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ORIGINAL ARTICLE

Calixarene complexes with metal ions

Wanda Sliwa · Tomasz Girek

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Abstract Selected complexes of metal ions are presented showing their syntheses and possible applications, an attention was paid to their usefulness in chemosensors design and in the environmental protection.

Keywords Actinides · Alkali metal ions · Alkaline earth metal ions · Complexation · Lanthanides

Introduction

Chemistry of calixarenes is today a focus of an intense research [1–6]. They belong to macrocyclic receptors, besides calixarenes encompassing cyclodextrins [7–9] and cucurbiturils [10–12].

The family of calixarene receptors includes also resorcinarenes [13] and pyrogallolarenes [14], as well as related compounds—cavitands [15, 16], dimeric [17, 18] and hexameric [19, 20] capsules and nanotubes [21]. One should mention also calixpyrroles [22, 23] and calixquinones [24, 25], as well as calixarene analogues, i.e. thiacalixarenes [26], oxacalixarenes [27] and azacalixarenes [28]. Calixarenes are building blocks for structures of supramolecular chemistry, the rapidly developing research area [29, 30]. It is noteworthy that calixarenes are synthesized from simple starting materials and their functionalization is not difficult.

Inclusion properties of calixarenes are their important feature, they may accomodate ionic and neutral species, among them a growing attention is paid now to complexes of metal ions [31–33]. These complexes are promising in the detection and removal of heavy metal ions from environment [34], as well as in the treatment of nuclear wastes, especially having in view the separation of cesium [35] and of actinides [36]. The application of calixarene metal complexes in the elucidation of enzymatic processes is also worthnoting [37]. It should be mentioned that metal complexes with other macrocyclic receptors, such as cyclodextrins also deserve an attention [38, 39].

The present review is connected with our papers dealing with calixarenes and related compounds [40–42] and is a continuation of our former articles concerning calixarene complexes with transition metal ions [43, 44] and with soft metal ions [45]; calixarene complexes with metal ions are described in [6] up to 2007. In the review the references are cited up to 2008. Since the number of reports concerning calixarene complexes with metal ions is enormous, only selected examples are given.

The following complexes are described in the present review:

(1) Calixarene complexes with alkali metal ions
(2) Calixarene complexes with alkaline earth metal ions
(3) Calixarene complexes with copper and zinc ions
(4) Calixarene complexes with silver, cadmium, mercury and lead ions
(5) Calixarene complexes with rhodium, palladium, lanthanide and actinide ions
(6) Calixarene complexes with metal ions and anions.

Calixarene complexes with alkali metal ions

Numerous works concern calixarene complexes with alkali metal ions [46, 47]; some examples will be shown here.

W. Sliwa (✉) · T. Girek
Institute of Chemistry and Environmental Protection, Jan Długosz University of Częstochowa, Armii Krajowej Ave 13/15, 42-201 Czestochowa, Poland
e-mail: w.sliwa@ajd.czest.pl

The complexation properties of calixarenes **1a**–**g** toward alkali metal cations have been investigated, among them calixarenes **1f** and **1g**, each substituted by four identical groups, served for comparison purposes. In experiments the alkali metal picrates were extracted from water into dichloromethane [48].

Study of stability constants of alkali metal complexes of **1a**–**g** in acetonitrile has shown that **1f** binds only Li^+ and Na^+ ions, the Li^+ complex being more stable than the Na^+ complex. Calixarene **1g** binds all alkali metal cations except Cs^+; **1g** forms with small cations Li^+ and Na^+ the ML_2 complexes while with large cations K^+ and Rb^+ the ML complexes are obtained (M and L denote metal ion and calixarene, respectively). Calixarene **1b** forms ML complexes with all alkali metal ions, except for Cs^+, and is selective for Na^+.

Calixarene **1e** affords stable ML complexes with all alkali metal cations; they are accompanied by ML_2 complexes in the case of Li^+ and Na^+. The ML_2 complex for Li^+ is more stable than that for Na^+. It was observed that **1e** is selective for Li^+. The performed experiments show that the ML complexes are more stable than ML_2.

One may conclude that the order of decreasing complexing properties with alkali metal ions is: calixarenes with ester groups > calixarenes with methyl groups > calixarenes with benzyl groups. The enthalpies and entropies of complexation of alkali metal ions by **1a**–**g** have been obtained using calorimetric measurements. It was established that the formation of ML complexes is enthalpically controlled, while the formation of ML_2 from ML is entropy driven.

Sulfonatocalixarene **2** forms with strongly fluorescent diazabicyclooctene **3** in aqueous solution the inclusion complex **2**·**3**. The complexation of **3** results in quenching of its fluorescence. It was observed that upon addition of Na^+, Mg^{2+} or La^{3+} ions, the displacement of **3** occurs, leading to formation of the **metal/2** complex, and release of **3**; this behavior is connected with the regeneration of fluorescence of **3** and is promising as a method to sensitively monitor and quantify the binding of metal ions by **2** in aqueous solutions [49].

Calixcrowns **4a**–**e** which are 1,2-bridged by thiacrown ether unit have been synthesized for investigation of their metal ion binding properties; for comparison purposes their oxa analogues **5a**–**e** were used. The efficiency and selectivity of **4a**–**e** were assessed for competitive solvent extractions of alkali metal ions and alkaline earth metal ions from aqueous solutions into chloroform [50]. It should be pointed out that 1,2-bridged calixcrowns are less common than 1,3-bridged species, the former ones being more difficult to synthesize.

Aqueous solutions of Li^+, Na^+, K^+, Rb^+ and Cs^+ chlorides were extracted with solutions of **4a**–**e** in chloroform. In these experiments the 1:1 metal ion/calixcrown complexes were formed. It was observed that **4a**,**b**,**e** are Na^+ selective, whereas **4c**,**d** are Li^+ selective. The comparison of **4a**–**e** and **5a**–**e** series shows that **4a** extracts Li^+ more efficiently than **5a**, this fact being opposite to expectation that the hard Li^+ ion should be more efficiently extracted by hard oxygen atoms of **5a** (Scheme 1).

Complexing properties of the fluorescent sensor **6** for potassium ion consisting of 1,3-alt calix[4]bisazacrown-5 as an ionophore and of two moieties of boron-dipyrromethene dye (BODIPY) as fluorophores have been investigated. It was observed that an efficient CT process occurring in **6** in the excited state in solvents of medium or high polarity leads to a strong quenching of fluorescence. This CT process can be hampered by cation complexation, resulting in a considerable fluorescence enhancement; when two cations are coordinated, the enhancement is stronger [51].

The stability constants of complexes of **6** with Na^+, K^+, Cs^+, Ca^{2+} and Ba^{2+} ions were determined. The sensor **6** has two azacrown-5 ether binding sites, well fitting the K^+ ion and therefore shows a very high K^+/Na^+ selectivity in acetonitrile, ethanol and ethanol/water mixtures; **6** is also selective for K^+ over other metal ions. It is noteworthy that the high K^+/Na^+ selectivity is valuable for use of **6** as a K^+ sensor in analytical tests under physiological conditions.

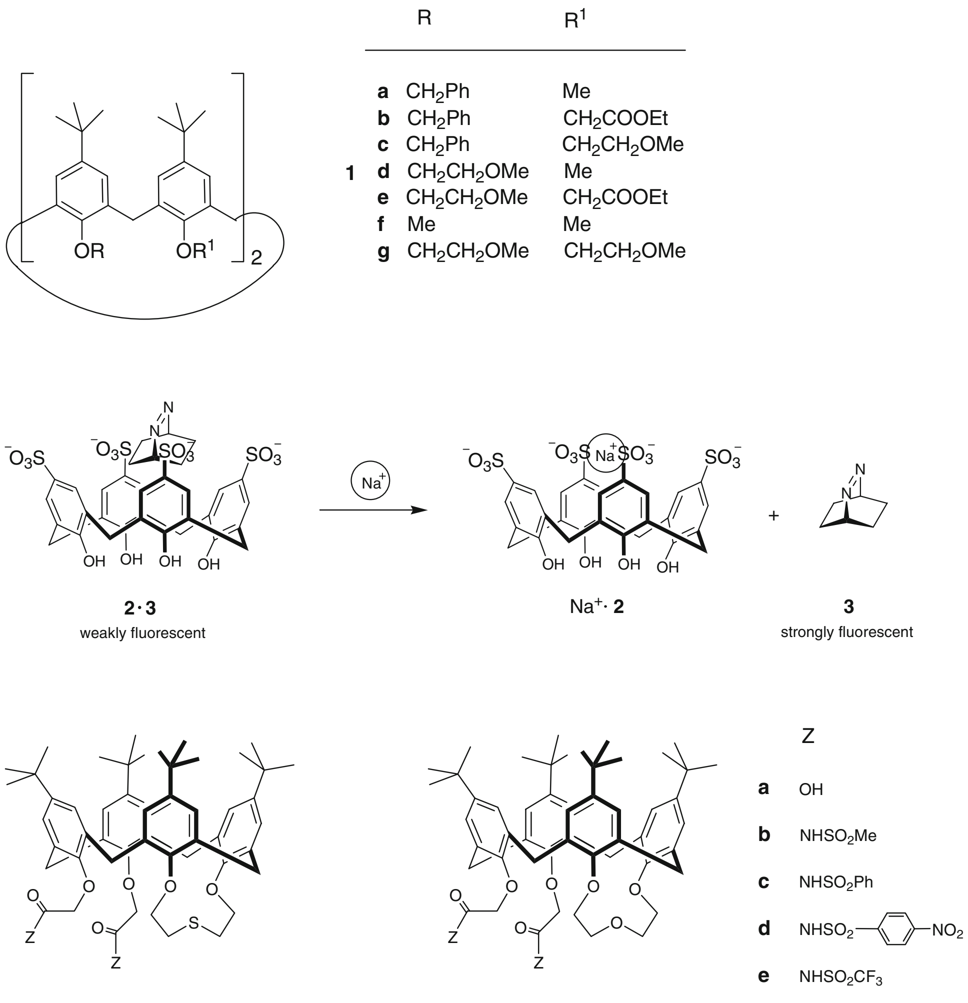
The reaction of 1,3-alt calixarene **7** with either rubidium or cesium hydroxide in water affords the nanocapsule structure. It was observed that the formed three-dimensional networks of nanocapsules interpenetrate with one another.

Crystals of rubidium complex have trigonal symmetry. The asymmetric unit contains two molecules of **7**; each of the resulting pseudo cavities is occupied by a rubidium centre coordinating to methoxy groups and phenyl rings of calixarenes. The rubidium centres are coordinated to three of the six aromatic carbon atoms of phenyl rings. Crystals of cesium complex have the cubic symmetry [52].

The properties of alkali metal binding of 3,6-*syn* and 3,6-*anti* isomers of calix[6]-biscrown **8** were studied using the metal picrate extraction method, i.e. aqueous solutions of the picrate salts were shaken with chloroform solutions of receptors. It was found that *syn*- and *anti*-**8** have high extraction ability and selectivity toward Cs^+, the Cs^+/Na^+ selectivity of *syn*-**8** being higher than that of *anti*-**8** [53] (Scheme 2).

The calixcrown **9** may be covalently attached to Au (111) chips, forming well ordered SAMs (self assembled monolayers) as it was shown by polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS). These SAMs may be used to determine trace amounts of Cs^+ or other metal ions by Fourier transform-surface plasmon resonance (FT-SPR)-based techniques; the method is simple and fast [54].

Scheme 1 Structures of compounds **1**–**5**



		R	R^1
1	**a**	CH_2Ph	Me
	b	CH_2Ph	CH_2COOEt
	c	CH_2Ph	CH_2CH_2OMe
	d	CH_2CH_2OMe	Me
	e	CH_2CH_2OMe	CH_2COOEt
	f	Me	Me
	g	CH_2CH_2OMe	CH_2CH_2OMe

2·3
weakly fluorescent

Na^+·2

3
strongly fluorescent

	Z
a	OH
b	$NHSO_2Me$
c	$NHSO_2Ph$
d	$NHSO_2-C_6H_4-NO_2$
e	$NHSO_2CF_3$

4

5

In the study of binding properties of 1,3-alt calix-bis-crown **10** which was designed originally for selective separation of Cs^+ from other alkali metals it was found that **10** shows high affinity for Tl^+ as compared with that for Cs^+ and Rb^+ [55]. Thallium compounds are widely used in technology and medicine despite of their strong toxicity, therefore detection and removal of Tl^+ ions is of a great importance.

The 1,3-alt calix-biscrowns are able to π-coordinate metal ions; they contain oxygen atoms able to bind hard cations and they have π-basic aromatic cavity which may bind soft electron acceptors. Therefore **10** may serve as a receptor for Cs^+ and for Tl^+ ions. The higher extraction efficiency of **10** toward Tl^+ as compared to alkali metal ions is due to the strong ability of Tl^+ for cation-π coordination with aromatic framework of **10**. The formation of complexes **Tl^+·10** and **Cs^+·10** has been established.

Extraction of thallium picrate from aqueous solutions into chloroform was made; for comparison also Li^+, Na^+, K^+, Rb^+ and Cs^+, as well as Ag^+ picrates were used in the experiments. The extraction efficiency of **10** decreases in the order $Tl^+ > Cs^+ > Rb^+$; for Li^+, Na^+, K^+ and Ag^+ ions the extraction efficiency is considerably lower.

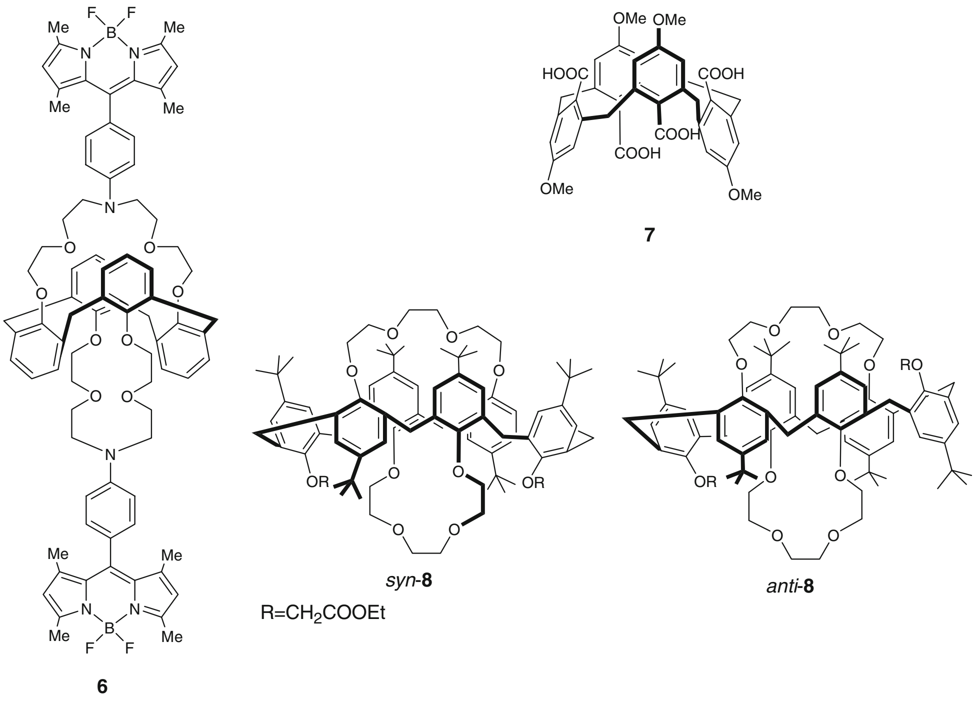
One should also mention here that calixbiscrown **11** bearing dansyl group as a fluorophore may serve as a fluorescent chemosensor for Tl^+; the fluorescence of **11** decreases upon complexation of Tl^+. The optical recognition of thallium by **11** shows selectivity over Na^+, K^+, Ca^{2+}, Ag^+, Hg^{2+} and Pb^{2+} ions [56] (Scheme 3).

