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REVIEW ON CALIXARENE-TYPE MACROCYCLES AND METAL EXTRACTION DATA

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Rainer LUDWIG *

日本原子力研究所
Japan Atomic Energy Research Institute

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Review on Calixarene-type Macrocycles and Metal Extraction Data

Rainer LUDWIG*

Department of Fuel Cycle Safety Research
Tokai Research Establishment
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken

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This paper gives an overview on the current state of solvent extraction studies with derivatized[1.n]-metacyclophanes and related compounds. 122 References from the last ten years are discussed and data on extractability, extraction equilibria, and complex formation are presented in graphical form.

Keywords: Solvent Extraction, Calixarenes, Macrocycles, Metacyclophanes, Metal Separation

* Research Fellow

カリックスアレーン型大環状化合物とその金属抽出データ

日本原子力研究所東海研究所燃料サイクル安全工学部
Rainer LUDWIG*

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これまでに知られている各種のメタシクロファン[1,n]誘導体と同系化合物による溶媒抽出実験の結果を調査し、まとめた。すなわち、過去10年間に発表された、全部で 122報の文献について、考察をくわえるとともに、抽出分配や錯体生成のデータをグラフ形式で示した。

東海研究所：〒319－11　茨城県那珂郡東海村白方白根2-4
* リサーチフェロー

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The class of calix[n]arenes has received significant attention in recent years due to readily available starting and intermediate materials, the possibility to synthesize ligands for ion and molecular recognition with high selectivities, applications of the selective host-guest binding in solvent extraction processes, ion-selective membranes and electrodes, sensors based on spectral and fluorescent changes, and others.

Since a number of books[1,2] and review articles[3-27] deal with the synthesis, conformations, structures, and coordination properties of calixarenes, the present report focuses on metal extraction studies. The aim is to allow a comparison of the extractability of compounds having different cavity sizes and bearing different functional groups at the calixarene backbone. The literature data are ordered according to the groups attached either to the 'lower' or 'upper' rim of the calixarene: Alkyl-, ether-, keto-, ester-, acid-, amino-, amido-, heteroatom-containing and crown ether moieties containing ligands are followed by bridged and double-calixarenes. Not in detail considered are here studies on transport through liquid membranes , for which fewer data are available.

2. Discussion of Extraction Data for Substituted Calixarenes

2.1 Ethers, Phenols and para-Substituted Calixarenes

Ikeda[28, 29] studied the solvent extraction of alkali metal and silver picrates with calixarenes carrying alkyl- and ether groups at the 'upper rim' as well as at the phenolic oxygen at the 'lower rim'. He found cation-π interaction to play an important role in the interaction with K^+ and Cs^+. This is also reflected in the association constants, which were determined in homogeneous media. As a result of cation-π interaction, 1,3-*alternate* conformers (alternating one phenyl ring up and down) show a higher K^+- and Cs^+- selectivity compared with the *cone* conformer (all phenyl rings look in the same direction). Compound **24** in 1,3-*alternate* conformation has a higher extractability towards Ag^+ than the *cone* conformer. No cation-π interaction takes place with Na^+, and the *cone* conformer shows the highest Na^+- selectivity among the different conformers of calix[4]arene (*cone*, *partial cone*, 1,2- and 1.3-*alternate*). The *tert*-butyl groups were found to suppress the extractability in case of 1,3- *alternate* conformers, probably due to steric hindrance. Compound **14** in *partial cone* and 1,3-*alternate* conformation is an efficient extractant for Ag^+. Compound **24** exhibits a low Li^+/Na^+-selectivity due to steric crowding of the propyl groups and the higher lipophilicity around the binding sites. Two examples of bridged calixarenes will be discussed in chapter **2.8**.

Yoshida[30] studied the extraction of copper(II) by using the underivatized p-*t*-butyl-calix[6]arene and established the extraction mechanism. Due to the low acidity of the hydroxyl groups, the pH of the aqueous phase has to be adjusted to above 11 for metal extraction according to a cation exchange mechanism. The stoichiometry of the extracted

1. Introduction

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species is 1:1 but the extraction is slow, because the solvent chloroform is complexed by the extractant and slowly exchanged for the metal ion.

Chang[31-33] synthesized a number of ether, diether, ester, acid and amide derivatives of calixarenes with different ring size n (n = 4, 6, 8) and examined the extraction and transport of alkali and alkaline earth metal picrates. The esters and amides will be discussed in chapters **2.3** and **2.5**. The ether and ethyleneoxy groups are much less effective for metal extraction compared with the ester groups. The ethers of calix[4]arene **64** and **34** show some selectivity for sodium, while the discrimination is low in case of the hexamers and octamers.

Conner[34] extracted alkali metal ions by using calix[4]arenes bearing ether or ester groups at the lower rim and ligating groups at the upper rim. The upper-rim ketone **74**, ester **84**, and amide **94** have a similar sodium/potassium selectivity, in contrast to calix[4]arenes carrying ligating groups at the lower rim. Compared with **104**, they are more flexible and their preorganization is lower as concluded from NMR studies. The stoichiometry of the extracted species is 1:1 (metal picrate: extractant).

Nomura[35] investigated the influence of the solvent polarity on the extraction of alkali metal picrates by calix[6]arene in 1,4-*anti* conformation bearing polyether groups at the lower rim. The extraction constants increase with increasing solvent polarity. The potassium/sodium- selectivity also increases from benzene to 1,2-dichloroethane. The order of extractability is $Rb^+ > Cs^+$, $K^+ >> Na^+ > Li^+$, different from the order of ion-radii. The high extractability of Rb^+, Cs^+, and K^+ is attributed to the flexibility of the 3,6,9-trioxadecyl groups attached to the phenolic oxygen. The stoichiometry is 1:1.

2.2 Ketones

Schwing[36] studied the extraction and complex formation of the ketone derivative **124** and of esters with alkali metal picrates. The esters are discussed in the following chapter. The ketone of calix[4]-arene is a better extractant than the ester due to the higher basicity of the ligating group. However, the selectivity of the calix[4]arene ketone and ester is similar, showing a peak for sodium ions, which is attributable to the cavity size. A good correlation between the stability constants in methanol solvent and the order of extractability was observed. The values and order of the stability constants in acetonitrile, the properties of which are very different from water, differ significantly from the values determined in methanol.

A series of ketones **12n** - **14R4** were synthesized by Arnaud[37, 38] and Ferguson[39] together with esters (chapter **2.3**). Their extraction properties towards alkali ions from alkaline and neutral aqueous solutions, stability constants and membrane transport were investigated. The extractability of the ketones towards alkali metal picrates is higher compared with esters, but the selectivity is lower. All calix[4]arene extract sodium better than potassium. The octamers **128** and **138** are the least effective ionophores. The extractability order is paralleled by the stability constants in methanol.

2.3 Ester

Brunink[40] studied the extraction of alkaline metal picrates by de-*t*-butylated calix[4]arenes bearing ester groups, ester- and ketone groups, as well as ester- and amide groups at the lower rim, the latter being discussed in chapter **2.5**. The sodium-selectivity is influenced by kind and number of ester groups. Compound **17$_4$** in *cone* conformation has the highest sodium-selectivity, which completely disappears in the *partial-cone* conformer. Compounds **15$_4$** and **16$_4$** show sodium-selectivity as well.

Calixarene-based extractants carrying ethylester groups attached to Ø-O-CH_2- were studied in detail by a number of research groups. The extraction of alkali metal thiocyanates from neutral solutions was compared with that of alkali metal picrates by Arnaud[41] by using the ethylester (**18$_4$** - **18$_6$**) and amide derivatives of p-*t*-butylcalix[n]arenes (n = 4, 5, 6) and extraction constants were calculated for the 1:1 complexes. The dissociation of the extracted species in the organic phase was neglected for the calculation of K_{ex}, although dichloromethane with a high dielectic constant was used as solvent in the experiments. The metal thiocyanates are extracted to a lower extent compared with the picrates. The calix[4]arene shows peak selectivity for sodium, independent from the kind of functional group at the lower rim. The mechanism of transport by calixarenes across liquid membranes is discussed in detail in the paper.

The extraction of alkali metal picrates from alkaline aqueous solutions was investigated by Chang[31-33] as well as by Arnaud[37, 42], Diamond[43], McKervey[44], and Ferguson.[39] Compared with the ethers, ester derivatives of calixarenes are better extractants and both the tetramer **18$_4$** and the hexamer **18$_6$** extract alkaline metal ions to a greater extent than alkaline earth ions. The hexamer shows some cesium-selectivity, which was confirmed by UV-spectroscopy.[33] The octamer assumes a loosely pitched conformation forming a pseudo cavity with plateau-selectivity for K^+, Rb^+, and Cs^+. Generally can be concluded, that the cavity size plays an crucial role in the discrimination of ionic guests and the extraction efficiency. The carbonyl oxygen was found to participate strongly in metal binding, compared with the poor extractability of the parent calixarenes bearing only hydroxyl groups and with the low efficiency of calixarene extractants bearing ether groups. The Na^+-selectivity of compound **18$_4$** (*cone* conformation) is reflected by the stability constant in methanol, while the stability in acetonitrile differs significantly. The *t*-butyl groups improve the sodium-selectivity compared with the de-butylated analogon. The cesium-selectivity of **18$_6$** for example is not reflected by the stability constants in acetonitrile solvent. Towards ammonium picrate both the ester **18$_4$** and the ketone **12$_4$** show a low extractability. The macrocyclic effect improves the extractability as can be seen from the data for the linear ester podand **19$_4$**. Compared with 18-crown-6, the selectivity of calixarenes is better.

The influence of the conformation of the calix[4]arene ethylester on its extraction towards alkali metal picrates as studied by Iwamoto[45] established that the *cone* conformers **18$_4$** and **15$_4$** display sodium-selectivity while the other conformers (*partial cone*, 1,2-*alternate* and

1,3-*alternate*) display potassium-selectivity. This effect can be utilized in the metal template-mediated synthesis of the different conformers. The 1,3-*alternate* conformers have two metal binding sites with negative allostericity. A metal-induced rotation of the phenyl groups was observed in the *partial cone* conformer. The flattened ester groups in the 1,2-*alternate* conformer are inefficient ligands and the proximal tweezing is weaker than the distal tweezing in the 1,3-*alternate* conformer.

Further data on the extractability of alkali, alkaline earth, and other metal picrates by ester derivatives of calix[n]arenes (n = 4, 5, 6, 7, 8) and the stability constants in methanol were obtained by Arnaud[46] and Schwing[47], who also investigated the tetrameric and hexameric amides and thioamides **21** and **22**. Their studies revealed the influence of the ring size in symmetrical calixarenes, the influence of the kind of ester group, the influence of the kind of ligating group (ketone, ester, amide, acid) attached to the phenolic oxygen, and the influence of mixed functionalities. The pentameric ester **10$_5$** and **18$_5$** are more efficient extractants compared with the hexameric and tetrameric analoga, and display plateau selectivity for the heavy alkaline ions. The *t*-butyl ester of calix[4]arene and calix[5]arene show higher extractability and stability constants than the corresponding ethylester. As expected, the thioamides **21S$_n$** and **22S$_n$** are poor extractants for the 'hard' alkali and alkaline earth ions. Ag^+ is extracted to a great extent by both the amides and the thioamides, while Pb^{2+} and Cd^{2+} are well extracted by the tetrameric amides **21O$_4$** and **22O$_4$** (and by **22S$_4$** as well). The amides **21O$_4$** and **21O$_6$** display a good barium/magnesium selectivity, while the sodium-selectivity of the tetramers is less pronounced.

Another thioamide **23$_4$** was described recently by Roundhill[48], who found it to be an effective extractant for Hg^{2+}, Hg_2^{2+}, Ag^+, and Au^{3+}, but not for the 'hard' metal ions Pb^{2+}, Cd^{2+}, Ni^{2+}, and Pt^{2+}.

The sodium/potassium selectivity of a variety of esters (**10$_4$**, **12$_4$**, **25$_4$**-**35$_4$**), amides and calix[4]arenes with mixed functionalities in *cone* conformation was studied by Arnaud[38, 46] in terms of extraction from neutral solutions and stability constants in methanol. All esters display sodium/potassium selectivity, which strongly depends on the nature of the ester group. A high selectivity coefficient of the β-values (e.g. **28$_4$** due to good ligating properties of the phenacyl group) is not always reflected by a large difference in extractability. Substitution of one or two ester groups in **33$_4$** and **34$_4$** has little influence compared with the tetra-ethylester **18$_4$**. The monoacid **35$_4$** extracts no picrate, but possibly the metal ion alone as neutral complex.

2.4 Carboxylic Acids and Hydroxamic Acids

With the aim to avoid the influence of counterions and to improve both extractability and selectivity, ionizable groups are introduced into the calixarenes. Shinkai[49] investigated the extraction and transport of uranyl ions in the absence and presence of competing metal ions with acid derivatives **37$_6$** and **38$_6$**, which provide a hexaedric planar coordination site. The

high selectivity observed for the comparable water-soluble, p-sulphonated calix[6]- and calix[5]-arene in aqueous solution is not observed in solvent extraction, because two uranyl ions are co-extracted as counterions, thus changing the coordination to bidentate. Tetramethylammonium ions improve the selectivity since they compete as better counterions and the extracted complex achieves the desired 1:1 stoichiometry.

The extraction of lanthanide ions by acid derivatives of *t*-octylcalixarenes was studied by Ohto.[50-53] The *t*-octyl group at the upper rim greatly improves the solubility in organic solvents compared with the *t*-butyl analoga, without a major change in the selectivity. The highest extractability is observed for the medium lanthanides and **39$_4$** and **39$_6$** as extractants. The dimeric compound **39$_4$** extracts lanthanides into toluene with a stoichiometry of 3:1 while the hexamer **39$_6$** forms 2:1- complexes (ligand:metal). Compound **39$_4$** is partly dissociated between pH 2 and pH 4.5, the proton dissociation number at pH 4.5 being about 0.3. The values of the pH at 50% extraction ($pH_{0.5}$) were determined at various compositions of the aqueous phase containing an excess of Li^+, Na^+, or K^+ ions. Lower values of $pH_{0.5}$ correspond to higher extractability at a certain pH. An significant impact is observed in the presence of Na^+ when **39$_4$** is used as extractant, because sodium fits the cavity of calix[4]arenes well and enhances the rigidity of the ligand. The 'tetrad'-effect was observed in the series of lanthanides and by comparing the extraction with monomeric **39$_1$** a significant decrease of $pH_{0.5}$ is achieved due to higher preorganization and the chelate effect.

Recently, Ohto[54] described the extractability of silver and palladium from acidic media by using the calix[4]arene acids **39$_4$** and ketones **40$_4$** A separation factor Ag(I)/Pd(II) in the order of 10^2 is achieved by extracting Ag^+ from a 100-fold excess of Pd(II) in 1 M HNO_3 with **40$_4$**.

Ungaro[55] in 1984 established that acid derivatives of calixarenes **37$_4$**, **41$_4$**, and **42$_4$** show good extractability towards metal ions compared with the monomeric **37$_1$**. The highest selectivity was observed for the crowned calixarene **42$_4$**, though the selectivity depends on the extraction conditions such as pH, additives, and competitive extraction.

The complex formation of carboxylic acid carrying calix[4]arenes with lanthanoides and Th^{4+} was studied by potentiometry.[56] Among lanthanoides, the selectivity is in favor of the smaller Yb^{3+}. Extractive separation of Th(IV) from Ln(III) in very acidic media might be possible due to differences in stability constants.

Our own studies[57-59] on competitive lanthanoide extraction at pH 2 to 4 by the acid derivatives **37$_4$** and **37$_6$** showed, that the lanthanoides are extracted as sandwich-complexes according to a cation exchange mechanism in the absence of excess alkali salts. Probably, the preorganization of the ligand and the hydrophobicity of the 1:1-complex are not sufficient for the phase transfer and a second ligand is required. The presence of excess Na^+ changes the extraction mechanism for **37$_6$**, the stoichiometry of the extracted complexes becomes 1:1, while sodium is extracted independent of the pH as ion pair with perchlorate anion. In case of **37$_4$**, positive allostericity is observed, excess Na^+ improves the extractability and the separation factors among the light to medium lanthanides, as shown for La, Nd, and Eu. This

is the same effect of improved ligand preorganization as observed with **394**, namely a more rigid ligand, the cavity size of which is suitable to accommodate the medium and heavy lanthanoides, and weakened intramolecular hydrogen bonding. The extraction of lanthanoides by [1.3.1.3]-metacyclophane **43** was not affected by Na^+, Ln^{3+} and Na^+ are extracted separately rather than co-extracted.

The extraction of other metals from weakly acidic sulphate media into toluene/octanol (5%) by **374** follows the order: Th(IV)> Fe(III) > U(VI) >> Mg(II)≈ Cu(II) ≈V(IV) > Zn(II) > Ni(II) ≈ Co(II) > Mn(II).[60] A kinetic study of UO_2^{2+} extraction by means of an analytical ultracentrifuge showed a diffusion-controlled transport. Substituting the *t*-butyl group by a more hydrophobic n-octadecyl group in **444** increases the distribution ration of lanthanides by a factor of 20. The stoichiometry of the Ln(III)-complexes extracted into toluene is 1:1. Only 2 protons are exchanged when either chloroform or toluene serve as diluent, which may indicate that the extractant exists as a 1:1- sodium complex and exchanges the Na^+ ion.

The extraction of lanthanoides and nobel metals by calix[4]arenes bearing mixed carboxylic acid and amide groups from weakly and strongly acidic media shows that lanthanoides are better extracted in the presence of one amide group in the macrocycle, if the hydrogen bonding is diminished, e.g. by the presence of Na^+ in the aqueous phase.[61] A calix[4]arene bearing 2 carboxylic acid and 2 amide groups readily extracts Pd(II), Pt(IV) and Au(III) from aqueous solutions at pH 1 to 2.5, as well as minor amounts of Ru(III), while the calix[4]arene with 3 carboxylic acid and one amide group extracts Au and Pd and traces of Pt, but none of the trivalent Ir, Rh, and Y.

A number of studies by Shinkai et.al. dealt with uranium extraction by hydroxamic acid derivatized calix[6]arenes, since water-soluble calix[6]arenes can selectively bind UO_2^{2+}. [62, 64-65] The extraction of uranyl by hydroxamic acids **456** and **454**, carried out by Nagasaki[62, 65] showed that these compounds have a lower pK_a compared with monomeric **451**. The calix[6]arenes provide hexaedric coordination for the bound metal, which is favorite for UO_2^{2+}. In competitive extraction, hydroxamic acid **456** is more selective towards UO_2^{2+} than the acid **376**. Since the pK_a of hydroxamic acid is higher compared with the carboxylic acid, the complex [L·UO2] is neutral at pH 6. In both **376** and **456** the number of ionizable groups doesn't match the metal charge and the excess of ligating groups cause the co-extraction of 3 UO_2^{2+} ions.[64] Compound **474** bearing a C_3-symmetry avoids this disadvantage and extracts only one UO_2^{2+} ion with high selectivity, together with K^+. The structure as proved by NMR shows a pseudoplanar hexacoordinated binding of UO_2^{2+}. The impact of carbonate anions, which form strong complexes with UO_2^{2+}, on its extractability is lower for the hydroxamic acid compared with the carboxylic acid.

Another type of hydroxamic acids, the flexible **46R4**, was found to effectively extract Th(IV) and U(VI) from weakly acidic media.[63]

A number of transition and nobel metal ions in the presence of excess alkali salts were extracted by Nagasaki[66] by using carboxylic acid, hydroxamic acids and amide derivatives of calixarenes. They have an improved extractability compared with their monomeric analoga

37$_1$, **45$_1$**, and **48$_1$**. At pH 2.2, compound **37$_4$** extracts only traces of metals, while **37$_6$** and **45$_n$** preferably extract Fe(III). Amides **48$_4$** and **48$_6$** extracted Pd and Pt over a wide range of pH. Extraction equilibria were established for Ni(II), both **37$_6$** and **45$_6$** form 1:1-complexes via a cation exchange mechanism, though **37$_6$** under the conditions of excess KCl in the aqueous phase exists as its 1:1-potassium complex.

Calixarene **49$_4$** bearing carboxylic acid and amide groups preferably extracts Ca^{2+} and high separation from the other alkali earth ions is achieved even in competitive extraction experiments.[67] The selectivity and high extractability stem from (i) the rigid cavity into which Ca^{2+} fits well, (ii) charge neutralization, and (iii) cooperativity of the ligating groups. The Ca^{2+}-selectivity disappears upon removal of the two amide groups as in **50$_4$**.

By using calix[4]arene **51$_4$** bearing two carboxylic acid groups, Soedarsono[68] extracted lanthanides from low acidic and neutral solutions. High separation was achieved in synergistic extraction by mixing **51$_4$** with versatic acid, as shown for La, Y, and Er. The extractability is increased by 2 to 3 orders of magnitude and the selectivity by a factor of 50 at pH > 4. The separation factors at pH 5.8 are 1.4 (Er/Dy) and 19 (Er/La).

The same extractant forms 1:1-complexes with Na^+, K^+, and Cs^+, while 2 Li^+-ions are extracted.[69, 70] The extraction proceeds according to a cation exchange mechanism, releasing one or two protons. The effect of different anions in the aqueous phase was investigated. The extraction constants follows the order Na > K > Rb > Cs, and the largest impact of the kind of anions is observed for Na^+. In competitive extraction, the separation factor Na/K diminishes. The stoichiometries were verified by mass spectra and slope analysis.

2.5 Amides

Compound **52$_4$** with two amide and two ester groups has a higher extractability towards alkali ions compared with calixarenes **15$_4$** - **17$_4$** carrying ester groups only. The sodium-selectivity, which is caused by the size of the cavity around the ethereal oxygens, is remained but weakened due to the higher donor strength of the amide groups. A similar effect, namely a higher extractability together with a lower selectivity was observed by Arduini and Calestani[71, 72] when extracting alkali ions by ester and amide derivatives of p-*t*-butylcalix[4]arene. The participation of the amide groups in alkali ion binding was established by X-ray crystal structure analysis of the 1:1-complexes. The tetra-amides **53$_4$**, compared with tetra-esters, extract divalent metal ions, e.g alkaline earths, to a greater extent than alkali ions, because the amide carbonyl group is more polar than the ester carbonyl group.[31-33] A high extraction of Sr^{2+} was observed with the hexamer **53$_6$**, but the tetramer and octamer display no peak-selectivity.

The de-butylated **21R$_4$** (R = H) was recently shown to have remarkably increased Cs/Na- as well as Sr/Na- selectivities, compared with the *t*-butylated analogon.[73] The higher flexibility, shown in its VTNMR spectra, seems to be the origin for the increased selectivity.

Tetra-amides **21$_4$** and **22$_4$** feature a peak-selectivity towards Na^+ among alkali ions as well as stable complexes and high extractability for alkaline earth ions.[41, 42] The amides are better extractants than the ester, and the pyrrolidinyl amide **22$_4$** is more effective for Li^+, Na^+, and K^+ compared with diethylamide **21$_4$**. Tertiary amides are better extractants than secondary amides, but in transport studies through BLM's the amides **21$_4$** and **22$_4$** show exceptional poor transport of Na^+, compared with the high stability constants of the complexes. The selectivity for Na^+ and Ca^{2+} is explained by the size effect since the radii of both ions are similar and the highly polar amide group promotes binding of alkaline earth ions. The Na/K-selectivity of calixarenes **54$_4$** and **55$_4$** with 3 ester and one amide group, measured by potentiometry in methanol is reduced, while the selectivity in phase transfer studies is still high. Probably, K^+ fits less deep into the cavity and is more exposed to hydration.

2.6 Other Nitrogen- and Phosphorous- Containing Calixarenes

Compound **56$_4$** with mixed pyridine and ester groups[74] exhibits a pronounced difference in selectivity for different conformers. The *cone*-conformer displays Na^+-selectivity and the extracted Na^+-complex has a 1:1-stoichiometry. The considerable percentage of extracted Li^+ means that the cavity is smaller compared with that of the tetra-ester. The *partial-cone* conformer displays plateau-selectivity for K^+ and Cs^+ as a result of a larger cavity. The stoichiometry of the complexes remains 1:1. Fully pyridine-derivatized **57$_n$** can extract alkali ions and Ag^+ from basic solutions,[75] the extractability is higher when the hexamer is used instead of the more flexible octamer. The observed Cs^+-selectivity is interpreted in terms of the cavity size of **57$_6$**. Cu(II), which is known to bind to pyridine-nitrogen is extracted to a small extent only, while the extraction of UO_2^{2+} is enhanced at elevated temperature. The slow kinetics of the complex formation and the higher flexibility at higher temperature are responsible for the latter effect.

Nomura[76, 77] used para-phenylazo-derivatized **58R$_n$** for extraction. Compounds **58H$_4$** and **58H$_6$** extract only 'soft' metals like Hg and Ag from neutral solution, while the methylated analoga (R=CH_3) are poor extractants. The hexamer **58H$_6$** is more effective for extraction than the tetramer **58H$_4$**, though the stability constants for the silver complexes show an opposite order. Silver is bound between two nitrogen atoms, one of which is neighbored to a tautomeric hydrazono nitrogen and the other is part of the azo-group. The monomeric **58$_1$** binds metal ions non-selectively to the phenolic oxygen, leading to higher extractability but poor selectivity.

Carbamoylmethylphosphineoxide (CMPO) containing calixarene **59R$_n$** with different alkyl chains R and ring sizes (4 or 5) were found to be better extractants for lanthanoides and actinides compared with the parent CMPO and much better than the monomeric analoga.[78-83] A high extraction of Np, Am, and Pu was observed.

A very high but non-selective extractability towards alkali ions is observed by using compound **60$_4$** with amino-groups at the upper rim, but not for the monomeric analoga and

the de-aminated calixarene **614**.[84] The high extractability is not observed in liquid membrane transport experiments.

Another azo-calixarene was described by Shimizu[85] to be very Li^+-selective. The Li/Na-selectivity depends on the kind of counter anion in the order $Cl^- > ClO_4^-$. The Li^+-selectivity is caused by the smaller cavity compared with the calixarene esters. The Li^+-ion is bound as counter-cation to the azophenolate anion and interacts with three ($-O^-$).

Oxime-derivatized **63n** selectively extracts metals in the order: $Hg^+ > Hg^{2+} > Ag^+ > Cu^{2+} > Cr^{3+}$ and the extractability is higher in case of the tetramer.[86] Compared with the ester **184**, the ketone **124**, and parent calixarenes **5n**, a reasonable discrimination between the 'soft' Hg and Ag and 'hard' alkaline ions is achieved with the oxime groups. Polymeric **64R4** preferably extracts Hg and Ag with a mechanism different from that of monomeric calix[4]arene.

Pyridine and pyridine-N-oxide carrying **654** to **704** were tested with respect to the extraction of alkali ions.[87] The N-oxides have a low extractability and selectivity due to hydrogen-bonding between N-O functionalities and water at the liquid-liquid interface. Compounds **684** and **704** in *cone*-conformation show selectivity for Na^+. The selectivity changes to K^+ and Rb^+in case of the 1,3-*alternate* **704**, while 1,2-*alternate* **704** is ineffective for extraction under these conditions. In aprotic solvents, however, *cone* **704** N-oxide was proved by NMR to be a better ligand with a faster kinetic compared with the pyridine.

Crowned **714** with one azo-group in para-position displays a high selectivity towards K^+ in extraction at pH 7 to 9, and a high discrimination against Li^+, Na^+, Cs^+, Mg^{2+}, and Ca^{2+}.[88] The extracted metal ions are bound to the phenolic oxygen and the extraction constant is influenced by the substituent attached to the phenylazo group.

