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REVIEW

Homooxacalixarenes: II.* Receptor Properties

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On the frontier of nineteen seventies and ‘eighties has arisen and vigorously develops a new field of chemistry, “supramolecular chemistry”, that is designated as the “chemistry beyond molecular limits” or the “chemistry of molecular ensembles and intermolecular bonds” [2]. A supramolecule (σC), the subject of the supramolecular chemistry, is the “next complexity level of molecular organization… after that of molecules” [2], its formation involves an interaction of at least two components: receptor (C) and substrate (σ) that are bound due to the process of “molecular recognition”. Therefore the creation of suitable receptors becomes an urgent task. The vigorous development of calixarene chemistry in the recent 10–15 years unambiguously demonstrates the importance and promise of their application for manufacturing of new highly efficient and selective receptors [3].

The goal of this article was to collect, systematize, and analyze the published data on receptor properties of homooxacalixarenes, compouns with homooxabriges between the aromatic fragments of a molecule. The synthesis and modifications of the oxacalixarenes we described in the preceding review [1]. The most easily available and the best studied are nowadays hexahomotrioxacalix[3]arenas, compounds related both to the “classic” calyx[4]arenas and to 18-crown–6 ethers. The unique features H of the oxacalix[3]arenas: the presence of an inner cavity formed by an 18-membered ring, a limited number of probable conformations (*cone* and *paco),* and C_3-symmetry of the main structure [4, 5] should significantly influence the receptor activity of the derivatives. C_3-Symmetry of the molecule is especially favorable for building up receptors for ammonium ions that play a significant part not only in chemistry but also in biology.

1. COMPLEXING OF HEXAHOMOTRIOXACALIX[3]ARENES WITH NEUTRAL MOLECULES

The analysis of published data showed that a special attention in the study on receptor properties of oxacalixarenes received their possible complexing with fullerenes, i.e. just the point in the investigations on molecular recognition where the interests of fundamental and applied chemistry were the most tightly intertwined.

It was shown in 1994 [6–8] that the “classic” 4-*tetr*-butylcalix[8]arene **1** selectively formed a complex with C_{60}-fullerene of 1:1 composition. Basing on this fact C_{60}-fullerene was prepared in a large quantity and of a high purity [9]. It turned out however that the complex obtained was stable only in the solid state and dissociated into initial components in solution [10]. This discovery

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For Communication I see [1].

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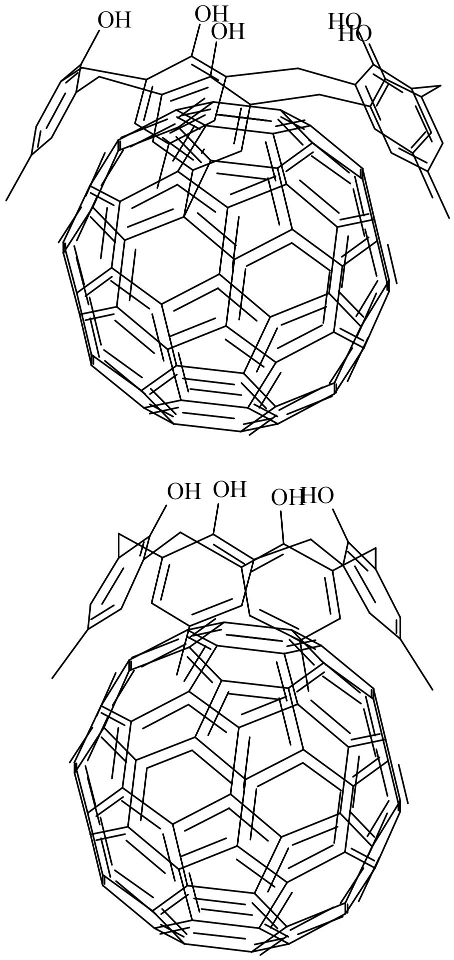
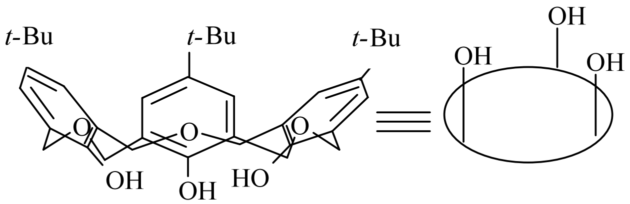
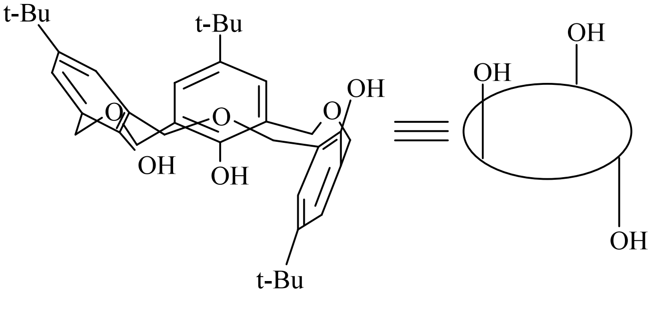


Fig. 1. Hypothetical structure of C_{60}-fullerene complexes with *p*-*H*-calixC[4]arene (up) and *p*-*H*-calix[5]arene (below).



2, crown (*cone*)

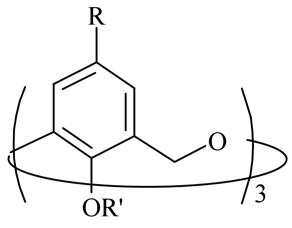


2, partial crown (*paco*)

promoted new research in the field, and in 1997–98 complexing of C_{60}-fullerenes in toluene was performed with over 30 calixarenes, and among the latter oxacalixarenes were present with free OH groups **2**, and also with methoxy groups **3** and ester groups **4–6**.

The studies were carried out applying spectroscopy in UV and visible region and ^{1}H and ^{13}C NMR spectra. The oxacalixarene **2** possessing free OH groups formed with fullerene a complex of 1:1 composition with a relatively small association constant (K_{ass}) 35 ± 5 l mol^{-1} [11]. The oxacalixarenes **3–6** with modified OH groups did not afford complexes with the C_{60}-fullerene.

As suggested in [11, 12], the main driving force of complex formation was the π–π interaction of the "guest" and the "host". The conformation of the molecule played the most significant role, whereas not only the depth of the cavity was important but also the tilt of the benzene rings constituting the cavity. The favorable tilt ensures multipoint contacts with the fullerene surface. The interaction occurs by the type of *«local cap»* for fullerene (Fig. 1).

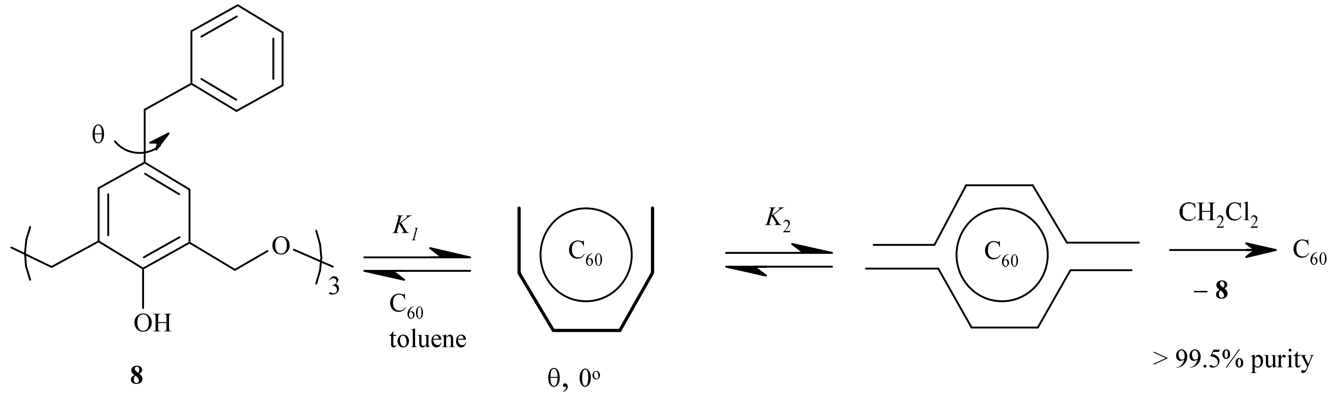


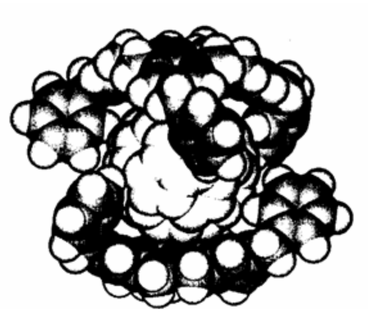
3 -13

3, R = *t*-Bu, R' = Me; **4**, R = *t*-Bu, R' = CH_2COOEt; **5**, R = Br, R' = CH_2COOEt; **6**, R = Me, R' = CH_2COOEt; **7**, R = Br, R' = OH; **8**, R = CH_2Ph, R' = OH; **9**, R = H, R' = OH; **10**, R = OMe, R' = OH; **11**, R = I, R' = OH; **12**, R = $CMe_2C_6H_4OCH_2OCH_3$-*p,* R' = OH; **13**, R = 4-Py, R' = CH_2COOEt.

A preliminary arrangement of the ligand molecule in the required direction should play an important part in the complexing process as was shown in [11]. It proved that in the presence of Li^+ cations oxacalixarene **4–6** esterified at the lower rim were excellent receptors for the C_{60}-fullerene. The complexes obtained were characterized by high values of K_{ass} (l mol^{-1}): 460 [$\mathbf{4} \cdot Li^+$], 80 [$\mathbf{5} \cdot Li^+$], 550 [$\mathbf{6} \cdot Li^+$]; thus a pronounced allosteric effect was observed. The K_{ass} values evidence also that the character of the *para*-substituent significantly influences the complexing process (the smallest K_{ass} arises in the presence of an electron-withdrawing substituent in the molecule **5**).

Scheme 1.





Supramolecule $[C_{60} \subset (\mathbf{8})_2]$.

The presence of free OH group on the lower rim of the ligand is one of prerequisite conditions for binding fullerene [11, 12]. In [13–16] the receptor activity was studied of derivatives of *p*-R-trioxacalix[3]arene (**2, 7–12**) with a free *para*-position, with various substituents at the upper rim, and free phenol hydroxy groups. The association constants (l mol^{-1}) of the complexes obtained from compounds **2,** R = *t*-Bu; **7,** R = Br; **9,** R = H; **10,** R = OMe; **12,** R = $CMe_2C_6H_4OCH_2OCH_3$-*p* with C_{60}-fullerene in toluene at 198 K were equal respectively to 35.6 ± 0.3, 14.9 ± 2.0, 9.1 ± 1.0, 20.7 ± 0.9, and 13.3 ± 0.4 showing that the efficiency of complexing was virtually independent of the electronic effects of sub-stituents attached to the "host" molecule.