Calixarene complexes with alkaline earth metal ions

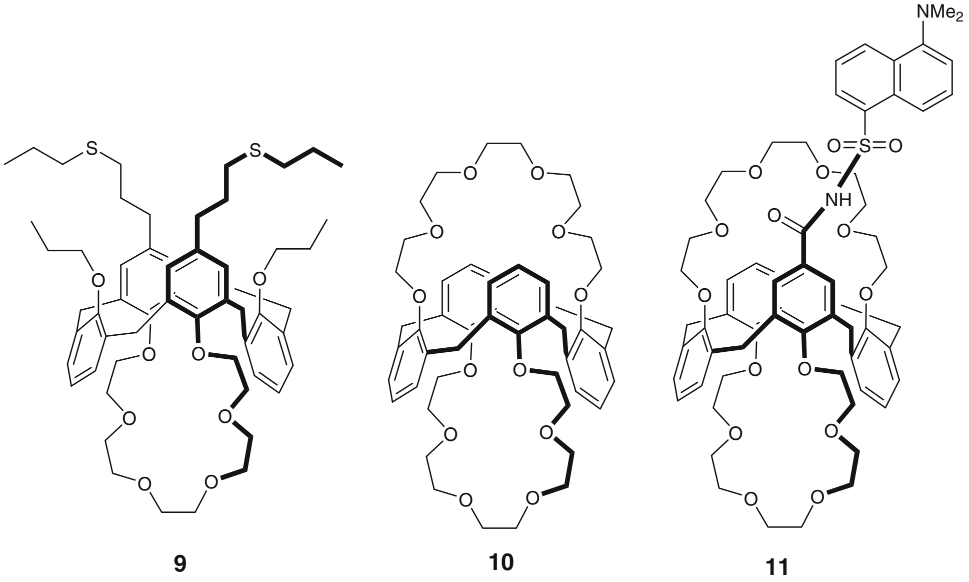
In the study of calixcrown complexes with alkaline earth metal ions [57, 58] it was found that cone, paco and 1,3 alt calixcrowns **12** extract alkaline earth metal ions from aqueous solutions into chloroform; the extraction efficiency decreases in their conformation order: cone ≫ 1,3-alt ≫ paco. For cone and 1,3-alt conformations the selectivity for Ba^{2+} was observed [59].

Investigation of **4a**–**e** and **5a**–**e** series has revealed the following extraction selectivity of **4a**: $Ca^{2+} > Ba^{2+} >$

Scheme 2 Structures of compounds **6–8**



Scheme 3 Structures of compounds **9–11**



$Mg^{2+} > Sr^{2+}$, however, in the case of **4b–e** for alkaline earth metals Ba^{2+} is the best extracted cation. It was observed that the selectivity of **4a–e** series among the alkaline earth metal ions is better than that of **5a–e** [50].

Calixarenes **1e**,**g** form 1:1 complexes with all alkaline earth metal ions, with a particular affinity for Ba^{2+}, while **1b**,**c** form 1:1 complexes with Ca^{2+}, Sr^{2+} and Ba^{2+}. In the case of **1e** the complex $\mathbf{Ca^{2+}{\cdot}(1e)_2}$ is also obtained, $\mathbf{Ca^{2+}{\cdot}1e}$ being stronger than $\mathbf{Ca^{2+}{\cdot}(1e)_2}$. Calixarene **1d** gives complexes only with Ca^{2+} and Sr^{2+} ions [48].

Photochromic properties of calixarene **13A** bearing two spiropyran groups were investigated. Upon UV irradiation of the colorless, closed spiropyran form **13A** the concentration of the colored, open merocyanine **13B** increases, whereas under dark conditions the concentration of the form **13A** increases. The process involves the thermal isomerization of colored form **13B** into the colorless form **13A** [60].

For elucidation of the thermal stability of the colored form **13B** in the presence and absence of metal ions, its thermal decoloration was studied. In **13**, the phenolic hydroxyl groups of calixarene provide the polar environment, profitable for stability of zwitterionic merocyanines.

Investigation of the first-order thermal decoloration rate constants has shown that the low rate constants indicate high stability of merocyanines. Addition of Mg^{2+}, Ca^{2+} or Eu^{3+} metal ions decreases these rate constants due to the complexation with metal ions, i.e. enhances stability of **13B**. Thermal decoloration was hardly observed in the presence of Eu^{3+}; the **Eu^{3+}·13B** complex is very stable. The stability of **metal ion·13B** merocyanine complexes decreases in order: **Eu^{3+}·13B > Mg^{2+}·13B > Ca^{2+}·13B**. Results of the above experiments reveal that **13** is promising for use in photochromic materials due to high stability of colored form **13B**.

By incorporating calixarene **14** as the ionophore in a PVC membrane, the highly selective and sensitive sensor for Ca^{2+} ion was obtained. Membrane of a composition **14**:NaTPB:PVC (2:2:120) showed the best performance, i.e. the widest working concentration range with a near Nernstian slope, the lowest response time and the satisfactory work in a partially non-aqueous medium, (NaTPB denotes tetraphenylborate) [61]. It should be mentioned that many ion selective Ca^{2+} sensors are known, however often they do not show a wide working concentration range or high selectivity, and their response time is long.

The selectivity investigation of the sensor, made with the fixed interference method showed that it is selective to Ca^{2+} over a large number of mono-, bi- and trivalent cations at pH 2.5–6.0. The sensor may work successfully in high-ionic-strength solutions, thus, with a variety of real samples, therefore it can be used for Ca^{2+} determination in the presence of other ions by direct potentiometry. It was established that the sensor may serve as an indicator electrode in the potentiometric titration of Ca^{2+} against EDTA.

In order to develop sensors for Ca^{2+} and Cu^{2+} ions, chemical field effect capacitors (Chem FECs) or Electrolyte-Insulator-Semiconductor (EIS) devices have been coated with calixarenes **15a–c**. The spin-coating method was used for deposition of thin calixarene **15a–c** layers on silicon nitride ($Si/SiO_2/Si_3N_4$) surfaces; the silicon nitride transducer showed to have better adhesion and better operational stability than silicon dioxide transducer.

The sensor responses resulted from the host–guest interaction between calixarene cavities and ions. The electrochemical capacitance measurements were carried out to evaluate the sensing properties of calixarenes **15a–c** towards Ca^{2+} and Cu^{2+} ions. It was found that the **15a** sensitive layer deposited on the silicon nitride substrate shows a high affinity toward Ca^{2+} ions [62].

The Chem FECs coated with **15b** and **15c** by spin-coating method, serving as Cu^{2+} sensors were compared to those prepared with thermal evaporation method. The results obtained for the both deposition procedures are comparable, however the spin-coating method is easier and simpler than the evaporation method (Scheme 4).

The fluorescent chemosensor consisting of calixarene **16** bearing BODIPY and Rhodamine units can selectively detect Ba^{2+} and Hg^{2+} ions. The FRET process between BODIPY (fluorescence donor) and Rhodamine units (fluorescence acceptor) in combination with the isomerization of two states of Rhodamine serves for modulation of the system (FRET = fluorescence resonance energy transfer). The BODIPY unit is linked to calix[4]arene via a crown-6 loop, able to bind effectively the main-group ions.

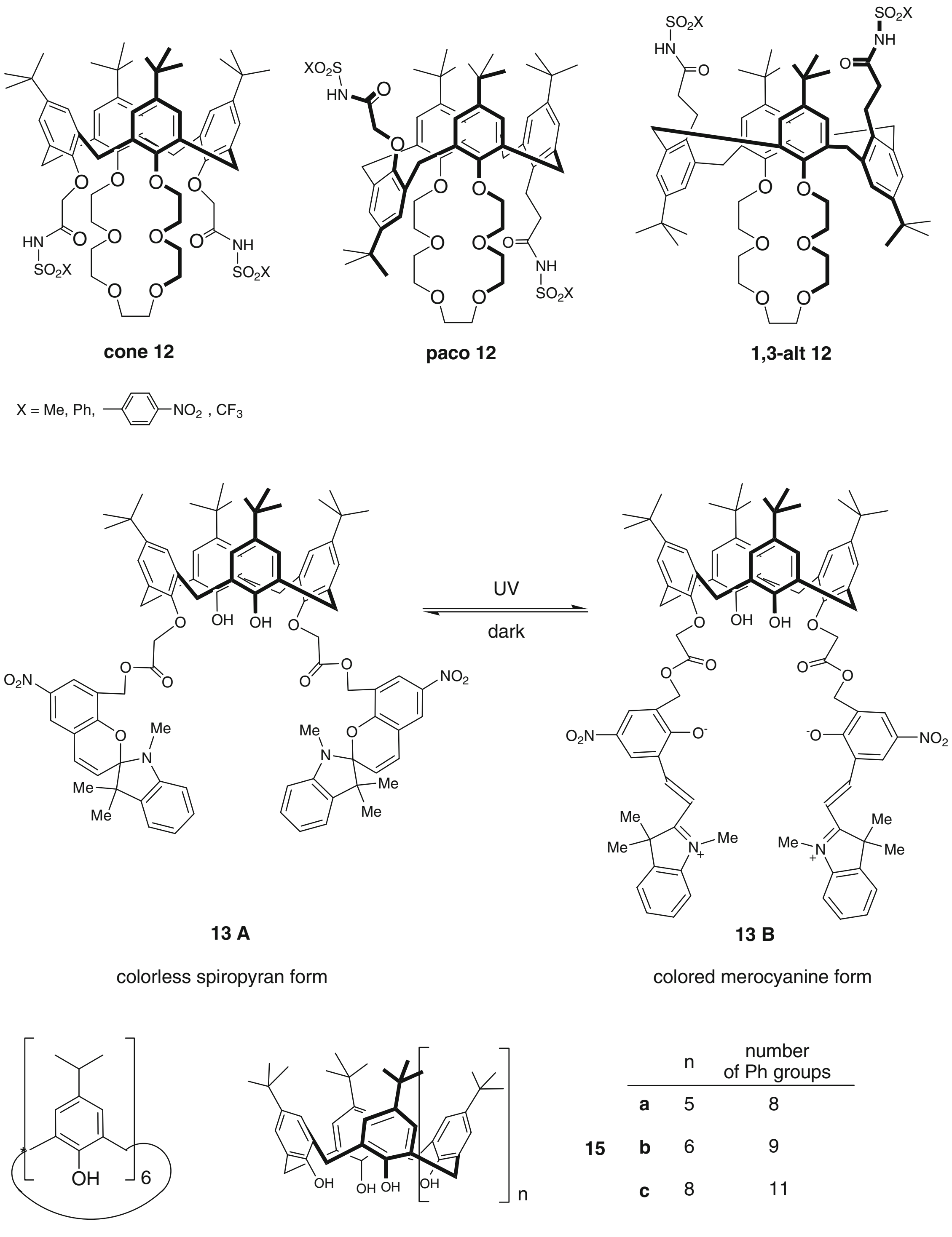
In **16**, the PET process occurs and BODIPY shows a weak fluorescence (PET denotes photoinduced electron transfer). Upon addition of Ba^{2+} ion to acetonitrile solution of **16**, the fluorescence of BODIPY is enhanced due to inclusion of Ba^{2+} ion by **16**. Therefore **16** can serve as a chemosensor for Ba^{2+}; it was established that the complex **Ba^{2+}·16** is formed.

Upon addition of Hg^{2+} ion to acetonitrile solution of **16**, the fluorescence of Rhodamine unit is enhanced due to isomerization of spirolactam Rhodamine to ring-opened form, entrapping Hg^{2+}; the FRET-ON process occurs. The absorption changes are visible to the naked eye (the yellow solution of **16** becomes red upon titration with Hg^{2+} ions). Therefore **16** can serve also as a “naked eye” chemosensor for Hg^{2+}; the formation of the complex **Hg^{2+}·16** was observed.

When the solution of the complex **metal ion·16** was treated with another metal ion (**Ba^{2+}·16** treated with Hg^{2+} ion, or **Hg^{2+}·16** treated with Ba^{2+} ion), PET is blocked, the complex **Ba^{2+}·Hg^{2+}·16** is formed, and FRET-ON process occurs. Since the above behavior may be analyzed with the combinational logic circuit, the selective detection of Ba^{2+} and Hg^{2+} ions by controlling a logic gate is possible [63] (Scheme 5).