Crowned Schiff bases of type **72R4** extract metal ions as 1:1-complexes.[89] Comparing the influence of the spacer length R, the binding ability turns out to depend on rigidity and length of the bridge. The more flexible compound with R=-$(CH_2)_4$- is less selective but shows considerable extractability towards Fe, Cu, Pb, and Eu. The phenolic hydroxyl groups of **72R4** (R=butyl), which dissociate above pH 12, are not involved in metal binding at pH 8. The rigid **72R4** (R=phenyl) preferably binds Eu^{3+} in homogeneous solution, but the selectivity is changed and reduced under solvent extraction conditions.

Triphenylphosphane-derivatized calixarene **6R4** shows high extractability towards all tested metal ions[90] compared with the *t*-butyl-analogon. Participation of P in metal binding is concluded from the selectivity towards Hg^+. In the Cu(II)-complex, calixarene **6R4** (R=-$P(Ø)_2$) adopts a 1,3-*alternate* conformation and binds two metal ions. The cyclic compound has a higher extractability than the monomeric triphenylphosphane, the selectivity order is different between both compounds.

2.7 Crowned Calixarenes

Crowned **73$_4$** in *cone* conformation in the extraction of alkali picrates shows the order: Rb^+, $K^+ >> Na^+ > Cs^+$.[91, 92] Double catechol-bridged **74R$_4$** in 1,3-*alternate* conformation extracts K^+ selectively among the alkali ions due to its rigid cavity.[28] The high extraction of Ag^+ can be explained by cation-π interaction. Crowned double-calixarene **75$_4$** forms 1:1-complexes with alkali ions in acetonitrile.[93] The extraction is highest for K^+ and Rb^+, and a high Rb/Cs-selectivity both in picrate extraction and in the values of the association constants is observed. The metal is bound in the central, major cavity while the minor cavities don't bind metal ions due to the 1,3-*alternate* conformation and the *t*-butyl groups.

2,4-Crown-6-calix[4]arenes **76R$_4$** and bis crown-6-calix[4]arene **77R$_4$** in fixed 1,3-*alternate* conformation were investigated as selective extractants and carriers in supported liquid membranes for Cs^+ from acidic media and other ions from industrial waste solutions.[94-97] The highest Cs/Na-selectivity in the presence of excess Na^+ is found for **76R$_4$** (R=*i*-propyl). Extraction and transport studies with Purex raffinate were conducted and high decontamination factors of Cs from fission products and actinides are obtained. Kinetic studies were undertaken in the same system. A detailed study about the influence of the conformation on the selective extraction of alkali ions by crowned calixarenes **76$_4$** and **78$_{4,n}$** was recently described by Casnati.[98] The selectivity order is in agreement with the order of association constants and stability constants. The affinity for Cs^+ is dramatically increased in 1,3-*alternate* **76$_4$** compared with *cone* **76$_4$**, the greatest difference is observed when bulky isopropoxy groups are introduced, which further reduce the low binding ability of the *cone*-conformer for steric reasons. The Cs^+-complexation by **76$_4$** is enthalpy driven. The flexible **78$_{4,6}$** interconverts to 1,3-*alternate* conformation in the presence of Cs^+ due to solvation effects. *Cone* **78$_{4,6}$** is more polar and less preorganized than the 1,3-*alternate* conformer. Desolvation during the complexation of Cs^+ enhances the ($T\Delta S_C$) term and decreases the ($-\Delta H_C$) term. Transport studies with **76$_n$** in SLM's show that the transport is diffusion limited.

Chromogenic calix[4]crowns with a high Na/K-selectivity both in extraction and in homogeneous solutions were described by Yamamoto.[99] Compounds **79$_4$** and more hydrophobic **80$_4$** show selectivity factors Na/K of $>10^{3.1}$ and Na/Li of 10 and can be applied as sensors by monitoring the spectral intensity (λ_{max} at 615 to 623 nm).

The extraction of alkaline ions by calix[4]crown telomers **81$_4$** was compared with the uncondensed calix[4]crowns **82R$_4$**. The compounds display K^+-selectivity in both picrate extraction and membrane transport. Among the telomers, ether- and amide-bridged **81$_4$** are the most effective extractants due to the additional binding sites in the bridges.

A study on the transport of Cs- salts through SLM's by a crowned calix[4]arene in 1,3-alternate conformation bearing an additional anion receptor group opposite to the crown moiety established that cooperative binding of both cation and anion greatly enhances the

flux.[101] This effect is more pronounced for the hydrophilic chloride than for the comparatively more hydrophobic nitrate.

A kinetic study and modeling of the transport of alkali ions through SLM's by using some crowned calix[4]arenes and calixspherands showed that the rate-limiting step is the release of the salt from the membrane as a result of a slow kinetics of decomplexation.[102] The slow kinetics can reduce the K/Na-selectivity which is found in diffusion-limited transport.

Alkali ion extraction by a calix[4]arene with a photoswitchable selectivity was reported from the Chemirecognics Project.[103-105] Compounds **844** and **854** photocyclizise at hν > 365 nm to **834** and **864**, respectively. The reversed monomerization takes place upon heating or/and at hν < 280 nm and this cycle can be repeated without a significant change in the extractability. The cavity of bridged **834** is more rigid compared with its precursor and leads to a more pronounced Na^+-selectivity. On the other hand, dimerized **864** preferably extracts Li^+ while its precursor is Na^+-selective. The association and dissociation rates decrease upon dimerization in case of **834** and the kinetics of decomplexation is influenced by the complexed metal ion.

2.8 Bridged Calixarenes and other Metacyclophans

A series of biscalix[4]arenes in immobilized *cone* conformation was synthesized by Ohseto and their ion recognition was studied by alkali picrate extraction.[105, 107, 108] The molecular motion of the ethyleneoxy groups in **904,3**, compared for example with calixarene **844** is suppressed in the ring and causes an increased extractability. All biscalix[4]arenes showed Na^+-selectivity like the mono-calix[4]arenes. Biscalixarene **894** can accommodate up to 2 alkali ions in its cavities with negative allostericity, the binding of one metal ion suppressing the further binding of the second one. The formation of 1:2 endo-complexes (L:M) of compound **904,3** with Na^+- or K^+-ions was verified by NMR. A change of the conformation is observed during complexation. The sodium ions in the 1:2-complex exhibit fast intramolecular and slow intermolecular exchange on the NMR-time scale.

Takemura[109] extracted alkali and alkaline earth picrates and uranyl chloride with the nitrogen-containing [3.3.3]-metacyclophane **914**. Uranyl is almost quantitatively extracted from neutral solutions. Among the alkali and alkaline earth ions, K^+ and Ba^{2+} are preferably extracted.

Okada studied the extraction of various metal ions with the rigid compounds **92R4** and **93R4**. The extraction of alkali ions is very low when ketone and diketone groups are attached to the phenolic oxygen, but strongly increases when ester groups are present. The larger alkali ions are preferred due to the cavity size, which is similar to the cavity size of the more flexible calix[6]arenes. Among several esters, the ethyl ester is superior for the extraction of K^+, Rb^+, and Cs^+, while the *t*-butylester extracts transition and heavy metals to a greater extent. Light lanthanides are better extracted than heavy ones, in difference to the extraction order for the smaller calix[4]arenes. The ethylester of the more flexible **934** can

extract Cr(III) and Hg(II), while the pyridino derivative almost quantitatively extracts Ag(I) and Hg(II) as well as considerable amounts of Cr(III) and the larger lanthanoides. By using functionalized **92**$_4$ and **93**$_4$, Nomura[113] compared the extraction of lanthanoides. A significant influence of the alkyl group of the ester and of the bridge of the skeleton is observed, but the selectivity among the lanthanoides is low.

Resorcinol-derived **94**$_4$ bearing alkyl chains of different length at the bridging carbon extracts alkali ions as 1:1-complexes (proved for n=12 by molar ratio method) in the order: $Cs^+ >> Rb^+ > K^+ > Na^+ > Li^+$. The two OH-groups are strongly acidic compared with the parent resorcinol and stable intramolecular hydrogen bonding is observed at room temperature by NMR spectroscopy, IR, and titration. Solvents were found to attract OH-groups in the order: $CH_2Cl_2 < C_6H_6 < CHCl_3$, which reduces the extractability of Cs^+ in this order. The long-chain compounds were tested in flotation and foam fractionation experiments.

A series of cyclophanes **95**$_2$ to **99**$_2$ with different ligating groups were studied by Inokuma.[115] Compounds **96**$_2$ and **97**$_2$ with a rigid paddlane skeleton are selective towards K^+ and Ag^+, respectively. The stoichiometry of the Ag^+-complex is 1:1. Crowned **99**$_{2,n}$ preferably extracts heavy alkali ions when crown-6- or crown-7 moieties are attached.

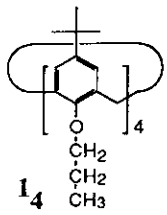
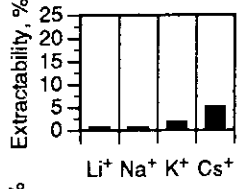
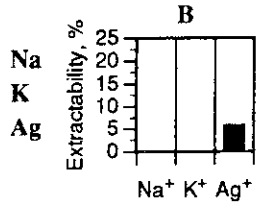
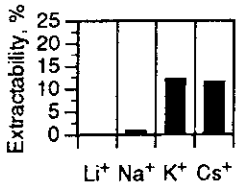
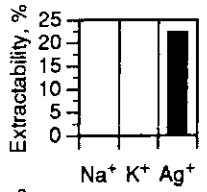
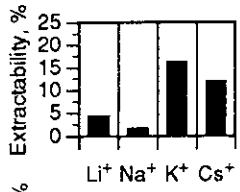
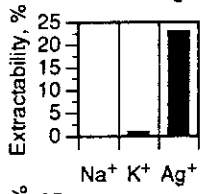
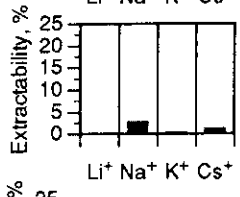
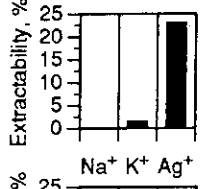
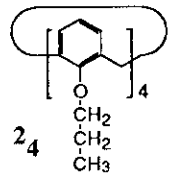
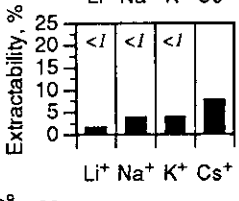
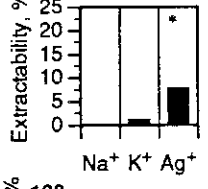
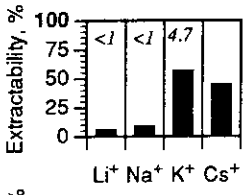
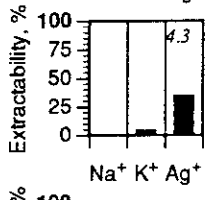
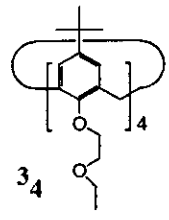
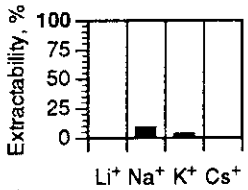
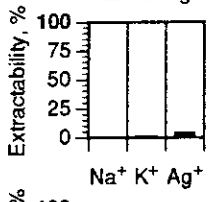
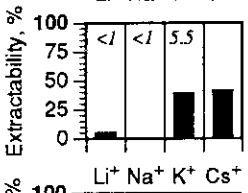
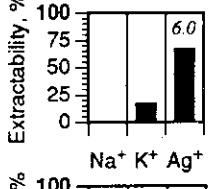
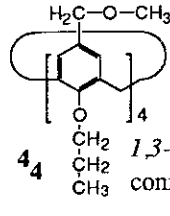
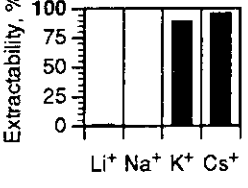
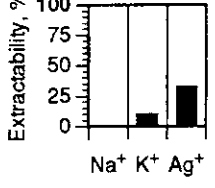
Ester- and polyether-functionalized **100**$_4$ as one example for 'resorcinarenes' preferably extracts Rb^+ among alkali ions and was tested with respect to its catalytic activity.[116]

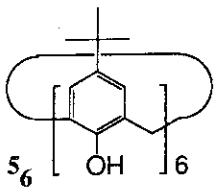
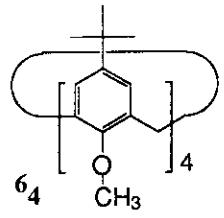
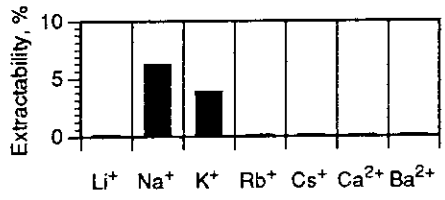
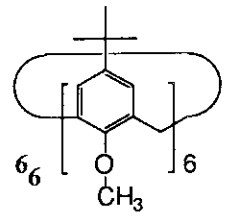
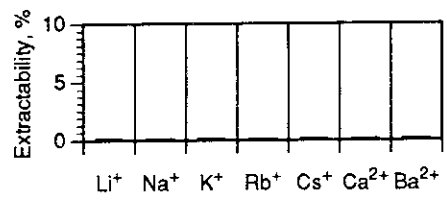
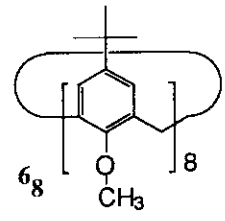
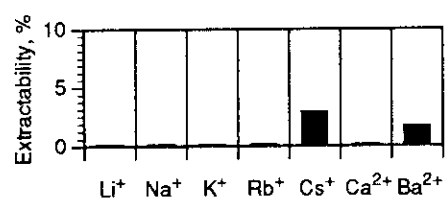
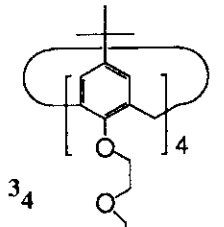
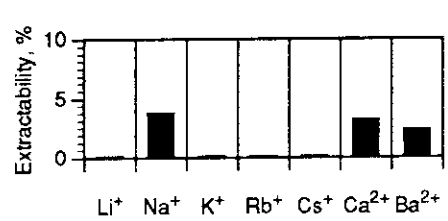
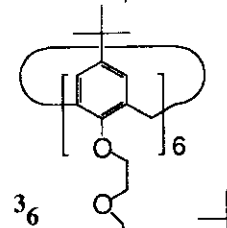
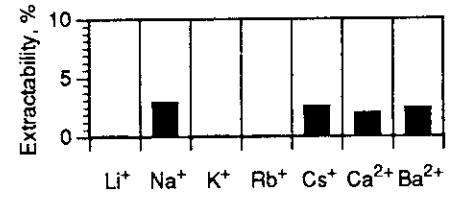
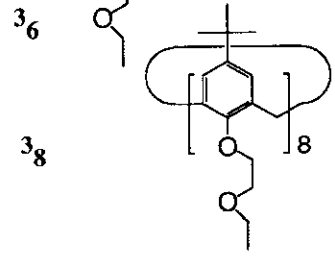
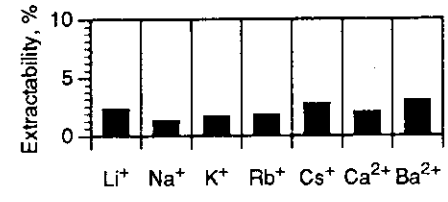
The functionalized [1.3.1.3]-metacyclophane **101R**$_4$ in 1,2-*alternate* conformation shows selectivity for Rb^+ in picrate extraction when R is an ester groups. The extractability is decreased upon removal of the *t*-butyl groups. Introducing amide groups strongly enhances the extraction of the light alkali ions. The extracted species have a 1:1 stoichiometry.

Derivatives of the [3.3.3]-metacyclophane **103**$_3$ were prepared by Yamato[118-120] and their metal extraction investigated. The flexible [3.3.3]-metacyclophane **104**$_3$ with ether bridges and conformationally fixed **105**$_3$ extract alkali ions in the order: $K^+ > Cs^+ > Na^+ > Li^+$. The *cone*-conformer of **105**$_3$ shows better extraction of K^+ and Cs^+, but lower extraction of Na^+ compared with the *partial cone* conformer. The K^+ interacts with the phenolic oxygen at the same side, while Na^+ interacts across the ring. The thermodynamics of the binding was established from NMR studies. Ammonium ions are well extracted due to C_3-symmetry.

The extraction of transplutonium elements Am and Cm as ion pairs by resorcinol-derived cyclophanes 106R was examined with supported liquid membranes.122) These cavitands possess an enforced concave cavity the rigidity of which is higher compared with calix[n]arenes. However, the compounds were found by NMR to be too rigid to complex lanthanides. Since the coordination requirements for lanthanide and actinide extraction are not fulfilled by the monodentate ligating groups, bidentate groups are proposed as binding sites.

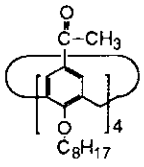
3. Charts on Solvent Extraction

Extractant Ether	Metal	Data A	Data B	Conditions and Remarks	Ref.
 **1_4** *cone* conformation	Li Na K Cs		 Na K Ag	**Aq.**, Series A (Li, Na, K, Cs): 0.25 mM metal picrate, 0.1 M MOH, 0.5 M MCl **Aq.**, Series B (Na, K, Ag): 0.238 mM Hpic, 0.01 MNO_3, pH 4.7 **Org.:** 2.5 mM L in CH_2Cl_2 Vol.: 5 ml/5 ml, T: 298 K, t: 12 h, analysis: spec.	[28, 29]
partial cone conformation					
1,3-alternate conformation					
1,2-alternate conformation				association constants K_{ass} from NMR data at 223 K in $CDCl_3/CD_3OD$ (4:1 v/v), $c_{MX} = c_L = 1$ mM MX = $LiClO_4$, $NaClO_4$, Kpic, $AgCF_3SO_3$ *: K_{ass} not determined due to line broadening	
 **2_4** *cone* conformation					
1,3-alternate conformation				values of log K_{ass} are indicated above bars	
 **3_4** *cone* conformation					
1,3-alternate conformation					
 **4_4** *1,3-alternate* conformation					

Extractant	Metal	Data	Conditions and Remarks	Ref.
Phenol and Ether				
	Cu^{2+}	$Cu(NH_3)_n^{2+} + \overline{H_2L} \rightleftarrows \overline{CuL} + 2H^+ + nNH_3$ $Kex' = D * [H^+]^2 * [H_2L]^{-1}$ $\log Kex' = -19.5$ ($CHCl_3$) $\log Kex' = -18.6$ (C_6H_6)	**Aq.:** 0.1 mM $Cu(NO_3)_2$ 1 M (NH_3 + NH_4Cl) (pH 11.3 - 11.8) stripping: 2M HCl (30 min) **Org.:** 1 mM in $CHCl_3$, 0.37 mM in C_6H_6 or variable 5 - 0.25 mM Vol.: 20 ml /10 ml(aq/org), t: 20 h Analysis: AAS	[30]
Ethers and Polyethers				
	Li Na K Rb Cs Ca Ba		**Aq.:** 10 mM MOH, MCl_2 or $M(NO_3)_2$, 0.07 mM picric acid **Org.:** 0.35 mM in CH_2Cl_2 Vol.: 5 ml /5 ml, T: 293 K, t: 5 min,	[31-33]
				
				
				
				
				

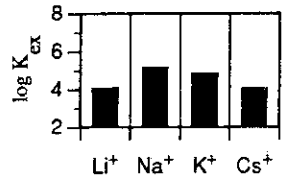
Extractant	Metal	Data	Conditions and Remarks	Ref.

Ether, ester and para-substituted calixarenes

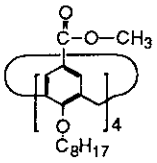


7_4

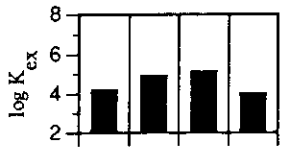
Li
Na
K
Cs



Aq.: metal picrates [34]
(Li-picrate: 8.4 mM,
Na-picrate: 1 mM,
Cs-picrate: 4.8 mM)
Org.: 1 mM L in $CHCl_3$

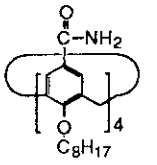


8_4

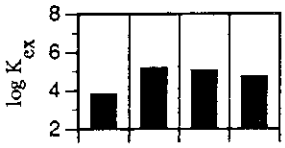


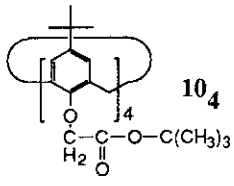
$$M^+ + pic^- + \overline{L} \overset{K_{ex}}{\rightleftarrows} \overline{[LM^+pic^-]}$$

$$K_{ex} = \frac{\overline{[LM^+pic^-]}}{\gamma^2 [M^+] [pic^-] (\overline{L}^0 - \overline{[LM^+pic^-]})}$$

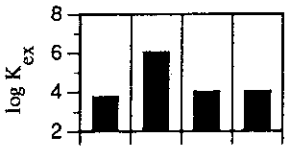


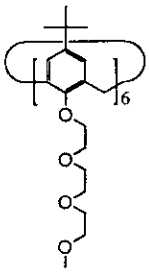
9_4





10_4

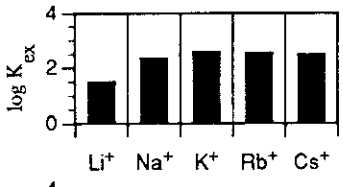




11_6

solvent: benzene

Li
Na
K
Rb
Cs



Aq.: 1 to 10 mM metal picrate
Org.: 1 mM L
Vol.: 5 ml /5 ml, T: 298 K,
t: 2 to 5 h
conformation of L: 1,4-*anti*
stoichiometry in THF: 1:1

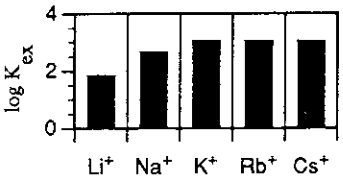
$$M^+ + pic^- + \overline{L} \overset{K_{ex}}{\rightleftarrows} \overline{[LM^+pic^-]}$$

$$K_{ex} = \frac{\overline{[LM^+pic^-]}}{\gamma^2 [M^+] [pic^-] (\overline{L}^0 - \overline{[LM^+pic^-]})}$$

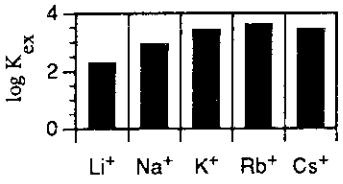
K_{ex} in M^{-2}

[35]

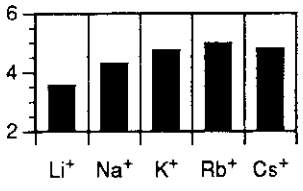
solvent: chlorobenzene



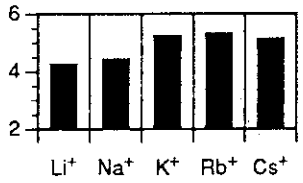
solvent: chloroform

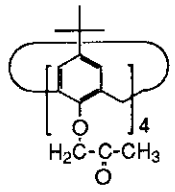
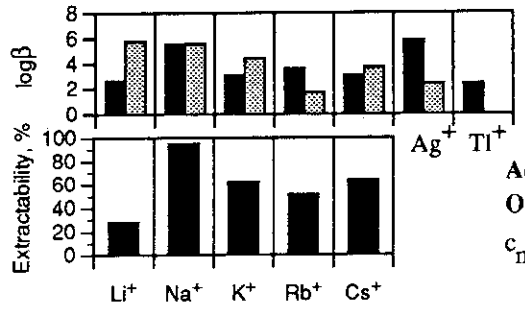
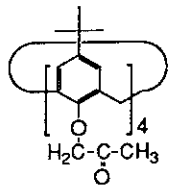
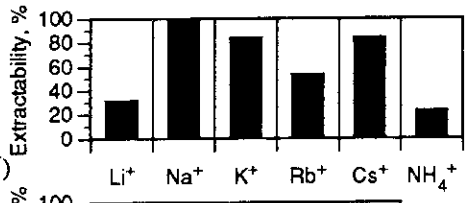
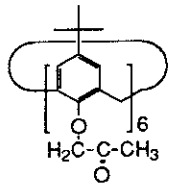
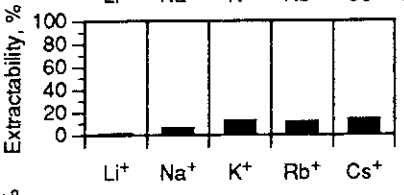
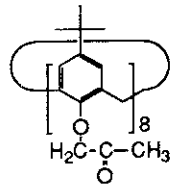
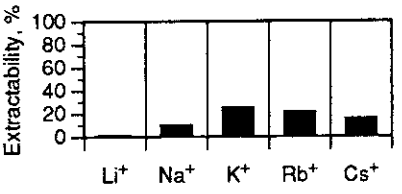
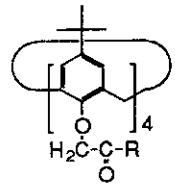
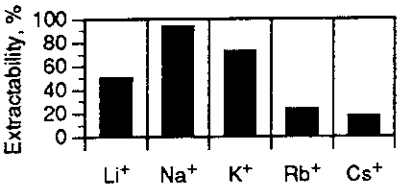
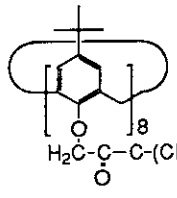
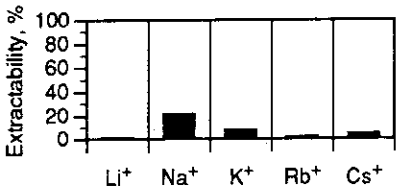
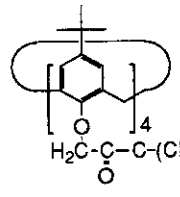
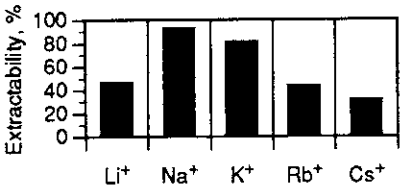
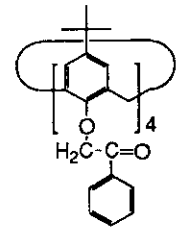
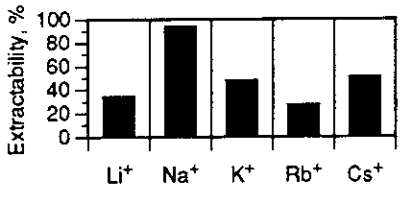
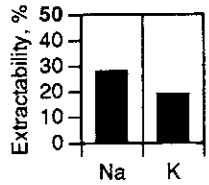