The inclusion complex of C_{60}-fullerene with ligand **7** was studied by X-ray diffraction analysis. The complex was shown to possess C_{3d}-symmetry, and the driving force of the complexing was found to be the van der Waals interaction. In the complex formed the hexagonal fullerene surfaces are located very close both to aromatic rings and to the dibenzyl ether oxygens of the ligand (the distance from the O atoms of the dibenzyl ether bridge of the ligand to the nearest six-membered ring of the "guest" is 3.290 Å).

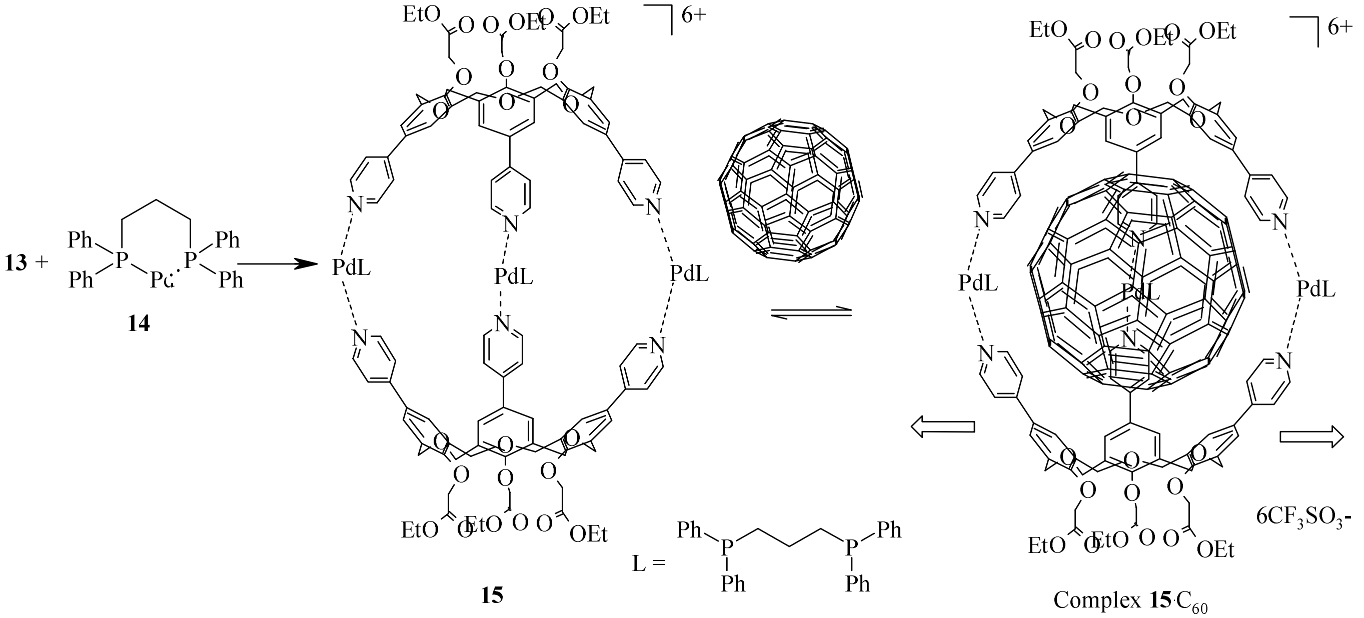
Tribenzyl derivative **8** formed a complex with C_{60}-fullere in toluene of composition 2 : 1 with K_{ass} 100 l mol^{-1} (Scheme 1) [15].

X-ray diffraction analysis demonstrated that in the complex the fullerene is "*shrouded*" by two "host" molecules in zigzag position possessing *cone* conformation. The benzyl substituents are located "*edge-on*" with respect to fullerene. Thus the symmetry of the "guest" and the "host" provides an agreement resulting in a maximum number of contact points between them and therefore in sufficiently effective π–π interaction. Mostly the distance $C \cdots C \approx 3.83$ Å, the shortest distances $O \cdots C_{fullerene}$ are 3.14 (ether O atom) and 3.64 Å (phenol O atom).

It is worth mentioning that *p*-bromo- and *p*-iodo-oxacalix[3]arenas (**7** and **11** respectively**)** possessing free OH groups on the lower rim ensure selective precipitation of C_{70}-fullerene from its mixture with C_{60}-fullerene in toluene.The purity of the separated fullerene homolog attained 92% [14, 16].

The complexing with C_{60}-fullerene was also carried out with molecular capsules built basing on the oxacalixarenes.

Pyridine-containing oxacalixarene **13** with ester groups on the lower rim of the molecule [17] dimerized in the presence of Pd(II) derivative **14** affording on the force of Pd(II)–pyridine interaction a capsule-like molecule **15** possessing D_{3h}-symmetry [18, 19]. This molecule proved to be capable to include into the inner cavity the C_{60}-fullerene as was unambiguously supported by ^1H and ^{13}C NMR spectra. The peak of free fullerene in the ^{13}C NMR spectrum is located at 142.87 ppm whereas that of the bonded fullerene is at 140.97 ppm. The K_{ass} of the



Complex **15**·C_{60}

complex was determined at 39 l mol^{-1} at 30°C and 54 l mol^{-1} at 60°C. The D_{3h}-symmetry was conserved in the fullerene complex although a "*flattening*" of the phenyl fragments of the oxacalixarene was observed.

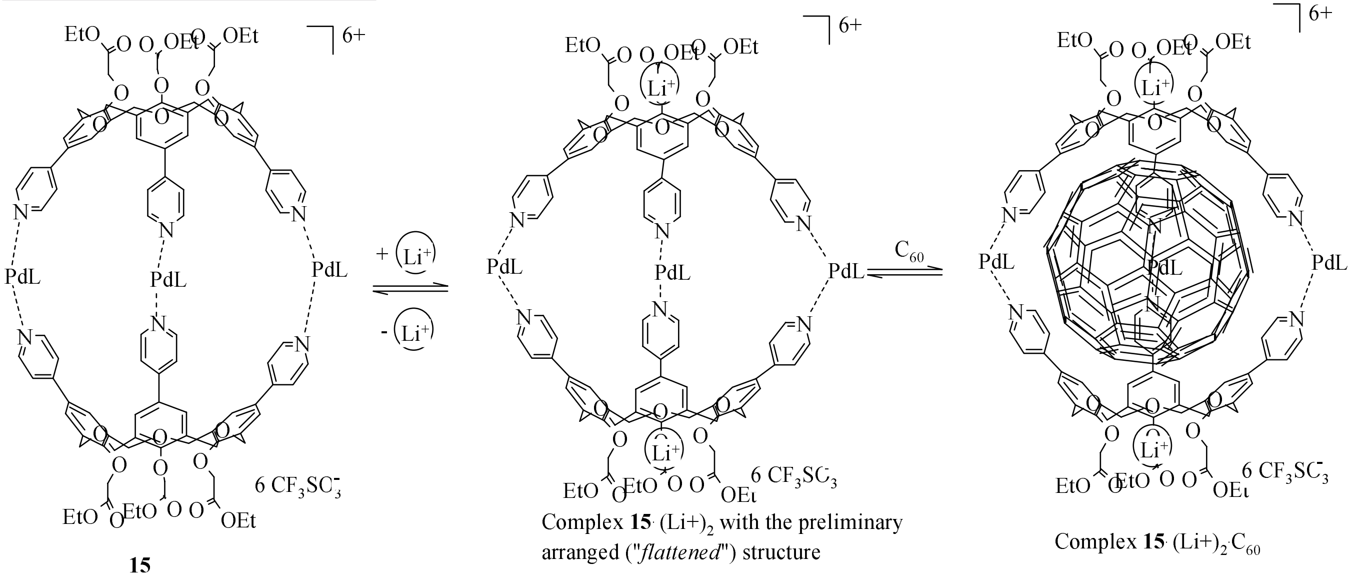
The addition to derivative **15** of Li$^+$ cations coordinated at the lower rims of the calixarene components resulted in altering the capsule geometry due to strong flattening of the aromatic fragments and in facilitating inclusion into the cavity of C_{60}-fullerene. This preliminary arrangement of the molecule by Li$^+$ cations led to increase in the K_{ass} of the fullerene complex to 2100 l mol^{-1} at 30°C [18].

The replacement of Li$^+$ by Na$^+$ cations also attached to the lower rim results in total removal of fullerene from the complex [18] (Scheme 2).

Ikeda *et al.* [18] presumed that the elliptic form of the cavity in the complex **15**·$(Na^+)_2$ was inconvenient for bonding of C_{60}-fullerene.

Note that a conformationally labile ligand **16** containing methoxy groups on the lower rim of the molecule did not form dimeric capsules.

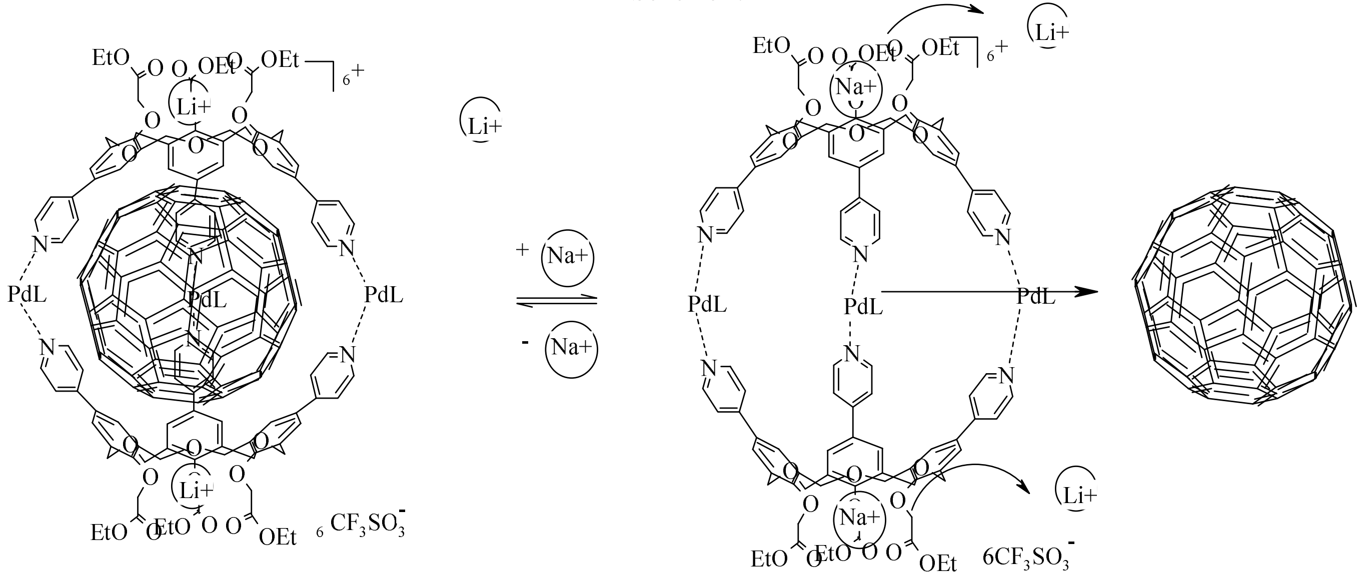
In 2000 [20] heterocapsules were built up proceeding from oxacalixarene **13** and derivatives of Zn^{2+}-porphyrin (**17**, **18**). The corresponding complexes (1:1) (**19**, **20**)