Calixarene complexes with copper and zinc ions

In investigation of calixarene complexes with copper [64–67] and with zinc [68, 69] ions it was found that calixarene **17** bearing four iminoquinoline moieties acts as a fluorescent chemosensor; it shows a strong fluorescence enhancement in the presence of Cu^{2+} ion from almost zero background and is highly selective over alkali metal ions (Li^{+}, Na^{+}, K^{+}), alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Ba^{2+}) and transition metal ions (Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+}, Hg^{2+}) [70]. Comparing the behavior of **17** and **18**, the latter bearing only two iminoquinoline units it was observed that the enhancement of fluorescence intensity by **18** is weaker (Scheme 6).



cone 12

paco 12

1,3-alt 12

13 A

colorless spiropyran form

13 B

colored merocyanine form

14

15

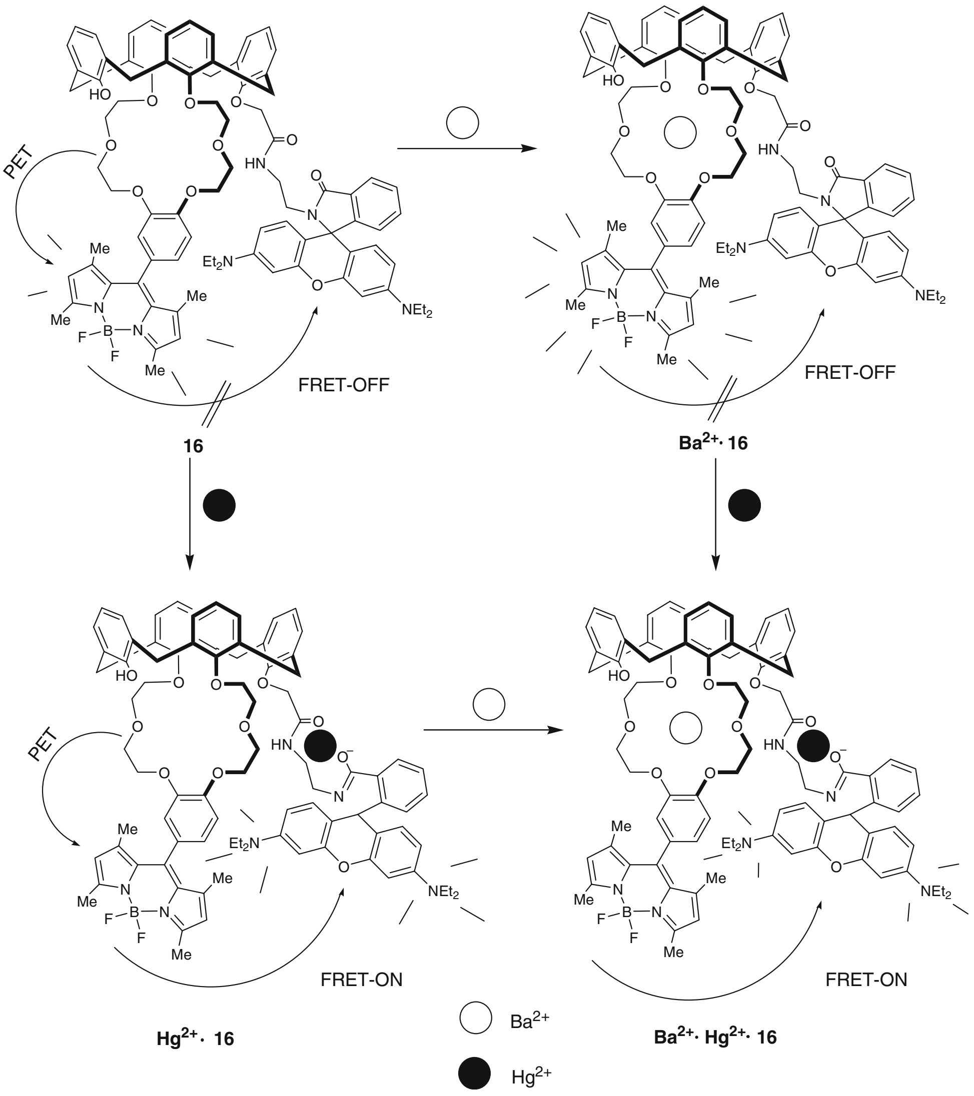
	n	number of Ph groups
a	5	8
b	6	9
c	8	11

Scheme 4 Structures of compounds **12**–**15**

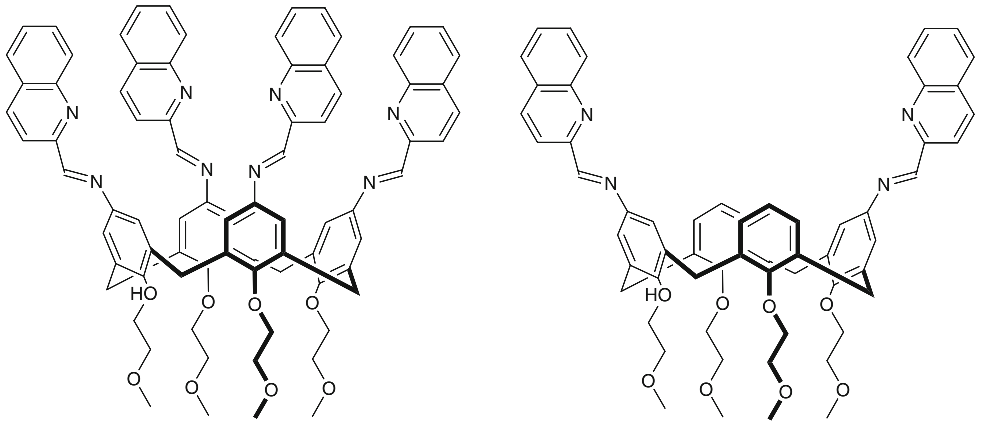
It is known that dioxygen activation at a metal centre for the functionalization of a C–H bond plays a crucial role so in biology as in chemistry. In the case of copper enzymes, the activation process is based on the Cu(II)/Cu(I) redox couple, at a dinuclear or at mononuclear centre.

For dinuclear copper systems the activation occurs via the bielectronic reduction of O_2 by two Cu(I) centres leading to a Cu(II)O_2Cu(II) peroxo dinuclear adduct [71]. However the reactivity at a mononuclear centre is not so much studied; this investigation is difficult since model

Scheme 5 Reactions of compound **16**



Scheme 6 Structures of compounds **17** and **18**



compounds often undergo dimerization, or their reactivity is weak due to steric hindrance around the copper centre [72, 73].

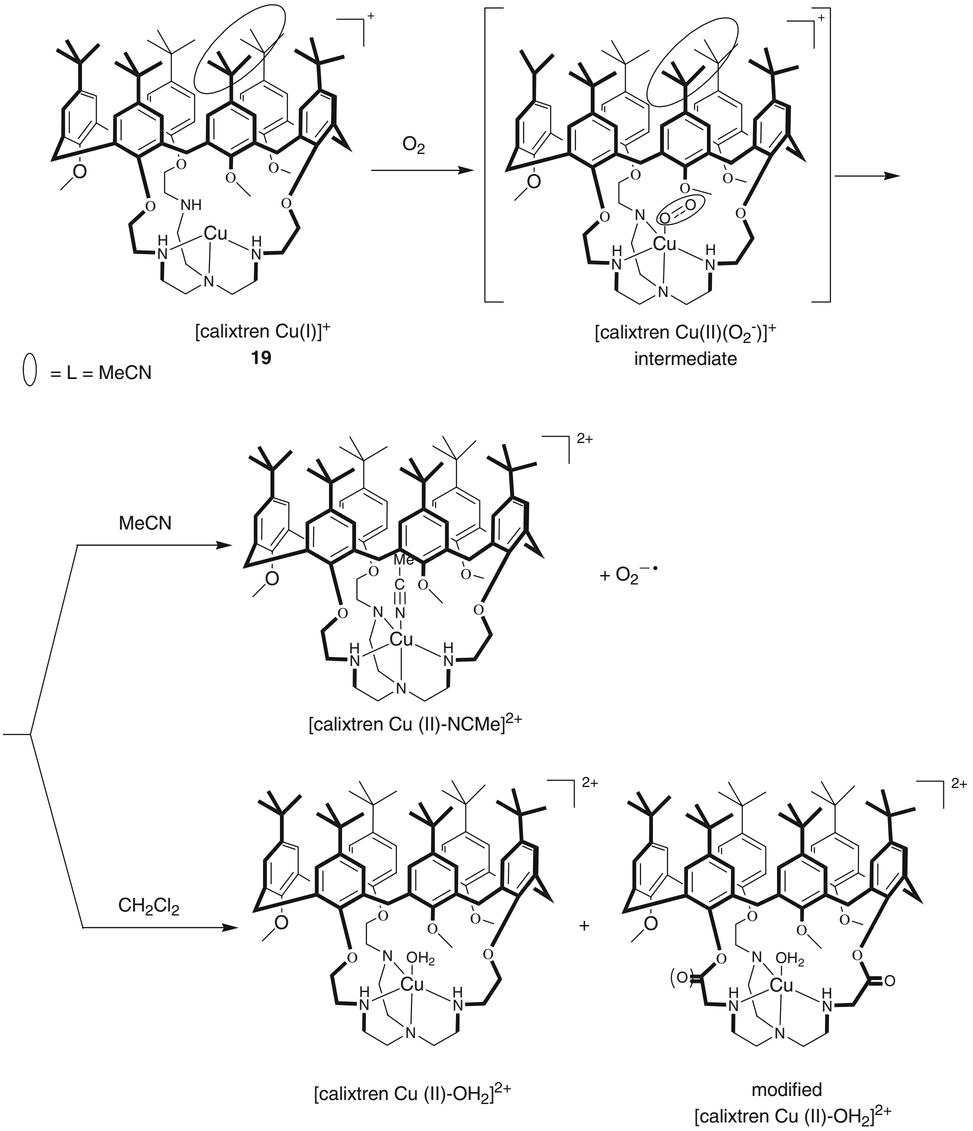
In order to explore the reactivity of mononuclear Cu(I) centre, a series of ligands based on cone calix[6]arenes capped at a narrow rim by a nitrogenous coordination core has been designed. Such “funnel complexes” have a metal centre embedded at the narrow rim.

One should point out that calix[6]arenes are less studied than calix[4]arenes, although calix[6]arenes are more suitable receptors than the tetramers. The 1,3,5-substituted calix[6]arenes have useful C_{3v} symmetry [74, 75]. It is worthnoting that examples of such readily available C_{3v}-symmetrical calixarenes are rare.

Calix[6]arenes have larger cavity than calix[4]arenes, this fact is of interest for their inclusion properties. However, the presence of six phenol units in calix[6]arenes causes their insolubility in aqueous solvents and makes the selective functionalization difficult. Moreover calix[6]arenes have higher flexibility than calix[4]arenes, this high flexibility must be restricted to constrain calix[6]arenes in the cone conformation. To overcome this problem, the “funnel complexes” have been designed; they are capped at the narrow rim by a nitrogeneous core coordinating the metal ion and are able to retain calix[6]arene in a cone conformation [76].

The [calixtren Cu(I)]$^{+}$ **19** is very reactive toward O_2, this behavior being contrary to calix[6]arenes capped by tris(imidazole) [77, 78] or by tris(pyridine) [79] core. It was observed that upon the very fast reaction of **19** with O_2, the Cu(I) centre is oxidized to Cu(II). It is proposed that the reaction of **19** with O_2 proceeds via the transient formation of a [calixtren $[\mathrm{CuII}(\mathrm{O}_2{}^{-})]^{+}$ intermediate, which is presumably a superoxide–Cu(II) species; its further reaction depends on the reaction medium: in coordinating solvent MeCN the formation of the well known complex [calixtren Cu(II)–NCMe]$^{2+}$ with the release of superoxide occurs, while in noncoordinating solvent CH_2Cl_2 the formation of the complex [calixtren Cu(II)–OH_2]$^{2+}$ along with one or more Cu(II) species

Scheme 7 Reaction of the complex **19** with O_2



probably resulting from modification of calixtren takes place [37].

Therefore in MeCN, i.e. in the presence of a guest suitable for stabilization of the Cu(II) state, $O_2^{-\bullet}$ is readily ejected from the complex into the reaction medium. However in the absence of such a guest the insertion of oxygen atoms into a C–H bond of the tren cap occurs affording modified calixtren Cu(II) species [80, 81].

This latter result is of interest, since it shows that a Cu(I) centre reacts with O_2 to afford a species able to oxygenate an organic compound without the need of an external electron input [37]. Such behavior confirms the hypothesis stating that in copper monooxygenases the $[CuO_2]^+$ adduct attacks the C–H bond of the substrate before the electron input from the second copper centre occurs (Scheme 7).

It was found that triple molecular recognition is directing the formation of inclusion complexes of *p*-sulfonatocalix[4]arene **2** and *β*-cyclodextrin (*β*-CD) with bicyclic azoalkanes **3** and **20** [82]. The mixture of **2**, *β*-CD and bicyclic azoalkanes **3** and **20** was investigated in the absence and in the presence of Zn^{2+} ions. It should be mentioned that *β*-CD does not bind Zn^{2+}. In the absence of Zn^{2+}, four equally populated inclusion complexes exist in solution, their binding constants being comparable.

However, when Zn^{2+} ions are added, the formation of the ternary complex $\mathbf{Zn^{2+}\cdot 2\cdot 3}$ is directed by triple molecular recognition, i.e. is induced by a synergy of three supramolecular interactions, namely hydrophobic, Coulombic, and weak metal–ligand bonding. The organic guest is held in the macrocycle by hydrophobic interactions, whereas the Zn^{2+} cation is bound by Coulombic interactions with *p*-sulfonato groups at the wide rim. The bicyclic azoalkane **3** has enough vacant space at the wide rim to allow the Zn^{2+} cation to dock and to reinforce the resulting complex by formation of a weak metal–ligand bond with the azo group; it is a cooperative binding.

However **20** cannot form such ternary complex due to steric hindrance, therefore the addition of Zn^{2+} results in the displacement of **20** and formation of the binary complex $\mathbf{Zn^{2+}\cdot 2}$. This is a competitive binding.

In a mixture of **3** and **20**, both **3** and **20** show a similar affinity for **2**, however upon addition of Zn^{2+} as a directing element, the complex $\mathbf{Zn^{2+}\cdot 2\cdot 3}$ predominates. When a second receptor, i.e. *β*-CD is added, which shows similar affinity for **3** and **20**, but does not bind Zn^{2+} cations, the complexity of the resulting multicomponent system decreases, although a more complicated system rather could be expected, and two complexes, namely $\mathbf{Zn^{2+}\cdot 2\cdot 3}$ and *β*-CD·**20** predominate. The result of this process is "sorting". The described sorting phenomenon in which calixarene **2** and *β*-CD take part as hosts involves the triple supramolecular recognition mediated by Zn^{2+} ion [82].

In the study of calixarenes serving as fluorescent sensors [83, 84], calixarenes **21** and **22** bearing pyrenyl units have been tested. It was found that **21** is highly selective for Zn^{2+} and Cd^{2+} over other metal ions, such as group 1 and group 2 metals, silver and lead [85].

The addition of Zn^{2+} or Cd^{2+} ion to acetonitrile solution of **21** resulted in a remarked ratiometry where the monomer emission increases as its excimer emission decreases. By contrast, no spectral changes occurred upon addition of most of other metal ions, except for heavy metal ions showing heavy metal ion effects resulting in the quenching of fluorescence in both monomer and excimer emission.

However in the case of **22**, which bears only one pyrene unit no spectral changes upon addition of metal ions were observed, except for heavy metal ions which cause fluorescence quenching. Therefore it may be concluded that the two triazole moieties of **21** create an efficient metal ion binding site, whereas **22** does not form complexes with metal ions albeit it contains an additional carbonyl binding site.