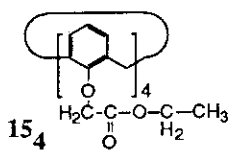
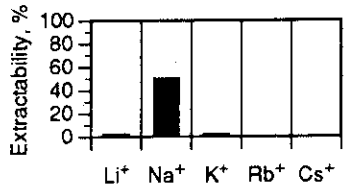
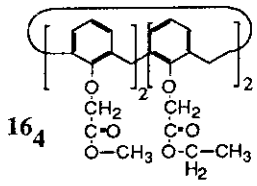
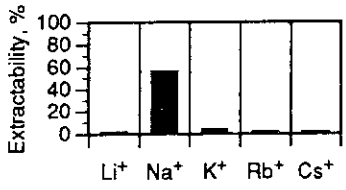
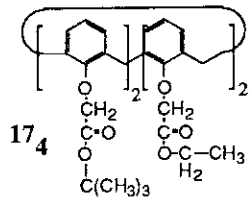
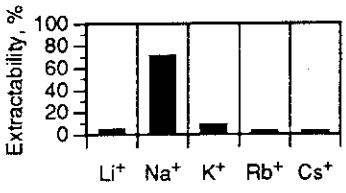
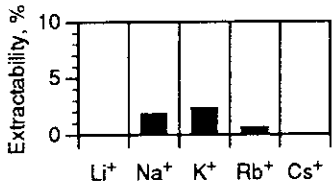
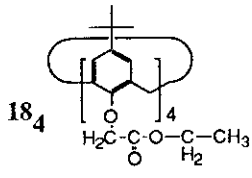
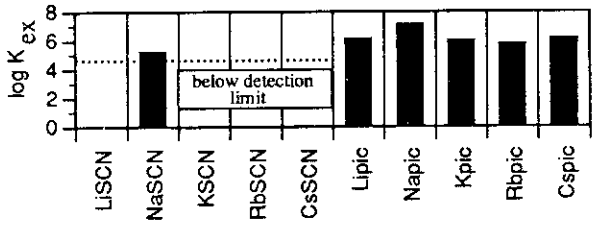
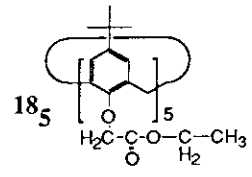
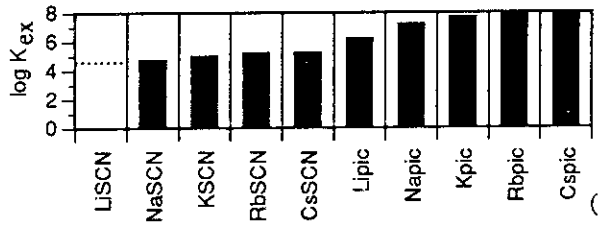
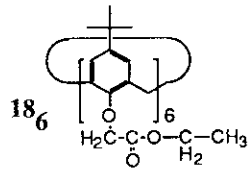
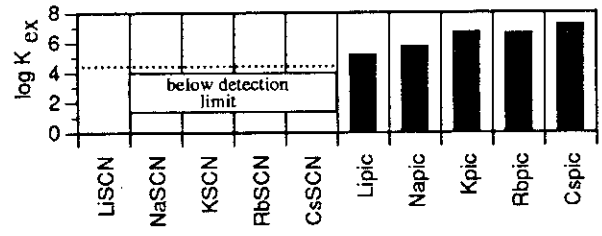
solvent: dichloromethane

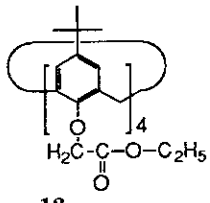
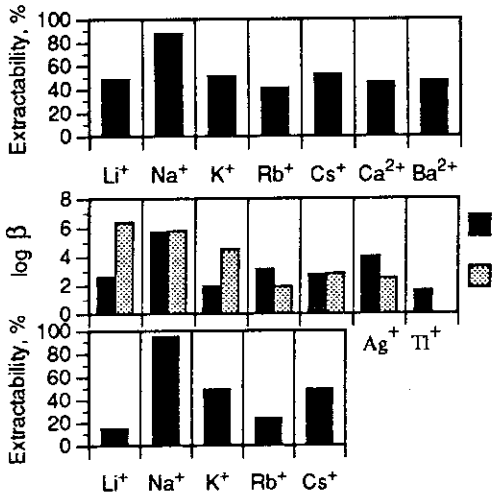
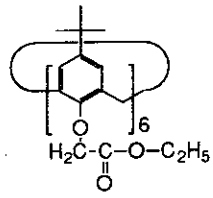
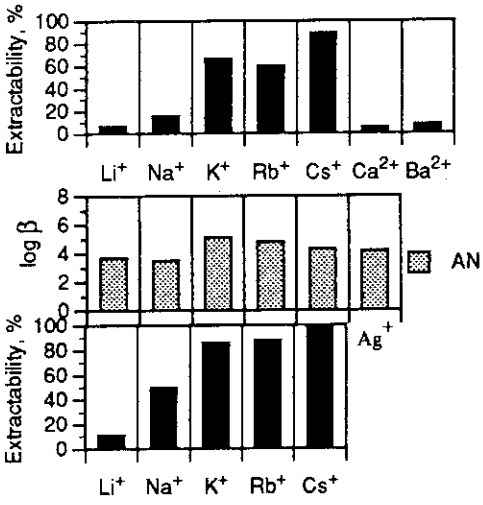
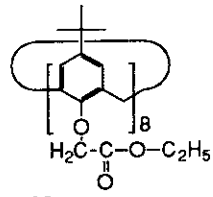
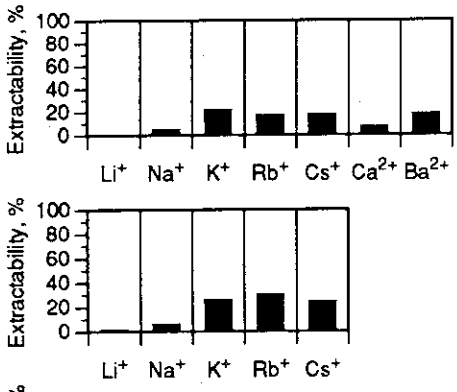
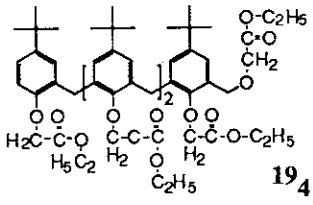
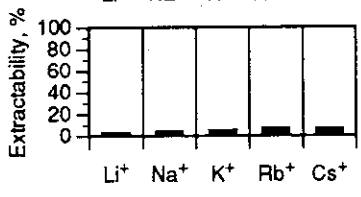


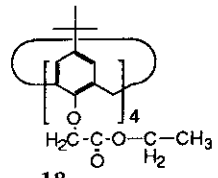
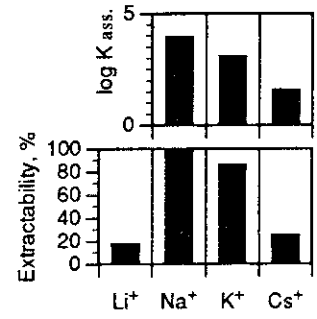
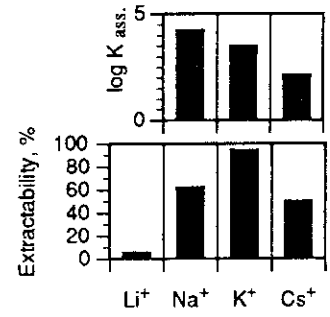
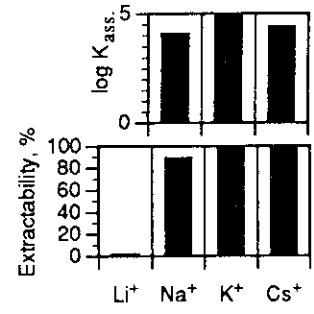
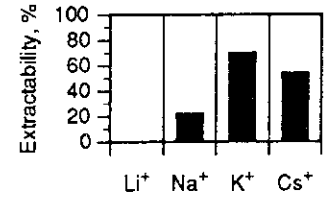
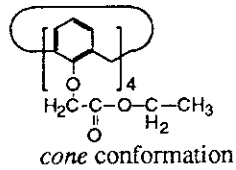
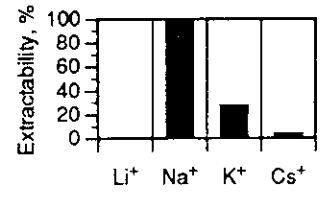
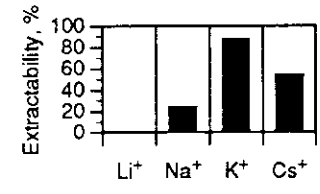
solvent: 1,2-dichloroethane

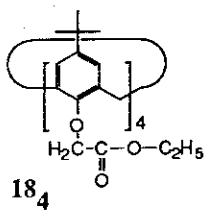
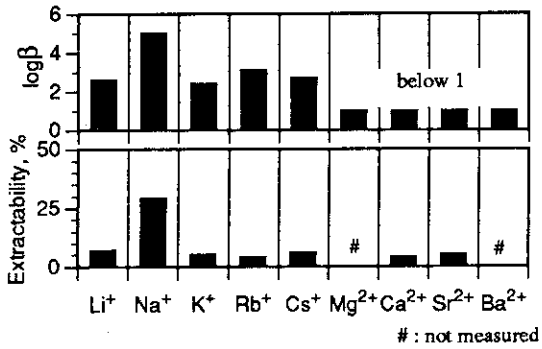
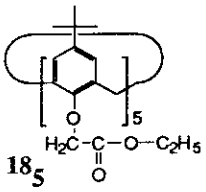
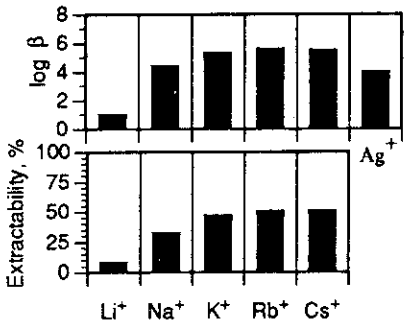
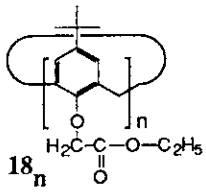
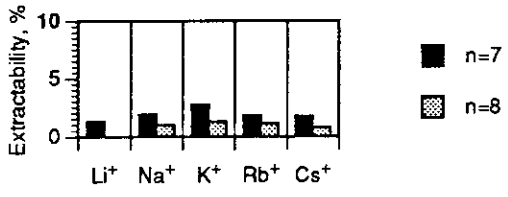
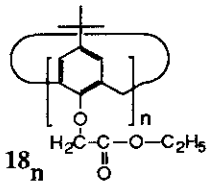
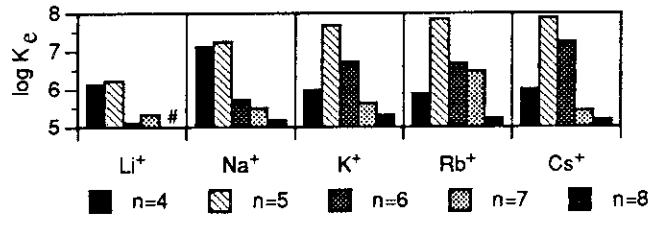
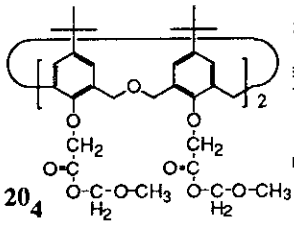
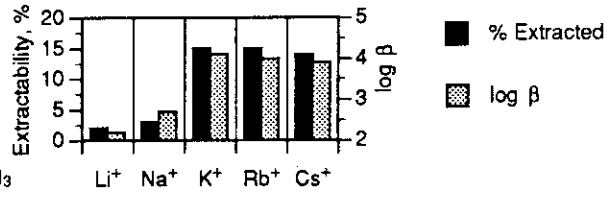
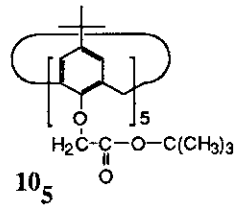
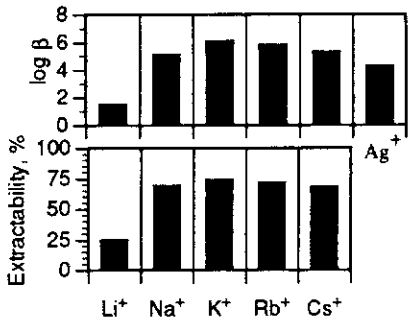


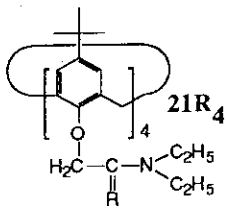
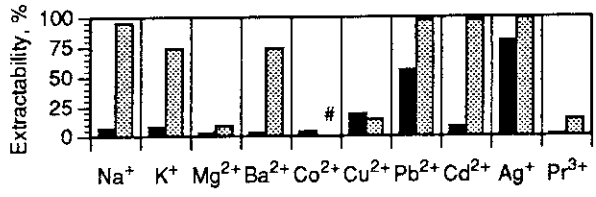
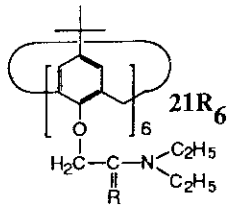
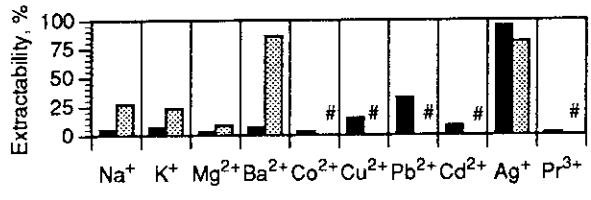
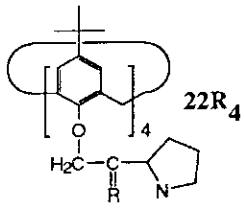
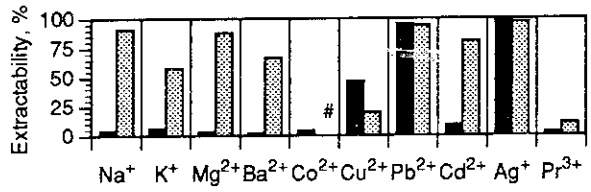
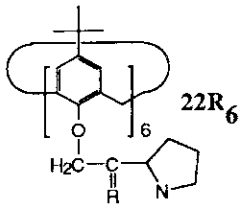
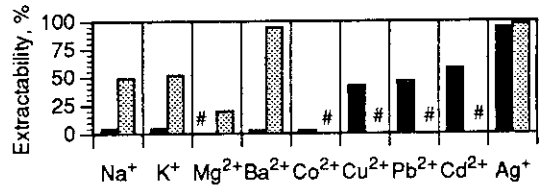
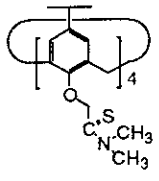
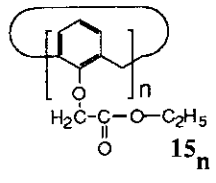
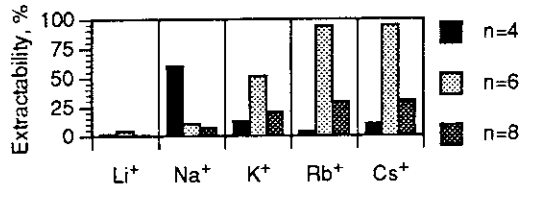
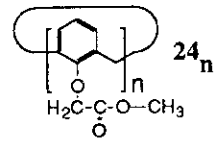
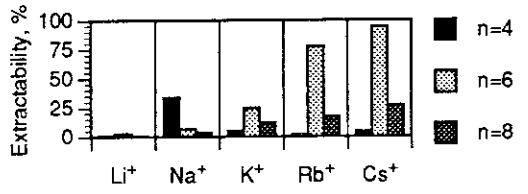
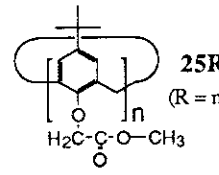
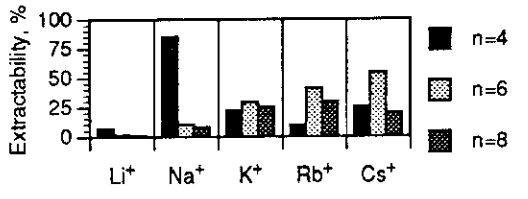
Extractant	Metal	Data	Conditions and Remarks	Ref.
Ketones				
 **12_4**	**Li Na K Rb Cs**		**Aq.:** alkali picrate **Org.:** CH_2Cl_2 $c_{metal} = c_{extractant}$	[36]
 **12_4**	**Li Na K Rb Cs (NH_4^+)**		**Aq.:** 10 mM MOH 0.25 mM picric acid **Org.:** 0.25 mM in CH_2Cl_2 Vol.: 5 ml /5 ml, T: 293 K, t: 3*1 min,	[37-39]
 **12_6**	**Li Na K Rb Cs**			
 **12_8**				
 **13_4**			R = adamantyl	
 **13_8**				
 **$14R_4$**	**Li Na K Rb Cs**		R = *t*-butyl	
 **$14R_4$**			R = phenyl	
			(from neutral aq. soln.)	[38]

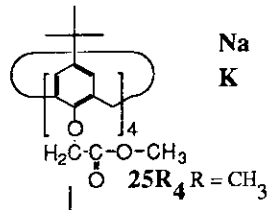
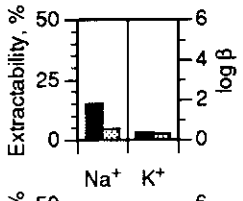
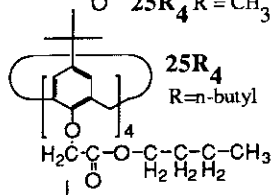
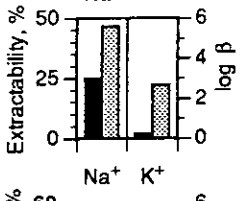
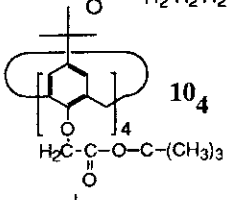
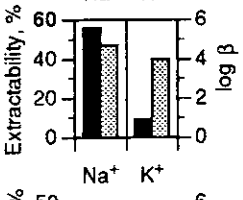
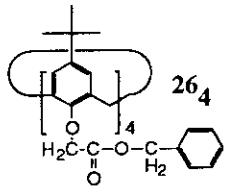
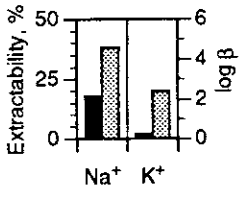
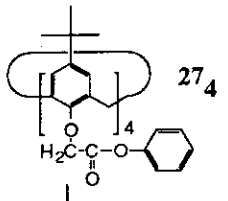
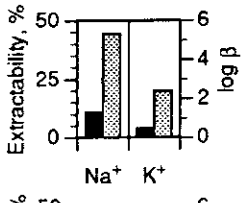
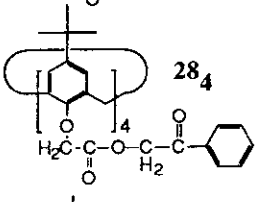
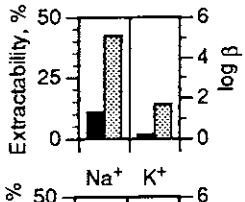
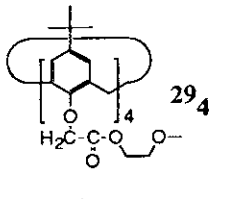
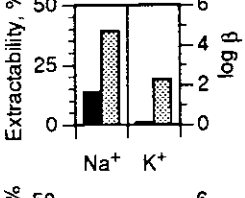
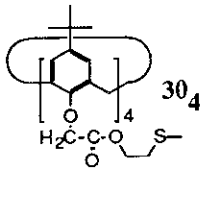
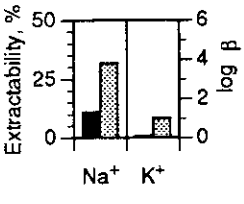
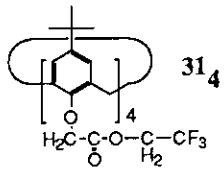
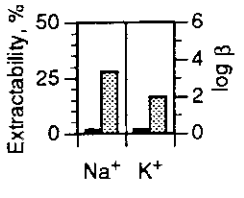
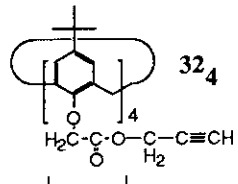
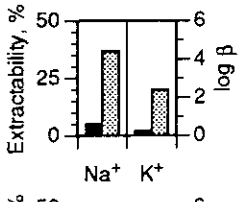
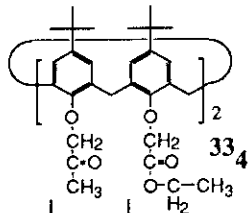
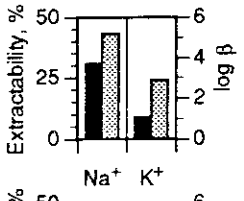
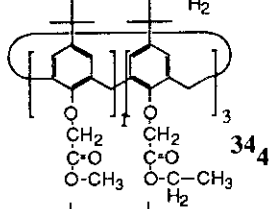
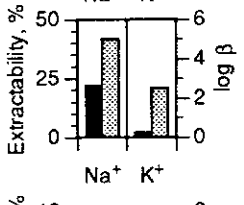
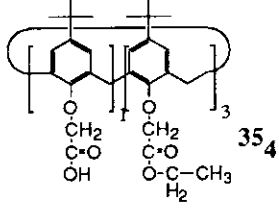
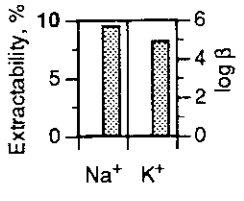
Extractant Ester	Metal	Data	Conditions and Remarks	Ref.
 **15**$_4$	Li Na K Rb Cs		**Aq.:** 0.1 M MCl, 0.25 mM metal picrate **Org.:** 0.25 mM L in CH_2Cl_2 Vol.: 5 ml/5 ml, T: 293 K,	[40]
 **16**$_4$				
 **17**$_4$			*cone* conformation	
			*partial cone* conformation	
 **18**$_4$			**Aq.:** metal picrate or metal thiocyanate **Org.:** CH_2Cl_2 2.5 mM L (for thiocyanates) 0.25 mM (for picrates)	[41]
 **18**$_5$			$(\gamma_{\pm})^2 * K_{ex} = \frac{P * C^0}{(C^0 - P*C^0)^2 * (L^0 - P*C^0)}$ with $\gamma_{\pm}$ about 1 C^0 cation initial conc. L^0 ligand initial conc. extractability $0 \le P \le 1$	
 **18**$_6$				

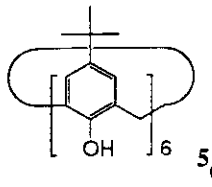
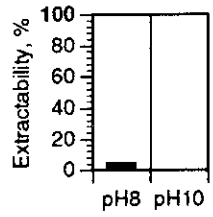
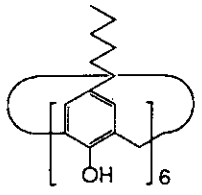
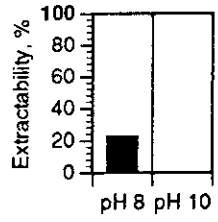
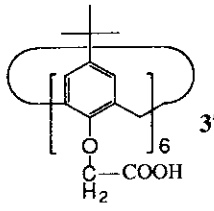
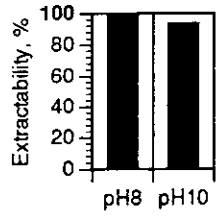
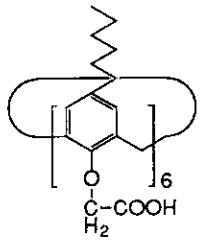
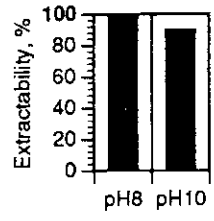
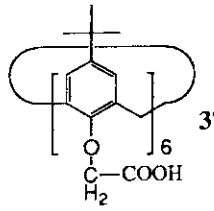
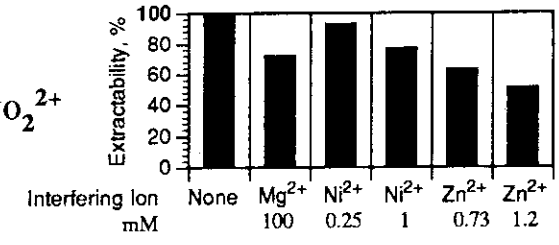
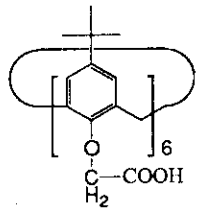
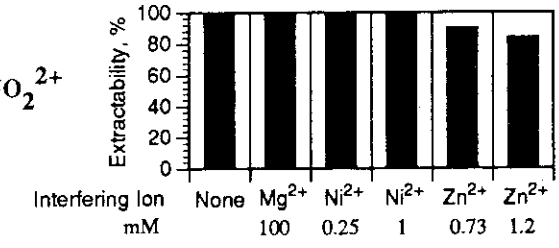
Extractant Ethylester	Metal	Data	Conditions and Remarks	Ref.
 18_4	Li Na K Rb Cs Ca Ba		**Aq.:** 10 mM MOH, 10 mM MCl_2 or $M(NO_3)_2$, 0.07 mM picric acid **Org.:** 0.35 mM L in CH_2Cl_2 T: 298 K, eq. vol.	[31-33]
				[36, 37, 39, 42, 43, 44]
			Aq.: 0.01 M MOH 0.25 mM picric acid **Org.:0.25** mMin CH_2Cl_2 Vol.: 5 ml /5 ml, t: 3 * 1 min T: 293 K	
 18_6			.....	[31-33]
			.....	[36, 37, 39, 42, 43, 44]
 18_8			.....	[31-33]
			.....	[37, 44]
 19_4				[37, 44]

Extractant	Metal	Data	Conditions and Remarks	Ref.
Ethylester				[45]
 **18_4** *cone* conformation	**Li Na K Cs**		**Aq.:** 0.1 M MOH, 0.5 M MCl, 0.25 mM metal picrate, **Org.:** 0.25 mM L in CH_2Cl_2 Vol.: 5 ml /5 ml, T:298 K association constants $K_{ass.}$ in THF at 303 K, 0.005 mM metal picrate c_L = 0 to 0.5 mM, spec.	
partial cone conformation				
1,3-alternate conformation				
1,2-alternate conformation			small association constants	
 *cone* conformation **15_4**				
1,3-alternate conformation				

Extractant	Metal	Data	Conditions and Remarks	Ref.
Ester				
 18_4	Li Na K Rb Cs Ca Sr	 # : not measured	**Aq.:** 0.25 mM metal picrate (neutral soln.) **Org.:**0.25 mMin CH_2Cl_2 Vol.: 5 ml /5 ml, t: 17 min T: 293 K Stability constant β in MeOH, 298 K, μ 0.01 M (Et_4NCl or Et_4NClO_4)	[42, 46, 47]
 18_5			**Aq.:** 0.25 mM metal picrate (neutral soln.) **Org.:** 0.25 mM L in CH_2Cl_2 T: 293 K Stability constants β in McOH at 298 K, μ=0.1 M (Et_4NCl or Et_4NClO_4), method: spec. and pot. $\beta = \frac{[ML^{m+}]}{[M^{m+}]\,[L]}$ $K_e = \frac{[\overline{ML(pic)_m}]}{[M^{m+}]\,[pic^-]^m\,\overline{[L]}}$	[46, 47]
 18_n				
 18_n			# : not measured	
 20_4				
 10_5				

Extractant Amides, Ester	Metal	Data	Conditions and Remarks	Ref.
 **$21R_4$**	Na K Mg Ba Co Cu Pb Cd Ag Pr		**Aq.:** 0.25 mM metal picrate (neutral soln.) **Org.:** 0.25 mM L in CH_2Cl_2 Vol.: 5 ml /5 ml, T: 293 K, t: 17 min, analysis: spec. Stability constants in MeOH at 298 K, method: spec. and pot., μ = 0.01 M # : not measured	[42, 47]
 **$21R_6$**				
 **$22R_4$**				
 **$22R_6$**				
 **23_4**		effective extractant for Hg^{2+}, Hg_2^{2+}, Ag^+, and Au^{3+} low extractability for Pb^{2+}, Cd^{2+}, Ni^{2+}, $MeHg^+$, and Pt^{2+}		[48]
 **15_n**	Li Na K Rb Cs		**Aq.:** 0.01 M MOH 0.25 mM picric acid **Org.:0.25** mM in CH_2Cl_2 Vol.: 5 ml /5 ml, t: 3 * 1 min T: 293 K	[37, 43, 44]
 **24_n**				
 **$25R_n$** (R = methyl)				