Complex **15**·$(Li+)_2$ with the preliminary arranged ("*flattened*") structure

Complex **15**·$(Li+)_2$·C_{60}

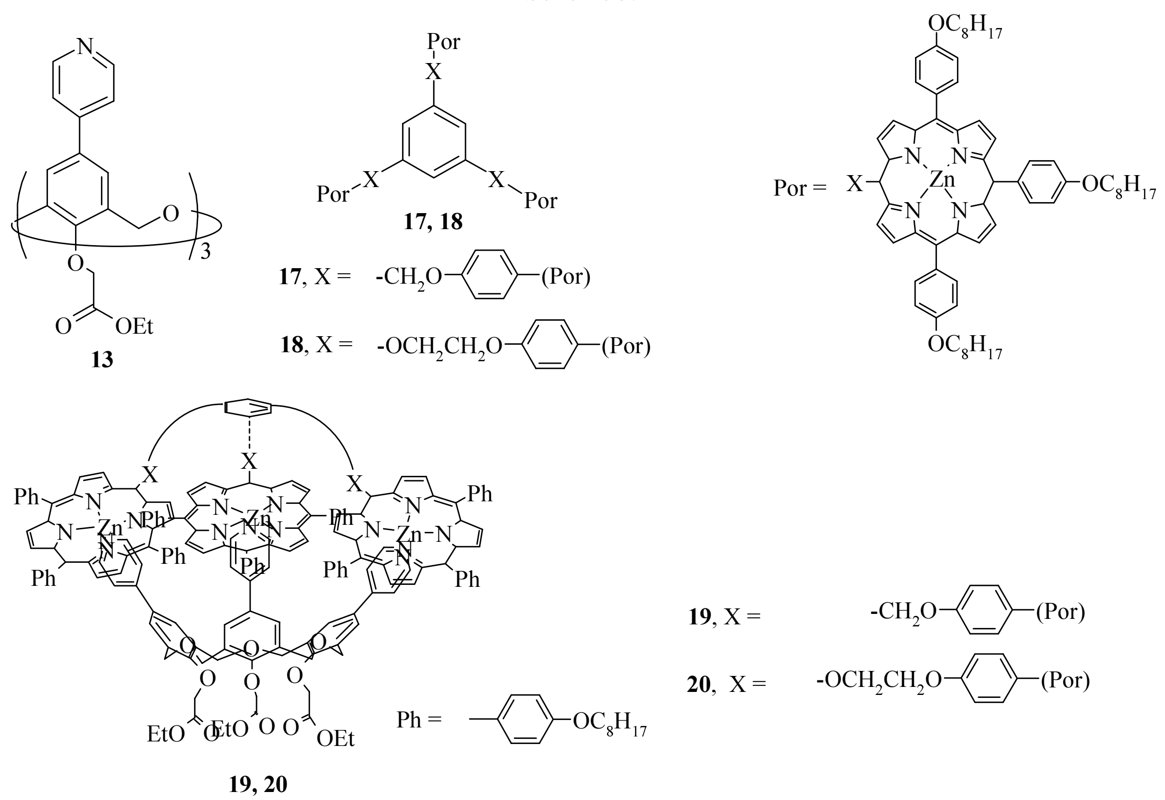
Scheme 2.



Complex **15**·(Li+)$_2$·C$_{60}$

Conplex **15**·(Na+)$_2$

Scheme 3.

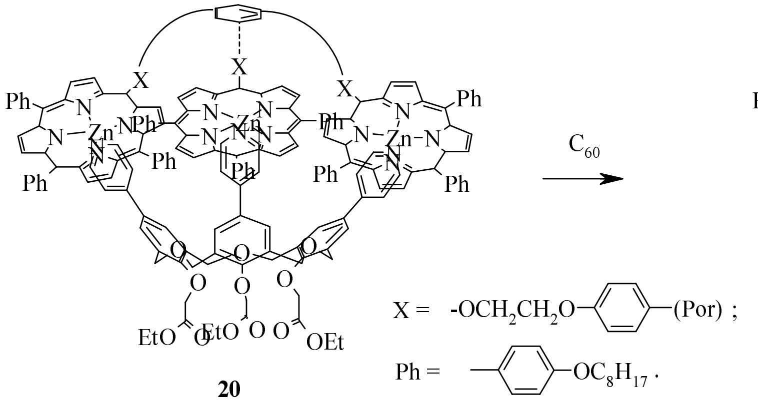


had the following formation constants (l·mol^{-1}): 5.6×10^5 for complex **19** in toluene, 7.2×10^4 for complex **19** in 1,1,2,2-tetrachloroethane, 8.5×10^5 for complex **20** in pyridine (Scheme 3).

The cavity arising in porphyrin complexes **19**, **20** due to π-basic components is capable to include C$_{60}$-fullerene with K_{ass} of the formed fullerene complex **21** equal to 60 l mol^{-1} at –30°C (Scheme 4).

In the most recent publications information appeared on practical applications of complexes between oxacalix[3]arene derivatives and C$_{60}$-fullerene [21–24]. It was demonstrated for the first time [23] that hexacation

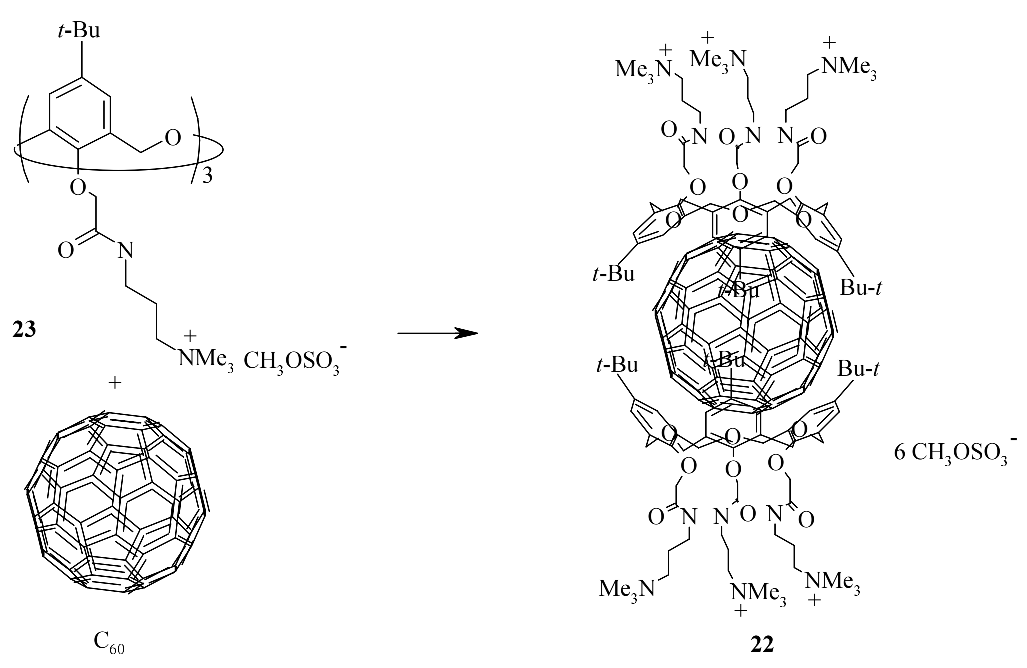
Scheme 4.



20

21

Scheme 5.



23

22

complex **22** of oxacalixarene **23** with C_{60}-fullerene (2 : 1) (Scheme 5) was readily adsorbed on the surface of gold electrode modified with anions providing an ultrathin film similar to monolayer (Fig. 2).

When the film obtained was irradiated with visible light a new photoelectric current response appeared (~360 nA cm^{-2}). The following scheme of the process was suggested (Fig. 3).

A ready formation of a C_{60}-fullerene-porphyrin double-layer film on an anion-modified surface of a golden or an In-TiO$_2$ electrode was reported in [24] (Fig. 4). First a hexacation complex **22** of oxacalixarene **23** with C_{60}-fullerene is deposited on the electrode surface, and then the electrode is treated with porphyrin derivative **24**.

On irradiation with the visible light of this double-layer film a current response was observed (Fig. 5); The high quantum yield was attributed to the presence of C_{60}-fullerene bound in a complex. These films may be used in preparation of new photocurrent generators.

C_{60}-Fullerene was extracted by ultrasound action into water containing “cationic” oxacalixarene **23**. The formation of complex **22** was proved by spectroscopy (absorption spectra in UV and visible region, ^{13}C NMR spectra) [21, 22]. Complex **22** was applied to photosplitting

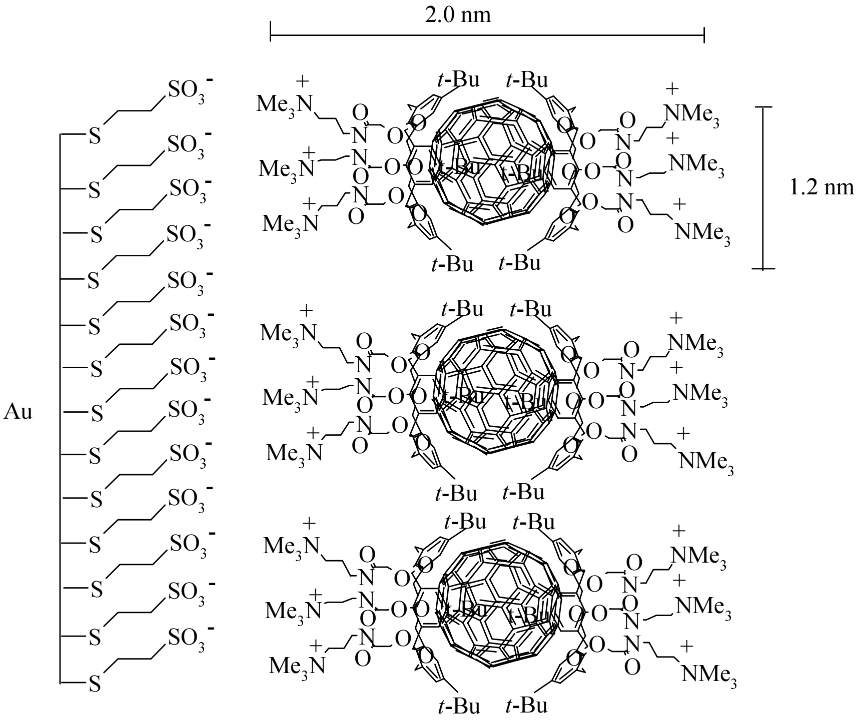


Fig. 2. Adsorption of sodium 2-mercaptoethanesulfonate (first layer) and complex **22** on gold-deposited QCM *(Quartz Crystal Microbalance: USI system* [25]) resonator.

of a *supercoil plasmid Col E1* [21]. It turned out that at irradiation with the visible light a pronounced splitting of DNA occurred: ~65% of the supercoiled DNA (form I) was transformed into nicked DNA (form II). Ligand **23** proper showed weak activity in the DNA splitting. Ikeda *et al.* [21] believed that "cationic" oxacalixarene **23** favored "dissolution" of C_{60}-fullerene in water and transported it to the anionic DNA due to electrostatic interaction. Thereafter a photoinduced electron transfer occurred from the guanine fragment in the DNA to the fullerene followed by the DNA splitting.