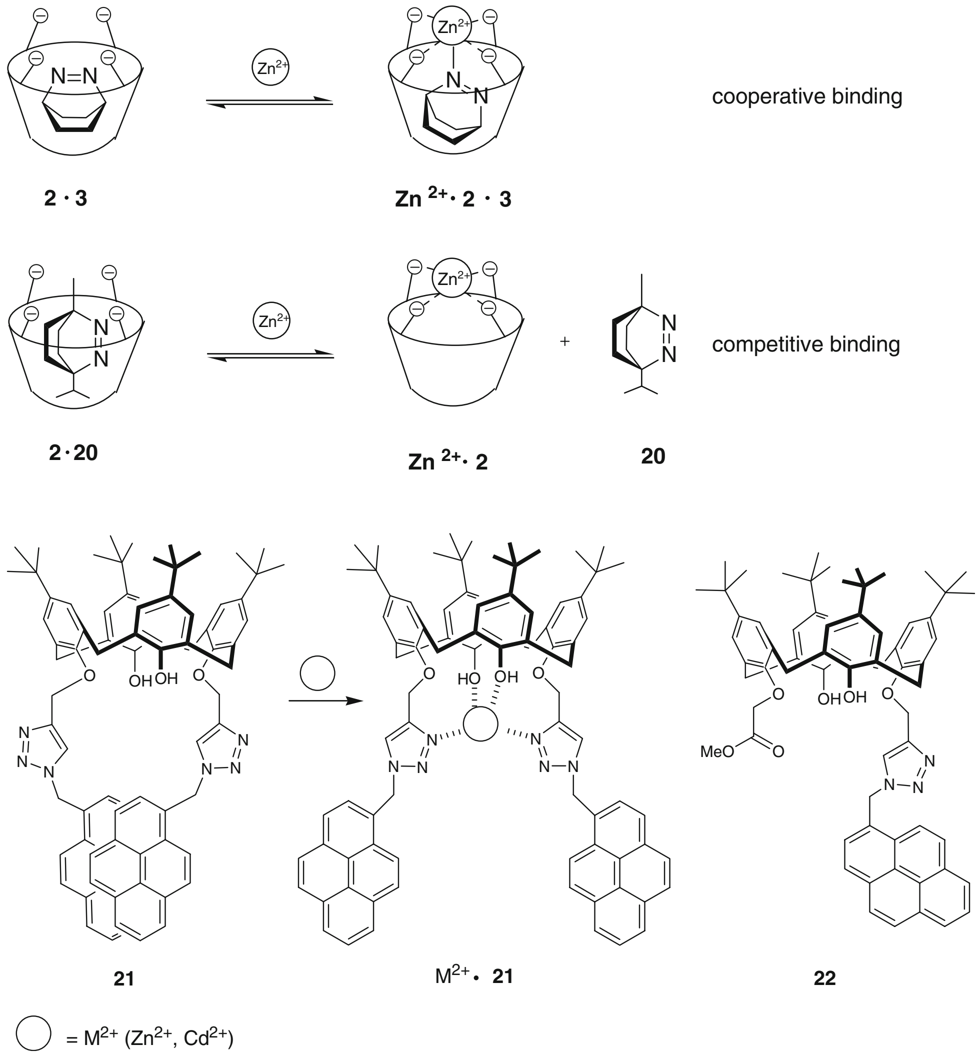
The Zn^{2+} and Cd^{2+} ions are bound with **21** in the complex $\mathbf{M^{2+}\cdot 21}$ by two nitrogen atoms of triazole rings and by two hydroxyl groups of calixarene. The complexation prevents the two pyrene units from maintaining the *π*–*π* interaction, necessary for excimer emission [86] but causes their separation which leads to the observed increasing monomer emission (Scheme 8).

It was established that the easily synthesized calix[4]hexamine **23** reacts with $Zn(ClO_4)_2{\cdot}6H_2O$ in CH_2Cl_2/MeOH mixture to give the complex **24a**. The reaction of **24a** with acetamide leads to the displacement of methanol by a better guest, i.e. acetamide, leading to complex **24b**. Upon treatment of **24b** with $PrNH_2$ or PhCOOH/TEA, which act as exogeneous ligands L, the complexes **25a** or **25b**, respectively, are formed.

In **25a** and **25b**, three alternating amino groups are coordinated to Zn^{2+} ion, while the three others remain free and are thus more reactive. The Zn^{2+} centre preorganizes the C_{3v}-symmetrical complex in such a way that the free amino groups are directed toward the outside of the cavity, and are accessible for reactions.

It was shown that **25b** was suitable for selective 1,3,5-tris-protection of three amino groups. As an example of such protection, the reaction of **24a** with Boc_2O was made; in this procedure **25b** was formed in situ. The subsequent basic washing leads to Zn^{2+} decoordination affording **26**. In order to show that **26** may be used as a building block, the remaining free amino groups were acetylated with Ac_2O, and then the Boc groups were removed by TFA to give **27**. It should be pointed out that 1,3,5-tris-protected **26** can be easily synthesized on a large scale and is a promising C_{3v}-symmetrical platform for further reactions [75] (Scheme 9).

Scheme 8 Reactions of complexes **2•3** and **2•20** along with structures of compounds **21** and **22**



The “funnel complex” $\mathbf{Zn^{2+}{\cdot}28}$ capped by *tris*-imidazole core coordinating Zn(II) ion and bearing three amino groups as compared with such complex $\mathbf{Zn^{2+}{\cdot}29}$ containing six *t*-butyl groups, has higher water solubility than $\mathbf{Zn^{2+}{\cdot}29}$, may include larger guests and has a higher flexibility than $\mathbf{Zn^{2+}{\cdot}29}$; this fact allows for **Zn·28** the existence of induced-fit phenomena in the inclusion of guest molecules [76].

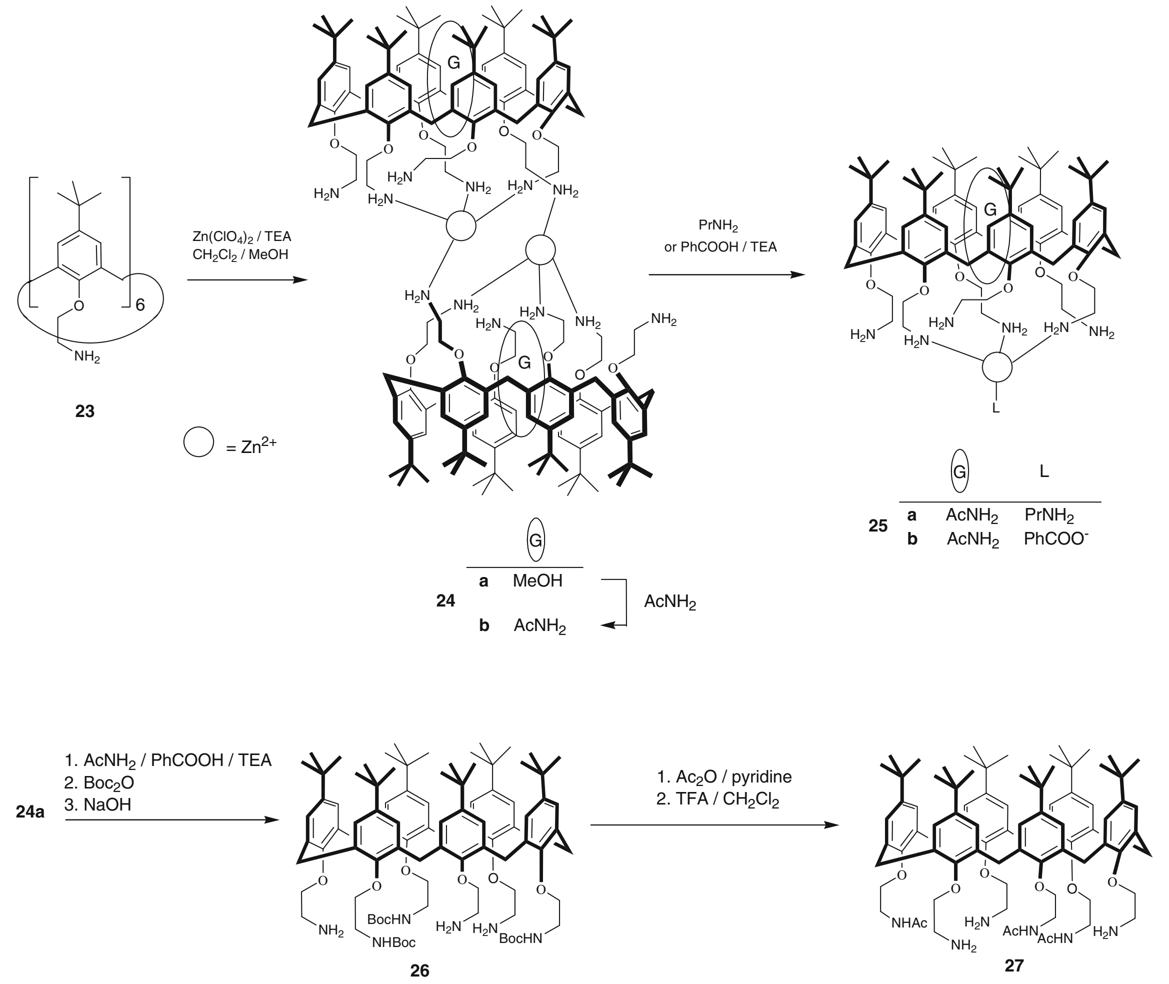
Both $\mathbf{Zn^{2+}{\cdot}28}$ and $\mathbf{Zn^{2+}{\cdot}29}$ encapsulate small guests (such as H_2O, EtOH, DMF, DMSO, acetamide), however their behavior is different, since $\mathbf{Zn^{2+}{\cdot}28}$ is soluble and stable in aqueous solvents and can include larger guests (e.g. benzylamine, dimethyldopamine and decarboxylated tryptamine, **30**–**32**, respectively) while $\mathbf{Zn^{2+}{\cdot}29}$ cannot.

It should be pointed out that the presence of three small amino groups in $\mathbf{Zn^{2+}{\cdot}28}$ (as compared to three bulky *t*-butyl groups in $\mathbf{Zn^{2+}{\cdot}29}$) increases the degree of freedom of phenol units to rotate. This fact enables the calixarene to tune its cavity space for a best fit to the guest size, ranging from a single water molecule to large dimethyldopamine.

This behavior is contrary to cyclodextrins, which entrap strongly organic guests, but only in the case when a good fit between the host cavity and the guest size exists, and this condition is a disadvantage of rigid hosts. Therefore one may state that the flexibility of $\mathbf{Zn^{2+}{\cdot}28}$ is advantageous, since cavity adapts to the size of the guest, i.e. the induced-fit process occurs [76] (Scheme 10).

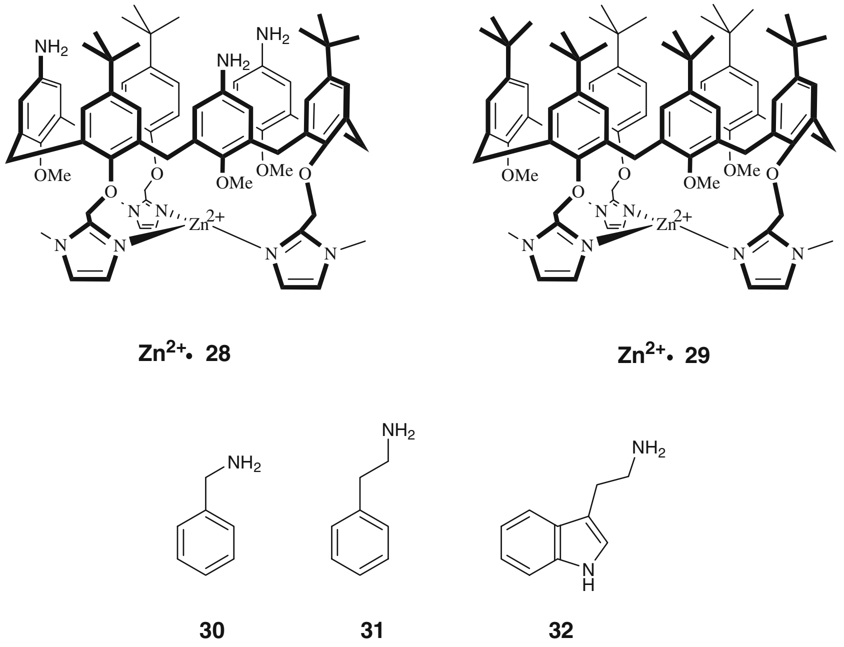
Calixarene complexes with silver, cadmium, mercury and lead ions

Calixarene complexes with silver [69, 87], cadmium [67, 88], mercury [67, 89, 90] and lead [67, 88, 90] are a topic of many reports; selected examples will be described. Calixarenes **33a**,**b** dissolved in dichloromethane have been used as extractants in order to recover silver from nitric acid solutions. It was found that complexes $\mathbf{Ag^{+}{\cdot}33a}$ and $\mathbf{Ag_2{}^{+}{\cdot}33b}$ are formed. A special attention was paid to a new silver stripping process, avoiding the



Scheme 9 Synthesis of complexes **24a,b** and their reactions

Scheme 10 Structures of complexes $\mathbf{Zn^{2+}{\bullet}28}$ and $\mathbf{Zn^{2+}{\bullet}29}$ and structures of compounds **30–32**



difficulties of conventional stripping silver back to the aqueous phase.

It was found that **33a** is an efficient Ag^+ extractant only in acidic solutions, whereas **33b** efficiently extracts silver independently on the nitric acid concentration. Therefore, **33b** may be used for the extraction of silver either from rinse waters, containing only a small amount of acid, or from mother liquors from salt production, containing a large amount of acid [91].

It is known that some calixarenes have affinity for sodium, which can be coextracted with silver. It was observed that that **33a** extracts sodium as successfully as silver, therefore can extract silver only in the absence of sodium. On the other side **33b** effectively extracts silver from solutions containing sodium ions, since it does not extract sodium.

Complexes of **33a**,**b** with silver cannot be stripped in a conventional way, therefore other methods are necessary to strip the metal from the organic phase. Using electrolytic reduction processes, the problem arises that calixarenes can be readily oxidized on the anode to give calixdiquinones. To avoid any anodic destruction of calixarenes, the electrochemical experiments were carried out using two-phase electrowinning method.