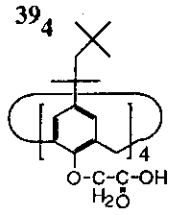
Extractant Ester	Metal	Data	Conditions and Remarks	Ref.
 $25R_4$ R = CH_3	Na K		**Aq.:** 0.25 mM metal picrate **Org.:** 0.25 mM L in CH_2Cl_2 Vol.: 5ml /5 ml, T: 293 K, t: 17 min Stability constants β in MeOH, T: 298 K, μ: 0.01 M, method UV /pot.	[38]
 $25R_4$ R=n-butyl				
 10_4				
 26_4				
 27_4				
 28_4				
 29_4				
 30_4				
			Extractability log β	
 31_4				
 32_4				
 33_4				
 34_4				
 35_4				

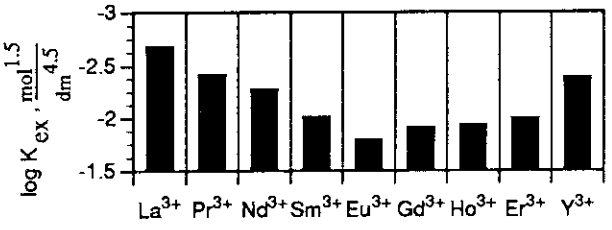
Extractant	Metal	Data	Conditions and Remarks	Ref.
Carboxylic acids, phenols				
	UO_2^{2+}		**Aq.:** uranyl acetate 0.037 mM borate buffer 4 mM (pH8-10) **Org.:** 2.1 mM L in o-dichlorobenzene Vol.: 25 ml /10 ml, T: 298 K, t: 15 h Analysis: Arsenazo III	[49]
	UO_2^{2+}			
	UO_2^{2+}		Stoichiometry of extracted complex: $[L(UO_2)_3]$	
	UO_2^{2+}			
	UO_2^{2+}		**Aq.:** uranyl acetate 0.02 mM bis-tris buffer 10 mM (pH 5.9) and competing metal ions **Org.:** 0.1 mM L in o-dichloro-benzene Vol.: 25 ml /5 ml, T: 298 K, t: 15 h, Analysis: Arsenazo III/AAS	
	UO_2^{2+}		**Aq.:** 1 mM trioctyl-methylammonium chloride added as counterion	

Extractant	Metal	Data	Conditions and Remarks	Ref.
Carboxylic acids				

[50]

39$_4$



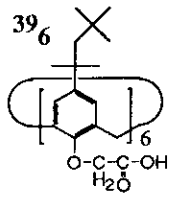


$$Ln^{3+} + 1.5\ \overline{(H_4L)_2} \rightleftarrows \overline{Ln(H_3L)_3} + 3H^+$$

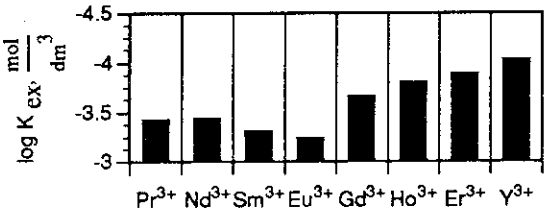
$$Ln^{3+} + 2\ \overline{H_6L} \rightleftarrows \overline{Ln(H_4L)(H_5L)} + 3H^+$$

$$K_{ex} = \frac{D\,[H^+]}{[(H_4L)_2]^{1.5}}$$

39$_6$

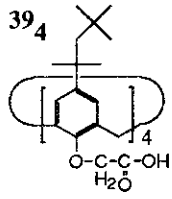


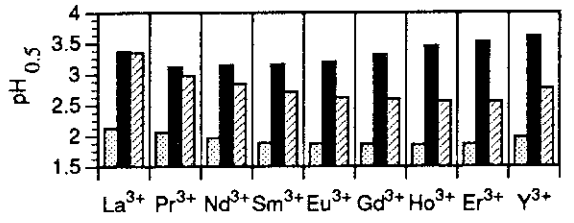
La
Pr
Nd
Sm
Eu
Gd
Ho
Er
Y



Aq.: 0.1 mM $LnCl_3$, 0.1 M K(H)Cl, pH 2-3
Org.: 5 mM L in toluene (pH var.)
0.8 - 10 mM (c_L var.)
Stripping: 2 M HNO_3
T: 303 K, t: 24 h
analysis: ICP-AES

39$_4$

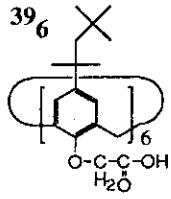


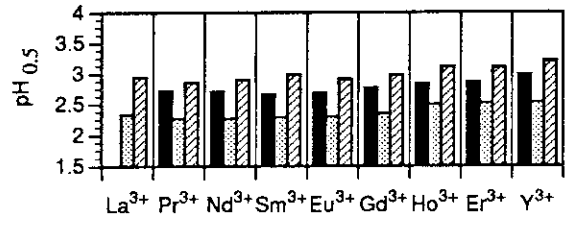


Nitrate system, solvent toluene [51-53]
Glycine system, solvent chloroform
Glycine/Na system, solvent chloroform

log D (Y^{3+}) = -2.9 + 1.65pH
log D (Y^{3+}) = -10.2 + 3pH
log D (Er^{3+}) = -10.3 + 3pH

39$_6$

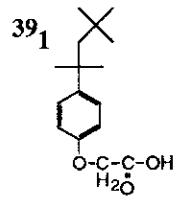


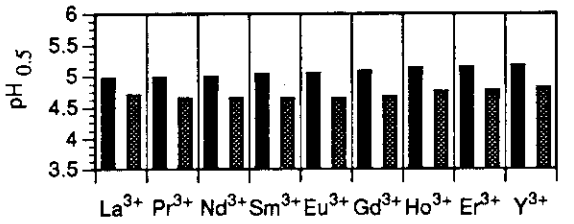


log D (Sm^{3+}) = -5.25 + 2.1pH
log D (Sm^{3+}) = -7.1 + 3pH
log D (Pr^{3+}) = -6.9 + 3pH

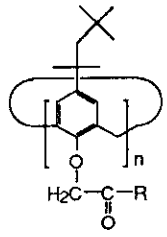
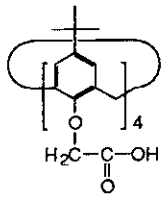
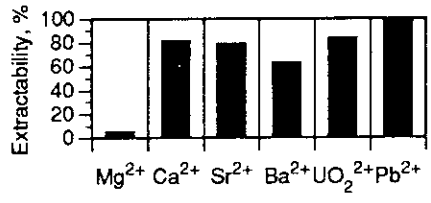
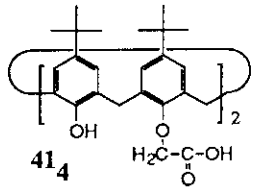
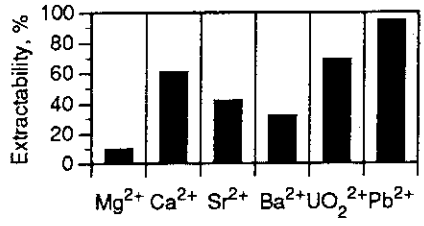
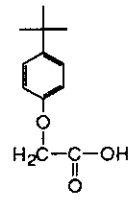
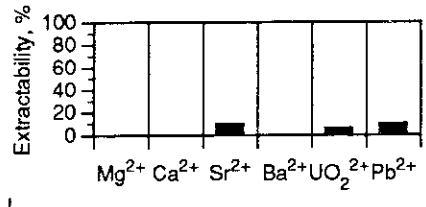
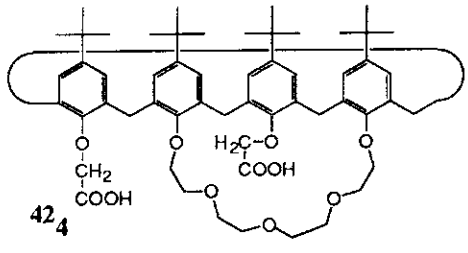
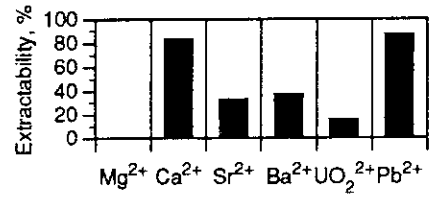
Aq.: competitive extraction of 3 or more lanthanides,
nitrate system:
3 * 0.1 mM $LnCl_3$ (H_4L),
8 * 0.05 mM $LnCl_3$ (H_6L)
0.1M $Na(H)NO_3$
glycine systems:
3 * 0.1 mM $LnCl_3$,
0.1M (HNO_3/glycin)e or
0.1 MHNO_3 + 0.1M (NaOH/glycine)
Org.: 5 mM calixarene (or 10 mM of monomer) in toluene or chloroform
T: 298 K, analysis: ICP-AES

39$_1$



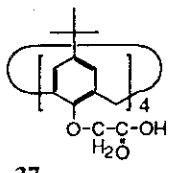


log D (La^{3+}) = -14.9 + 3pH
log D (La^{3+}) = -13.65 + 3pH
log D (Eu^{3+}) = -13.35 + 3pH

Extractant	Metal	Data	Conditions and Remarks	Ref.
Carboxylic acids				
 *cone*-conformation	**Pd** **Ag**	extractability of Ag(I) and Pd(II) at vari. HNO_3 conc.	**Aq.:** 10 ppm Pd^{2+} + 10 ppm Ag^+ and 250 ppm Pd + 2.5 ppm Ag **Org.:** 3.3 mM calix in $CHCl_3$ (13.3 mM monomer) T: 303 K, t: 72 h	[54]
39$_n$ R = OH **40**$_n$ R = CH_3		n = 4, 6		
 **37**$_4$	**Mg** **Ca** **Sr** **Ba** **U** **Pb**		c_L = 0.5 mM	[55]
 **41**$_4$			**Aq.:** 0.5 mM metal acetate **Org.:** CH_2Cl_2 c_L = 1 mM	
 **37**$_1$			c_L = 1 mM	
 **42**$_4$			c_L = 1 mM	

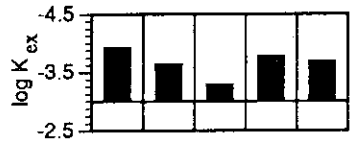
Extractant	Metal	Data	Conditions and Remarks	Ref.

Carboxylic acids



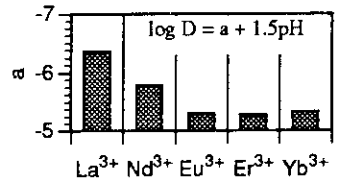
37_4

La
Nd
Eu
Er
Yb



solvent: toluene

$Ln^{3+} + 2(\overline{H_4L}) \rightleftarrows \overline{[Ln(H_2L)(H_3L)]} + 3H^+$

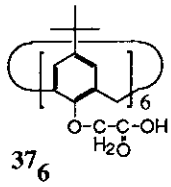


solvent: chloroform

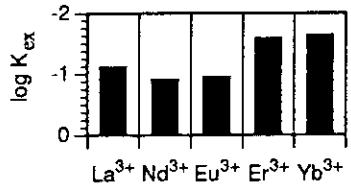
log D (Na^+) ca. 2.2

[57-59]

Aq.: competitive extraction of 5 lanthanides, 5 * 0.05 mM $Ln(ClO_4)_3$, $HClO_4$ (■) or $HClO_4$ + 0.1 M $NaClO_4$ (▩)
stripping: 0.1 M HCl
Org.: 0.5 mM L in toluene or chloroform or vari. 1 mM - 0.01 mM
T: 298 K, t: 2 h,
Vol.: 15 ml /15 ml
analysis: ICP-AES

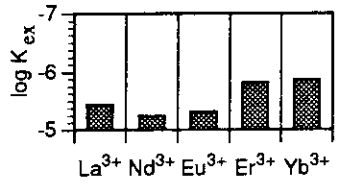


37_6



$Ln^{3+} + 2(\overline{H_6L}) \rightleftarrows \overline{[Ln(H_4L)(H_5L)]} + 3H^+$

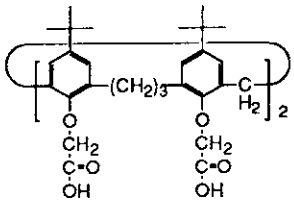
solvent: chloroform



$Ln^{3+} + (\overline{H_6L}) \rightleftarrows \overline{[Ln(H_3L)]} + 3H^+$

$Na^+ + ClO_4^- + (\overline{H_6L}) \rightleftarrows \overline{[Na(H_6L)ClO_4]}$

log K_{ex} (Na^+) = 1.25



43_4

log D (La^{3+}) = -8.08 + 2pH

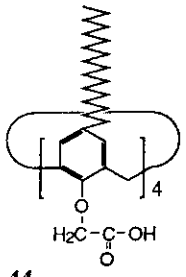
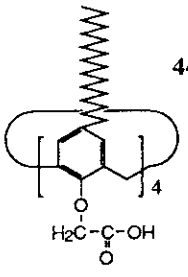
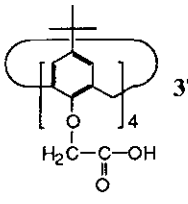
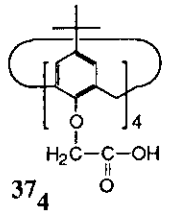
log D (Nd^{3+}) = -11.19 + 3pH (pH 2.5 - 3
slope 2 above pH 3.5

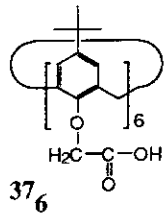
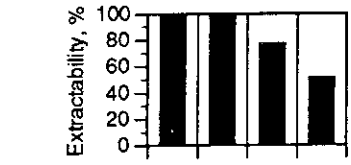
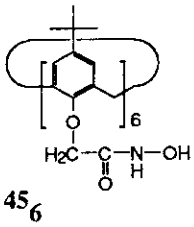
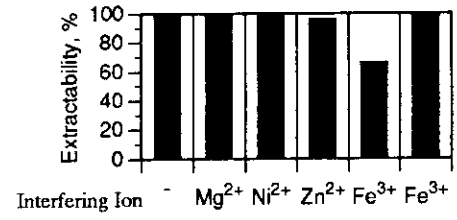
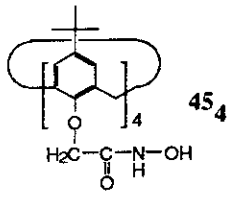
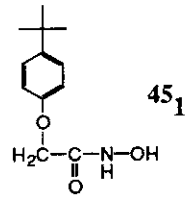
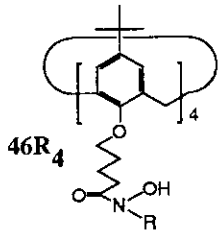
log D (Eu^{3+}) = -11.05 + 3pH

log D (Er^{3+}) = -10.75 + 3pH

log D (Yb^{3+}) = -10.56 + 3pH

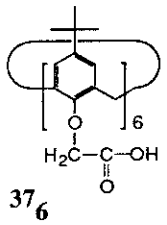
log D (Na^+) = -5.78 + pH

Extractant	Metal	Data	Conditions and Remarks	Ref.
Carboxylic acids				[60, 61]
 **44_4**	**La** **Nd** **Eu** **Tb** **Dy** **Er**	log D (La^{3+}) = -9.9 + 2.4pH log D (Nd^{3+}) = -8.9 + 2.2pH log D (Eu^{3+}) = -8.0 + 2.1pH log D (Tb^{3+}) = -7.45 + 1.95pH log D (Dy^{3+}) = -7.4 + 1.9pH log D (Er^{3+}) = -7.1 + 1.8pH	**Aq.:** competitive extraction of 6 lanthanides, 6 * 0.005 mM $Ln(ClO_4)_3$, HNO_3 + 50 mM $NaNO_3$ (pH 2.5 - 4.1) or 50 mM Na(H)ac (pH 4.0, c_L vari.)	
	solvent toluene	log D (La^{3+}) = 2.77 + 0.83 log c_L log D (Nd^{3+}) = 3.00 + 0.88 log c_L log D (Eu^{3+}) = 3.60 +1.01 log c_L log D (Tb^{3+}) = 3.88 + 1.06 log c_L log D (Dy^{3+}) = 4.00 + 1.08 log c_L log D (Er^{3+}) = 4.14 + 1.12 log c_L	**Org.:** 0.2 mM (pH vari.) or 3 - 0.05 mM L (c_L vari.) in toluene contg. 3 % 1-octanol (vol./vol.) or in chloroform $Ln^{3+} + \overline{NaLH_3} \rightleftarrows 2H^+ + Na^+ + \overline{LnLH}$	
	solvent chloroform	log D (La^{3+}) = -9.3 + 2.3pH log D (Nd^{3+}) = -8.05 + 2.0pH log D (Eu^{3+}) = -7.6 + 2.0pH log D (Tb^{3+}) = -8.0 + 2.1pH log D (Dy^{3+}) = -7.7 + 2.1pH log D (Er^{3+}) = -7.8 + 2.1pH	log D (Ln^{3+}) = a + 2 log c_L (below 0.1 mM L)	
 **44_4**	**Eu**	log D (Eu^{3+}) = -10.8 + 3.3pH log D (Eu^{3+}) = -9.4 +2.9pH (Na^+ present)	**Aq.:** 0.01 mM $Eu(ClO_4)_3$ + $^{152}Eu^{3+}$ + $HClO_4$ or $HClO_4$ + 0.05 M $NaClO_4$ (pH 2.5 - 3.8) **Org.:** 0.5 mM L in $CHCl_3$ T: 298 K, t: 1h, analysis: Ge(Li)	
 **37_4**		log D (Eu^{3+}) = -12.0 + 3.3pH log D (Eu^{3+}) = -4.6 +1.5pH (Na^+ present)		
 **37_4**	**Th** **Fe** **U** **Na** **Mg** **Cu** **V** **Zn** **Ni** **Co** **Mn**	log D (Th^{4+}) = -30.3 +12pH log D (Fe^{3+}) = -17.6 + 6.9pH log D (UO_2^{2+}) = -20.8 +8.1pH log D (Na^+) = -12.2 + 4.4pH log D (Mg^{2+}) = -19.3 + 7.0pH log D (Cu^{2+}) = -23.7 +8.7pH log D (VO^{2+}) = -5.2 +1.2pH log D (Zn^{2+}) = -11.3 +3.6pH log D (Ni^{2+}) = -20.3 + 7.1pH log D (Co^{2+}) = -20.5 +7.2pH	**Aq.:** competitive extraction 10 * 1 mM metal sulfate (except Na^+), pH 2.3 - 2.5 H_2SO_4 + 0.01 M Na_2SO_4 **Org.:** 25 mM L in toluene contg. 5 % 2-octanol (v./v.) T: 298 K, t: 2 h, analysis: ICP-AES log D (Mn^{2+}) < -3	

Extractant	Metal	Data	Conditions and Remarks	Ref.
Carboxylic acid and hydroxamic acids				
 **37_6**	UO_2^{2+}	$\log D\,(UO_2^{2+}) = -3.4 + pH$ $\log D\,(UO_2^{2+}) = f([CO_2^-])$ $UO_2^{2+} + \overline{LH_5^-K^+} \rightleftarrows \overline{LH_4UO_2} + K^+ + H^+$ 	**Aq.:** 0.0106 mM $K_4UO_2(CO_3)_3$ (carbonate interference) at pH 10.4 0.106 mM $K_4UO_2(CO_3)_3$ (contineous variation) at pH 6.2 0.02 mM $K_4UO_2(CO_3)_3$ (competitive extraction) at pH 5.9 competing metal ions if indicated 10 mM buffer: acetate (pH 3.6-6.2) Tris (pH 9) ammonia (pH 10.4)	[62]
 **45_6**		$\log D\,(UO_2^{2+}) = -7.7 + 2pH$ $\log D\,(UO_2^{2+}) = f([CO_2^-])$ $UO_2^{2+} + \overline{LH_6} \rightleftarrows \overline{LH_4UO_2} + 2H^+$ 	**Org.:** 0.53 mM L in $CHCl_3$ (0.1 mM L for competitive extr.) Vol.: 25 ml / 5 ml (aq:org) T: 303 K, t: 12h (equil. after 3 h) stoichiometry at high loading: 3:1 (metal:ligand)	
 **45_4**		$\log D\,(UO_2^{2+}) = -3.2 + pH$ $\log D\,(UO_2^{2+}) = f([CO_2^-])$ $UO_2^{2+} + \overline{LH_5^-K^+} \rightleftarrows \overline{LH_4UO_2} + K^+ + H^+$	stoichiometry at high loading: 2:1 (metal:ligand)	
 **45_1**		$\log D\,(UO_2^{2+}) = -9 + 2pH$ $\log D\,(UO_2^{2+}) = f([CO_2^-])$	stoichiometry at high loading: 1:2 (metal:ligand)	
 **$46R_4$**	**Th** **U**	high extractability for Th(IV) at pH 2-3 complete extraction of UO_2^{2+} at pH 4-5 extraction of transition metals	**Aq.:** pH 2 - 5 **Org.:** $CHCl_3$	[63]
		R = H, CH_3		

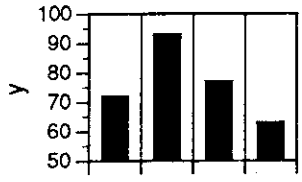
Extractant	Metal	Data	Conditions and Remarks	Ref.

Carboxylic acids and hydroxamic acids



37_6

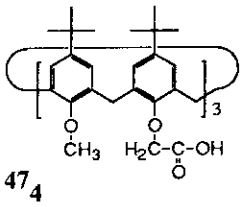
UO_2^{2+}



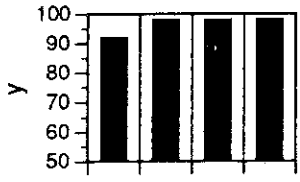
stoichiometry 1:3
(ligand: uranyl)
K^+ co-extracted
$pH_{0.5} = 3.5$

$$y = \frac{\text{Extractability of } UO_2^{2+}}{\text{Extractability without competing metals}}$$

[64]

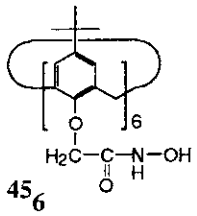


47_4



stoichiometry 1:1
(ligand: uranyl)
$pH_{0.5} = 4.2$

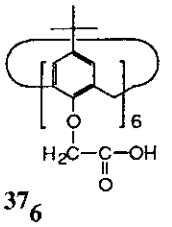
$$UO_2^{2+} + \overline{LH_2^-K^+} \rightleftarrows \overline{L^{3-}UO_2K^+} + 2H^+$$



45_6

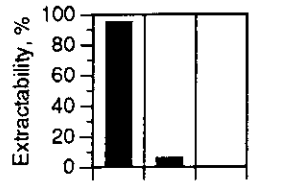
$pH_{0.5} = 3.8$

Aq.: 0.106 mM $K_4UO_2(CO_3)_3$
10 mM buffer (CH_3COOK)
pH 5.9 (competitive extr.)
pH 6.2 (loading test)
Org.: 0.53 mM L in $CHCl_3$
Vol.: 25 ml /5 ml (aq.:org.),
T:303 K



37_6

UO_2^{2+}

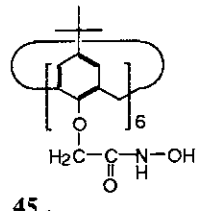


extractability = f([CO_3^{2-}])
and f (pH)

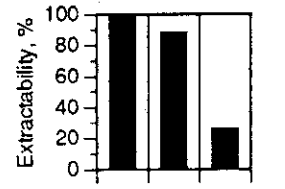
Aq.: 0.106 mM $K_4UO_2(CO_3)_3$
Extr. from carbonate at pH 10.4:
0.0106 mM $K_4UO_2(CO_3)_3$ or
$UO_2(CH_3COO)_2$
buffer: acetate (pH 3.7 - 6.2),
Tris (pH 9), or ammonia (pH 10.4)
Org.: 0.53 mM L in $CHCl_3$
Vol.: 25 ml /5 ml (aq./org.), T:303 K

$$UO_2^{2+} + \overline{LH_5^-K^+} \rightleftarrows \overline{LH_4^{2-}UO_2^{2+}} + H^+ + K^+$$

[65]



45_6

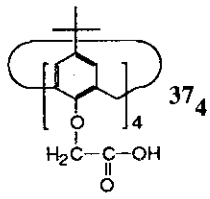


extractability = f([CO_3^{2-}])
and f(pH)

$$UO_2^{2+} + \overline{L_2H_6} \rightleftarrows \overline{L_2H_4^{2-}UO_2^{2+}} + 2H^+$$

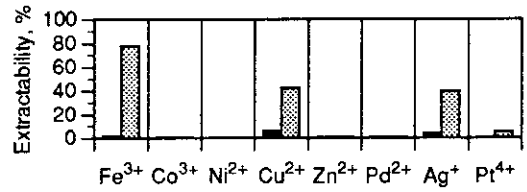
Extractant	Metal	Data	Conditions and Remarks	Ref.

Carboxylic acids, hydroxamic acids, and amides



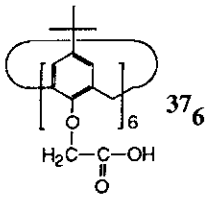
37_4

Fe
Co
Ni
Cu
Zn
Pd
Ag
Pt

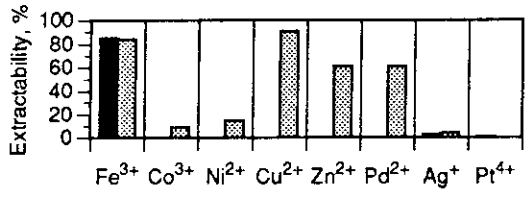


pH 2.2
pH 5.4

[66]

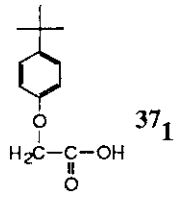


37_6

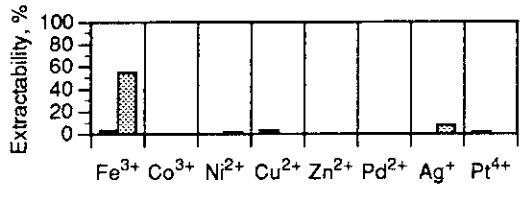


$pH_{0.5}(Ni^{2+}) = 5.38$

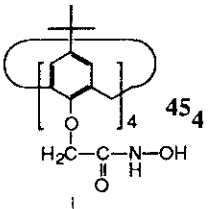
$Ni^{2+} + \overline{LH_5K} \rightleftarrows K^+ + H^+ + \overline{NiLH_4}$



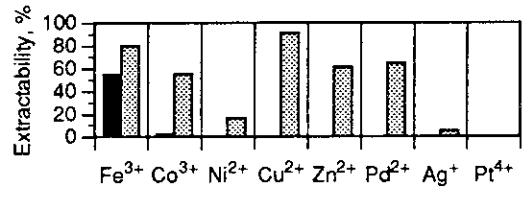
37_1

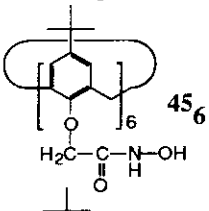


Aq.: 0.106 mM metal salt (nitrates, K_2PtCl_6, K_2PdCl_4), $\mu = 0.1$
(0.01 $Na(H)NO_3$ + KCl, pH 2.2)
(0.01 Na(H)ac + KCl, pH 5.4)
Org.: 0.53 mM calixarene or 3.18 mM monomer in $CHCl_3$
Vol.: 25 ml /25 ml (aq.:org.)
T: 303 K, t: 12 h

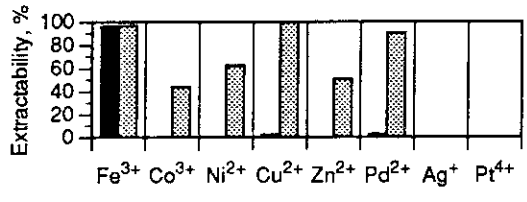


45_4



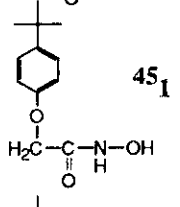


45_6

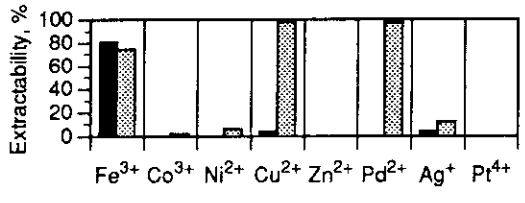


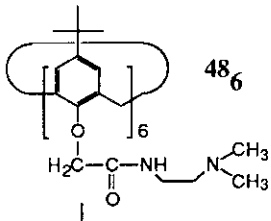
$pH_{0.5}(Ni^{2+}) = 4.77$

$Ni^{2+} + \overline{LH_6} \rightleftarrows 2H^+ + \overline{NiLH_4}$

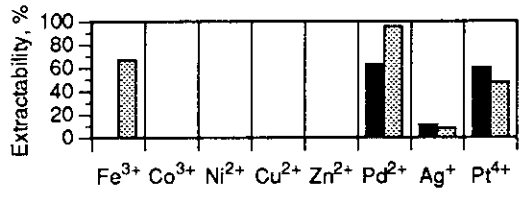


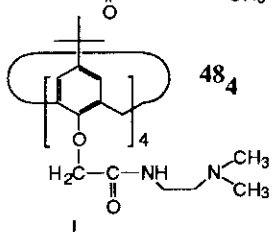
45_1



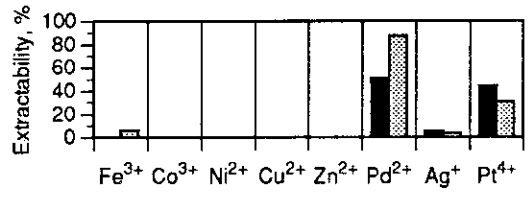


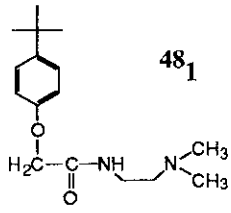
48_6



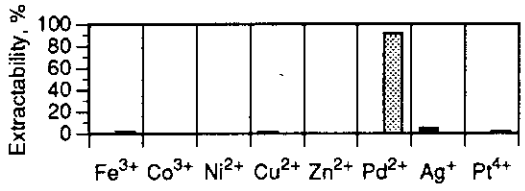


48_4



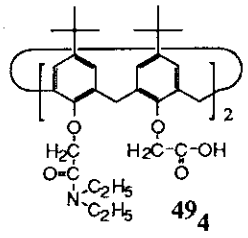


48_1



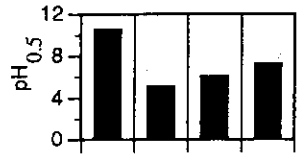
Extractant	Metal	Data	Conditions and Remarks	Ref.

