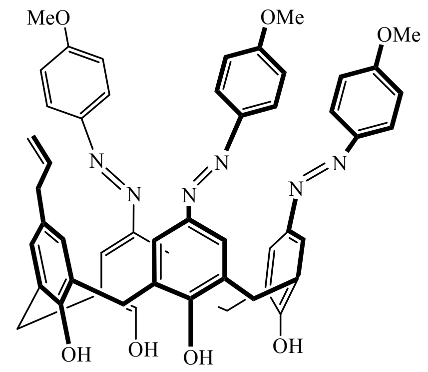
		X
93	**a**	H
	b	OMe



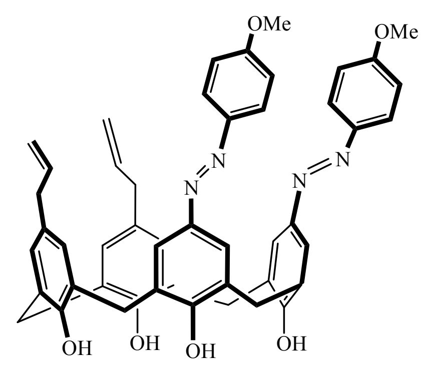
		X
94	**b**	OMe
	c	NO_2



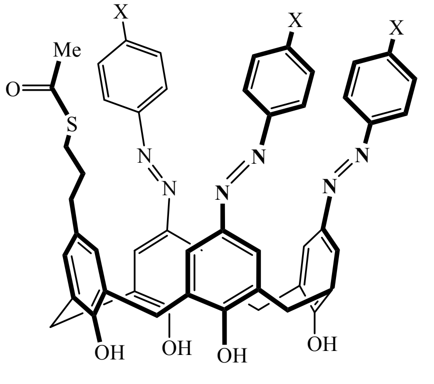
Hg^{2+} • **91b**



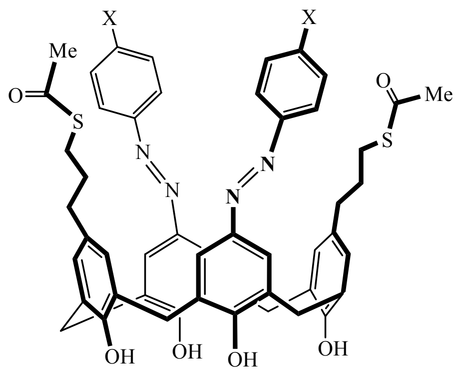
95



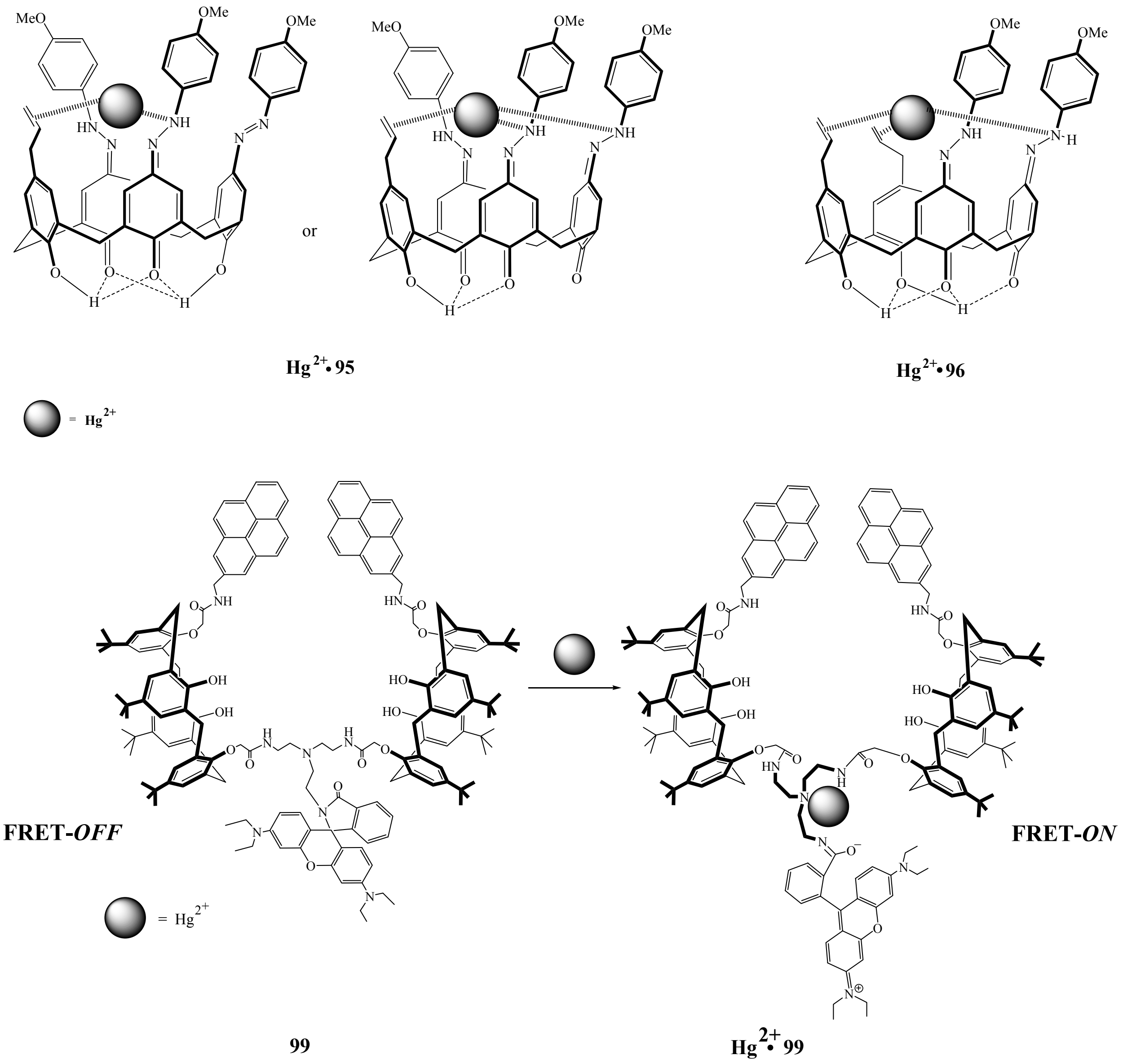
96



		X
97	**a**	OMe
	b	H



		X
98	**a**	OMe
	b	H



Scheme 9

Conclusions and future outlook

The above review, albeit describing only selected examples, sheds some light on the chemistry of calixarene metal complexes. This field of science develops rapidly due to promising properties of such complexes in chemistry as well as in other research areas; [148-154] here their use as sensors for metal ions[26,27] and as catalysts [22] deserves a special attention. One should point out formation of calixarene complexes with lanthanides [155-157] and actinides [158-160] in view of the importance of radioactive waste disposal for the environmental protection. Due to the technical progress, one may expect that the work concerning complexation of calixarenes with metal ions will develop so from the theoretical and practical viewpoints.

Acknowledgements

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