In order to perform the extraction of silver, the solution of the extractant and solution of silver nitrate were shaken in a separating funnel, left for phase separation and introduced into the cell; there the two layers were formed—an upper aqueous phase and a lower silver-bearing organic phase. The cathode was placed in the organic phase, and the anode was immersed in the aqueous phase to protect calixarene from a destruction by anodic oxidation. Therefore the anodic reaction was simply the electrolysis of water.

As a supporting electrolyte *t*-butylammonium perchlorate (TBAPC) was used; it was dissolved in organic phase prior to electrolysis. The concentration of nitric acid serving as supporting electrolyte in the aqueous phase was sufficiently high to assure its high conductivity, and as a result, an acceptably low cell voltage. Therefore, the energy consumption by this two-phase electrowinning of silver is not high.

Using the above procedure the deposition of silver from the organic phase is feasible and efficient. An important fact is that calixarenes do not change their extraction properties during electrowinning and can be reused many times. The process is an effective way of electro-reductive stripping, integrating the two separate consecutive operations, i.e. stripping and electrowinning into one step; in this way the time of the solvent extraction is shorter [91].

Three series of calixarenes **34**–**36** containing azo groups, and functionalized at narrow rim by acetyl and benzoyl (**34**, **35**) and by ketone groups (**36**) have been used for extraction with metal picrates from aqueous solution into chloroform; all studied compounds have the cone conformation in solution. The functionalization of narrow rim of calixarenes by acetyl, benzoyl and ketone groups was made in order to increase their solubility and their extraction efficiency. The experimental results have shown that **36c** efficiently extracts Ag^+ and Hg^{2+} ions, **34b** efficiently extracts Ag^+, Hg^{2+}, Cu^{2+} and Cr^{3+}, and all investigated calixarenes except **35c** are good extractants for Hg^{2+} [92].

It was found that paco calixarene **37** bearing a dansyl unit is a fluorescent chemosensor showing selective optical recognition of Hg^{2+} and Cu^{2+} ions, it exhibits the ratiometric sensing of Hg^{2+} and an "ON–OFF" type of fluorescence behavior in the presence of Cu^{2+} ions [93].

In **37** the intramolecular PET from the electron-rich nitrogen atom of the dimethylamino group to the electron-deficient naphthalene moiety is strong in the absence of Hg^{2+}, while in the presence of Hg^{2+} is decreased. Calixarene **37** shows a characteristic fluorescence emission band, upon addition of Hg^{2+} this band decreases, and two new, blue-shifted emission bands appear, resulting from the formation of the complex $\mathbf{Hg^{2+}}\cdot\mathbf{37}$. It is proposed that the fluorescence spectral changes are due to the protonation of the dansyl unit resulting from the deprotonation of the phenolic hydroxyl group; such deprotonation of the phenolic hydroxyl group was reported in the presence of lead and indium perchlorates [94]. It was established that **37** shows high selectivity toward Hg^{2+} in the presence of Li^+, Na^+, K^+, Ni^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+} ions.

Using Hg^{2+} and Cu^{2+} as inputs, this system was utilized as a NOR logic gate with a YES logic function. Addition of Cu^{2+} to the solution of **37** quenches the intensity of fluorescence. This behavior results from the reverse PET from the naphthalene unit to the nitrogen atom of the dimethylamino group; the electron density of the nitrogen atom is diminished by metal coordination. Addition of Hg^{2+} to the complex $\mathbf{Cu^{2+}}\cdot\mathbf{37}$ completely quenches the fluorescence emission and two new blue-shifted bands appear. Due to the above facts, the dual output molecular switch was designed.

The solid/liquid extraction of three toxic Cu^{2+}, Cd^{2+} and Pb^{2+} ions with unsupported calixarenes **38**–**41** serving as solid extractants, has been studied. This procedure showed to be effective and convenient and may be compared to classic liquid/liquid extraction. The selective extraction was also investigated.

All the considered calixarenes have been used for solid/liquid and liquid/liquid extraction of the above metal ions, and results of both methods have been compared. The aim of the work was to find a simple and effective method of extraction of toxic metal ions by calixarenes [95]. It should be mentioned that the use of unsupported calixarene as solid phase in extraction of ions from aqueous solution is a new process.

It was found that **38a** is a poor extractant in acidic and neutral media for metal ions investigated, but its extraction ability increases at pH 8.8 in the solid/liquid extraction. The extraction of Cu^{2+} by **38a** in basic media using solid/liquid method is more efficient than in the case of liquid/liquid method.

Calixarene **38b**, similarly as **38a** is a poor extractant of investigated metal ions in acidic and neutral media, only a low affinity for Cd^{2+} and Pb^{2+} was observed. The fact that the extraction results of **38a** and **38b** are comparable shows that the presence of *t*-butyl groups is not important for the extraction process. Calixarene **38b** is an efficient extractant for Cu^{2+} in basic media, the results of solid/liquid and liquid/liquid methods are similar.

In the study of calixarene carboxylic acids **39a–c** it was observed that they are efficient Cu^{2+}, Cd^{2+} and Pb^{2+} extractants, especially in basic media. The extraction efficiency in solid/liquid and liquid/liquid methods is similar (except for extraction of Cu^{2+} and Cd^{2+} by **39b**).

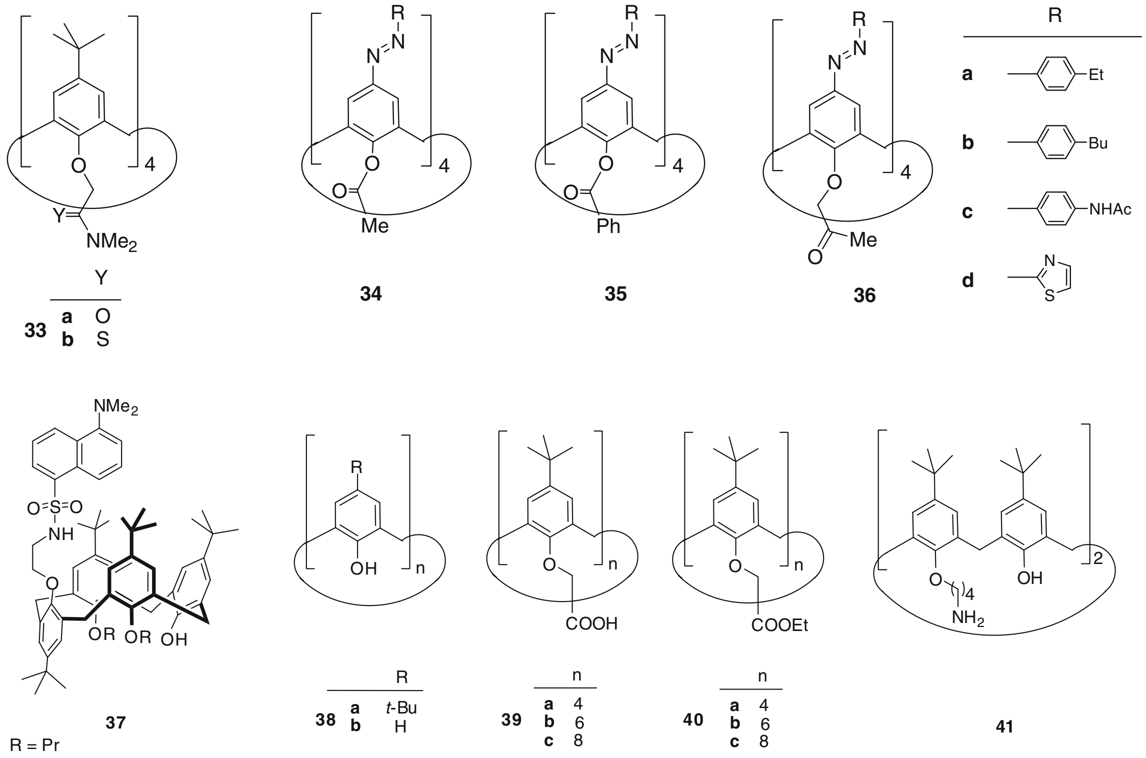
In the case of calixarene esters **40a–c**, the results obtained by solid/liquid and liquid/liquid methods are similar. Calixarene carboxylic acids **39a–c** are more efficient extractants than calixarene esters; this observation confirms the fact that the ionisable groups play an important role in extraction process.

In investigation of the solid/liquid extraction method it was found that **39c** extracts metal ions in order $Cu^{2+} > Pb^{2+} > Cd^{2+}$, showing good reproducibility. The washing of **39c** with HCl solution allows its full regeneration. Calixarenes **39a–c** are good extractants for Cu^{2+}, Cd^{2+}, and Pb^{2+}, but are not very selective. The most selective solid extractants so in solid/liquid as in liquid/liquid methods showed to be **38a** (for Cd^{2+}) and **41** (for Cu^{2+}).

The extraction mechanism involves the exchange between the metal ions dissolved in the aqueous phase and the calixarene (as a solid or as dissolved in organic medium). The exchange occurs by interfacial complexation between the phases. This process is probably based on the presence of hydrophilic groups of calixarenes containing oxygen donor atoms, able to selectively bind metal ions [95] (Scheme 11).

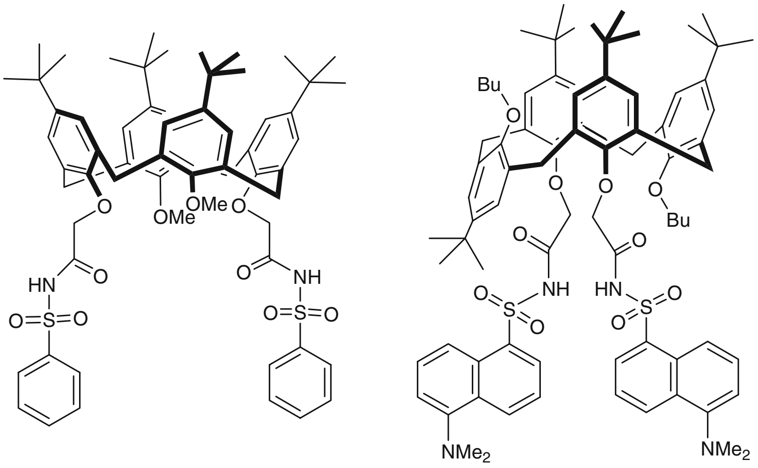
The separation of heavy metals with the use of polymer inclusion membranes (PIMs) was investigated. PIMs are interesting for their stability as compared to other types of liquid membranes [38, 39, 96–98]. With the use of lipophilic calixarene **42** in a PIM system, Hg^{2+} ions were transported with high selectivity from acidic aqueous source phase solutions of Cd^{2+}, Hg^{2+} and Pb^{2+} of a large $NaNO_3$ concentration into aqueous receiving solutions containing EDTA.

The PIM was prepared by evaporation of solvent from a dichloromethane solution of carrier **42**, cellulose triacetate (CTA), dinonylnaphthalenesulfonic acid (DNNS, a cation transport promoter), and 2-nitrophenyl octyl ether (NPOE,



Scheme 11 Structures of compounds **33**–**41**

Scheme 12 Structures of compounds **42** and **43**



42 **43**

the plasticizer). The aqueous receiving phase contained the di-lithium salt of EDTA and lithium acetate. In the experiments the separation of Hg^{2+} from Cd^{2+} and Pb^{2+} in an acidic, high salt aqueous solution was achieved. In this competitive heavy metal ion transport, the selectivity order was $Hg^{2+} \gg Cd^{2+} \cong Pb^{2+}$ [34].

In the investigation of metal ion complexation, NPOE was not a convenient solvent, therefore acetonitrile served as a medium; metal perchlorates had to be used instead of metal nitrates, since metal perchlorates are fully dissociated in acetonitrile. The stability constants of complexes of Cd^{2+}, Hg^{2+}, Pb^{2+}, and Na^+ ions with **42** were determined.

The mechanism for membrane transport involves the diffusion of metal ion through the boundary layer together with nitrate. The cation forms a complex with a carrier within the membrane. This complex, together with the accompanying nitrate ions slowly diffuses through the membrane. In the final step, both the metal ion and the anions are released into the receiving phase. The free carrier diffuses back through the membrane, beginning another cycle.

Investigation of calixcrowns **4a–e** and their oxa analogues **5a–e** has shown that they extract Hg^{2+} and Pb^{2+} ions from aqueous solutions into chloroform; for these both ions **4a–e** proved to be better extractants than **5a–e** [50].

It was found that paco calix[4]arene **43** bearing two dansyl groups is a highly sensitive and selective fluorescent chemosensor for Pb^{2+} ion. In acidic MeCN/H_2O (1:1 v/v) solutions, **43** can detect Pb^{2+} at the 2.5 ppb level [99] (Scheme 12).

Calixarene complexes with rhodium, palladium, lanthanide and actinide ions

Numerous calixarene complexes with rhodium [100] and palladium [100, 101] have been studied in view of their catalytic activities; investigation of calixarene complexes with lanthanides [102–104] and actinides [105], or with both lanthanides and actinides [106–108] in the aspect of nuclear waste management deserves a special attention. Examples of the above calixarene complexes are presented.