Carboxylic acids and amides



49_4

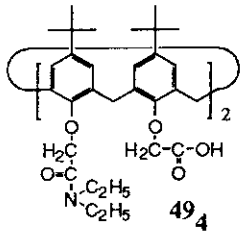
Mg
Ca
Sr
Ba



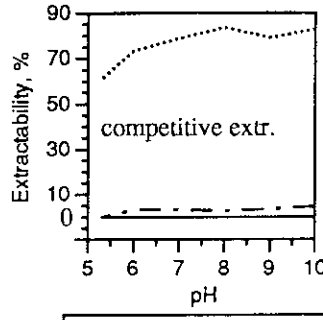
single element: Mg^{2+} Ca^{2+} Sr^{2+} Ba^{2+}

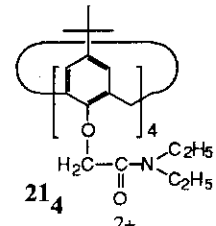
max. extractability >95 %

Aq.: single element and competitive extraction [67]
0.1 mM $M(NO_3)_2$, stripping: 1 M HCl
buffers: succinic acid/ammonia (pH 4-6)
Tris/HCl (pH 7-9)CAPS/ammonia (pH 10)
Org.: 0.05 mM L in $CHCl_3$
Vol.: 4 ml /4 ml, T: 298 K, t: 30 min



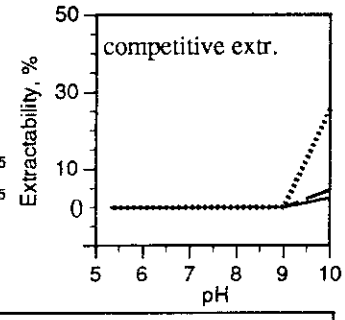
49_4

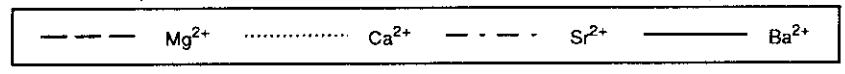


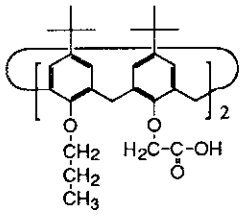


21_4

$pH_{0.5}$ (Ca^{2+}) = 10.2
(single element extr.)

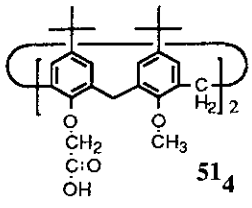






50_4

no extraction of alkaline earth ions up to pH 10



51_4

conditional extraction constants

	Y, La, Er	Na	K	Rb	Cs
	D (Ln^{3+}) = f(pH) (Ln = La, Y, Er), pH = 4 - 7 synergistic extraction with versatic acid				
single ion extraction					
$\log K_{111}$ (from chloride media)		-4.77	-5.76	-6.11	-7.04
$\log K_{111}$ (from acetate media)		-4.44	-5.8	-6.09	-7.02
$\log K_{111}$ (from nitrate media)		-4.62	-5.64		

[68]
solvent: 1,2-dichloroethane
[69, 70]

Aq.: 0.5 M MX (X^-=Cl^-, NO_3^-), vari. MOH/MX, or 0.2 M metal acetate/acetic acid stripping with $HClO_4$ (pH 1.3)
Org.: 1 to 3 mM L in 1,2-dichloroethane
Vol.: 60 ml /60 ml
T: 298 K, t: 20 min
analysis: ICP-AES

	Li
$\log K_{102}$ (from chloride media)	-11.57
$\log K_{102}$ (from acetate media)	-12.52

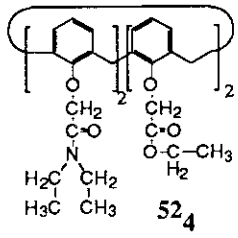
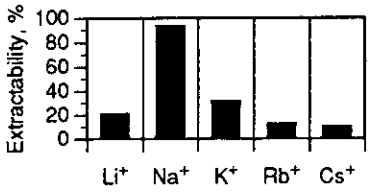
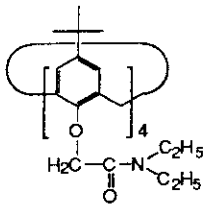
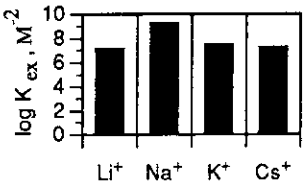
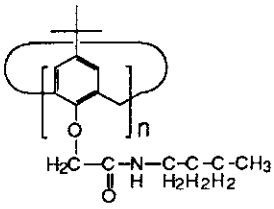
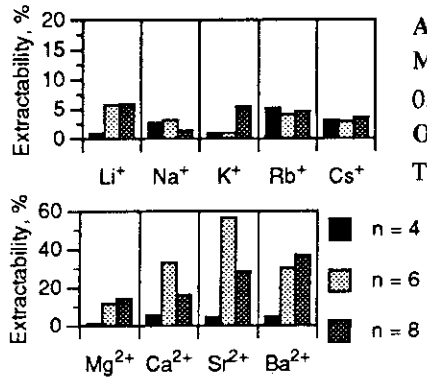
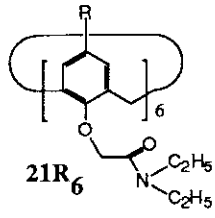
$$\overline{LH_2} + M^+ \overset{K_{111}}{\rightleftarrows} \overline{LHM} + H^+$$
(M = Na, K, Cs)

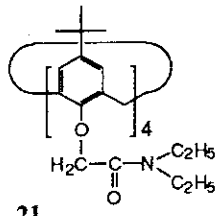
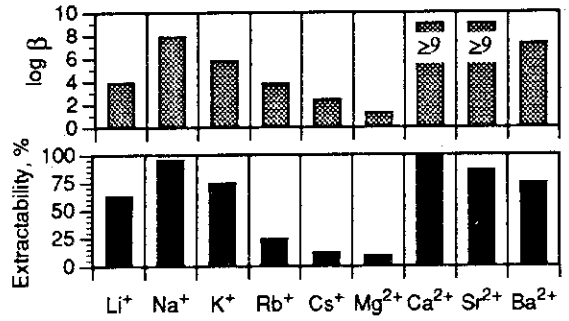
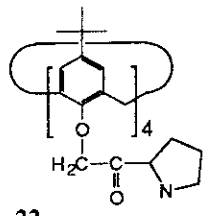
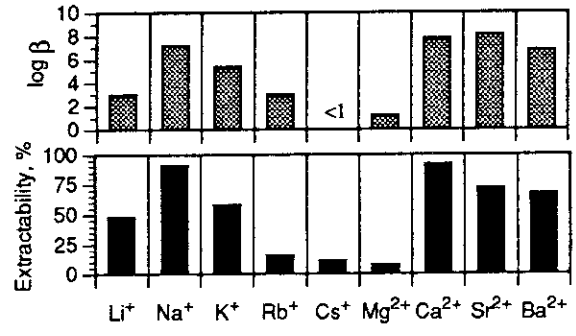
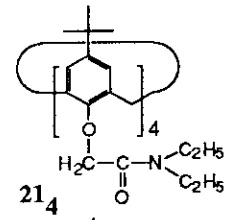
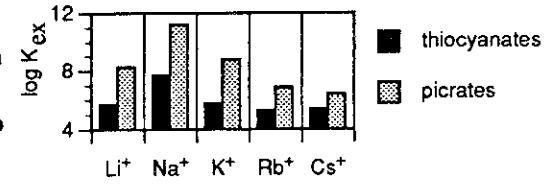
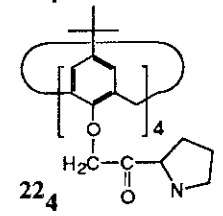
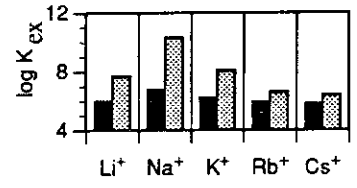
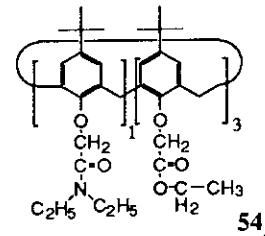
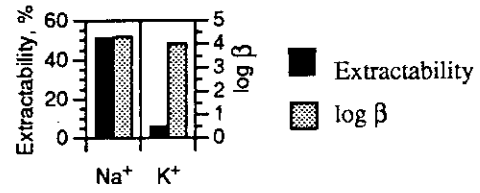
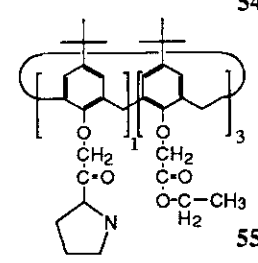
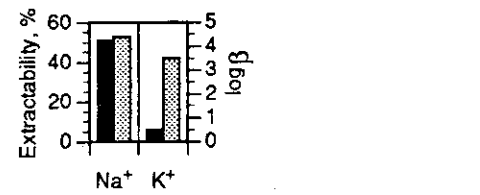
$$\overline{LH_2} + 2M^+ \overset{K_{102}}{\rightleftarrows} \overline{LM_2} + 2H^+$$
(M = Li)

stoichiometry verified by slope analysis and mass spectra

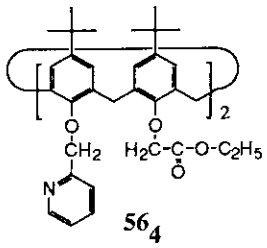
competitive extraction

	Na	K
$\log K_{111}$ (from chloride media)	-4.62	-5.64
$\log K_{111}$ (from acetate media)	-4.81	-5.5

Extractant	Metal	Data	Conditions and Remarks	Ref.
Amides				
 **52_4**	**Li** **Na** **K** **Rb** **Cs**		**Aq.:** 0.1 M MCl, 0.25 mM metal picrate **Org.:** 0.25 mM L in CH_2Cl_2 Vol.: 5 ml/5 ml, T: 293 K,	[40]
 *cone* conformer **21_4**	**Li** **Na** **K** **Cs**	 $M^+ + pic^- + L \overset{K_{ex}}{\rightleftarrows} \overline{LM^+pic^-}$	**Aq.:** 0.5 - 1 mM picrate **Org.:** 1 mM L in $CHCl_3$ T: 293 K log K (Na^+) = 4.07 in THF log K (K^+) = 3.95 in THF K: stability constant	[71, 72]
 **53_n**	**Li** **Na** **K** **Rb** **Cs** **Mg** **Ca** **Sr** **Ba**		**Aq.:** 10 mM MOH, 10 mM MCl_2 or $M(NO_3)_2$, 0.07 mM picric acid **Org.:** 0.35 mM L in CH_2Cl_2 T: 298 K, equal volumes	[31-33]
 **$21R_6$**		enhanced Cs^+/Na^+ and Sr^{2+}/Na^+ - selectivity in solvent extraction for R = H compared with R = *t*-butyl		[73]

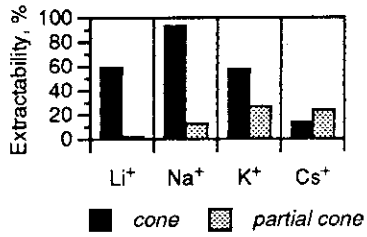
Extractant Amides	Metal	Data	Conditions and Remarks	Ref.
 21_4	Li Na K Rb Cs Mg Ca Sr Ba		**Aq.:** 0.25 mM metal picrate (neutral soln.) **Org.:** 0.25 mM L in CH_2Cl_2 Vol.: 5 ml /5 ml, T: 293 K, t: 17 min, analysis: spec. Stability constants in MeOH at 298 K, method: spec. and pot., μ = 0.01 M	[42]
 22_4				[41]
 21_4	Li Na K Rb Cs		**Aq.:** metal picrate or metal thiocyanate **Org.:** CH_2Cl_2 2.5 mM L (for thiocyanates) 0.25 mM (for picrates and pyrrolidinyl amide)	
 22_4			$(\gamma_\pm)^2 * K_{ex} = \frac{P * C^0}{(C^0 - P*C^0)^2 * (L^0 - P*C^0)}$ with $\gamma_\pm$ about 1 C^0 cation initial conc., L^0 ligand initial conc. extractability $0 \le P \le 1$	
 54_4			**Aq.:** 0.25 mM metal picrate **Org.:** 0.25 mM L in CH_2Cl_2 Vol.: 5ml /5ml, T: 293 K, t: 17 min Stability constants in MeOH, T: 298 K, μ: 0.01 M, method: UV /pot.	[38]
 55_4				

Extractant	Metal	Data	Conditions and Remarks	Ref.
Nitrogen- containing				



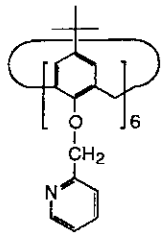
56_4

Li
Na
K
Cs



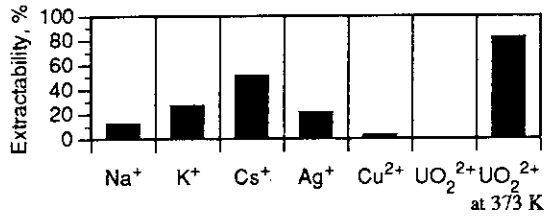
Aq.: 0.1 M MOH, 0.5 M MCl, 0.25 mM metal picrate
Org.: 2.5 mM L in CH_2Cl_2
Vol.: 5 ml / 5ml, t: 30 min

[74]



57_6

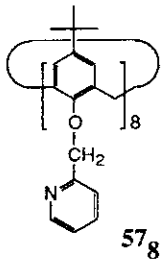
Na
K
Cs
Ag
Cu
U



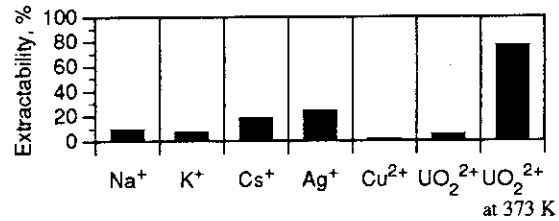
extractability of pic^- = f (pH), pH 2-11
(conditions: 0.25 mM Hpic, 0.02 M Na^+, 0.02 M buffers (acetate, phosphate, pH 4-8) or NaOH (pH 11) (no extraction of Na^+)

[75]

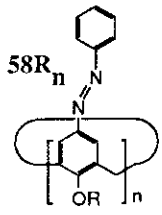
Aq.: (Na^+, K^+, Cs^+): 0.25 mM Hpic, 0.5 M MCl, 0.1 M MOH,
(Ag^+): 2.5 mM Hpic, 0.5 mM $AgNO_3$, pH 11 (0.01 M ammonia)
(Cu^{2+}): 2.5 mM Hpic, 0.5 mM $Cu(NO_3)_2$, pH 8 (0.01 M Bis-Tris)
(UO_2^{2+}): 0.02 mM $UO_2(ac)_2$, pH 8 (0.01 M Tris)
Org.: 2.5 mM L in CH_2Cl_2
(for UO_2^{2+}):0.1 mML in o-dichloro-benzene, or 0.25 mM L (for Hpic)
T: 298 K (and 373 K for UO_2^{2+}),
t: 30 min, analysis: AAS, absorption spec, Arsenazo III



57_8

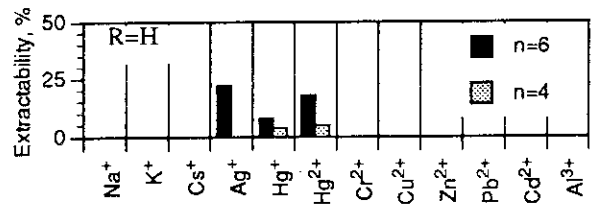


extractability of pic^- = f (pH), pH 2-11



$58R_n$

Na
K
Cs
Ag
Hg
Cr
Cu
Zn
Pb
Cd
Al

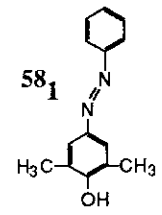


(para-*tert*-butyl-analogue and $58R_n$ with R=CH_3 don't extract metal ions under these conditions)

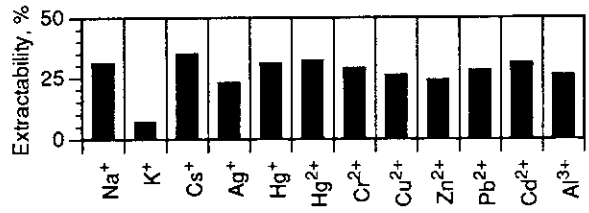
[76, 77]

Aq.: 10 mM metal nitrate, 0.018 mM Hpic,
Org.: 1 mM calix (or 6 mM monomer) in $CHCl_3$
Vol.: 5 ml /5 ml, T: 298 K,
t: 24 h

Stability constants in THF at 298 K,
$AgNO_3$/L = 0.5 - 2.0,
c_L = 0.005 mM (hexamer)
c_L = 0.01 mM (tetramer)
c_L = 0.25 mM (monomer)
analysis: spec.



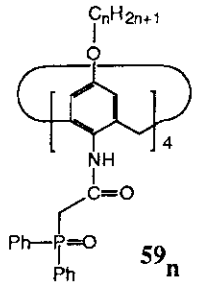
58_1



log K (Ag) = 4.34 ($58H_6$)
log K (Ag) = 4.85 ($58H_4$)
log K (Ag) = 4.56 (58_1)

$$AgNO_3 + L \overset{K}{\rightleftharpoons} L(AgNO_3)$$

Extractant	Metal	Data	Conditions and Remarks	Ref.
Nitrogen-containing				



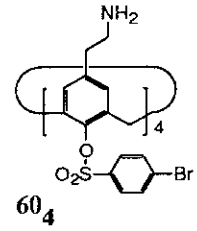
59_n

Ln
Np
Pu
Am
Th

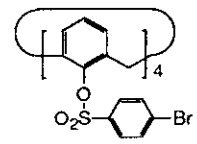
higher extractability for Ln^{3+}, Np, Pu, Am, and Cm than monomeric analogue (n=4)
D (Th^{4+}) > 1, independent of chain length n
D (Th^{4+}) > D (Eu^{3+}) $c_L = c_M = 0.1$ mM
stoichiometry 1:2 for Eu^{3+} - complex (n=4)
D (Np) > 1.5, D (Pu, Am) > 19

[78-83]

Aq.: 1 M HNO_3
Org.: CH_2Cl_2

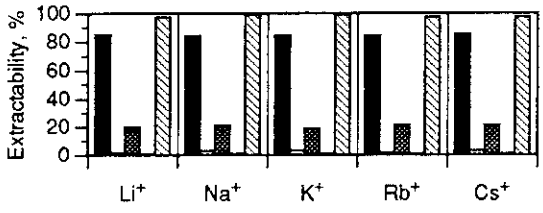


60_4



61_4

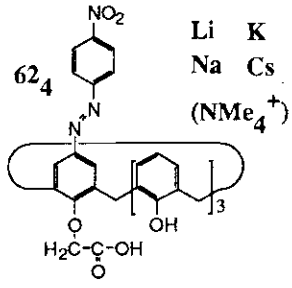
Li
Na
K
Rb
Cs



[84]

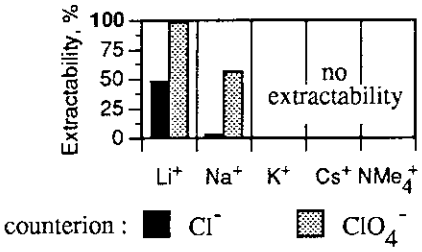
Aq.: 0.07 mM metal picrate
Org.: 0.2 mM L in CH_2Cl_2
Vol.: 5 ml / 5 ml, t: 5 min

- p-Br-benzenesulfonate of 2-aminomethylcalix[4]arene
- monomeric 2-aminomethylbenzene
- monomeric p-Br-benzenesulfonated 2-aminomethylbenzene
- p-Br-benzenesulfonate of calix[4]arene (≤ 1% extracted)
- monomeric 6-cetyl-1,4,7,11-tetraazaundecane



62_4

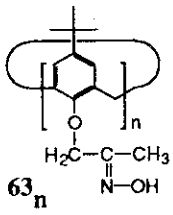
Li **K**
Na **Cs**
(NMe_4^+)



Solid Phase: 0.2 mmol MCl or $MClO_4$
Org.: 0.05 mM calixarene + 50 mM imidazole in 1,2-dichloroethane
Vol.: 4 ml, T: 298 K, t: 1 h
(imidazole added to facilitate the metal-induced deprotonation)

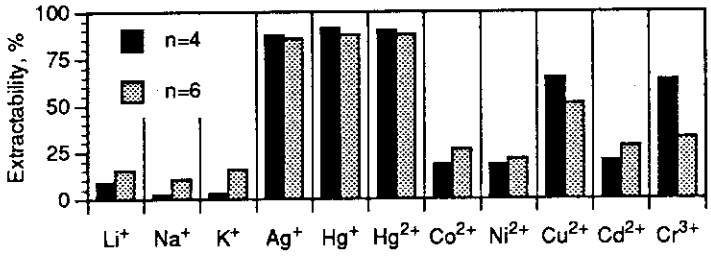
[85]

Extractant	Metal	Data	Conditions and Remarks	Ref.
Nitrogen-containing				



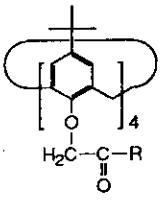
63_n

Li
Na
K
Ag
Hg
Co
Ni
Cu
Cd
Cr

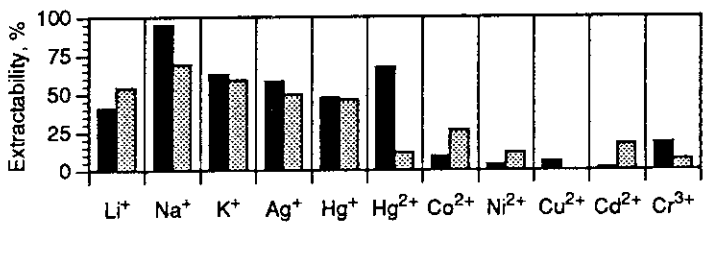


[86]

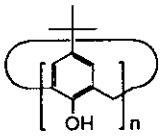
Aq.: 10 mM metal hydroxide (Li^+, Na^+, K^+) or 10 mM metal nitrate (other metals)
0.02 mM Hpic
Org.: 1 mM L in $CHCl_3$
Vol.: 10 ml /10 ml
T: 298 K
t: 1 h
analysis: UV-spec.



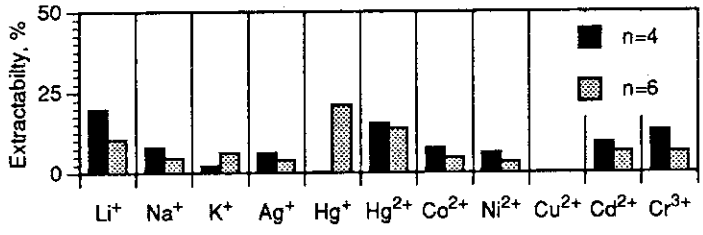
18_4 **12_4**



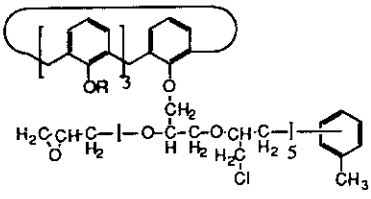
■ R= $-O-C_2H_5$ ▨ R= $-CH_3$



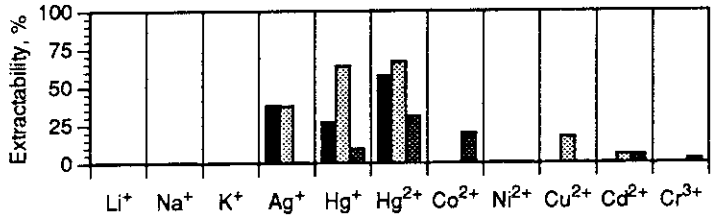
5_n



(no extraction of Fe^{3+} with picrate counterion by all ligands due to complexes in th aq. phase (extractable from nitrate media))



$64R_4$

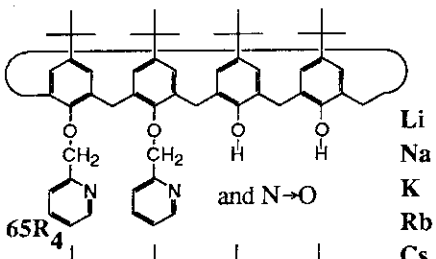


■ R= H ▨ R= $-\overset{O}{\overset{\|}{C}}-$⬡ ■ calixarene-free oligomer

Extractant **Metal** **Data** **Conditions and Remarks** **Ref.**

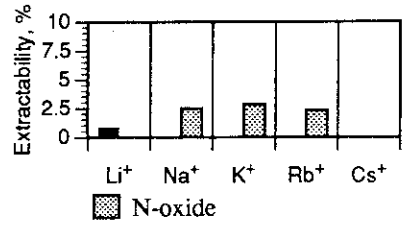
Pyridines and Pyridine N-oxides

[87]

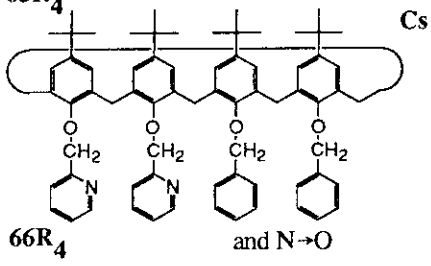


65R$_4$

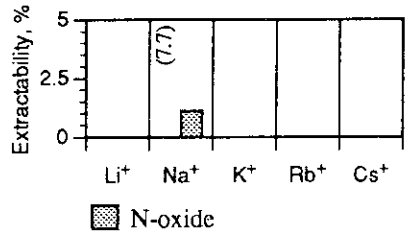
Li
Na
K
Rb
Cs

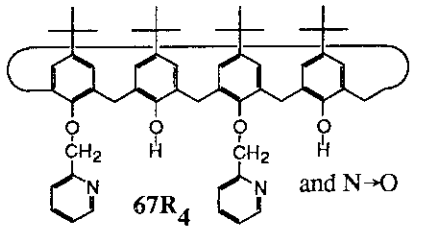


Aq.: 0.25 mM metal picrate (neutral soln.)
Org.: 0.25 mM L in CH_2Cl_2
Vol.: 5 ml /5 ml
T: 296 K, t: 24 h
analysis: UV-spec.