Some information appeared on complex formation of C_{60}-fullerene with unconventional oxanaphthylcalixarenes (**25, 26**). It was demonstrated that supramolecular (i.e. noncovalent or ionic) complexes of oxacalixnaphthalenes (**25, 26**) with C_{60}-fullerene could exist both in solid state and in solution. In the first case the complex possessed C_{3i}-symmetry and contained an incapsulated fullerene molecule in the cavity formed by two ligand molecules (Fig. 6).

The fullerene molecule is located between two concave surfaces of calixnaphthalene at a distance close to van der Waals radii. The structure obtained ensures the maximum π–π interaction of the ligand and the substrate.

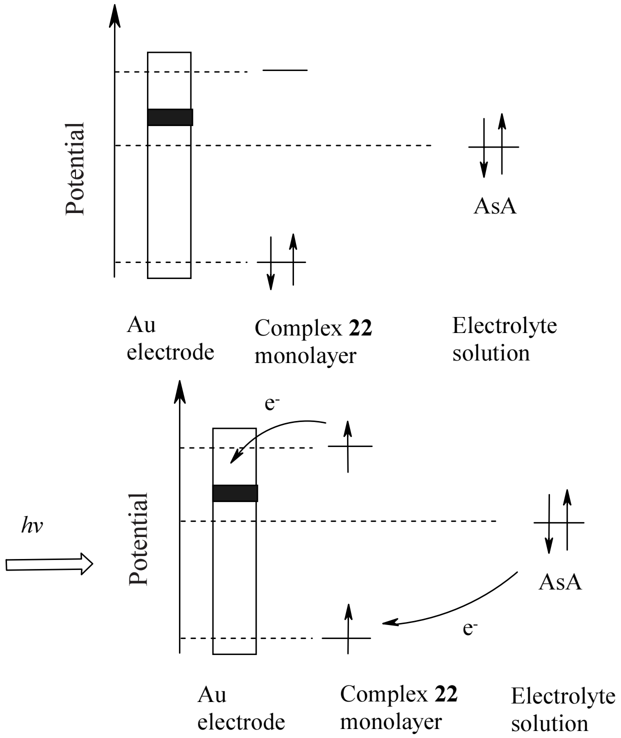


Fig. 3. Schematic representation of the mechanism of the photovoltammatric response of complex **22** in the presence of electron donor (ascorbic acid AsA).

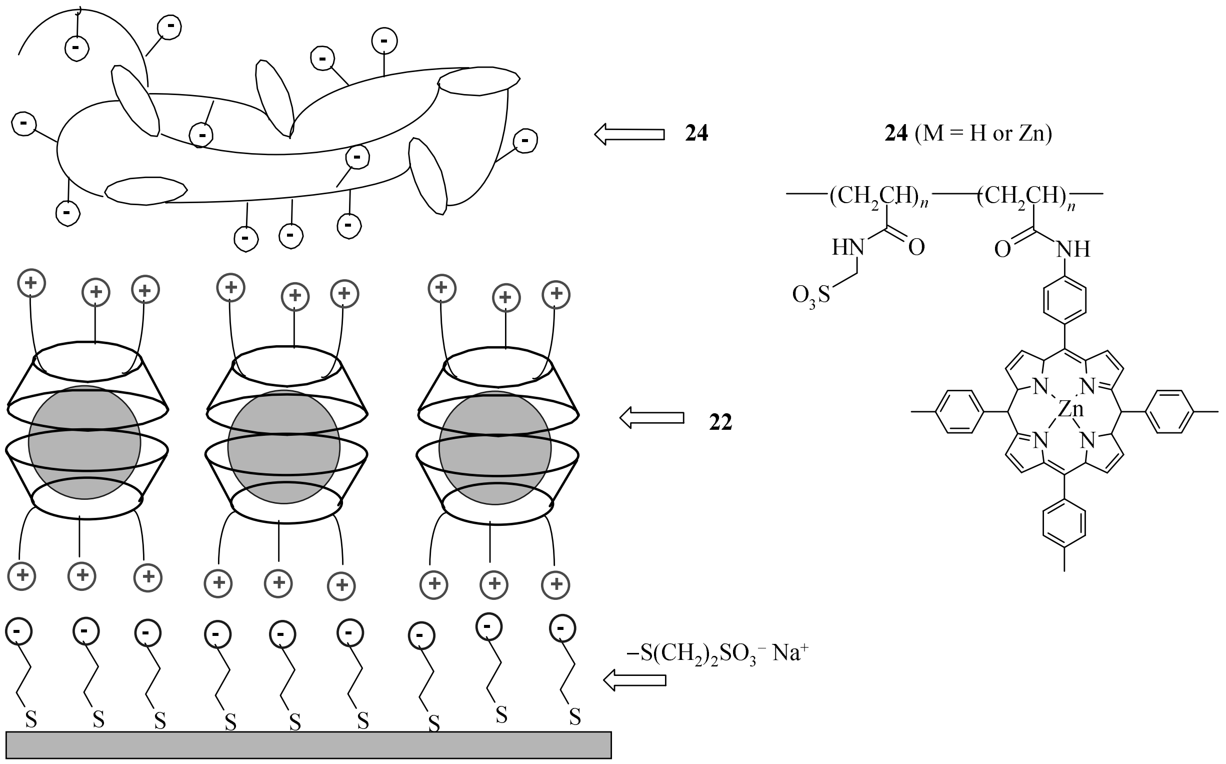


Fig. 4. Schematic representation of self-adjusting polylayers: 2-mercaptoethanesulfonic acid (first layer), complex **22** (second layer), and porphyrin **24** (third layer) on a In-TiO$_2$ electrode.

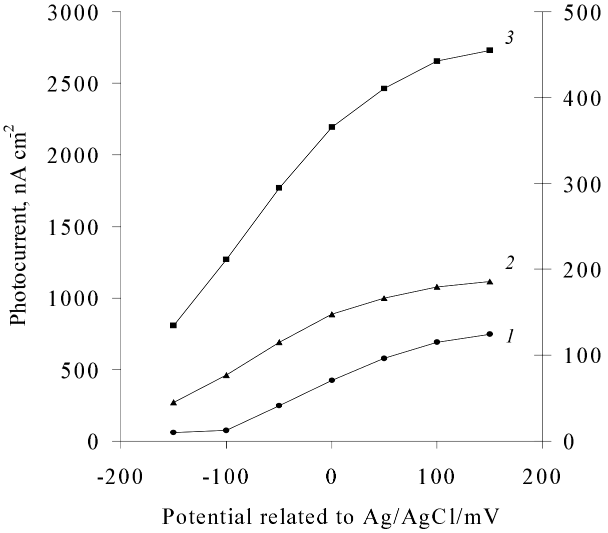


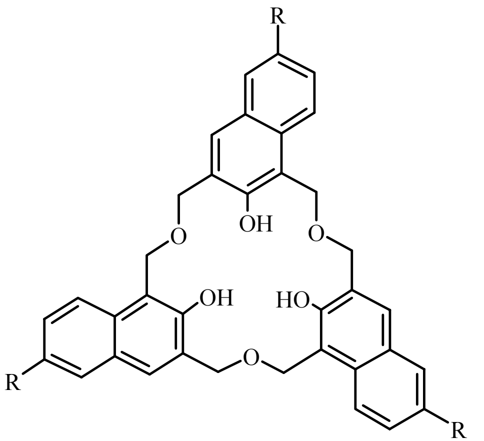
Fig. 5. Photocurrent as a function of applied potential at monochromatic irradiation of an In-TiO$_2$ electrode modified by: complex **22** (l = 400 ± 16 nm, 0.56 mW cm^{-2}) (*1*), complex **24** (M = 2H) (l = 420 ± 16 nm, 1.36 mW cm^{-2}) (*2*), complex **24** (M = Zn) (l = 430 ± nm, 1.53 mW cm^{-2}) (*3*) in 0.1 M. solution of Na$_2$SO$_4$ containing 50 mmol l^{-1} of ascorbic acid, pH 3.5.

Each of the two oxacalixarene **26** molecules is present in the *cone* conformation, and they are staggered with respect to each other thus decreasing the mutual steric repulsion.

The values of K_{ass} (l mol^{-1}) for the complexes were equal to 150 ± 5 in toluene and 116 ± 5 in benzene for complex **25**·C$_{60}$-fullerene, 296 ± 9 in toluene and 441±23 in benzene for complex **26**·C$_{60}$-fullerene. The large K_{ass} values are apparently due to the π–π interactions between the "guest" and "host" molecules. The stoichiometry of complexes in both solvents was 1:1, and the spectral data indicated that the fullerene molecule entered deep into the ligand cavity.

While the complex formation between oxacalix[3]arenes and fullerene is well documented, the data on the receptor activity of the oxacalix[3]arenas with respect to other neutral molecules are scarce [15, 27, 28].

A complex of 1:1 composition between tribenzyloxacalixarene **8** and CHCl$_3$ was reported in [15]. The interaction character between the "guest" and "host"molecules is worth mentioning: The hydrogen atom of chloroform is involved into hydrogen bonds with three



25, R = H; **26**, R = *t*-Bu

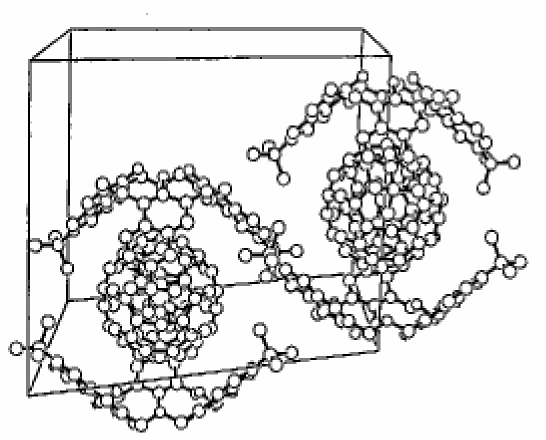
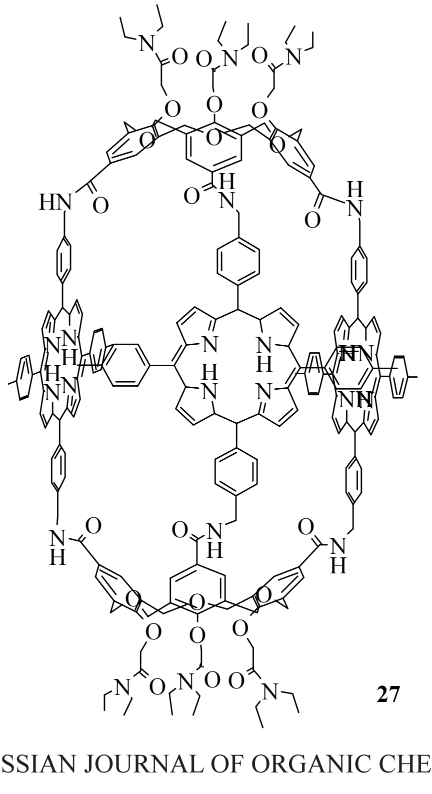


Fig. 6. A fragment of packing of the oxacalixarene **26** complex with fulleren.

phenol oxygen atoms. The distance $Cl_3C–H\cdots O$ amounts to 2.73 Å, whereas the shortest distance from the same $CHCl_3$ molecule and the second molecule of calixarene ($HCCl_2Cl\cdots$oxacalixarene) is 3.71 Å.