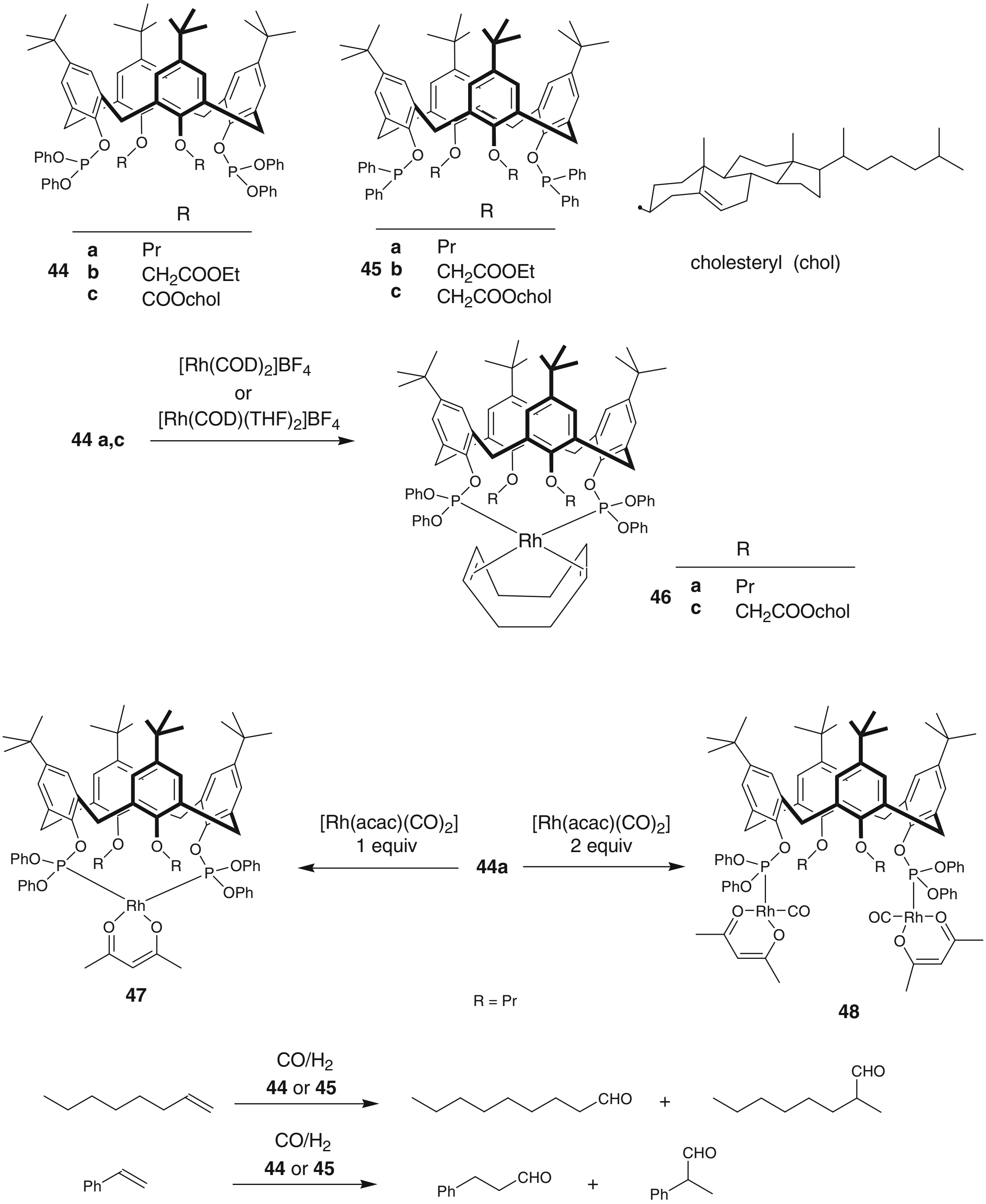
Complexes with rhodium and palladium ions

Three bisphosphite calixarenes **44a–c** and three bisphosphinite calixarenes **45a–c** were studied for their coordination properties with rhodium and palladium. It was found that **44a–c** readily form chelate complexes [109]. The reactions of **44a** and **44c** with $[Rh(COD)_2]BF_4$ or $[Rh(COD)(THF)_2]BF_4$ afford complexes **46a,c** while reaction of **44a** with $[Rh(acac)(CO)_2]$ yields monometallic or bimetallic complex **47** or **48**, respectively, according to conditions.

It was established that **44a–c** and **45a–c** mixed with $[Rh(acac)(CO)_2]$ effectively catalyze the hydroformylation of octene and styrene. In the case of octene, the selectivity of linear over branched aldehyde is higher for **44b** and **44c** as compared with that of **44a** and **45a–c**. In the case of styrene, all calixarenes **44a–c** and **45a–c** show high selectivity of linear over branched aldehyde (Scheme 13).

Studying coordination properties of **44b** and **44c** toward palladium it was established that **44b** reacts with cyclometallated complex $[Pd(o\text{-}C_6H_4CH_2NMe_2)(THF)_2]BF_4$ **49** to give the complex **50**, and the reaction of **44c** with $[Pd(COD)Cl_2]$ yields the complex **51** (Scheme 14).

Monophosphite calixarenes **52** and **53**, as well as bisphosphite calixarenes **54**, distally (i.e. 1,3)disubstituted and **55**, proximally (i.e. 1,2)disubstituted have been investigated in view of their coordination with palladium [110]. One should mention that monophosphite calixarenes are less studied than bisphosphite species .



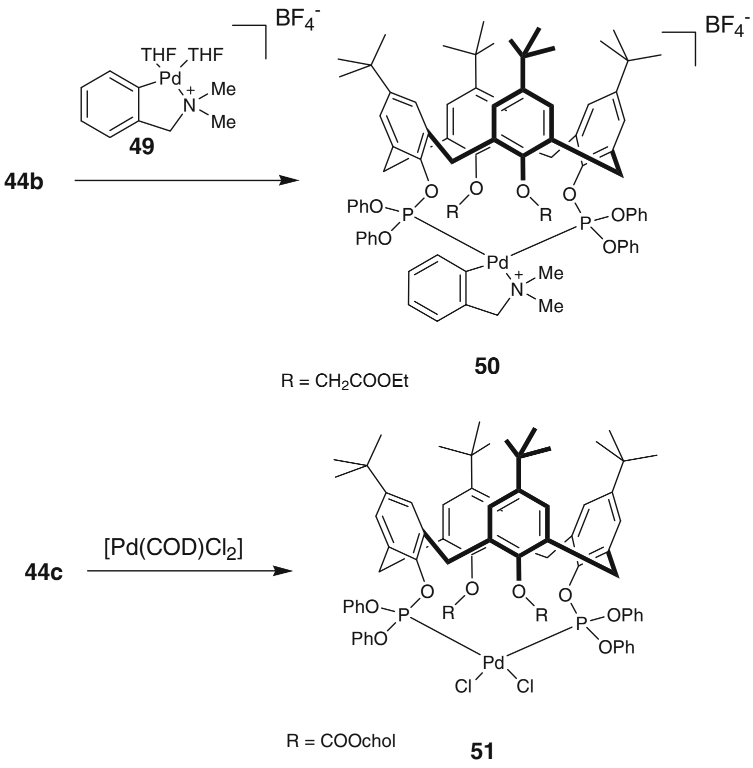
Scheme 13 Structures of compounds **44** and **45** along with synthesis of complexes **46**–**48**; examples of catalytic activity of **44** and **45** mixed with [Rh(acac)(CO)$_2$]

Calixarenes **52** and **53** react with allyl palladium precursor [η^3-1,3-R, R^1-C$_3$H$_4$) Pd(Cl)]$_2$ (**56**) yielding neutral allyl complexes **57a**–**c** and **58a**–**d**, respectively. Complexes of **58a**,**d** show two diastereomers in solution due to the inherently chiral structure of **53** (Scheme 15).

The reaction of **54** with **56** in the presence of NH$_4$PF$_6$ yields cationic allyl palladium complexes **59a**–**d**, whereas in the absence of NH$_4$PF$_6$ neutral allyl complexes **60a**–**c** are formed. The reaction of **55** with **56** in the presence of NH$_4$PF$_6$ affords cationic allyl palladium complexes **61a**,**b** whereas with [Pd(COD)Cl$_2$] the palladium dichloride complex **62** was obtained.

The catalytic activity of **54** and **60b** was studied in allylic alkylation of crotyl acetate using dimethyl malonate

Scheme 14 Syntheses of complexes **50** and **51**



as a nucleophile. It was observed that the relative yield of the branched isomer is higher in the case of **60b** than in the case of **54** used with the Pd-precursor [110] (Scheme 16).

Complexes with lanthanide ions

It was found that cationic or anionic calixarenes form with oppositely charged polyelectrolytes multilayered films to give calixarene based separation membranes which show a highly selective transport of metal ions. Sulfonatocalixarenes **63a**–**c** are anionic macrocycles, therefore cationic polyelectrolytes such as poly(vinylamine) (PVA) may be used. Membranes were prepared from **63a**–**c** and PVA upon alternating electrostatic adsorption of the charged species at solid substrates [111].

The ring size of calixarenes is very important in the formation and stability of multilayered films, the larger rings are easier adsorbed than the smaller ones. One should also take into account that small and large calixarene rings have different conformations; **63a** exists in a cone conformation, **63b** is mostly present in the double partial-cone conformation, more favorable for adsorption, and **63c** has a flat conformation, which is sterically the most favorable for adsorption.

The study of transport of lanthanide salts has shown that the permeability of yttrium, lanthanum, cerium, praseodymium and samarium chloride is low. Since sodium ions can easily pass the membrane, the separation factors α (Na^+/Ln^{3+}) (Ln = Y, La, Pr) are high. It was found that **63c**-based membranes are convenient for enrichment of lanthanide ions.

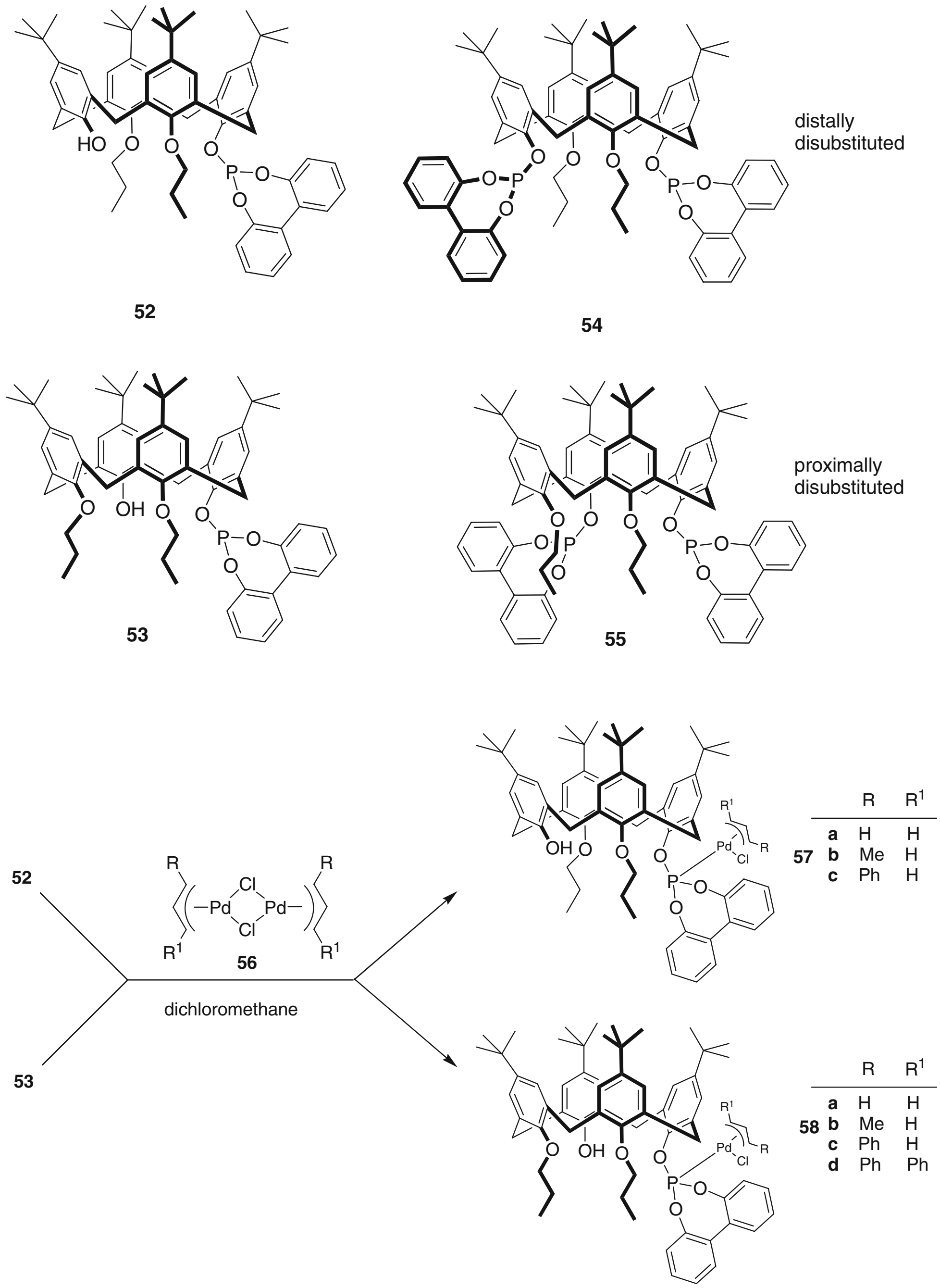
The binding properties of calixarene **64** toward La^{3+}, Gd^{3+} and Lu^{3+} ions have been evaluated using liquid/liquid extraction. The aqueous metal picrate solution buffered at pH 6.0 was magnetically stirred with the solution of **64** in $CDCl_3$. The extraction properties of **64** are higher than those of the acyclic monomeric analogue **65**, this fact showing that the platform of the calixarene **64** considerably improves metal binding properties [112].

In the search for extractants separating lanthanides, the mass transfer kinetics of Nd^{3+} extraction by calixarene **40a'** was investigated along with the interfacial behavior of **40a'**. These data are useful for understanding the nature of the separation process and for predicting the extraction rate. In experiments a constant interfacial cell with laminar flow based on the Lewis cell was used for study of extraction kinetics [113].

It is known that the extractant molecules adsorb at the interface, and create a surface excess. Some of the molecules diffuse, therefore an interface double layer is formed. Metal ions cannot enter into the organic phase due to their very low dielectric constant, but they can approach the surface because of the double layer.