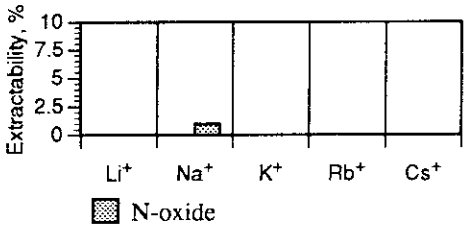


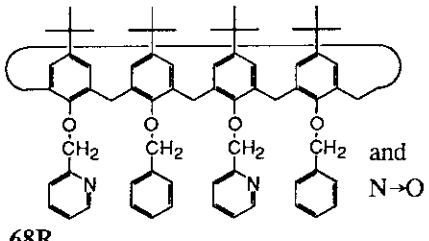
66R$_4$



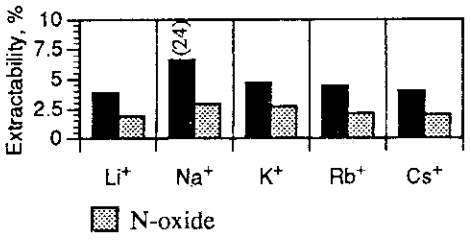


67R$_4$

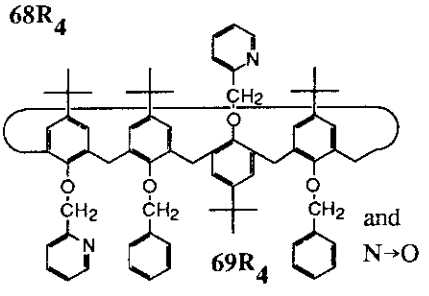




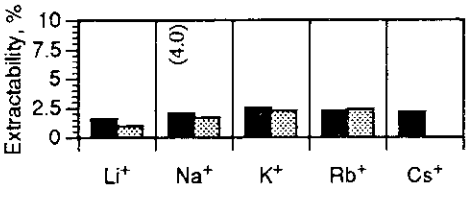
68R$_4$

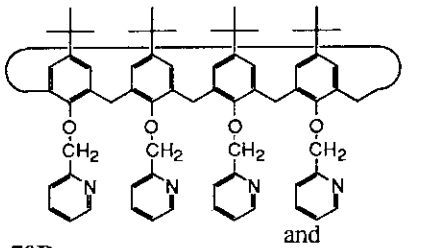


values in paranthesis are for 0.1 M $NaClO_4$ in aqueous phase

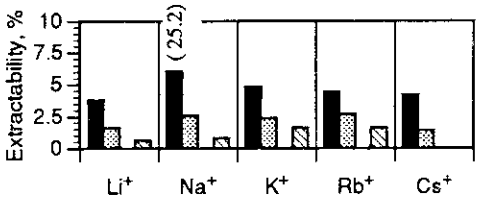


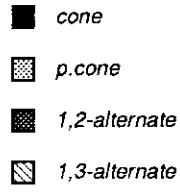
69R$_4$





70R$_4$

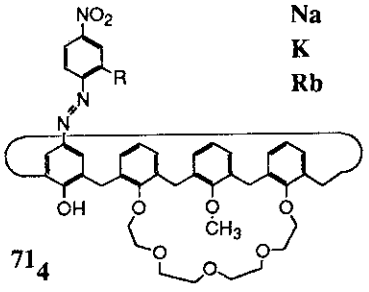




no extraction by N-oxide (11.1 % Na^+ at 0.1 M $NaClO_4$

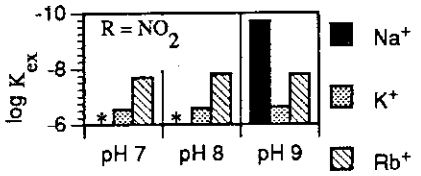
Extractant **Metal** **Data** **Conditions and Remarks** **Ref.**

Nitrogen-, Phosphorous- containing



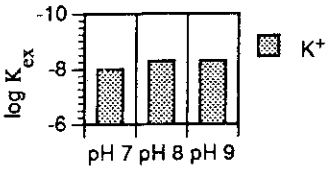
71_4

Na
K
Rb



*: low extractability

R = H

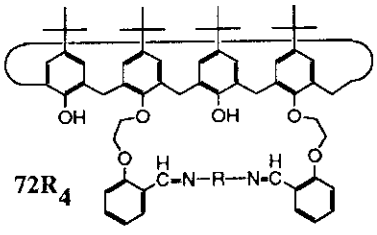


[88]

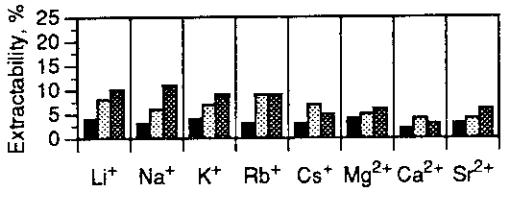
Aq.: 0.1 mM - 1 M MCl, buffer: (tris(hydroxymethyl)methyl-amine/HCl
Org.: 0.03 mM L in $CHCl_3$
analysis: spec

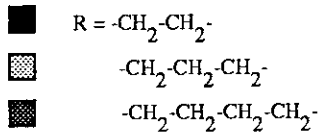
$M^+ + HL \overset{K_{ex}}{\rightleftarrows} H^+ + M^+L^-$

no extractability towards Li, Cs, Mg, Ca at pH 7 - 9



$72R_4$

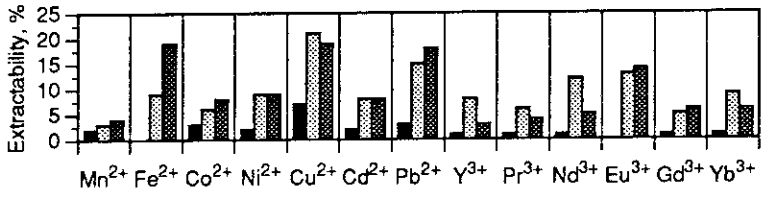


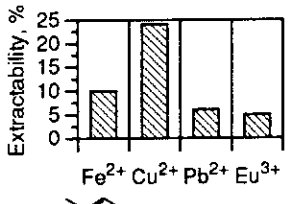


[89]

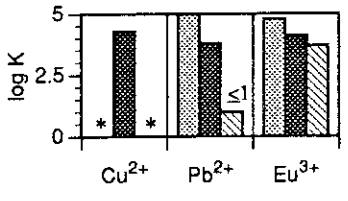
Aq.: 0.25 mM metal picrate (neutral)
Org.: 0.25 mM L in CH_2Cl_2
Stability constants in MeOH at 298 K, analysis: spec, stoichiometry: 1:1

Li **Ni**
Na **Cu**
K **Cd**
Rb **Pb**
Cs **Y**
Mg **Pr**
Ca **Nd**
Sr **Eu**
Mn **Gd**
Fe **Yb**
Co

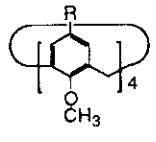




R =

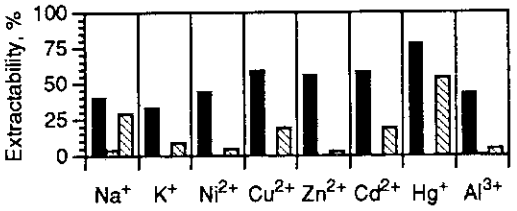


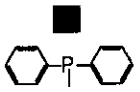
* : slow kinetics



$6R_4$

Na
K
Ni
Cu
Zn
Cd
Hg
Al



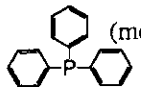
R:  R: $-C(CH_3)_3$

stoichiometry: 1:2 (calix:Cu^{2+}) in THF, cont. vari. method

[90]

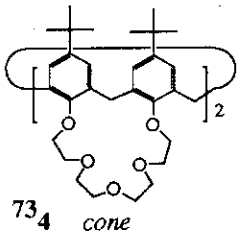
Aq.: 0.02 mM Hpic, 10 mM metal nitrate,
Org.: 1 mM L in $CHCl_3$
Vol.: 10 ml /10 ml,
T: 298 K, t: 24 h,
analysis: UV

Extractant:



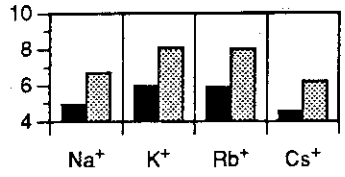
(monomer)

Extractant	Metal	Data	Conditions and Remarks	Ref.
Crowned calixarenes				[91, 92]



73_4 *cone* conformation

Na
K
Rb
Cs



K_{ass} in M^{-1}

ΔG in kcal mol^{-1}

Aq.: metal picrates
solvent: $CDCl_3$ (sat. H_2O)
T: 295 K

$$M^+ + pic^- + \overline{L} \overset{K_{ass.}}{\rightleftarrows} \overline{M^+pic^-L}$$

selectivity order: $Rb^+ \geq K^+ >> Na^+ > Cs^+$

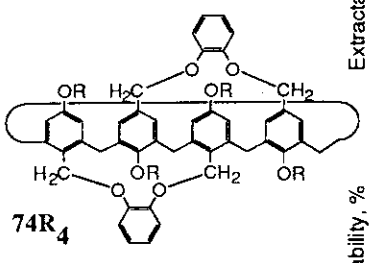
---

[28]

Aq., Series **A**
(Li, Na, K, Cs): 0.25 mM metal picrate, 0.1 M MOH, 0.5 M MCl
Aq., Series **B**
(Na, K, Ag): 0.238 mM Hpic, 0.01 MNO_3, pH 4.7
Org.: 2.5 mM L in CH_2Cl_2
Vol.: 5 ml/5 ml, T: 298 K,
t: 12 h, spec.
Association constants K_{ass} from NMR data at 223 K in $CDCl_3/CD_3OD$ (4:1 v/v),
$c_{MX} = c_L = 1$ mM
MX = $LiClO_4$, $NaClO_4$, Kpic, $AgCF_3SO_3$

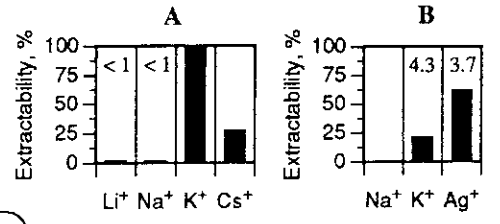
R = Propyl

Li Cs
Na Ag
K

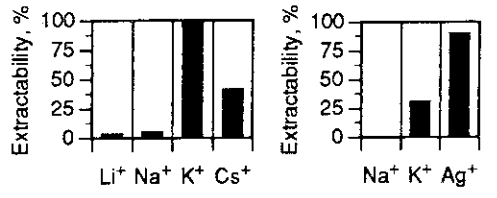


$74R_4$

R = $-CH_2-CH_2-O-CH_2-CH_3$



values of log K_{ass} are indicated above bars



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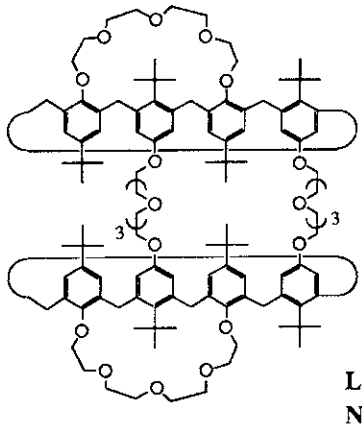
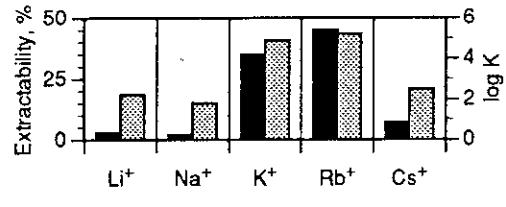
[93]

Aq.: 0.25 mM metal picrate
Org.: 0.25 mM L in CH_2Cl_2
T: 298 K, t: 70 min
Association constants K in acetonitrile solvent
at $\mu = 0.01$ (Et_4NClO_4)



75_4



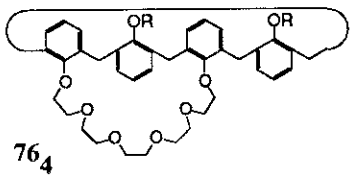
Li Rb
Na Cs
K

stoichiometry in acetonitrile: 1:1

Extractant **Metal** **Data** **Conditions and Remarks** **Ref.**

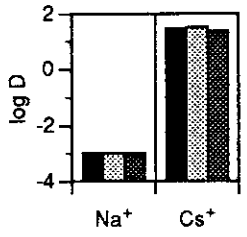
Crowned Calixarenes

[94-97]



76_4

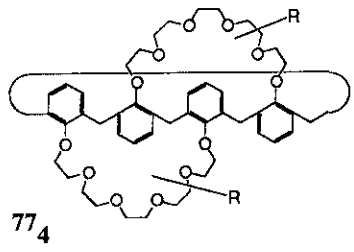
Na
Cs
Ru
Sb
Ce
Eu
Nd
Ce
Mo
Zr
Fe
Am
Cm



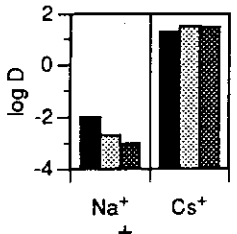
Single element extraction:
Aq.: 0.5 mM MNO_3, 1 M HNO_3
Org.: 10 mM L in o-nitrophenyloctylether

$$Cs^+ + NO_3^- + \overline{L} \rightleftarrows \overline{L(CsNO_3)}$$

R: ■ $-CH(CH_3)_2$ ▒ n-octyl ■ 2-nitrophenoxy-octyloxy



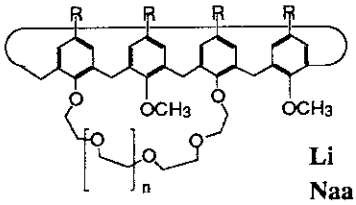
77_4



■ bis crown-6-calixarene
▒ bis-(1,2-benzo-crown-6)calixarene
■ bis-(1,2-naphto-crown-6)calixarene

distribution of Cs^+ in real PUREX raffinate liquid extraction (acidity 4M, activity ca. 30 Ci/L)
Cs decontamination factors towards Ru, Sb, Ce, Eu, Mo, Zr, Fe, Nd, Ce, and actinides, kinetics , (analysis: alpha-/gamma-spectrometry, ICP-AES)

[98]

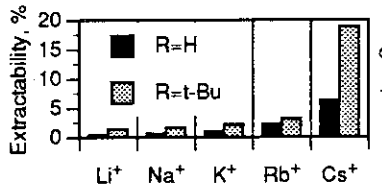


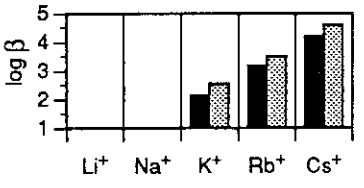
$78R_{4,n}$

Li
Naa
K
Rb
Cs

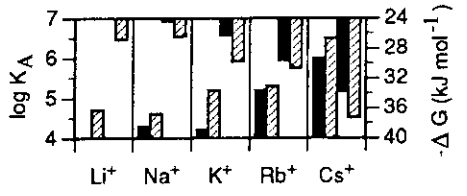
Ø-O-CH_3 conformationally mobile for R=H,

n=2





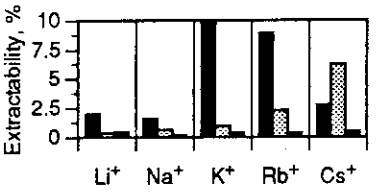
n=2



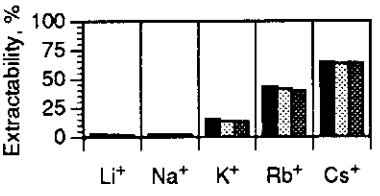
■ R=H ▨ R=t-Butyl

Aq.: 0.25 mM metal picrate (neutral soln.)
Org.: 0.25 mM L in CH_2Cl_2
Vol.: 5 ml /5 ml
T: 293 K, t: 30 min
analysis: spec
Association constants K_A in $CHCl_3$ (sat H_2O) at 295 K
Stability constants in MeOH at μ=0.01 M (Et_4NCl or Et_4NClO_4), 298 K, and MCl (spec.) or $MClO_4$ (pot.), c_L = 0.005 - 0.25 mM

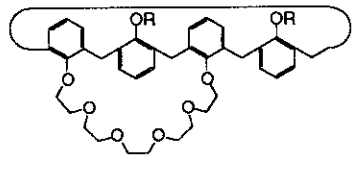
R = H



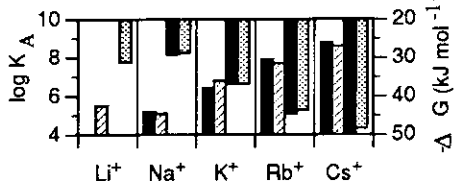
■ n=1 ▒ n=2 ■ n=3

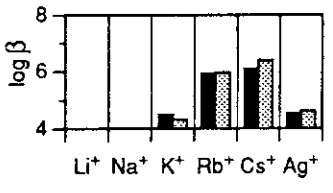


■ $R = -CH(CH_3)_2$
▒ $R = -CH_2-CH_2-CH_3$
■ $R = -(CH_2)_7-CH_3$



$79R_4$ 1,3-*alternate* conformation



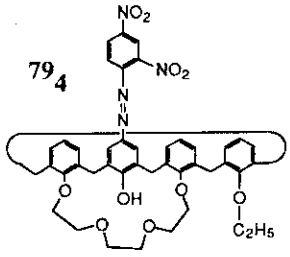


no extraction with *cone*-conformer when R=*i*-propyl

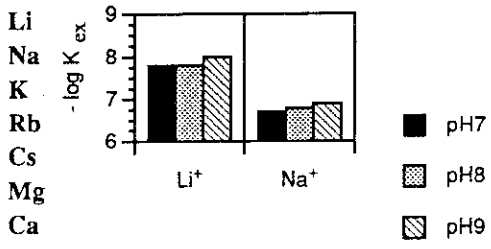
Extractant | **Metal** | **Data** | **Conditions and Remarks** | **Ref.**

Crowned Calixarenes

[99]



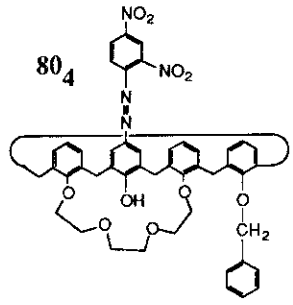
79_4



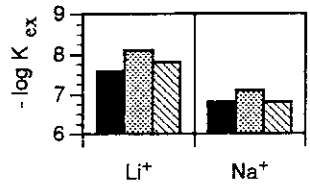
log K_{ex} of K^+, Rb^+, Cs^+, Mg^{2+}, and Ca^{2+} < -10

Aq.: 0.1 mM to 1.0 M MCl and 0.1 M buffer (tris(hydroxymethyl)-methylamine/HCl, pH 7 - 9
Org.: 0.01mM to 0.01 M L in $CHCl_3$
Vol.: 3 ml /3 ml, T: 298 K, analysis: spec

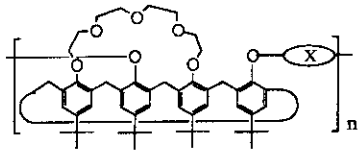
$$Kex = \frac{[H^+]\,\overline{[M^+L^-]}}{[M^+]\,\overline{[HL]}}$$



80_4

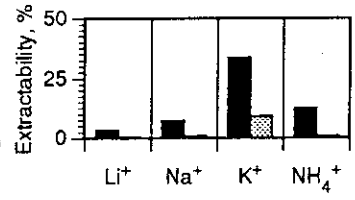


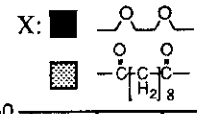
[100]

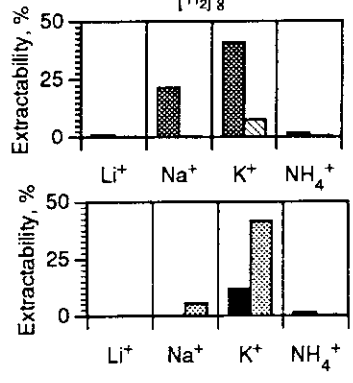


Telomer

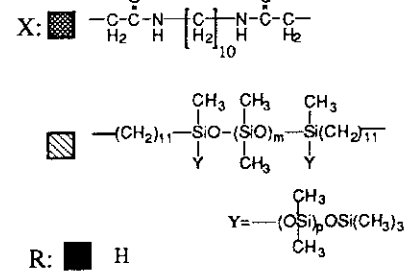
$81X_4$

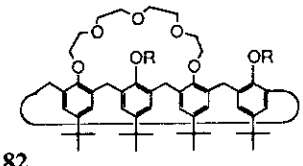




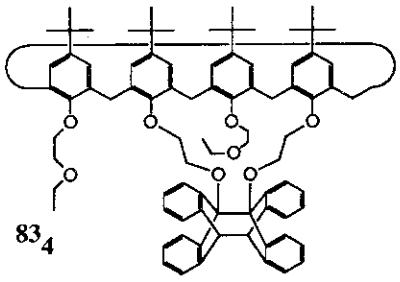
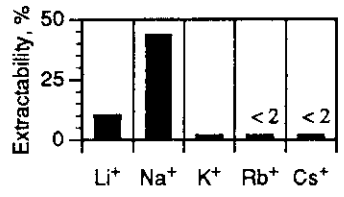
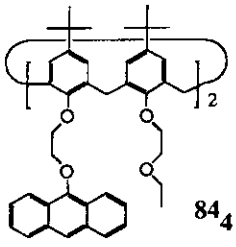
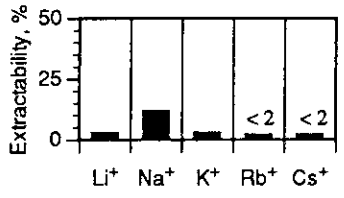
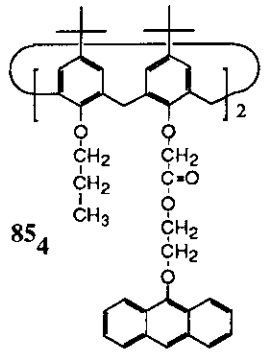
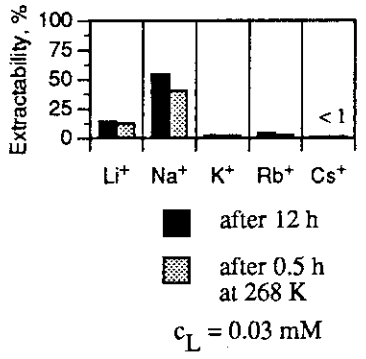
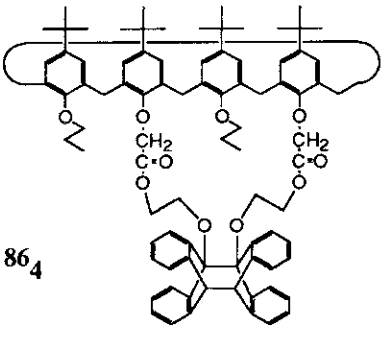
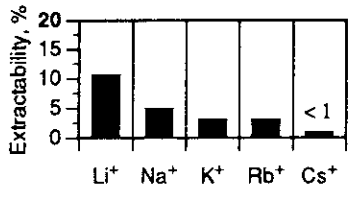
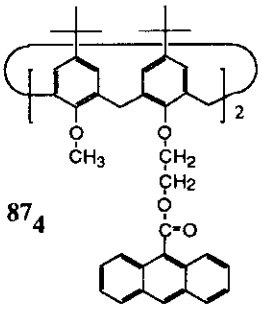
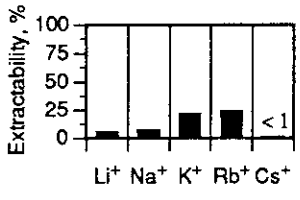
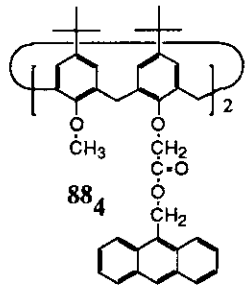
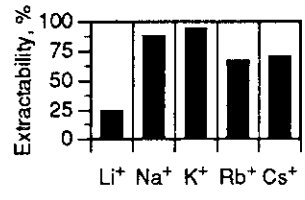


Aq.: 5 mM metal picrate
Org.: 5 mM L in $CHCl_3$
Vol.: 1 ml /1 ml, t: 10 min
analysis: spec



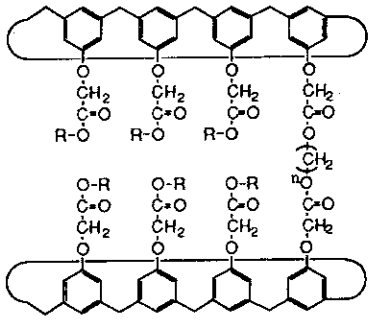


82_4

Extractant	Metal	Data	Conditions and Remarks	Ref.
Bridged Calixarenes				
 **83_4**	**Li** **Na** **K** **Rb** **Cs**		**Aq.:** 0.1 M MOH, 0.5 M MCl, 0.0226 mM Hpic, Stripping: water **Org.:** 0.0804 mM L in CH_2Cl_2 Vol.: 5 ml /5 ml, t: 30 min T: 268 K	[103-105]
 **84_4**				
 **85_4**			**Aq.:** 0.1 M MOH, 0.5 M MCl, 0.022 mM Hpic, **Org.:** ligand in $C_2H_2Cl_4$:CH_2Cl_2 (4:1 v/v) Vol.: 5 ml /5 ml, t: 12 h T: 298 K (268 K for dimerized ligand)	[106]
 **86_4**				
 **87_4**				
 **88_4**				

Extractant	Metal	Data	Conditions and Remarks	Ref.