In 2001 [28] as a receptor of neutral amines was used molecular capsule **27** of C_3-symmetry that contained ionophore coordination sites on the lower rims of the calixarene fragments. The reaction of compound **27** with $Zn(OAc)_2$ due tu the presence of porphyrin moiety in the molecule afforded complex with Zn **28** where the intramolecular hydrogen bonds (revealed by ^1H NMR spectrum in $CDCl_3$) suppressed the conformational lability of the molecule. On addition of $NaClO_4$ to complex **28** the latter bound Na^+ cations that resulted in flattening of the benzene rings and in increase of the distance between C=O and NH groups within the column inducing a cleavage of the hydrogen bonds.

Compound **28** was shown to form a complex of 1:1 composition with $N(CH_2CH_2NH_2)_3$ (TREN), K_{ass} 1.72×10^5 l mol^{-1} [29]. In the presence of $NaClO_4$ K_{ass} became 1.5×10^8 l mol^{-1} thus increasing by three orders of magnitude. Probably the addition of Na^+ cations destroyed



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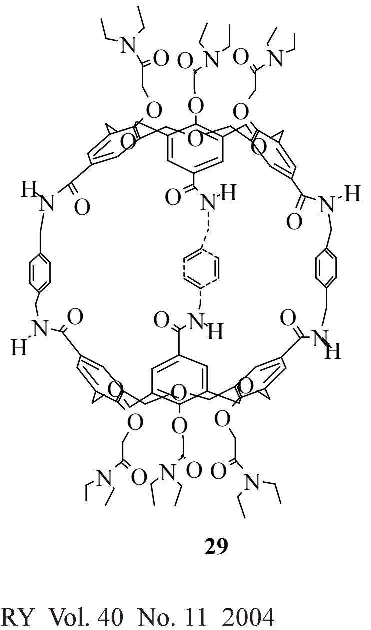

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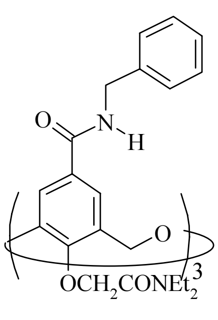

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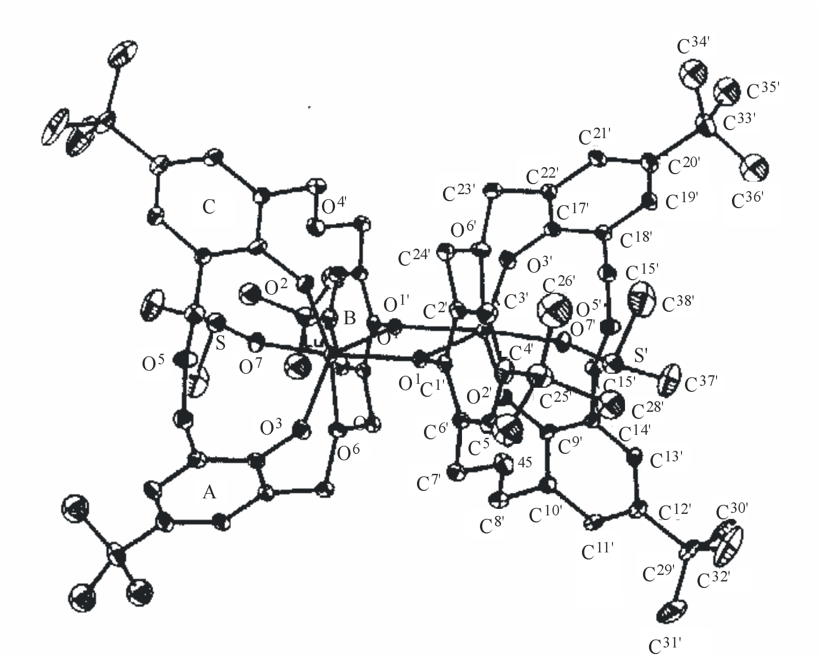
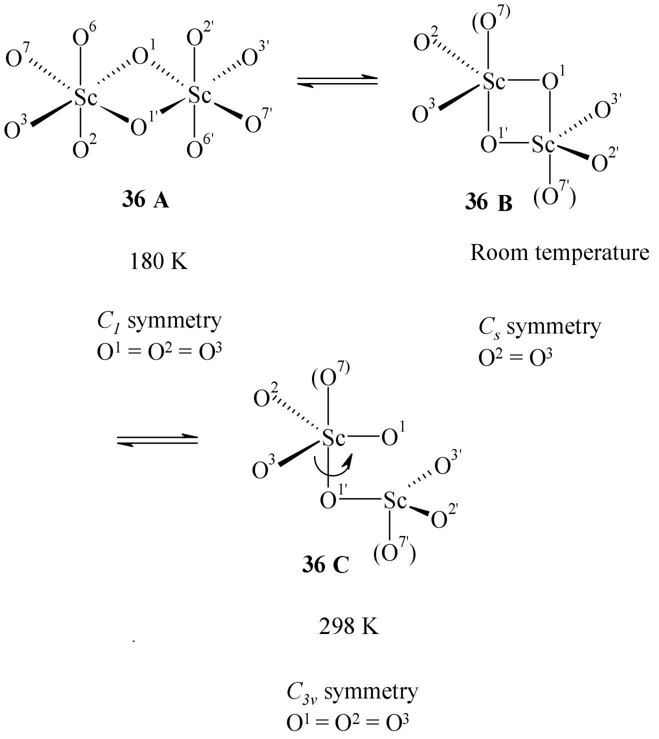


Fig. 7. The crystal structure of complex **33** $[Lu(L)(DMSO)]_2{\cdot}(MeCN)_4(H_2O)_{0.67}$ where L is trianion of macrocycle **2**.

the intramolecular hydrogen bonds in ligand **28** supplying the latter with higher symmetry favorable for binding TREN. A similar pattern was also observed on addition of CH_3OH where K_{ass} reached a value of 2.63×10^6 l mol^{-1}.

Scheme 6.



36 A

180 K

C_1 symmetry
$O^1 = O^2 = O^3$

36 B

Room temperature

C_s symmetry
$O^2 = O^3$

36 C

298 K

C_{3v} symmetry
$O^1 = O^2 = O^3$

Oxygen atoms: O^1, O^2, O^3 - aryloxide, O^6 - ether, O^7 - atom DMSO.

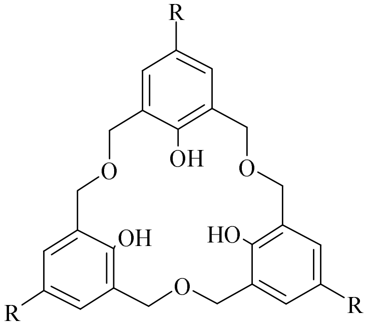
Therefore it is possible to describe this behavior as due to allosteric effect of Na^+ cation and CH_3OH. K_{ass} of the complex at the addition of $CH_3OH/NaClO_4$ attained 1.11×10^7 l mol^{-1}. Note that K_{ass} of the oxacalixarene **28** complex with a primary amine $C_3H_7NH_2$ was equal to 1.69×10^2 l mol^{-1} and virtually was not sensitive to addition of either $NaClO_4$ or CH_3OH.

^1H NMR spectroscopy was applied to a study of complex formation of dimer molecular capsule **29** with 1,1'-dialkyl-4,4'-bipyridyl tosylates (*alkyl viologen*) [30]. In $Cl_2CDCDCl_2$–CD_3OD medium complexes formed of 1:1composition possessing the following K_{ass}: 430 for Me-derivative, 116 for Et-derivative, 97 for Pr-derivative, and 210 l mol^{-1} for 1,2-bis(1-methyl-4-pyridinio)ethylene-ditosylate [under similar conditions the monomer molecule of oxacalixarene **30** formed a complex with Methyl Violet with K_{ass} 120 l mol^{-1}]. These data suggest that the Methyl Violet molecule is located in the inner cavity of capsule **29**.

2. COMPLEXING OF HEXAHOMOTRIOXACALIX[3]ARENAS WITH METAL CATIONS AND AMMONIUM IONS

2.1. *Receptor Properties of Hexahomotrioxacalix[3]arenes with Free OH Groups on the Lower Rim of the Molecule*

The study of complexing ability of oxacalix[3]arenes **2, 31, 32** by extraction from water solution of Li, Na, or



31, 32

R = Me (**31**), Cl (**32**).

K picrates into CH_2Cl_2 and by ^1H NMR spectroscopic measurements during titration with metal triflates [31] revealed that *p*-alkyl derivatives 2 and 31 bound alkali metal cations only in the presence of strong bases. Chloroderivative **32** bound Na^+ cation in the absence of bases, and in the presence of Et_3N it bound Na^+ and K^+ ions more efficiently than Li^+. The constants of complex formation amounted respectively for Na^+ cation to 0.39 l mol^{-1}, for ions K^+ and Li^+ to 0.32 and 0.11 l mol^{-1}.

Oxacalixarenes **2** and **32** form stronger complexes with trivalent metals Sc^{3+}, Lu^{3+}, Y^{3+}, and La^{3+} than with alkali or alkaline-earth metals [32, 33]. The constants of complex formation grow in the following sequence: Na^+, Li^+, $Ca^{2+} < Mg^{2+} < La^{3+} \ll Y^{3+} < Lu^{3+} \ll Sc^{3+}$, and the constants for ligand **2** are smaller than those of ligand **32** [33].

A reaction of oxacalixarene **2** with Lu^{3+}, Y^{3+}, or La^{3+} triflates in a mixture DMSO–CH_3CN in the presence of Et_3N furnished complexes $[M(L)(DMSO)_2]_2$ (**33–35**) [32] where M = Lu (**33,** 74%**)**, Y (**34,** 83%), La (**35,** 48%); L is the trianion of macrocycle **2**. All complexes in solid state or non-coordinating solvents (toluene) exist as dimers with a symmetry center whose core is constituted by μ-aryloxo bridges. Macrocycle **2** always operates as trianion donor. The complexes with Lu^{3+} and Y^{3+} ions (**33, 34**) are hexacoordinate. Into the metal coordination are involved three aryloxide oxygens of the macroring, one ether O atom of the same ligand molecule, and the O atom of dimethyl sulfoxide (Fig. 7).

With growing ion size the number of coordinated ether oxygen atoms increases. In complex **35** with La^{3+} cation already three ether O atoms are involved, and the complex is octacoordinate.

The macrocyclic ligand in complexes **33–35** assumes the *cup* conformation resembling that of "classic" calixarenes in their complexes with metals. The data obtained in [32] indicate that "*degree of cupping*" increased with growing metal ion whereas the μ-aryloxy bonds weakened.