The chemical reactions controlling the rate of extraction may occur either at the interfacial zone or in the bulk phase. If metal ions react quickly with the extractant

Scheme 15 Structures of compounds **52**–**55** and syntheses of complexes **57** and **58**

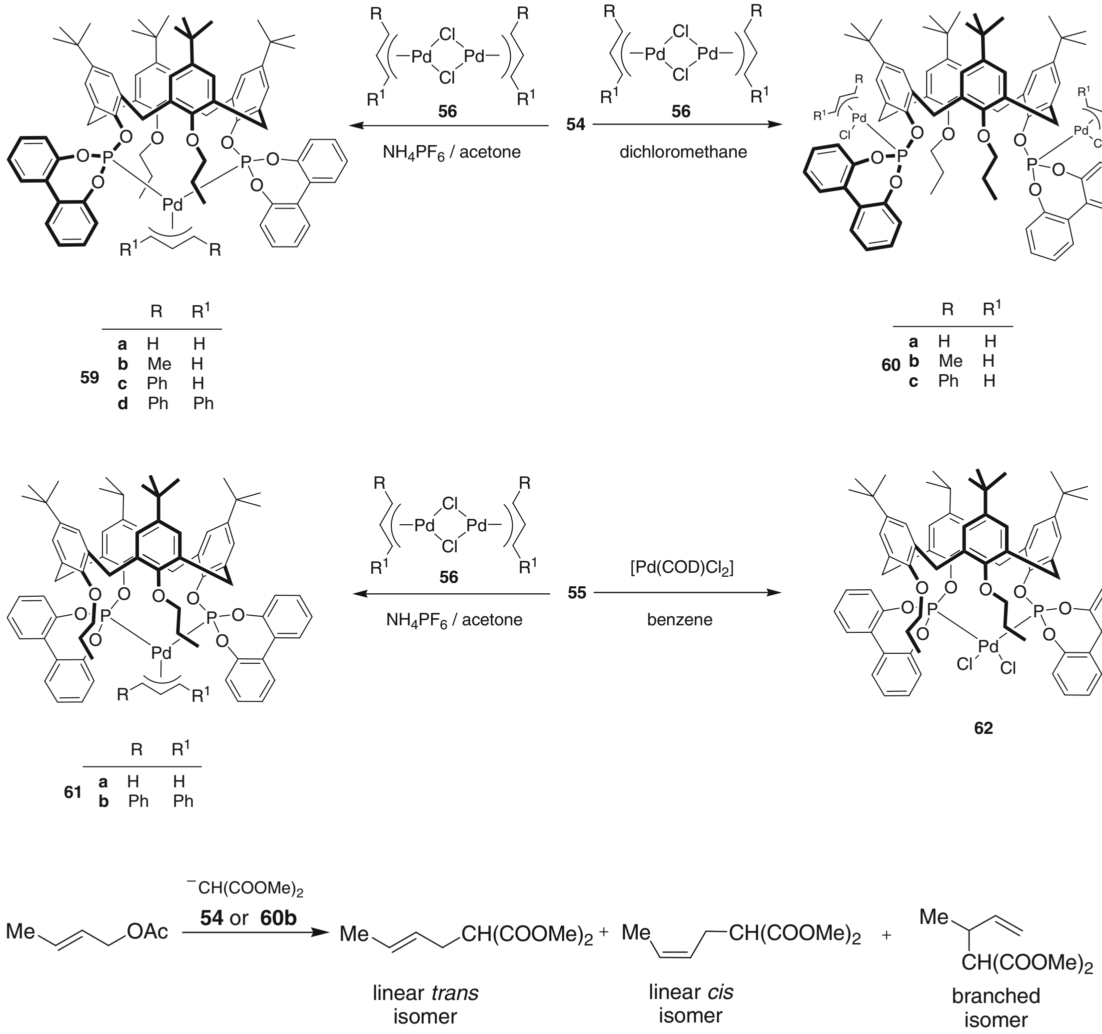


molecules at the interface, the process is an interfacial reaction of a rate directly proportional to the specific interfacial area. However, if metal ions react slowly with the extractant molecules, the reaction zone extends to the bulk phase and the initial rate is independent on the specific interfacial area.

The extraction of Nd^{3+} ions with **40a’** is a complex kinetic process involving an interfacial reaction. It was found that the chemical reaction which accompanies mass transfer occurs in a region close to the interfacial zone [113] (Scheme 17).

Calixarenes **66a**–**c** and **67** bridged with diethylene triamine pentaacetic acid (DTPA) on the narrow rim (**66a**–**c**) and on the wide rim (**67**) form with Eu^{3+} ion the 1:1 inclusion complexes **68**–**71** in which the Eu^{3+} ion is embraced by DTPA ring. Complexes **68**–**70** are depicted. It was established that calixarenes **66a**–**c** and **67** may also be used for complexation of gadolinium [114].

In the study of nanoporous materials it was found that sulfonatocalix[4]arene **2** and bisphosphonium cation **72** afford in aqueous solutions with Er^{3+} and Yb^{3+} ions complexes **73** and **74** [115]. Complexes **73** and **74** form



59

	R	R^1
a	H	H
b	Me	H
c	Ph	H
d	Ph	Ph

60

	R	R^1
a	H	H
b	Me	H
c	Ph	H

61

	R	R^1
a	H	H
b	Ph	Ph

Scheme 16 Reactions of compounds **54** and **55** along with an example of catalytic activities of **54** used with the Pd-precursor and of the complex **60b**

porous materials due to existence of a bilayer arrangement. Complex **73** crystallizes in the monoclinic space group *P*1; the asymmetric unit contains two calixarene molecules and one bisphosphonium cation in a *trans* configuration. Complex **74** crystallizes in the triclinic space group *P*1; the asymmetric unit contains three calixarene molecules and 3.5 bisphosphonium cations (Scheme 18).

Complexes with actinide ions

In the search for extractants of actinides and lanthanides it was established that the phosphinoylated *p*-*t*-butylcalix[6]arene **75** efficiently extracts actinides, but not lanthanides, using liquid/liquid extraction [36].

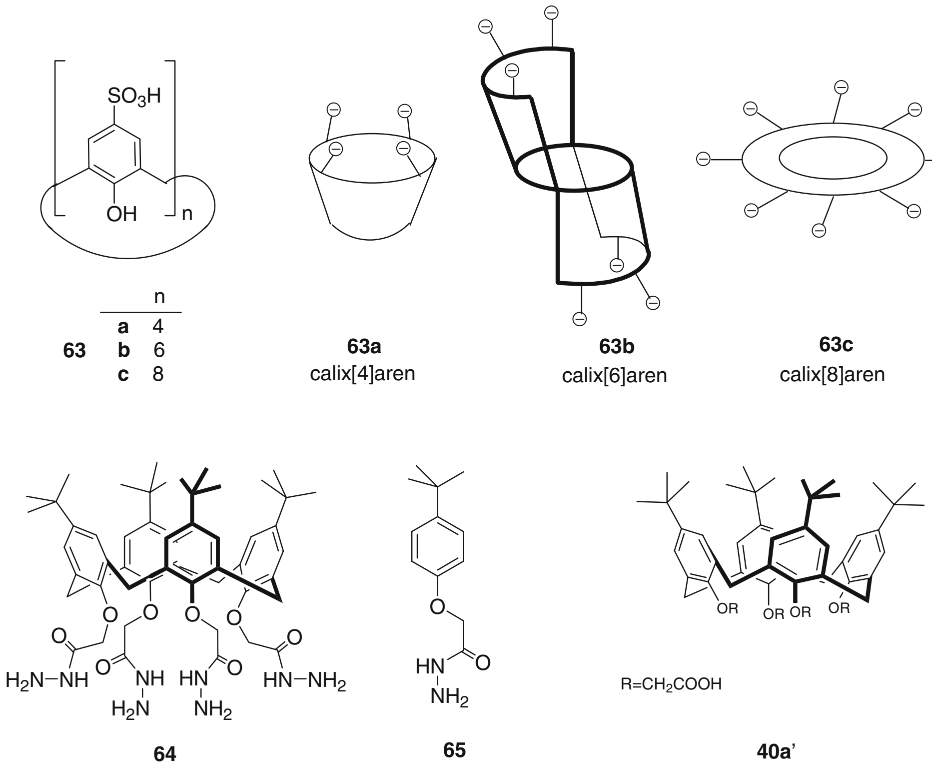
The coordination of **75** with actinide cations, especially with UO_2^{2+} and Th(IV), as well as with trivalent lanthanides (La^{3+}, Eu^{3+}, Y^{3+}) was investigated. These experiments were carried out in the aspect of confinement of nuclear wastes in deep geological repositories.

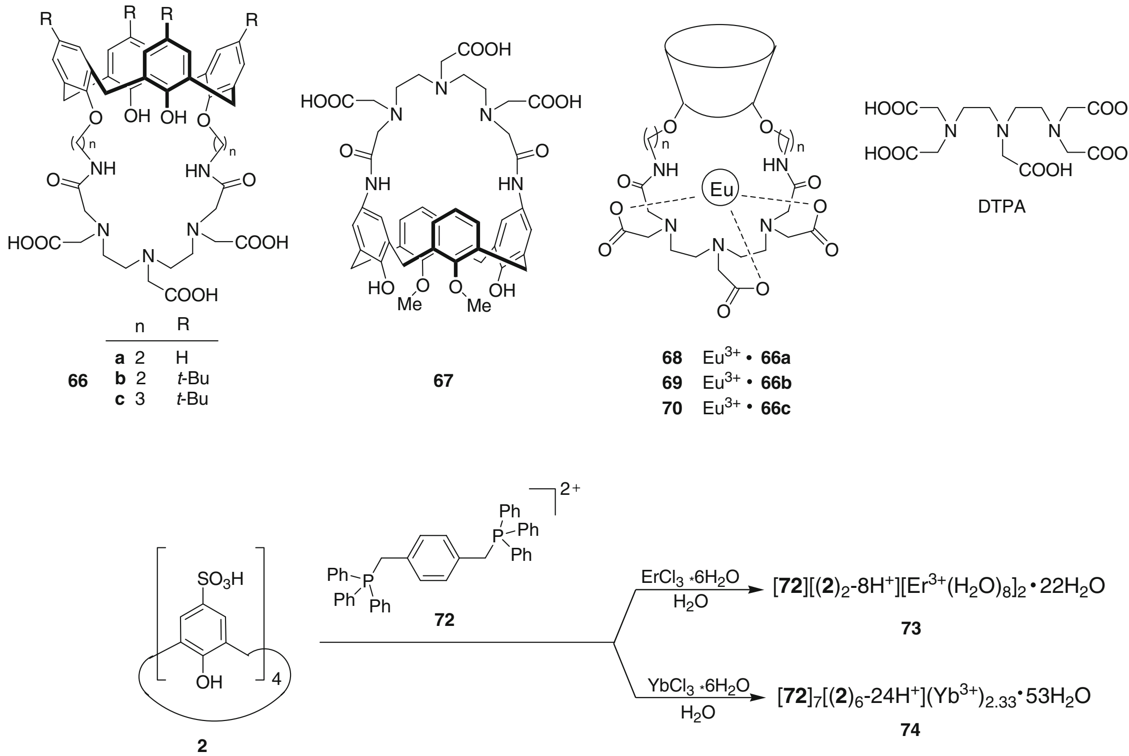
Actinides are radiotoxic, therefore their investigation is difficult. In order to circumvent this problem, the analogous cations are often examined, e.g. Eu(III) for Pu(III), Am(III) and Cm(III); Th(IV) for U(IV) and Pu(IV); and UO_2^{2+} for NpO_2^{2+} and PuO_2^{2+}. Among actinides, the complexes of uranium and thorium are the most explored.

Calixarene **75** gives with $An(NO_3)_x{\cdot}yH_2O$ (An = UO_2^{2+}, Th(IV), $x = 2$ and 4 and $y = 6$ and 5, respectively), in EtOH the 1:1 complexes $UO_2(\mathbf{75})(NO_3)_2{\cdot}3H_2O$ and $UO_2(\mathbf{75})(NO_3)_4{\cdot}3H_2O$, however in MeCN the 1:2 (M/L) complexes $UO_2(\mathbf{75})_2(NO_3)_2{\cdot}12H_2O$ and $Th(\mathbf{75})_2(NO_3)_4{\cdot}8H_2O$ are formed. It was found that **75** has higher affinity to uranyl ion than to thorium ion.

Aqueous phases of the actinide (An = UO_2^{2+}, Th(IV)) and/or trivalent lanthanide nitrates ($Ln^{3+} = La^{3+}$, Eu^{3+},

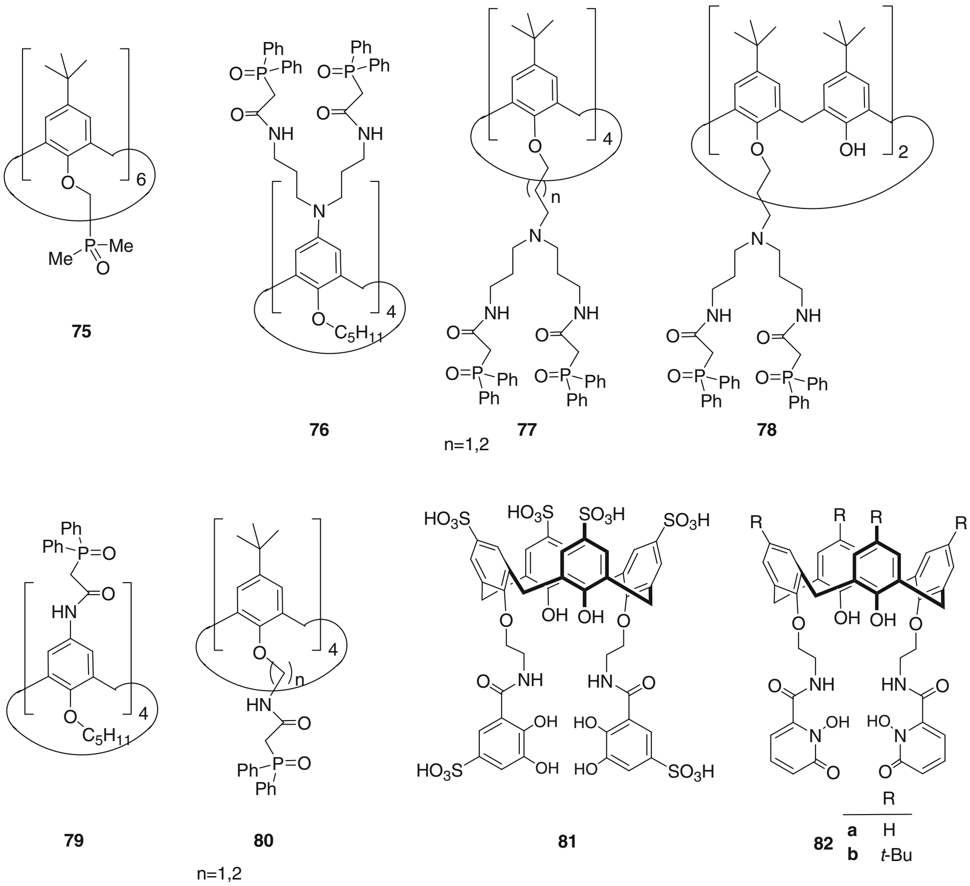
Scheme 17 Structures of compounds **40a’** and **63–65**





Scheme 18 Structures of compounds **66**, **67** and of complexes **68–70**; syntheses of complexes **73** and **74**

Y^{3+}) were prepared in water containing nitric acid and/or sodium nitrate. Organic phases of calixarene were prepared in chloroform. It was established that the formation of 1:1 complexes of uranyl, thorium and europium with **75** from an aqueous medium rich in nitrate ions is predominant.



Scheme 19 Structures of compounds **75**–**82**

Calixarenes substituted at the wide (**76**) or narrow (**77**, **78**) rim by carbamoylmethyl-phosphine oxide (CMPO) groups in a dendritic manner were investigated for extraction of Eu^{3+} and Am^{3+} from aqueous nitric acid into *o*-nitrophenyl hexyl ether. Calixarenes **76** and **77** contain eight CMPO units, calixarene **78** contains four CMPO units. For comparison purposes calixarenes **79** and **80**, having only four CMPO units at wide and narrow rim, respectively, were used [116]. It was found that the extraction efficiency of **76**–**78** is lower than that of **79** and **80** which contain four CMPO units, i.e. that the larger number of CMPO groups in calixarenes does not increase their extraction properties.