Double calixarene and metacyclophanes



89_4

Metal		$\frac{\overline{(Napic)}}{\overline{(calix\text{-}unit)}}$	$K_{ex\,1}$ (M^{-1})	$K_{ex\,2}$ (M^{-1})
Li	R = Et, n = 2	0.42	2.66	0.015
Na	R = Et, n = 5	0.55	4.9	0.206
K	R = Et, n = 10	0.65	5.57	0.689
Rb	R = *t*-Bu, n = 2	0.77	19.22	0.897
Cs	calix[4]arene tetraethylester	0.91	6.48	-
	calix[4]arene tetra-*t*-butylester	0.98	85.82	-

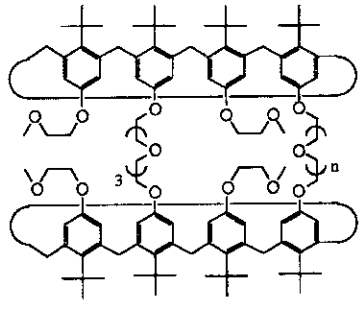
$$K_{ex\,1} = \frac{\overline{[pic^-]}\ \overline{[LM^+]}}{[M^+]\ [pic^-]\ \overline{[L]}}$$

$$K_{ex\,2} = \frac{\overline{[pic^-]}\ \overline{[LM_2^+]}}{[M^+]\ [pic^-]\ \overline{[LM^+]}}$$

Concentration:
Napic: calixarene-unit = 20

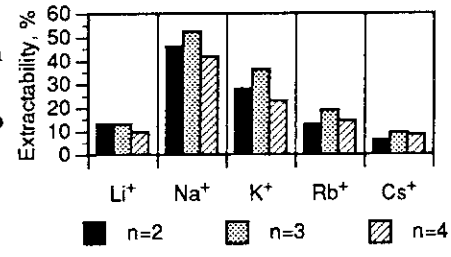
107]

[105, 108]



$90_{4,\,n}$

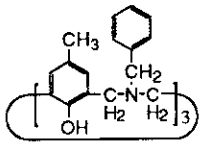
Li
Na
K
Rb
Cs



stoichiometry: 1:1 and 1:2 ($L:Na^+$)

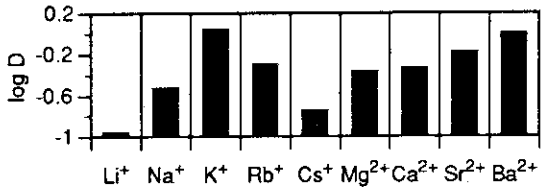
Aq.: 0.5 M MCl,
0.1 M MOH,
0.0275 mM Hpic
Org.: 0.0802 mM L
in CH_2Cl_2
Vol.: 5 ml /5 ml

[109]



91_4

Li
Na
K
Rb
Cs
Mg
Ca
Sr
Ba
U



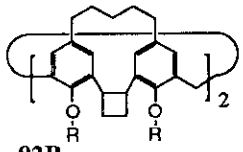
$D(UO_2^{2+}) = f(pH)$ (pH 2 - 10)

maximum extractability of UO_2^{2+} (D ca. 100) at pH 6 - 7

Aq.: 0.7 mM [pic^-],
0.1 M metal ions, pH 6
Org: 1 mM L in $CHCl_3$
(sat. water)
UO_2^{2+} extraction:
10 ppm UO_2^{2+}, 0.5 M
NaCl, buffer (pH 2-10)
0.49 mM L
T: 298 K, t: 12h,
analysis: spec

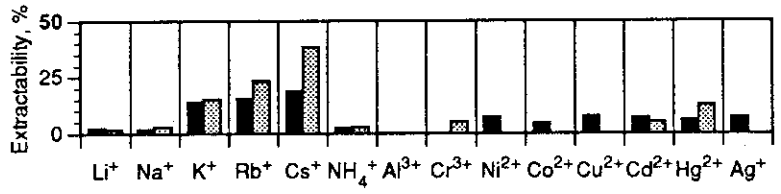
Extractant **Metal** **Data** **Conditions and Remarks** **Ref.**

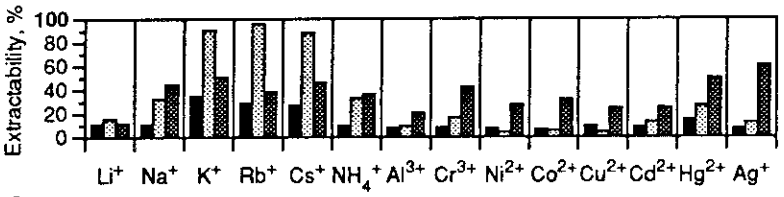
Bridged metacyclophanes

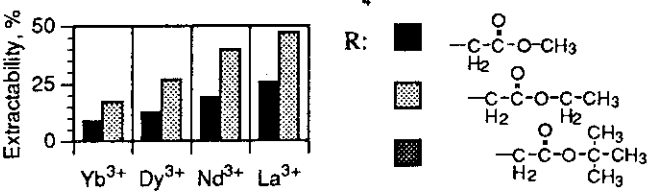


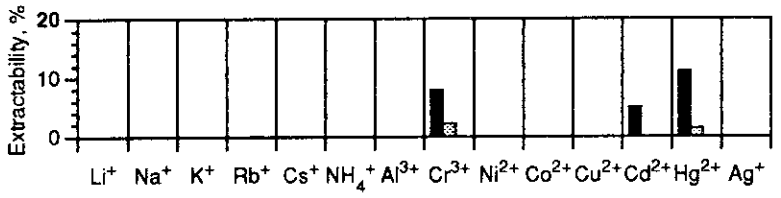
$92R_4$

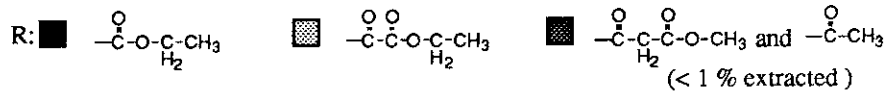
Li	**Cu**
Na	**Cd**
K	**Hg**
Rb	**Ag**
Cs	**Yb**
(NH_4^+)	**Dy**
Al	**Nd**
Cr	**La**
Ni	
Co	



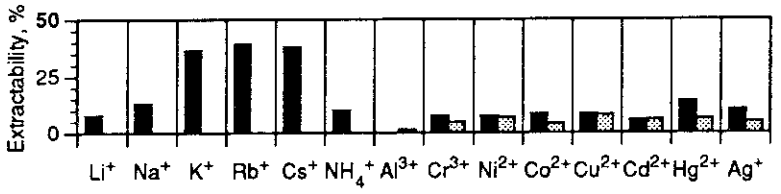




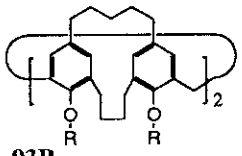




(< 1 % extracted)

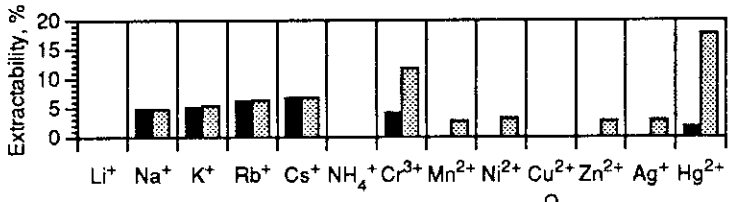


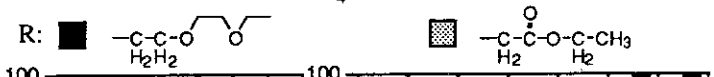
[112]

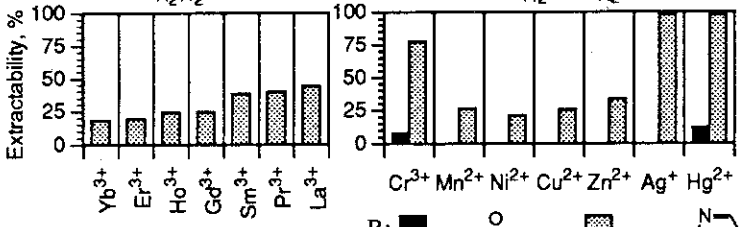


$93R_4$

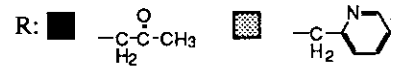
Li	**Zn**
Na	**Ag**
K	**Hg**
Rb	**Yb**
Cs	**Er**
(NH_4^+)	**Ho**
Cr	**Gd**
Mn	**Sm**
Ni	**Pr**
Cu	**La**







(no extractability for alkali ions)



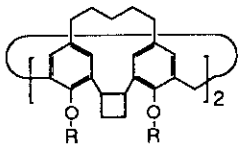
Aq.: 0.25 mM Hpic in 0.1 M alkali hydroxide, or 0.025 mM Hpic in 1 mM metal nitrate (other metals)
Org.: 0.25 mM L in CH_2Cl_2
Vol.: 5 ml /5 ml
T: 295 K
t: 10 min
analysis: spec deviation ± 2%

[110, 111]

Aq.: 0.25 mM Hpic in 0.1 M alkali hydroxide, or 0.025 mM Hpic in 1 mM metal nitrate (other metals)
Org.: 0.25 mM L in CH_2Cl_2
Vol.: 5 ml /5 ml
T: 295 K
analysis: spec deviation ± 2%

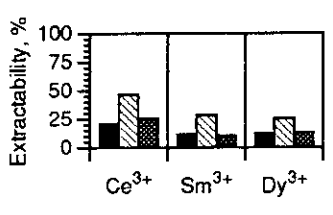
Extractant	Metal	Data	Conditions and Remarks	Ref.

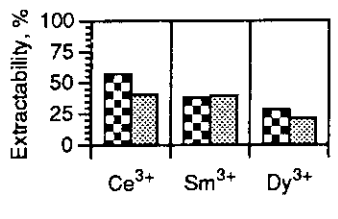
Bridged metacyclophanes



$92R_4$

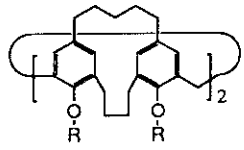
Ce
Sm
Dy



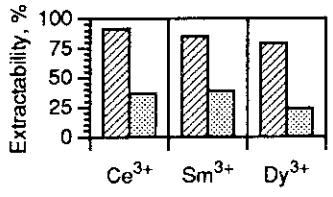


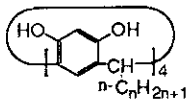
[113]

Org.: 0.1 mM L in CH_2Cl_2



$93R_4$



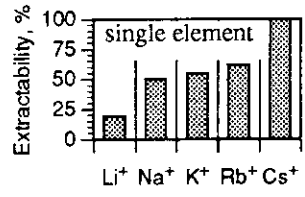


$94_{4,n}$

Li
Na
K
Rb
Cs

Extractability of M^+ = f(pH) (pH 9-13, single elememt)

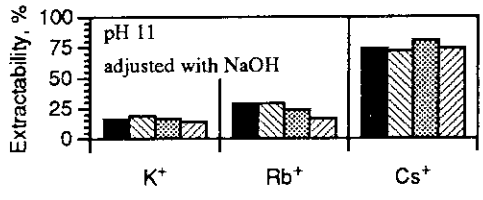
maximum extractability at pH 12:

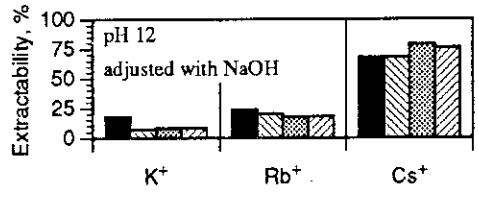


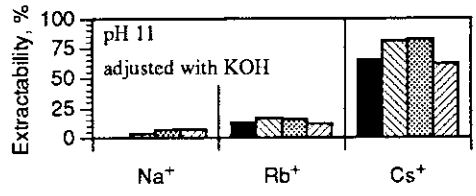
[114]

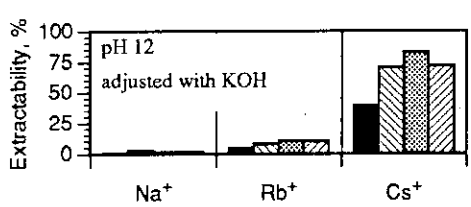
Single element extraction:
Aq.: 0.1 M MOH, HNO_3/NaOH for vari. pH
Org.: 0.5 mM L in C_6H_6

mixed element extraction





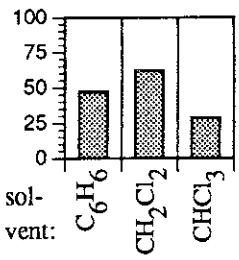


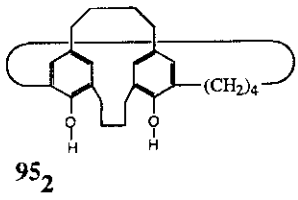
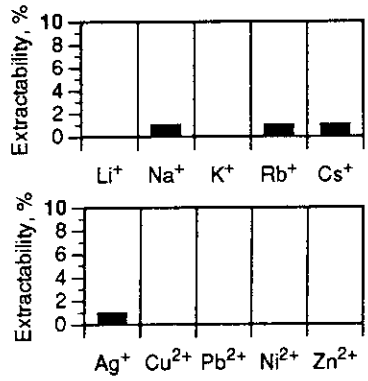
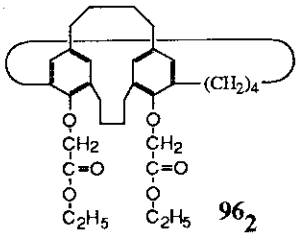
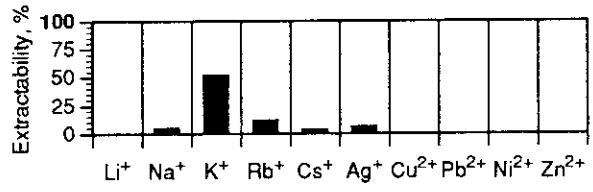
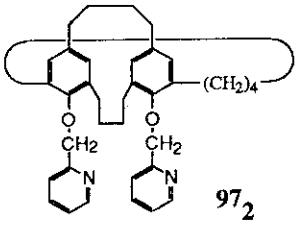
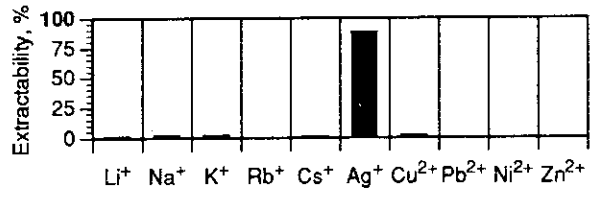
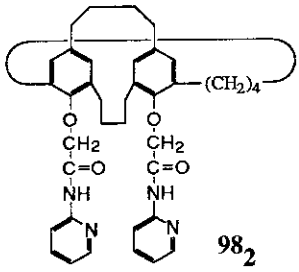
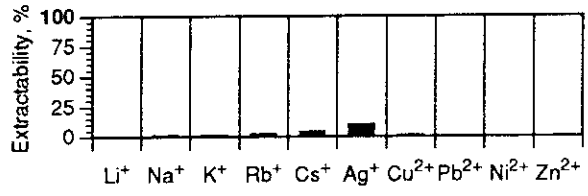
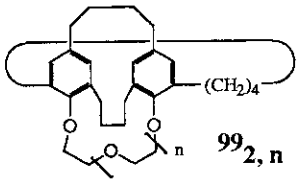
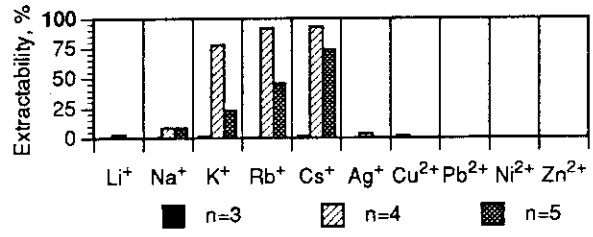


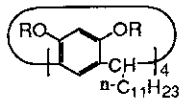
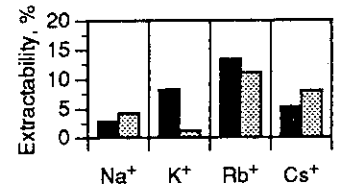
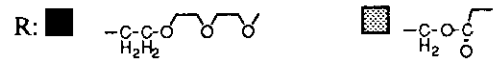
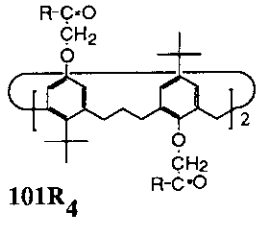
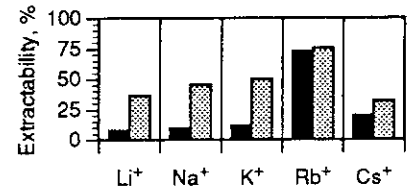
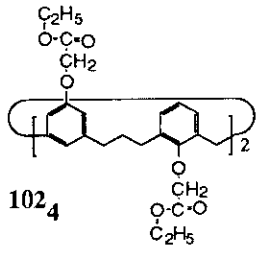
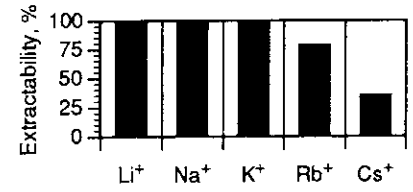
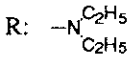
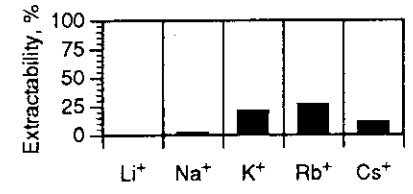
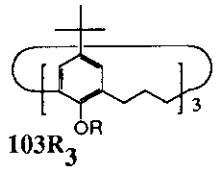
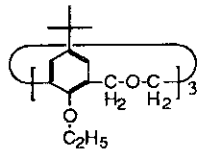
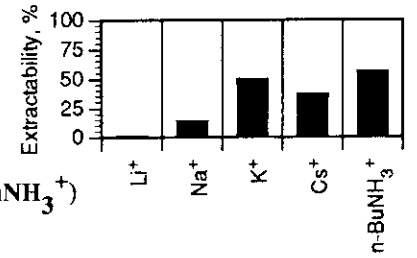
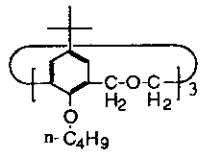
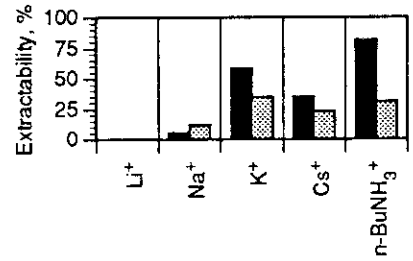
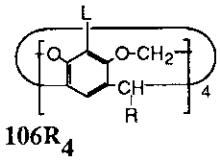
Mixed element extraction:
Aq.: 3 * 0.075 mM M+, pH 11-12 adjusted with NaOH or KOH
Org.: 1.125 mM L in C_6H_6
Stripping: 1 M HNO_3
Vol.: 30 ml /20 ml (single) 60 ml /20 ml (mixed), t: 15 min, analysis: AAS

■ n=6 ▨ n=12
▧ n=8 ▨ n=16

Extractability of Cs^+ with L (n=12) (equi-molar with Cs^+)at pH 12:



Extractant	Metal	Data	Conditions and Remarks	Ref.
Bridged metacyclophanes				
 **95_2**	**Li** **Na** **K** **Rb** **Cs** **Ag** **Cu** **Pb** **Ni** **Zn**		Alkali metal ions: **Aq.:** 0.1 mM MOH, 0.05 mM Hpic **Org.:** 1 mM L in CH_2Cl_2 Vol.: 5 ml /5 ml, T: 295 K, t: 1 h Other metal ions: **Aq.:** 0.1 M metal nitrate pH 7 (Ag), pH 4-5 (Cu, Pb), pH 3.5-4.6 (Ni), pH 5-6 (Zn) **Org.:** 0.1 mM L in CH_2Cl_2 Vol.: 5 ml /5 ml	[115]
 **96_2**				
 **97_2**			1:1 complexes with Ag^+ in acetone-d_6 and in methanol-d_4/acetone-d_6 (1:1 v./v.)	
 **98_2**				
 **$99_{2,n}$**				

Extractant	Metal	Data	Conditions and Remarks	Ref.
Metacyclophanes				
 **$100R_4$**	**Na** **K** **Rb** **Cs**	 	**Aq.:** 0.01 M MOH 0.07 mM Hpic **Org.:** 0.35 mM L in CH_2Cl_2 Vol.: 10 ml/10 ml,	[116]
 **$101R_4$**	**Li** **Na** **K** **Rb** **Cs**	 	**Aq.:** metal picrates **Org.:** L in CH_2Cl_2	[117]
 **102_4**		 R:  		
 **$103R_3$**		extraction of alkali and ammonium ions		[118-120]
 **104_3** (conformation not fixed)	**Li** **Na** **K** **Cs** **($BuNH_3^+$)**		**Aq.:** 0.1 M MOH, 0.5 M MCl, 0.25 mM metal picrate, or 0.07 mM $BuNH_3^+pic^-$ **Org.:** 2.5 mM L in CH_2Cl_2 (3.5 mM for $BuNH_3^+$) T:298 K	[121]
 **105_3**			■ *cone*-conformation ▨ *partial cone*-conformation	
 **$106R_4$**		extraction of lanthanides and actinides L = amide, phosphate, ester group, R = C_5H_{11}, C_9H_{19}		[122]

4. Conclusions

Extraction studies with calixarene-based macrocyclic compounds show that a pronounced metal-selectivity and a high extractability can be achieved by attaching functional groups to the calixarene skeleton which match the properties of the metal ion. Several calixarene compounds have properties which make them superior to crown ethers and conventional extractants. A great advantage over conventional extractants is the possibility of fine-tuning of the extraction properties by varying functional groups, cavity size, hydrophobicity, and other parameters.

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References

1) Gutsche, C. D.: "Calixarenes". Cambridge, UK: The Royal Society of Chemistry (1989).
2) Vicens, J.,Böhmer, V.: "Calixarenes. A Versatile Class of Macrocyclic Compounds" . Dortrecht/Boston/London: Kluwer Academic Publ. (1990).
3) Araki, K., Shinkai, S.: "Novel asymmetric compounds based on higher structure". Kagaku (Kyoto), **45** (2), 134-135 (1990) (jap.).
4) Arnaud-Neu, Fanni, S., F., Guerra, L., McGregor, W., Ziat, K., Schwing-Weill, M.-J., Barrett, G., McKervey, M. A., Marrs, D., Seward, E. M.: "Cation complexation by chemically modified calixarenes. Part 7. Transport of alkali cations by p-tert-butylcalix[n]arene esters and amides". J. Chem. Soc., Perkin Trans. 2, 113-118 (1995).
5) Asfari, Z., Vicens, J.: "Calixarenes". Janssen Chimica Acta, (24), 3-10 (1992).
6) Asfari, Z., Weiss, J., Vicens, J.: "Double-calixarene design, synthesis, and properties". Synlett, 719-725 (1993).
7) Atwood, J. L., Orr, G. W., Robinson, K. D.: "First structural authentication of third-sphere coordination: [p-sulfonatocalix[4]arene]$^{5-}$ as a third sphere ligand for Eu^{3+}". Supramol. Chem., **3**, 89-91 (1994).
8) Atwood, J. L., Orr, G. W., Robinson, K. D., Hamada, F.: "Calixarenes as enzyme models". Supramol. Chem., **2**, 309-317 (1993).
9) Böhmer, V.: "Calixarene - Makrocyclen mit (fast) unbegrenzten Möglichkeiten". Angew. Chemie, **107**, 785-818 (1995).
10) de Namor, A. F. D., Blackett, P.M., Pardo, M.T.G., Tanaka, D.A.P., Velarde, F.J.S.,: "From molecules to electolytes. Electrochemical and thermodynamic aspects of the interaction of phenol and resorcinol based calixarenes with amines". Pure & Appl. Chem., **65** (3), 415-422 (1993).
11) Gutsche, C. D.: "Calixarenes". Accounts of Chemical Research, **16**, 161-170 (1983).
12) Gutsche, C. D.: "The calixarenes" in Vögtle, F., Weber, E. (Eds.), "Host guest complex chemistry". New York: Springer Verlag (1985).

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1) Gutsche, C. D.: "Calixarenes". Cambridge, UK: The Royal Society of Chemistry (1989).
2) Vicens, J.,Böhmer, V.: "Calixarenes. A Versatile Class of Macrocyclic Compounds" . Dortrecht/Boston/London: Kluwer Academic Publ. (1990).
3) Araki, K., Shinkai, S.: "Novel asymmetric compounds based on higher structure". Kagaku (Kyoto), **45** (2), 134-135 (1990) (jap.).
4) Arnaud-Neu, Fanni, S., F., Guerra, L., McGregor, W., Ziat, K., Schwing-Weill, M.-J., Barrett, G., McKervey, M. A., Marrs, D., Seward, E. M.: "Cation complexation by chemically modified calixarenes. Part 7. Transport of alkali cations by p-tert-butylcalix[n]arene esters and amides". J. Chem. Soc., Perkin Trans. 2, 113-118 (1995).
5) Asfari, Z., Vicens, J.: "Calixarenes". Janssen Chimica Acta, (24), 3-10 (1992).
6) Asfari, Z., Weiss, J., Vicens, J.: "Double-calixarene design, synthesis, and properties". Synlett, 719-725 (1993).
7) Atwood, J. L., Orr, G. W., Robinson, K. D.: "First structural authentication of third-sphere coordination: [p-sulfonatocalix[4]arene]$^{5-}$ as a third sphere ligand for Eu^{3+}". Supramol. Chem., **3**, 89-91 (1994).
8) Atwood, J. L., Orr, G. W., Robinson, K. D., Hamada, F.: "Calixarenes as enzyme models". Supramol. Chem., **2**, 309-317 (1993).
9) Böhmer, V.: "Calixarene - Makrocyclen mit (fast) unbegrenzten Möglichkeiten". Angew. Chemie, **107,** 785-818 (1995).
10) de Namor, A. F. D., Blackett, P.M., Pardo, M.T.G., Tanaka, D.A.P., Velarde, F.J.S.,: "From molecules to electolytes. Electrochemical and thermodynamic aspects of the interaction of phenol and resorcinol based calixarenes with amines". Pure & Appl. Chem., **65** (3), 415-422 (1993).
11) Gutsche, C. D.: "Calixarenes". Accounts of Chemical Research, **16**, 161-170 (1983).
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1) Gutsche, C. D.: "Calixarenes". Cambridge, UK: The Royal Society of Chemistry (1989).
2) Vicens, J.,Böhmer, V.: "Calixarenes. A Versatile Class of Macrocyclic Compounds" . Dortrecht/Boston/London: Kluwer Academic Publ. (1990).
3) Araki, K., Shinkai, S.: "Novel asymmetric compounds based on higher structure". Kagaku (Kyoto), **45** (2), 134-135 (1990) (jap.).
4) Arnaud-Neu, Fanni, S., F., Guerra, L., McGregor, W., Ziat, K., Schwing-Weill, M.-J., Barrett, G., McKervey, M. A., Marrs, D., Seward, E. M.: "Cation complexation by chemically modified calixarenes. Part 7. Transport of alkali cations by p-tert-butylcalix[n]arene esters and amides". J. Chem. Soc., Perkin Trans. 2, 113-118 (1995).
5) Asfari, Z., Vicens, J.: "Calixarenes". Janssen Chimica Acta, (24), 3-10 (1992).
6) Asfari, Z., Weiss, J., Vicens, J.: "Double-calixarene design, synthesis, and properties". Synlett, 719-725 (1993).
7) Atwood, J. L., Orr, G. W., Robinson, K. D.: "First structural authentication of third-sphere coordination: [p-sulfonatocalix[4]arene]$^{5-}$ as a third sphere ligand for Eu^{3+}". Supramol. Chem., **3**, 89-91 (1994).
8) Atwood, J. L., Orr, G. W., Robinson, K. D., Hamada, F.: "Calixarenes as enzyme models". Supramol. Chem., **2**, 309-317 (1993).
9) Böhmer, V.: "Calixarene - Makrocyclen mit (fast) unbegrenzten Möglichkeiten". Angew. Chemie, **107**, 785-818 (1995).
10) de Namor, A. F. D., Blackett, P.M., Pardo, M.T.G., Tanaka, D.A.P., Velarde, F.J.S.,: "From molecules to electolytes. Electrochemical and thermodynamic aspects of the interaction of phenol and resorcinol based calixarenes with amines". Pure & Appl. Chem., **65** (3), 415-422 (1993).
11) Gutsche, C. D.: "Calixarenes". Accounts of Chemical Research, **16**, 161-170 (1983).
12) Gutsche, C. D.: "The calixarenes" in Vögtle, F., Weber, E. (Eds.), "Host guest complex chemistry". New York: Springer Verlag (1985).