The study of NMR spectra of complexes **33–35** in toluene-d_8 [32] revealed their fluxional behavior. The spectral data indicate that in **35** in toluene-d_8 occurred a rupture of a μ-aryloxy bond followed by rotation around the remaining μ-aryloxy bond. Coalescence temperatures were determined and for each complex free energies of activation at the coalescence temperatures were estimated having the following values of $\Delta G^{\#}$, kcal mol^{-1} (T_b, K): **33** 12.2 (250), **34** 11.4 (235), **35** 10.6 (220). For complex **35** with La^{3+} the enthalpy $\Delta H^{\#}$ (12.8 kcal mol^{-1}) and entropy $\Delta S^{\#}$ (7.2 kcal mol^{-1}) were evaluated.

The study of the ability of macrocycles **2** and **32** to transfer cations Li^+, Mg^{2+}, and Sc^{3+} through a liquid membrane showed that oxacalixarene **32** selectively transferred ion Sc^{3+} (44%) from solutions containing also cations Li^+ (transfer <0.5%) and Mg^{2+} (<0.2%) [33].

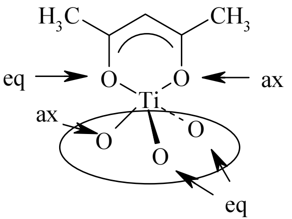
Reacting $Sc(OTf)_3$ with oxacalixarene **2** in the presence of Et_3N a neutral complex $[Sc_2L_2(DMSO)_2]\cdot$ 2DMSO·acetone (**36)** was obtained where L was the ligand trianion [34]. In the crystalline state the complex exists as a dimer of C_I-symetry with a 4-membered bimetalloring $Sc_2(\mu\text{-}O)_2$ where two oxygen atoms of the aryloxy groups serve as binding bridges. The macrocyclic ligand in the complex has a cup form each of which includes a DMSO molecule. The structure of the complex is similar to that of the dimer complex of monooxacalix[4]-arene **37** with Eu [35].

Under the conditions of registering ^1H NMR spectra complex **36** showed a fluxional behavior whose presumed mechanism is depicted in Scheme 6 [34].

Structure **36A** was identical to that of the complex in the solid state containing octahedral Sc-centers. The alternative structure **36B** contained trigonal or tetrahedral Sc-centers and corresponds to the ^1H NMR spectrum in toluene-d_8 at room temperature. The rising of temperature resulted in the rupture of the μ-aryloxide bridge affording structure **36C**.

The reaction of macrocycle **2** with 1 equiv of $Ti(OPr\text{-}i)_4$ in CH_2Cl_2 gave rise to a mixture of two titanium complexes: monomer $[Ti(L)(OPr\text{-}i)]$ (**37)** and bridging dimer $[Ti(L)(\mu\text{-}OPr\text{-}i)]_2$ (**38)** where (L) is oxacalixarene **2** trianion [36]. The mixture of complexes **37**and **38** reacted with2,4-pentanedione to yield acetylacetonate complex **39**. Mizyed *et al.* [36] on the strength of the ^1H, ^{13}C, and FTIR NMR spectra stated that complex **39** had a structure of a trigonal bipyramide where the oxygen atoms of the macrocycle occupied two equatorial and one axial positions, and the oxygens of the acetylacetonate moiety take an equatorial and axial ones.

During the registering of NMR spectra a fast isomerization was observed due to interconversion of the



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axial and equatorial positions. The macrocyclic ligand in the complex at room temperature possesses C_{3v}-symmetry, and the methyl groups in the acetylacetonate are equivalent. At low temperature the symmetry of the macrocycle becomes C_s, and the CH$_3$ groups are non-equivalent.

In 1999 [37] two isomorphic oxacalixarene **2** complexes were obtained with uranyl cation UO_2^{2+} with different counter ions [triethylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO)] and solvent molecules. The complexes were of following compositions: $[(UO_2^{2+})(L^{3-})(HNEt_3^+)]\cdot 3H_2O$ and $[(U)(L^{3-})(HDABCO^+)]\cdot 3MeOH$ where L^{3-} was the ligand trianion. The structure of complexes was studied by X-ray diffraction method. The uranyl cation in both complexes is located along the pseudoaxial crystal axis in the center of the lower rim and is connected to three deprotonated phenol oxygen atoms. The average U–O distance is 2.20(3) Å. A distinquishing feature of these complexes is a very low coordination number of UO_2^{2+} cation equal to three whereas in all known uranyl complexes it is 4, 5, or 6 [38].

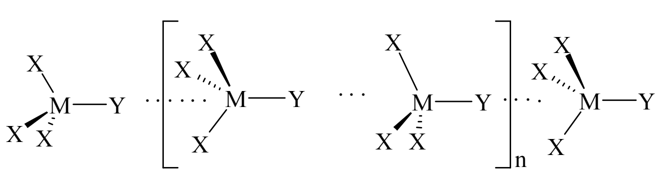
The structure of uranyl complexes of two trioxacalix[3]arenes **2** and **31C** prepared in the presence of various bases (NEt$_3$, NPr$_3$, H$_2$NBu, HNBu$_2$, and 4-methylpiperidine, MePi) was studied in [39]. In all cases the ligand was totally deprotonated, and the arising complexes had the following compositions: [HNEt$_3$][UO$_2$(**31**-3H)] **(40)**, [HNPr$_3$][UO$_2$(**2**-3H)]·MeOH **(41)**, [H$_3$NBu][UO$_2$(**2**-3H)] **(42)**, [H$_2$NBu$_2$][UO$_2$(**2**-3H)]·MeOH **(43)**, [HMePi]·[UO$_2$(**2**-3H)]·2MeOH·H$_2$O **(44)**. The structure of the complexes was studied in the solid state (by X-ray diffraction analysis) and solution (by ^{1}H NMR spectroscopy). In the solid state the observed coordination was trigonal equatorial in complex **42**, distorted tetragonal in complexes **40** and **41**, distorted pentagonal in complex **44,** and intermediate between the two latter in complex **43**. The bridging O atoms also take part in the coordination of the UO_2^{2+} cation. Besides everywhere the counter ion was included into the aromatic cavity of the ligand due to cation-π interaction.

In CDCl$_3$ and CD$_2$Cl$_2$ solutions the existence of two forms of complexes **40–44** with a C_{3v}-symmetry was observed. The stability of the latter considerably changed with temperature (the definite inversion occurred between 193 and 213 K). The inclusion of ammonium counter ion into the aromatic cavity of the liganda depended on the form of the complex (form I corresponded to high temperature, form II to low temperature). It was demonstrated that the relative stability of form I decreased in the series **41 > 40 > 43 = 44**. Thus the formation of form I is favored by *tert*-alkylammonium ions (compared to those with secondary alkyls) and tripropylammonium ions compared to triethylammonium ones. With lowering temperature a substantial exit of the counter ion from the ligand cavity was observed, and also the change of the complex form.

When in the synthesis of uranyl complexes with trioxacalixarenes **2** and **45** [2.2.2]cryptand **46** was used as deprotonating agent a formation of supramolecular ensembles was observed [40].

In the ensemble complex–cryptand, 1:1, the ammonium end of the *endo*-monoprotonated cryptand is included into the complex cavity, whereas in ensembles complex–cryptand, 2:1, the *endo*-diprotonated cryptand is located between two molecules of the complex convergent to each other (*sandwich* form) (Fig. 8). This was the first example of the use of [2.2.2]cryptand as “connector” [41] in building up supramolecular systems proceeding from calixarenes.

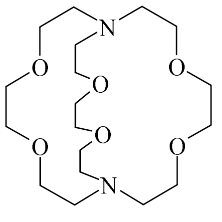
Oxovanadium complex **47** is easily prepared from the tri-OLi-derivative of *p*-methyloxacalix[3]-arene **31** and VOCl$_3$ [42]. In the arising complex in the solid state exist V=O···V interactions resulting in a linear polymer with μ-oxo bridges.



Polymer where M = V, Y = O, 3X is trianion of macrocycle **31**.

X-ray diffraction and ^{1}H NMR data of Hampton et al. [42] suggest that the complex has a structure with the oxovanadium groups located inside the ligand cup.

Complexing activity of trioxacalix[3]arene **2** with respect to a series of quaternary alkylammonium iodides was investigated in [43]. The measurement of ^{1}H NMR spectra in CDCl$_3$ solution at 30°C was used to estimate



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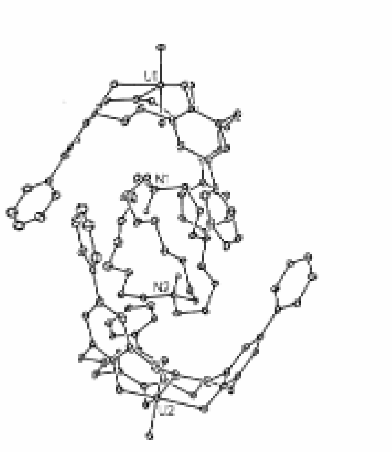


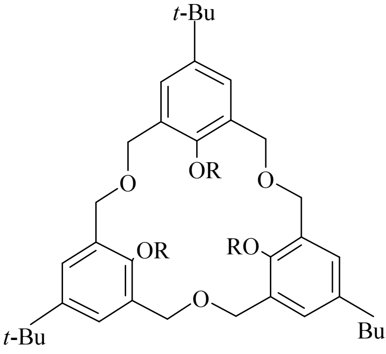
Fig. 8. Complex $(H_2\,\mathbf{46})[UO_2(\mathbf{45}\text{-}3H)]_2$.

the K_{ass} (l mol^{-1}) and free energies (kcal mol^{-1}) of the complexes formed. The maximum values of these parameters correspond to the complex with N,N-dimethylpyrrolidinium iodide (K_{ass} 90, $-\Delta G^{\#}$ 2.70), and the minimum values correspond to trimethylphenylammonium iodide (K_{ass} 38, $-\Delta G^{\#}$ 2.18). For the complexes obtained with the salts of trimethylethyl-, trimethylallyl-, trimethyl(2-acetyloxyethyl)-, and N-methyl-1-azabicyclo-[2.2.2]-octylammonium the values obtained were K_{ass} 60–64, $-\Delta G^{\#}$ 2.45–2.49.

As the main driving force of the complex formation the interaction of the cation positive charge with the π-electrons of the aromatic system is considered [43]. The effect of the ammonium salt structure on the complex formation is unquestionable.

2.2. *Receptor Properties of Hexahomotrixacalix[3]arenas Derivatives with Modified OH Groups on the Lower Rim of the Molecule*

The extraction activity with respect to alkali metal and ammonium ions of oxacalixarene **2** trialkyl ethers (conformationally labile **48**, conformationally immobilized *cone*-**49** and *paco*-**49)** was studied in [5]. The data obtained revealed that the chosen ligands had a greater affinity toward K^+ cation than to the other alkali metal cations; therewith the ligands in the *cone* conformation were more active than those in the *paco* conformation. Tributyl ether *cone*-**49** showed a high affinity to an ammonium ion $BuNH_3^+$ because both the ligand and “guest” possessed C_3-symmetry. Extraction degree (*E,%)* of cations K^+ and $BuNH_3^+$ from water phase into CH_2Cl_2 at 25°C equaled for *cone*-**49** 58.8 and 82.0, for *paco*-**49** 34.9 and 31.5, for compound **48** 49.6 and 56.4 respectively.