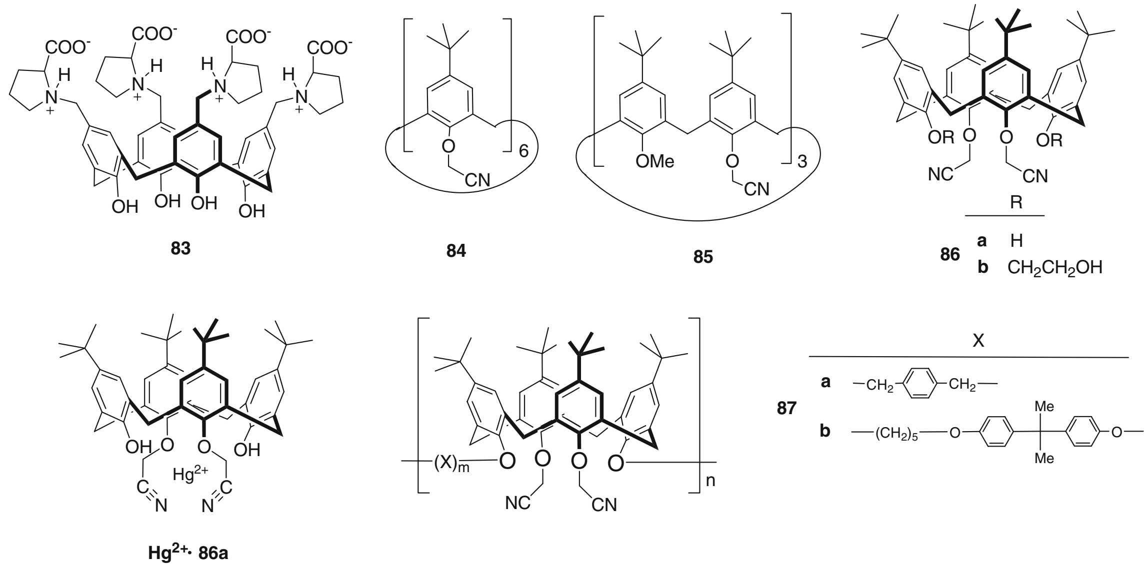
One should point out that the trivalent actinides are very similar to lanthanides, therefore their separation is difficult, especially when Am^{3+} should be separated from Eu^{3+} ions from strongly acidic media, as it is the case in nuclear fuels.

Calixarenes **81** and **82a**,**b** bearing sulfocatechol and hydroxypyridinone moieties, respectively, show affinity toward uranyl ion. It was found that calixarene **81** has high affinity toward UO_2^{2+} at basic pH, whereas **82a**,**b** are more efficient at acidic and neutral pH [117] (Scheme 19).

Calixarene complexes with metal ions and anions

Besides metal ions, calixarenes bind also anions [118–120] and ion pairs [121, 122]; some examples of calixarene complexes with metal ions and anions are shown below. It was found that the water soluble, proline-functionalized calixarene **83** forms low molecular weight hydrogels in the presence of specific anions; the gel properties are modified by associated cations. The gels are stable over a pH range 0–7, and are reversibly disassembled at pH above 7 [123]. Low molecular weight hydrogelators are promising as sensors and drug-release formulations. It should be mentioned that low molecular weight gelators are less studied than more common polymeric gelators.

The treatment of the aqueous solution of **83** with lithium chloride leads to the gel formation. In these experiments it was found that the gel formation is highly dependent on the anion added to the solution, while the kind of the cation has a weaker influence. Gel formation is the most successful with nitrate ions. When gelation fails, the mixture remains as a solution, or is transformed into a microcrystalline precipitate. Gels were characterized using atomic force microscopy; they have a fibrous network structure of the



Scheme 20 Structures of compounds **83**–**87**

density depending on the kind of electrolyte; if the network is dense, the hydrogels are robust.

The fact that the influence of anions is stronger than influence of cations is bound with the Hofmeister effect [124, 125]. The Hofmeister series is: $I^- < ClO_4^- < NO_3^- < Br^- < Cl^- < SO_4^{2-}$. The less hydrated anions to the left are salting-in or chaotropic anions, while strongly hydrated anions are salting-out or kosmotropic anions. The chaotropic ions induce gelation, whereas the kosmotropic ions result in a liquid phase, i.e. the tendency to form gels increases from right to left across the Hofmeister series.

The liquid/liquid two-phase extraction properties of calixarenes **84** and **85** serving as ionophores toward alkali (Li^+, Na^+, K^+, Rb^+, Cs^+) and transition metal (Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Hg^{2+}) ions, as well as $HCr_2O_7^-$/$Cr_2O_7^{2-}$ anions were investigated; calixarenes **86a**,**b** served for comparison purposes. Two-phase solvent extraction experiments for metal cation extraction and for dichromate anion extraction were made by Pedersen's procedure; metal picrates and sodium dichromate were used, respectively [126–128].

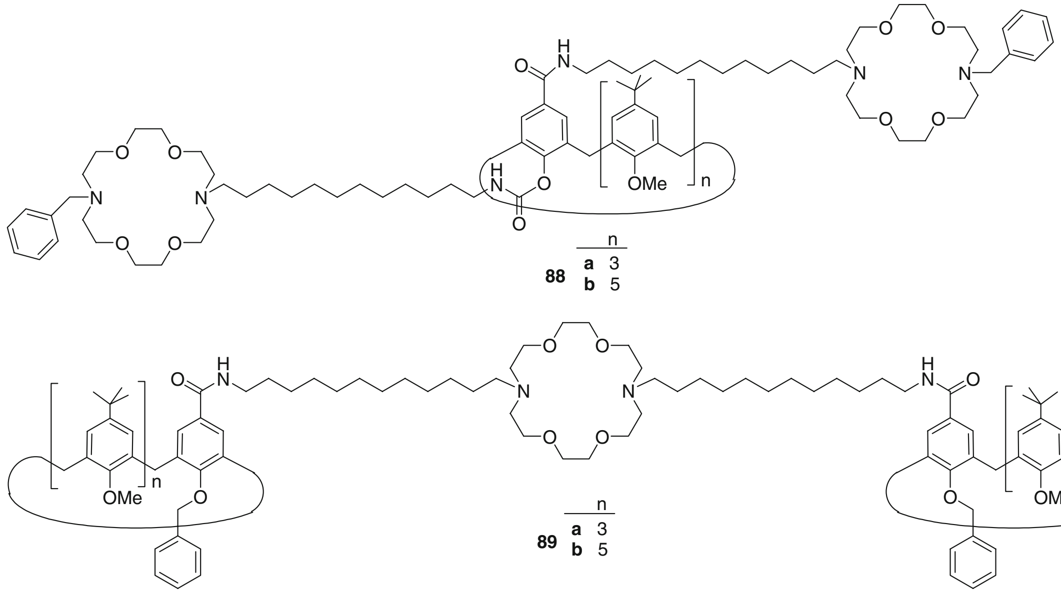
The results indicate that **84** selectively transfers Ni^{2+} ions, however its transferring ability for $HCr_2O_7^-$/$Cr_2O_7^{2-}$ anions from aqueous into a dichloromethane layer is low. Calixarene **85** does not extract alkali/transition metal cations effectively, but shows affinity toward $HCr_2O_7^-$/$Cr_2O_7^{2-}$ anions. It was found that **86a**,**b** are effective extractants for Hg^{2+} ion, the complex **Hg^{2+}·86a** is depicted.

One should mention that the selective extraction efficiency of the calixarenes under study may be enhanced by anchoring them into polymer structure. As an example may serve **86a** which by anchoring into polymeric backbones affords calixarene polymers **87a**,**b** showing higher extraction ability for dichromate anion that **86a** (Scheme 20).

Cation transporters **88a**,**b** and **89a**,**b** bearing calix[4]arenes (**88a**, **89a**) and calix[6]arenes (**88b**, **89b**) have been investigated. Compounds **88a**,**b** contain calixarene as a central unit whereas diaza-18-crown-6 molecules are headgroups; **89a**,**b** however bear calixarenes as headgroups and diaza-18-crown-6 as a central unit. Transport in these systems was assayed by planar bilayer methods [129]. It should be noted that only few works concerning calixarenes as ion transporters are reported [130].

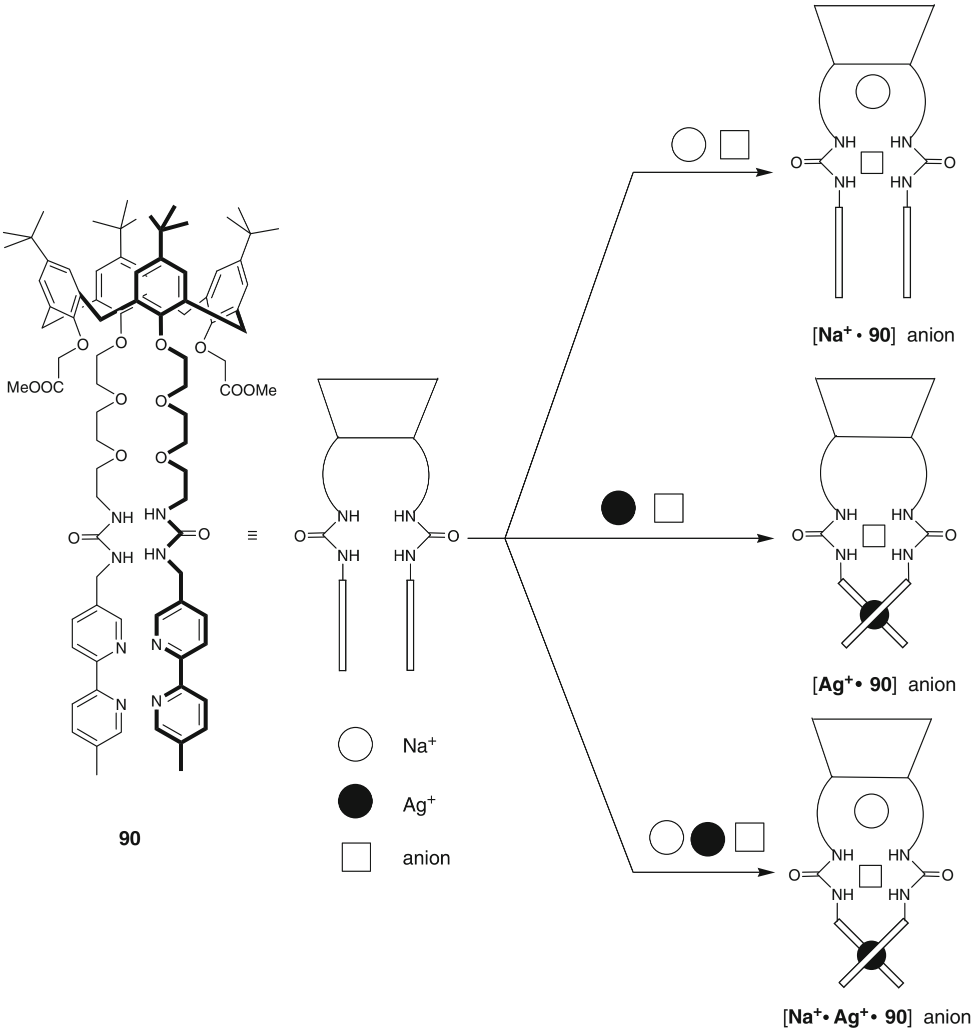
The ion release was studied by detecting either Na^+ or Cl^- release from phospholipid vesicles. The ion selective electrode methods were applied to assess ion egress from liposomes. The liposomes used in experiments were prepared from 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC). To achieve conductance pathway, the molecule should insert into the upper leaflet of the bilayer and then unfold into the lower leaflet. Then the molecule should pass half of the structure through the midplane of the bilayer to the opposite surface.

The formation of the conductance pathway requires compounds **88a**,**b** and **89a**,**b** to extend through both leaflets of the bilayer membrane. If calixarene is too large or too polar it may be unable to penetrate the hydrocarbon regime of the bilayer and anchor on the opposite membrane surface. The problem is the most difficult for **89b**, in which calix[6]arene is both large and polar; therefore **89b** shows no activity for transport of cations and anions. It was established that the ion transport activity of **88a** and **89a** bearing calix[4]arenes is modest, and nearly does not exist in **88b** and **89b** bearing calix[6]arenes (Scheme 21).



Scheme 21 Structures of compounds **88** and **89**

Scheme 22 Complexation reactions of compound **90**



It was found that calixarene **90** is a triple-site receptor which recognizes Na^+ and Ag^+ ions simultaneously and quantitatively and binds an anionic guest. Calixarene **90** is able to multistep regulation of anion recognition by using two different cationic guests [131].

It was observed that the affinity of **90** for anions may be increased due to the electrostatic interactions of hard and soft cationic guests Na^+ and Ag^+ which are bound by ester and bipyridine units, respectively. The complexation of bipyridine units with a cationic guest results in the conformational change of **90**, bringing two urea moieties into a close proximity; this fact facilitates the anion binding.

It was found that **90** forms 1:1 complexes with Na^+ and with Ag^+, **90** binds Na^+ with ester and polyether groups to give $\mathbf{Na^+{\cdot}90}$, and binds Ag^+ with the bipyridine units to give $\mathbf{Ag^+{\cdot}90}$. Upon addition of Na^+ and Ag^+ ions to **90**, the very stable ternary complex $\mathbf{Na^+{\cdot}Ag^+{\cdot}90}$ is formed.

The affinity of **90** for anions is weaker than that for cations. The anion capturing occurs by relatively weak hydrogen bonding with the urea units. The affinity of **90** toward anions is strongly enhanced in the presence of Na^+ or Ag^+. When both Na^+ and Ag^+ are added, the anion binding is stronger. The K_a values toward NO_3^- decrease in the order: $\mathbf{Na^+{\cdot}Ag^+{\cdot}90} > \mathbf{Na^+{\cdot}90} > \mathbf{Ag^+{\cdot}90} > \mathbf{90}$.

It was observed that $\mathbf{Na^+{\cdot}90}$ shows higher affinity for NO_3^- and BF_4^- anions than $\mathbf{Ag^+{\cdot}90}$ does. One should mention that the ternary complex $\mathbf{Na^+{\cdot}Ag^+{\cdot}90}$ strongly binds $CF_3SO_3^-$ and BF_4^- anions, in general difficult to capture by artificial anion receptors (Scheme 22).

Conclusion

Calixarene complexes with metal ions are intensively studied, a large number of reports is a reflection of the rapid development of this chemistry area [132–140].

One should point out the theoretical aspects in the study of the above species, as well as their applications in design of sensors for detection and determination of toxic metal ions, followed by their separation in view of environmental protection.

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