13) Gutsche, C. D.: "Calixarenes and the art of molecular basket making". Progr. Macrocycl. Chem., **3**, 93-165 (1987).
14) Gutsche, C. D., Alam, I., Iqbal, M., Mangiafico, T., Nam, K. C., Rogers, J., See, K. A.: "Topics in calixarene chemistry". J. Inclusion Phen. and Molec. Recognition in Chem., **7** (1), 61-72 (1989).
15) Gutsche, C. D., Iqbal, M., Nam, K. S., Alam, I.: "Conformational and complexational characteristics of calixarenes". Pure & Appl. Chem., **60** (4), 483-488 (1988).
16) Gutsche, C. D., Rogers, J. S., Steward, D., See, K. A.: "Calixarenes: Paradoxes and paradigms in molecular baskets". Pure Appl. Chem., **62** (3), 485-491 (1990).
17) Ikeda, A., Tsuzuki, H., Shinkai, S.: "NMR spectroscopic and x-ray crystallographic studies of calix[4]arene Ag^+ complexes. Influence of bound Ag^+ on C_{2v} - C_{2v} interconversion in cone-calix[4]arenes". J. Chem. Soc., Perkin Trans. II, 2073-2080 (1994).
18) Kunitake, T.: "Molecular recognition by surface monolayers". Kagaku (Kyoto), **44** (8), 560-561 (1989).
19) Linnane, P., Shinkai, S.: "Calixarnes: Adaptable hosts par excellence". Chemistry & Industry, (20), 811-814 (1994).
20) Lipkowitz, K. B., Pearl, G.: "Structural features of solid-state calix[4]arene in the cone conformation". J. Org. Chem., **58** (24), 6729-6736 (1993).
21) McKervey, A., Böhmer, V.: "Calixarenes - supramolecular pursuits". Chem. in Britain, (Aug.), 724-727 (1992).
22) Nakamoto, Y.: "Synthesis of functional cyclic phenol oligomers". Kobunshi Kako, **38** (12), 602-607 (1989).
23) Perrin, R. : "Potential industrial applications of calixarenes: New separation chemistry techniques for radioactive waste and other specific applications. Proceedings of the technical seminar on new separation chemistry techniques for radioactive waste and other specific applications" in Ceciller, L., Casarci, M., Pietrelli, L., (Ed.), Technical seminar on new separation chemistry techniques for radioactive waste and other specific applications, pp. 125-132, Rome, Italy: ENEA, Rome (1990).
24) Shinkai, S.: "Molecular recognition of calixarene-based host molecules". J. Inclusion Phen. Molec. Recogn. Chem., **7** (2), 193-201 (1989).
25) Shinkai, S.: "Calixarenes - The third generation of supramolecules". Tetrahedron, **49** (40), 8933-8968 (1993).
26) Thonforf, I., Hillig, G., Brandt, W., Brenn, J., Barth, A., Böhmer, V.: "Molecular modelling study of a disymmetric calix[4]arene and its methyl ethers". J. Chem. Soc., Perkin Trans. II, 2259-2267 (1994).
27) vanDienst, E., Bakker, W. I. I., Engbersen, J. F. J., Verboom, W., Reinhoudt, D. N.: "Calixarenes, chemical chameleons". Pure & Appl. Chem., **65** (3), 387-392 (1993).
28) Ikeda, A., Shinkai, S.: "Unusually high ionophobicity of 1,3-alternate calix[4]arenes: π-Donor participation in the complexation of cations?". Tetr. Lett., **33** (48), 7385-7388 (1992).
29) Ikeda, A., Shinkai, S.: "On the origin of high ionophoricity of 1,3-alternate calix[4]-arenes: p-Donor participation in complexation of cations and evidence for metal-tunneling through the calix[4]arene cavity". J. Amer. Chem. Soc., **116** (7), 3102-3110 (1994).
30) Yoshida, I., Fujii, S., Ueno, K., Shinkai, S., Matsuda, T.: "Solvent extraction of Cu(II) with p-tert-butylcalix[6]arene from ammonia alkaline solution". Chem. Letters, (9), 1535-1538 (1989).

31) Chang, S. K., Cho, I.: "New metal cation-selective ionophores derived from calixarenes". Chem. Letters, 477-478 (1984).
32) Chang, S.-K., Kwon, S.-K., Cho, I.: "Calixarene-based amide ionophores for group IIA metal cations". Chem. Letters, (5), 947-948 (1987).
33) Chang, S.-K., Cho, I.: "New metal cation-selective ionophores derived from calixarenes: their synthesis and ion-binding properties". J. Chem. Soc., Perkin Trans. I, (2), 211-214 (1986).
34) Conner, M., Janout, V., Regen, S. L.: "Synthesis and alkali metal binding properties of "upper rim" functionalized calix[4]arenes". J. Org. Chem., **57** (13), 3744-3746 (1992).
35) Nomura, E., Taniguchi, H., Kawaguchi, K., Otsuji, Y.: "Catalytic ability of flexible octopus-type calix[6]arene in ester-forming reactions and its structural properties". J. Org. Chem., **58** (17), 4709-4715 (1993).
36) Schwing, M.-J., Arnaud, F., Marques, E.: "Cation binding properties of alkyl calixaryl derivatives. A new family of molecular receptors". Pure & Appl. Chem., **61** (9), 1597-1603 (1989).
37) Arnaud-Neu, F., Collins, E. M., Deasy, M., Ferguson, G., Harris, S. J., Kaitner, B., Lough, A. J., McKervey, M. A., Marques, E., Ruhl, B. L., Schwing-Weill, M., Seward, E. M.: "Synthesis, X-ray crystal structure, and cation binding properties of alkyl calixaryl esters and ketones, a new family of macrocyclic molecular receptors". J. Amer. Chem. Soc., **111** (23), 8681-8691 (1989).
38) Arnaud-Neu, F., Barrett, G., Cremin, S., Deasy, M., Ferguson, G., Harris, S. J., Lough, A. J., Guerra, L., McKervey, M. A., Schwing-Weill, M. J., Schwinte, P.: "Selective alkali-metal cation complexation by chemically modified calixarenes. Part 4. Effect of substituent variation on the Na^+/K^+ selectivity in the ester series and x-ray crystal structure of the trifluoroethyl ester". J. Chem. Soc., Perkin Trans., 1119-1125 (1992).
39) Ferguson, G., Kaitner, B., McKervey, M. A., Seward, E. M.: "Synthesis, x-ray crystal structure, and cation transfer properties of a calix[4]arene tetraketone, a new versatile molecular receptor". J. Chem. Soc., Chem. Commun., 584-585 (1987).
40) Brunink, J. A. J., Verboom, W., Engbersen, J. F. J., Harkema, S., Reinhoudt, D. N.: "Synthesis and cation complexation selectivity of bis(syn-proximally) functionalized calix[4]arenes". Recl. Trav. Chim. Pays-Bas, **111** (11/12), 511-516 (1992).
41) Arnaud-Neu, F., S., F., Guerra, L., McGregor, W., Ziat, K., Schwing-Weill, M.-J., Barrett, G., McKervey, M. A., Marrs, D., Seward, E. M.: "Cation complexation by chemically modified calixarenes. Part 7. Transport of alkali cations by p-tert-butylcalix[n]arene esters and amides". J. Chem. Soc., Perkin Trans. 2, 113-118 (1995).
42) Arnaud-Neu, F., Schwing-Weill, M.-J., Ziat, K., Cremin, S., Harris, S. J., McKervey, M. A.: "Selective alkali and alkaline earth cation complexation by calixarene amides". New J. Chem., **15** (1), 33-37 (1991).
43) Diamond, D., Svehla, G., Seward, E. M., McKervey, M. A.: "A sodium ion-selective electrode based on methyl-p-t-butylcalix[4]arylacetate as the ionophore". Analyt. Chim. Acta, **204**, 223-231 (1988).
44) McKervey, M. A., Seward, E. M., Ferguson, G., Ruhl, B., Harris, S. J.: "Synthesis, x-ray crystal structure, and cation transfer properties of alkyl calixaryl acetates, a new series of molecular receptors". J. Chem. Soc., Chem. Commun. (7), 388-390 (1985).

45) Iwamoto, K., Shinkai, S.: "Synthesis and ion selectivity of all conformational isomers of tetrakis((ethoxycarbonyl)methoxy)calix[4]arene". J. Org. Chem., **57** (26), 7066-7073 (1992).
46) Barrett, G., McKervey, M. A., Malone, J. F., Walker, A., Arnaud-Neu, F., Guerra, L., Schwing-Weill, M.-J., Gutsche, C. D., Stewart, D.: "Cation complexation by chemically modified calixarenes. Part 6. Alkali and silver cation complexation by p-tert-butylcalix[5]arene derivatives and x-ray structure detremination of a pentaester". J. Chem. Soc., Perkin Trans. 2, 1475-1479 (1993).
47) Schwing-Weill, M. J., Arnaud-Neu, F., McKervey, M. A.: "Modulation of the cation complexing properties in the 'lower rim' chemically modified calixarene series". J. Phys. Org. Chem., **5**, 496-501 (1992).
48) Yordanov, A.T., Roundhill, D.M.: "Synthesis and chemistry of sulfur derivatized calixarenes". Int. Conf. on Calixarenes 1995, p. 25, Texas (USA) (1995).
49) Shinkai, S., Shiramama, Y., Satoh, H., Manabe, O., Arimura, T., Fujimoto, K., Matsuda, T.: "Selective extraction and transport of uranyl with calixarene-based uranophiles". J. Chem. Soc., Perkin Trans. II, (8), 1167-1171 (1989).
50) Ohto, K., Yamamoto, T., Goto, M., Nakashio, F., Nagasaki, T., Shinkai, S.: "Extraction of rare earth metals with new extractants of calixarene derivatives" Symposium on Solvent Extraction, pp. 61-66, Osaka (Japan) (1991).
51) Ohto, K., Inoue, K., Goto, M., Nakashio, F., Nagasaki, T., Shinkai, S.: "Extraction of rare earth metals with new extractants of calixarene derivatives" ISEC'93, **1** pp.364-369, York (UK).
52) Ohto, K., Yano, M., Inoue, K.: "Solvent extraction of rare earths with derivatives of phenolic oligomers" Symposium on Solvent Extraction, pp.187-190, Tokyo (1992) .
53) Ohto, K., Yano, M., Inoue, K., Goto, M., Nakashio, F., Nagasaki, T., Shinkai, S. : "The effect of alkali cations on the extraction of rare earths with calixarene derivatives" Symposium on Solvent Extraction, pp.75-76, Sendai, Japan (1993), and Analytical Science, (1995) (in press).
54) Ohto, K., Inoue, K., Murakami, E., Terada, H., Iwasaki, H.: "The extraction of silver and paladium with p-tert-octylcalixarene ketone derivatives". Autumn Conf. Chem. Eng., p. 435, Hokkaido University (Japan) (1995).
55) Ungaro, R., Pochini, A., Andreetti, G. D.: "New ionizable ligands from p-tert-Butylcalix[4]arene". J. Inclusion Phen., **2**, 199-205 (1984).
56) Arnaud-Neu, F., Schwinte, P., Schwing-Weill, M.J.: "Complexation of lanthanides(III) and thorium(IV) by ionizable calixarenes". Int. Conf. on Calixarenes 1995, p. 72, Texas (USA) (1995).
57) Ludwig, R., Inoue, K., Shinkai, S. : "Solvent extraction of lanthanide ions using a calix[6]arene compound" Symposium on Solvent Extraction , pp. 53-60, Toyonaka, Osaka (1991); Ludwig, R., Inoue, K. : "About solvent extraction of rare earth metal ions with carboxymethoxy-p-tert-butylcalix[6]arene" Symposium on Rare Metals, Sendai (Jap.) (1991).
58) Ludwig, R., Inoue, K., Yamato, T.: "Solvent extraction behaviour of calixarene-type cyclophanes towards trivalent La, Nd, Eu, Er, and Yb". Solvent Extr. Ion Exchange, **11** (2), 311-330 (1993).
59) Ludwig, R., Inoue, K., Shinkai, S., Gloe, K. : "Solvent extraction behaviour of p-tert-butylcalix[n]arene carboxylic acid derivatives towards trivalent lanthanides and sodium" in

Logsdail, D. H., Slater, M. J. (Ed.), Solvent Extraction in the Process Industries, Proc. ISEC'93, **1**, pp.273-278, York (UK): Elsevier Applied Science (1993).
60) Ludwig, R.: "Neue Extraktionsmittel vom Typ der Cyclophane zur Metallionentrennung für die Endlagerungradioaktiven Abfalls". Vortragstagung der FG Nuklearchemie der GDCh, Berlin 1994; Ludwig, R., Gauglitz, R. : "Calixarene type extractants for metal ions with improved properties" ISEC'96 Melbourne (Australia) (in press).
61) Ludwig, R., Tachimori, S.: " Metal extraction with calixarene-type extractants bearing amide and carboxylic acid functional groups" Symposium on Solvent Extraction, Fukuoka (1995) (in press).
62) Nagasaki, T., Shinkai, S.: "Synthesis and solvent extraction studies of novel calixarene-based uranophiles bearing hydroxamic acid groups". J. Chem. Soc., Perkin Trans. II, (7), 1063-1066 (1991).
63) Dasaradhi, L., Stark, P., Huber, V.J., Gopalan, A.S., Smith, P.H., Jarvinen, G.D.: "Synthesis and evaluations of some new calixarene tetrahydroxamates for selective extraction of actinide ions". Int. Conf. on Calixarenes 1995, p. 49, Texas (USA) (1995)
64) Araki, K., Hashimoto, N., Otsuka, H., Nagasaki, T., Shinkai, S.: "Molecular design of a calix[6]arene-based super-uranophile with C_3 symmetry. High UO_2^{2+} selectivity in solvent extraction". Chem. Letters, 829-832 (1993).
65) Nagasaki, T., Shinkai, S., Matsuda, T.: "Synthesis and solvent extraction properties of a novel calixarene-based uranophile bearing hydroxamate groups". J. Chem. Soc., Perkin Trans. I, (9), 2617-2618 (1990).
66) Nagasaki, T., Shinkai, S.: "Solvent extraction of transition metal cations by calixarene-based cyclic ligands". Bull. Chem. Soc. Japan, **65** (2), 471-475 (1992).
67) Ogata, M., Fujimoto, K., Shinkai, S.: "Molecular design of calix[4]arene-based extractants which show high Ca^{2+} selectivity". J. Amer. Chem. Soc., **116** (10), 4505-4506 (1994).
68) Soedarsono, J., Asfari, Z., Le Cornec, F., Burgard, M., Vicens, J. : "Selectivities in the liquid-liquid extraction of rare earths by systems containing 25,27-dicarboxylic 26,28-dimethoxy 5,11,17,23-tetra-tert-butyl calix[4]arene", Workshop on calixarenes and related compounds, (P 18) Mainz (Ger.) (1991).
69) Soedarsono, J., Burgard, M., Asfari, Z., Vicens, J.: Liquid-liquid extraction properties of 25,27-dicarboxy-26,28-dimethoxy-5,11,17,23-tetra-tert-butylcalix[4]arene towards the alkali ions". Solvent Extr. Ion Exchange, **13** (4), 755-769 (1995).
70) Soedarsono, J., Burgard, M., Asfari, Z., Vicens, J., New J. Chem. **17**, 601, (1993)
71) Arduini, A., Ghidini, E., Pochini, A., Ungaro, R., Andreetti, G. D., Calestani, G., Ugozzoli, F.: "p-t-Butylcalix[4]arene tetra-acetamide: a new strong receptor for alkali cations". J. Inclusion Phen., **6**, 119-134 (1988).
72) Calestani, G., Ugozzoli, F., Arduini, A., Ghidini, E., Ungaro, R.: "Encapsulated potassium cation in a new calix[4]arene neutral ligand: synthesis and x-ray crystal structure". J. Chem. Soc., Chem. Commun., 344-346 (1987).
73) Arnaud-Neu, F., Fanni, S., McKervey, M.A., Schwing-Weill, M.J., Walker, A.: "Dramatic effect ot the removal of the p-t-butyl groups on the binding abilities of calix[6]arene amides towards metal ions". Int. Conf. on Calixarenes 1995, p. 71, Texas (USA) (1995).
74) Shinkai, S., Otsuka, T., Fujimmoto, K., Matsuda, T.: "Metal selectivity of conformational isomers derived from p-tert-butylcalix[4]arenes". Chem. Letters, (5), 835-838 (1990).

75) Shinkai, S., Otsuka, T., Araki, K. M., T.: "(2-Pyridylmethoxy)calixarenes: New versatile ionophores for metal extraction". Bull. Chem. Soc. Japan, **62** (12), 4055-4057 (1989).
76) Nomura, E., Taniguchi, H., Tamura, S.: "Selective Ion Extraction by a Calix[6]arene Derivative containing Azo Groups". Chem. Letters, (7), 1125-1126 (1989).
77) Nomura, E., Taniguchi, H., Otsuji, Y.: "Binding properties of p-(phenylazo)calixarenes for metal ions". Bull. Chem. Soc. Japan, **66** (12), 3797-3801 (1993), Nomura, E., Taniguchi, H.: "Preparation of p-arylazocalix[4]arenes and their use for selective extraction of silver ions". JP 02.124.863/90.124.863, 14. May 1990, (Appl. 88/277.633, 1. Nov. 1988), (1990).
78) Grüttner, C., Böhmer, V., Jacobi, R.A., Kraft, D., Vogt, W.: "Calixarenes with phosphine-oxide-acetamide structures at the upper rim". Int. Conf. on Calixarenes 1995, p. 30, Texas (USA) (1995).
79) Dozol, J.F., Simon, N., Delmau, L.H., Arnaud, F., Schwing, M.-J., Mauprivez, O., Böhmer, V., Jacobi, R.A., Grüttner, C.: "Extraction and transport of actinides and lanthanides with CMPO-like calixarenes". Int. Conf. on Calixarenes 1995, p. 76, Texas (USA) (1995).
80) FP 95-01158E (1995).
81) McKervey, M.A.: "Synthetic and photochemical aspects of cation complexation using chemically modified calixarenes". Int. Conf. on Calixarenes 1995, p. 21, Texas (USA) (1995).
82) Arnaud-Neu, F., Schwing-Weill, M.-J., McKervey, M.A., Comprehensive Supramolecular Chemistry (subm.).
83) Schwing-Weill, M.J., Mauprivez, O., Arnaud-Neu, F..: "New calixarene derivatives for the separation of actinides". Int. Conf. on Calixarenes 1995, p.38, Texas (USA) (1995).
84) Gutsche, C. D., Nam, K. C.: "Calixarenes. 22. Synthesis, properties, and metal complexation of aminocalixarenes". JACS, **110** (18), 6153-6162 (1988).
85) Shimizu, H., Iwamoto, K., Fujimoto, K., Shinkai, S.: "Chromogenic calix[4]arene". Chem. Letters, 2147-2150 (1991).
86) Deligöz, H., Yilmaz, M.: Liquid-liquid extraction of transition metal cations by calixarene-based cyclic ligands". Solvent Extr. Ion Exchange, **13** (1), 19-26 (1995).
87) Pappalardo, S., Ferguson, G., Neri, P., Rocco, C.: "Synthesis and complexation studies of regioisomers and conformational isomers of p-tert-butylcalix[4]arene bearing pyridine or pyridine N-oxide pendant groups at the lower rim". J. Org. Chem., **60** (14), 4576-4584 (1995).
88) King, A. M., Moore, C. P., Sandanayake, K. S., Sutherland, I. O.: "A highly selective chromoionophore for potassium based upon a bridged calix[4]arene". J. Chem. Soc., Chem. Commun., 582-584 (1992).
89) Seangprasertkij, R., Asfari, Z., Arnaud, F., Vicens, J.: "Schiff base p-tert-butylcalix[4]-arenes. Synthesis and metal ion complexation.". J. Org. Chem., **59** (7), 1741-1744 (1994).
90) Hamada, F., Fukugaki, T., Murai, K., Orr, G. W., Atwood, J. L.: "Liquid-liquid extraction of transition and alkali metal cations by a new calixarene: Diphenylphosphino calix[4]-arene methyl ether". J. Inclusion Phen. Molec. Recognition in Chemistry, **10**, 57-61 (1991).
91) Arduini, A., Casnati, A., Dodi, L., Pochini, A., Ungaro, R.: "Selective 1,2-functionalization of calix[4]arenes at the lower rim. Synthesis of a new type of bis-calixcrown ether". J. Chem. Soc., Chem. Commun., (22), 1597-1598 (1990).

92) Arduini, A., Casnati, A., Fabbi, M., Minari, P., Pochini, A., Sicuri, A. R., Ungaro, R.: "New artificial receptors from selectively functionalized calix[4]arenes". Supramol. Chem., **1**, 235-246 (1993).
93) Asfari, Z., Abidi, R., Arnaud, F., Vicens, J.: "Synthesis and complexing properties of a double-calix[4]arene crown ether". J. Inclusion Phen. and Molec. Recogn ition in Chem., **13**, 163-169 (1992).
94) Viallesoubranne, C., Masson, M., Dozol, J.-F.: Extraction and transport of cesium from a PUREX raffinate by crown calixarenes". 2nd CEA/JAERI Meeting on Partitioning of Actinides and Long-Lived Fission Products, September 18-20, France (1995).
95) Ungaro, R.: "Selective recognition of ions and polar organic molecules using calixarene receptors". Int. Conf. on Calixarenes 1995, p. 11, Texas (USA) (1995).
96) Asfari, Z., Vicens, J.: "Calixcrowns and related molecules". Int. Conf. on Calixarenes 1995, p. 47, Texas (USA) (1995).
97) Egberink, R.J.M., Casnati, A., de Jong, F., Ungaro, R., Reinhoudt, D.N.: "Membrane transport studies of 1,3-alternate calix[4]arene crown-6 conformers: A new class of Cs^+ selective ionophores". Int. Conf. on Calixarenes 1995, p. 70, Texas (USA) (1995).
98) Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud, F., Fanni, S., Schwing, M.-J., Egberink, R.J.M., de Jong, F., Reinhoudt, D.N.: Synthesis, complexation, and membrane transport studies of 1,3-alternate calix[4]arene-crown-6 conformers: A new class of Cesium selective ionophores". J. Am. Chem. Soc. **117** (10), 2767-2777 (1995).
99) Yamamoto, H., Ueda, K., Sandanayake, K.R.A.S., Shinkai, S.: "Molecular design of chromogenic calix[4]crowns which show very high Na- selectivity". Chem. Letters, 497-498 (1995).
100) Zhong, Z.-L., Tang, C.-P., Wu, C.-Y., Chen, Y.-Y.: "Synthesis and properties of calixcrown telomers". J. Chem. Soc., Chem. Commun., 1737-1738 (1995).
101) Rudkevich, D.M., Mercer-Chalmers, J.D., Verboom, W., Ungaro, R., de Jong, F., Reinhoudt, D.N.: "Bifunctional recognition: Simultaneous transport of cations and anions through a supported liquid membrane". J. Amer. Chem. Soc. **117** (22), 6124-6125 (1995).
102) Reichwein-Buitenhuis, E.G., Visser, H.C., de Jong, F., Reinhoudt, D.N.: Kinetic versus diffusion control in carrier-mediated cotransport of alkali cations through supported liquid membranes". J. Amer. Chem. Soc. **117** (14), 3913-3921 (1995).
103) Deng, G., Sakaki, T., Nakashima, K., Shinkai, S.: "Light-responsive metal encapsulation in calix[4]arene". Chem. Letters, 1287-1290 (1992).
104) Deng, G., Sakaki, T., Kawahara, Y., Shinkai, S.: Supramol. Chemistry 2, 71 (1993).
105) Ohseto, F., Shinkai, S.: "Synthesis and metal cation oscillation in ionophoric biscalix[4]arenes". J. Chem. Soc., Perkin Trans. II, 1103-1109 (1995).
106) Deng, G., Sakaki, T., Kawahara, Y., Shinkai, S.: "Light-switched ionophoric calix[4]arenes". Tetr. Lett., **33** (16), 2163-2166 (1992).
107) Ohseto, F., Sakaki, T., Araki, K., Shinkai, S.: "Synthesis and metal recognition of biscalix[4]arenes. Intramolecular metal-hopping as detected by ^1H NMR spectroscopy". Tetr. Lett., **34** (13), 2149-2152 (1993).
108) Ohseto, F., Shinkai, S.: "Metal vibration in an ionophoric biscalix[4]arene". Chem. Letters, 2045-2048 (1993).

109) Takemura, H., Yoshimura, K., Khan, I. U., Shinmyozu, T., Inazu, T.: "The first synthesis and properties of hexahomotriazacalix[3]arene". Tetr. Lett., **33** (39), 5775-5778 (1992).
110) Okada, Y., Ishii, F., Kasai, Y., Nishimura, J.: "A new type ionophore made from a rigid calixarene analog". Tetr. Lett., **34** (12), 1971-1974 (1993).
111) Okada, Y., Kasai, Y., Nishimura, J. : "Synthesis and characterization of new receptors from rigid calixarene analogs" Workshop on Calixarenes and Related Compounds, (PS/A-31, OP-9) Kurume, Fukuoka (Japan) (1993).
112) Okada, Y., Kasai, Y., Ishil, F., Nishimura, J.: "Synthesis and characterization of macrocycles as enlarged calix[4]arene analogues". J. Chem. Soc., Chem. Commun., 976-978 (1993).
113) Nomura, K., Ozawa, M., Tanaka, Y., Togashi, A.: "Macrocyclic compound, its chemistry and partitioning application (j)". PNC Report (Japan), (94), 78-84 (1995).
114) Koide, Y., Oka, T., Imamura, A., Shosenji, H., Yamada, K.: "Studies of collectors. XIII. The selective flotation of cesium ion with resorcinol-type calix[4]arenes with alky side chains". Bull. Chem. Soc. Japan, **66** (8), 2137-2142 (1993).
115) Onokuma, S., Gao, S.-R., Nishimura, J.: "Strikingly selective ionophoric properties of rigid cyclophanes having a small number of ligating sites". Chem. Letters, 689-690 (1995).
116) Kikukawa, K., Sagara, Y., Kawaguchi, K., Nomura, E., Taniguchi, H. : "Catalytic ability of octopus-type resorcinol calixarene in the phase transfer raction" Workshop on Calixarenes and Related Compounds, (PS/A-23) Kurume, Fukuoka (Japan) (1993).
117) Iwasa, T., Saruwatari, Y., Yamato, T.: "Molecular design of "1,2-alternate" type calixarene analogous [3.1.3.1]metacyclophanes". Workshop on Calixarenes and Related Compounds, (PS/A-22) Kurume, Fukuoka (Japan) (1993)
118) Yamato, T., Doamekpor, L.K., Tashiro, M.: "Synthesis and ion selectivity of conformers derived from calixarene-analogous trihydroxy[3.3.3]metacyclophane". Int. Conf. on Calixarenes 1995, p. 82, Texas (USA) (1995).
119) Yamato, T., et.al., Chem. Letters, 89 (1995).
120) Yamato, T., et.al., Chem. Ber. (in press).
121) Araki, K., Inada, K., Otsuka, H., Shinkai, S.: "Conformational isomerism in and binding properties to alkali-metals and an ammonium salt of O-alkylated homooxacalix[3]arenes". Tetrahedron, **49** (42), 9465-9478 (1993).
122) Boerrigter, H., Konings, R.J.M., Cordfunke, E.H.P., Verboom, W., Reinhoudt, D.N.: "A novel approach towards the design of ligands for the selective extraction of trivalent actinides'. GLOBAL'95, pp. 1252-1257, Paris (1995).