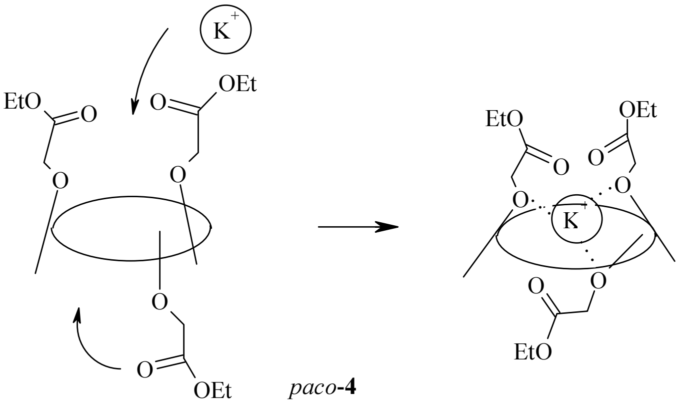


R = Et (**48**); *n*-Bu (**49**); 2-$PyCH_2$ (**50**); CH_2CONEt_2 (**51**); CH_2CONH(4-MePh) (**52**); 2-$PyNHCOCH_2$ (**53**).

Tri(2-pyridylmethyl)oxyderivatives **50** show pronounced affinity to ions Ag^+ and $BuNH_3^+$ affording 1:1 complexes with large K_{ass} [29]. The values *E*, %, for metal picrates extraction from the water phase into CH_2Cl_2 and ($K_{ass} \times 10^3$) in THF–$CHCl_3$ (1:1 by volume) at 25°C are as follows: at the use of calixarene *cone*-**50** 23.4 (29.4) for ion $BuNH_3^+$ and 84.4 (42.4) for Ag^+, at the use of conformer *paco*-**50** 13.5 (40.4) and 80.0 (35.2) respectively.

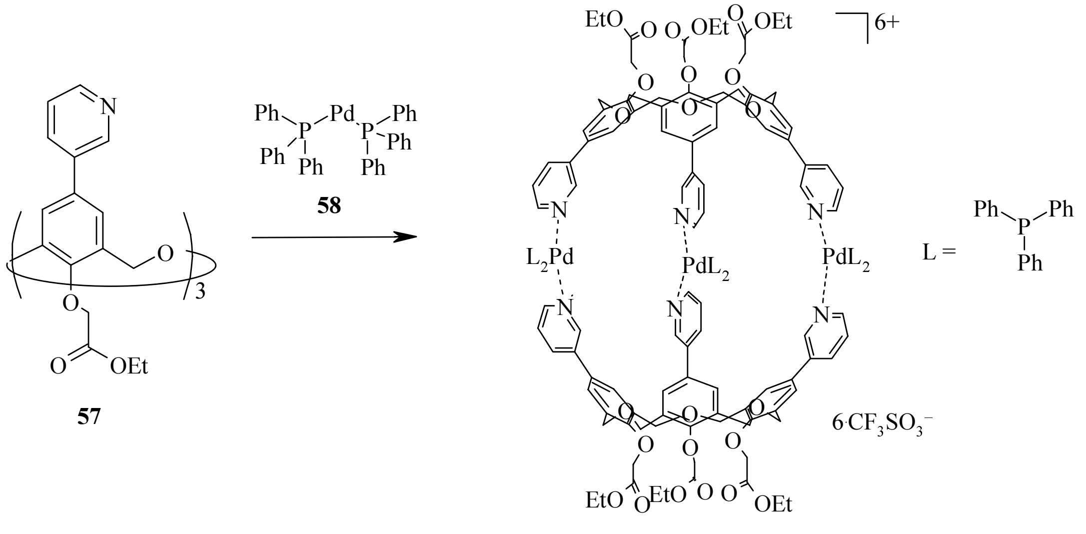
The extraction of alkali metal cations from the water phase into CH_2Cl_2 was studied using oxacalixarenes *cone*-**4** and *paco*-**4** with ester groups OCH_2COOEt on the lower rim of the molecule [4]. The following “classic” calixarenes were also used for comparison: tetra-(ethoxycarbonylmethoxy)-*p*-*tert*-butylcalix[4]arene **54**, hexaethoxycarbonylmethoxy-*p*-*tert*-butylcalix[6]arene **55,** and hexa(*tert*-butyloxycarbonylmethoxy)-*p*-*tert*-butylcalix[6]arene **56**. The data obtained show the high selectivity of derivative *cone*-**4** with respect to ion Na^+ (*E* 78.9%) [as well as *cone*-**54** (*E* 100%)] and *paco*-**4**

(*E* 88.4%) with respectr to ions K^+ [similarly to *paco*-**54** (*E* 94.3%)] although the degree of extraction with the oxacalixarene is somewhat lower than by the "classic" analog. Thus the ionophore quality of the cavity in trioxacalix[3]arene **4** with three OCH_2COOEt groups is comparable in efficiency with calix[4]arene **54** possessing four substituents. The increased size of the ring in the oxacalix[3]-arene as compared to "classic" calix[4]-arene is insufficient for the change in the ion-selectivity. A high affinity was revealed of derivative *paco*-**4** to cation Cs^+ (*E* 81.9%) significantly exceeding that of *paco*-**54** (*E* 49.9%). Especially interesting is the found efficiency of compound *cone*-**4** with respect to cations $BuNH_3^+$ (*E* 77.1%) evidencing that its structure of C_3-symmetry is very favorable for fixing cations of the same symmetry.



paco-**4**

It was found with the use of ^1H NMR spectroscopy [4] that the phenyl groups in conformer *cone*-**4** are more flattened than in the calix[4]arenes, and they lift up when the Na^+ cation enters the ionophore cavity. The fixing of K^+ ions with conformer *paco*-**4** is a more complicated process; Araki *et al.* [4] suggest that cation K^+ is coordinated by two usual ether groups and one inverted group.



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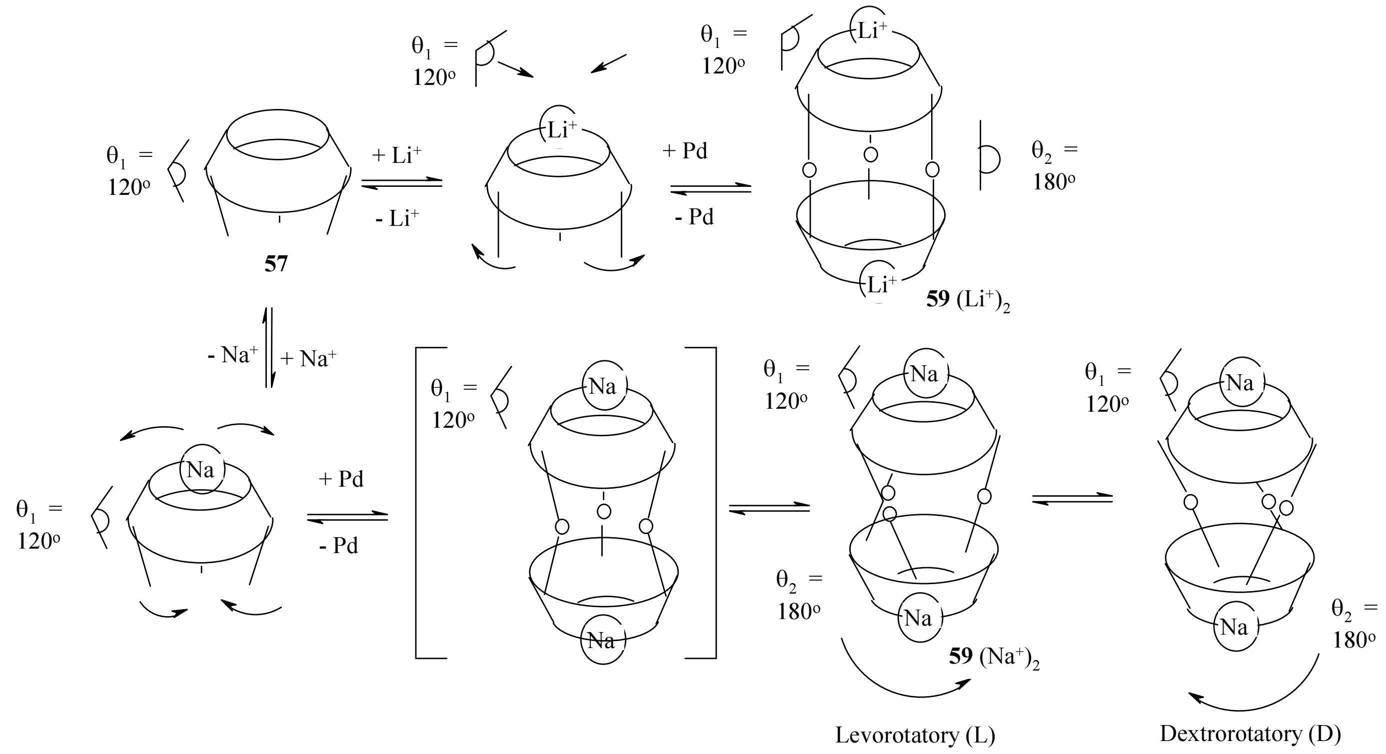
From 3-pyridyl-substituted oxacalixarene **57** equipped with ester groups on the lower rim of the molecule and complexa $Pd(II)(Ph_3P)_2{\cdot}(OTf)_2$ (**58**) a dimer molecule **59** was built up analogous to molecular capsule **15** prepared proceeding from 4-pyridylcalixarene **13**. The "designed" molecule **59** can be prearranged with cations of alkali metals Li^+ and Na^+ by complexing the latter at the lower rim of the calixarene fragments [44].

The composition of complexes [$\mathbf{58}{\cdot}(M^+)_2$] and their high D_{3h}-symmetry was established with the use of ^1H NMR spectra [44]. Curiously, the complexing of the bulky Na^+ cation caused turning of the three 3-pyridyl groups resulting in twisting of dimer [$\mathbf{59}{\cdot}(Na^+)_2$] and formation of a spiral structure (Fig. 9).

Therefore it is conceivable that the constructed molecular capsule possesses intrinsic chirality. The presence



θ_1 is the angle phenylpyridyl–Pd^{2+}; θ_2 is the angle pyridyl–Pd^{2+}–pyridyl.

Fig. 9. Rationalization of the internal chirality of molecular capsule [**59**·(Na$^+$)$_2$].

of two enantiomers in complex [**59**·(Na$^+$)$_2$] was proved by ^{1}H NMR spectra registered in the presence of chiral shift-reagents. Taking into account that C_{3v}-symmetry of oxacalix-[3]arenas is favorable for bonding ammonium ions Ikeda et al. [44] studied the presumable affinity of dimer **59** to chiral ammonium cations. It proved that under conditions of preparation of a complex between derivative **59** and Na$^+$ cation an analogous complex with a chiral (*S*)-2-methylbutylammonium triflate **60**:[**59**·(**60**)$_2$] readily formed [44]. The complex structure as showed ^{1}H NMR spectrum corresponded to the picture on Fig. 10.

Most interesting was the fact that inclusion of a chiral "guest" into the cavity of molecule **59** affected the ratio of its dextro- and levorotatory enantiomeric forms (chiral induction 70%).

Complexing properties with respect to cations of alkali and alkaline-earth metals of triamido derivative **51** in *cone* and *paco* conformations was studied in [45] in the THF–CHCl$_3$ mixture, 1:1 by volume, at 25°C. The data obtained demonstrated a high receptor activity of oxacalixarene *cone*-**51** conformer with respect to selected metal cations, especially to the alkaline-earth ones (log K_{ass} 4.9 for Mg^{2+} and > 7 for Ca^{2+} and Ba^{2+}). This compound operates as an excellent neutral ionophore because of the presence of three coordinated amido groups whose location provids the C_3-symmetry of the molecule. It should be noted that the binding quality of the respective triethylacetate derivative *cone*-**4** is considerably weaker, especially with regard to the alkaline-earth metal cations (log K_{ass} < 2). Arduini *et al.* [46] ascribe this fact to stronger electron-donating effect of amido groups as compared with ester groups.

In 2001 the ionophore activity was studied [47] of triamides **52** and **53** with tolyl (**52**) and pyridyl (**53**)

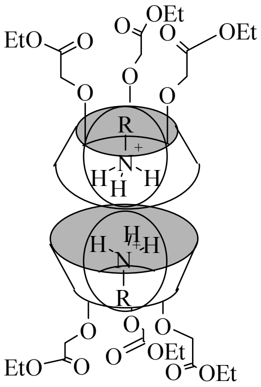


Fig. 10. Structure of the cpmplex between dimer molecule **59** and (*S*)-2-methylbutylammonium triflate **60**.

Table 1. Extraction (%) of metal and ammonium picrates from the water phase into CH_2Cl_2 by calixarene **51** and oxacalixarene **53** conformers

Ionophore	Na^+	K^+	Ag^+	Cu^{+2}	Al^{3+}	$BuNH_3^+$	*i*-$BuNH_3^+$	*t*-$BuNH_3^+$
cone-**51**	93.0	71.6	90.4	27.5	19.0	97.8	48.0	35.4
paco-**51**	27.9	72.9	77.1	24.0	8.9	93.2	36.8	14.2
cone-**53**	0	0	76.9	16.6	11.5	38.1	1.9	0.8
paco-**53**	0	0	31.1	3.1	2.6	2.2	0.4	0.4

fragments on the lower rim of the molecule. These compounds were presumable double-centered receptors with respect to metal cations, alkylammonium ions, and halide anions. The complexing with cations was studied by means of extruction, that with anions by ^1H NMR titration. For the sake of comparison diethylamide **51** was used. The extraction results are presented in Table 1.

Yamato *et al.* [47] for the first time tried to establish the relation of ionophore quality of oxacalixarene ligands to the presence of intramolecular hydrogen bonds and the C_3-symmetry of their conformations. It turned out that the presence of strong hydrogen bonds between neighboring NH and CO groups in oxacalixarenes **52** and **53** weakened the binding properties of these compounds with respect to metal and ammonium cations. Conformer *cone*-**52** showed only a certain selectivity toward ion $BuNH_3^+$ (*E* 18.7%), and conformer *paco*-**52** hardly possessed affinity to cations. Unlike amide *cone*-**52** its analog *cone*-**53** proved to be a sufficiently selective receptor for cations Ag^+ affording a 1:1 complex. In the course of complexing the nitrogen atoms of the pyridine fragments turn from the position "outside the cavity" into position "inside the cavity". Only two pyridine rings undergo this process in the case of *paco*-**53** conformer. After formation of complexes between amides **53** and Ag^+ cation the symmetry of the initial conformers is retained: C_3 for *cone*-**53** and C_2 for *paco*-**53**. The O atoms of ether bridges are not infolved into the complex formation.

A study was also carried out on complexing of amide *cone*-**52** with butylammonium halides $BuNH_3^+Hlg$ (Hlg = I, Br, Cl) [47]. It was proved that the complexes formed had 1:1composition and the binding of halogen atoms occurred by the NH groups of the substituents (Fig. 11). The formation of the complex with Cl^- anion was preferable (K_{ass} for Cl^- was 8250 l mol^{-1}, for Br^- 1720 l mol^{-1}).

The fluorescence intensity at 480 nm was used for estimation of complexing equilibrium constant (*K*) with ammonium for conformers *cone*-**61** and *paco*-**61** having three pyrene-containing fragments on the lower rim of molecule [48]. Conformer *paco*-**61** can be applied to the quantitative analysis of the primary ammonium ions in the presence of the secondary ammonium ions and alkali metal cations (for instance, for *n*-$C_6H_{13}NH_3ClO_4$ *K* 2920, for $NaClO_4$ 25, for $KClO_4$ 330). The following scheme of binding was suggested based on the ^1H and ^{13}C NMR spectra (Scheme 7).

The change in fluorescence of ligand on complex formation provides a useful tool for investigating the complexing process.

Relatively complicated artificial receptors **62** and **63** with N-hydroxypyrazine fragments on the lower rim of

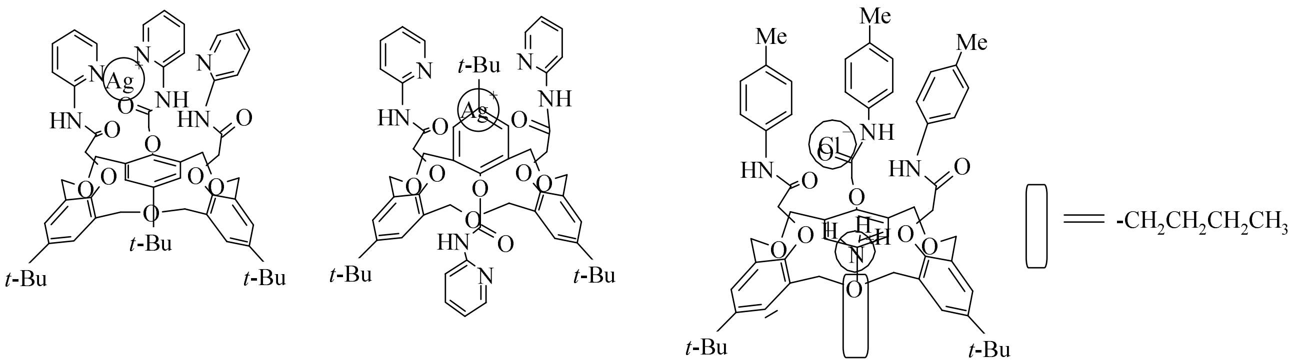
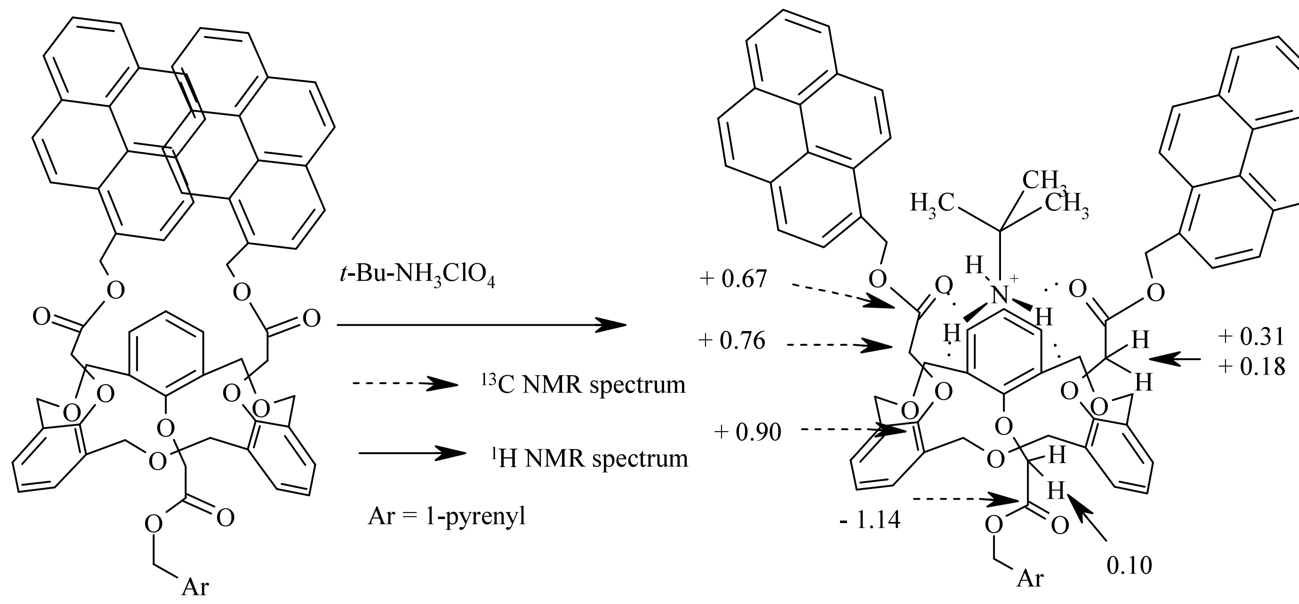


Fig. 11. Models of Ag^+ cation binding by derivatives *cone*-**53** and *paco*-**53**, and of butylammonium chloride binding by derivatives *cone*-**52**.

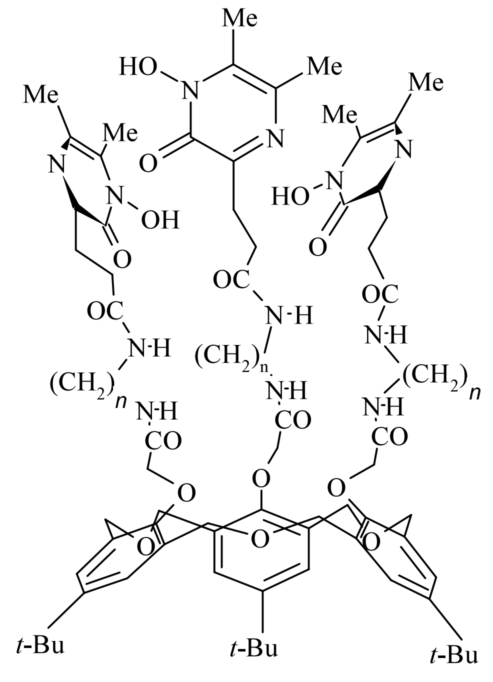
Scheme 7.



paco-**61**

the molecule were tested as “host molecules” for recognition of ammonium ions [49]. Extraction of primary alkylammonium picrates into the organic phase was performed by solutions of compounds **62** or **63** in CH_2Cl_2 or by a solution of oxacalixarenes **62** or **63** mixed with an equimolar amount of Ga(*acac*)$_3$. The results are presented on Fig. 12.

The data obtained demonstrated that t-BuNH$_3^+$ was extracted less efficiently than primary cations BuNH$_3^+$ and $C_6H_{11}NH_3^+$: it was ascribed to the effect of spatial



62, *n* = 4; **63**, *n* = 6

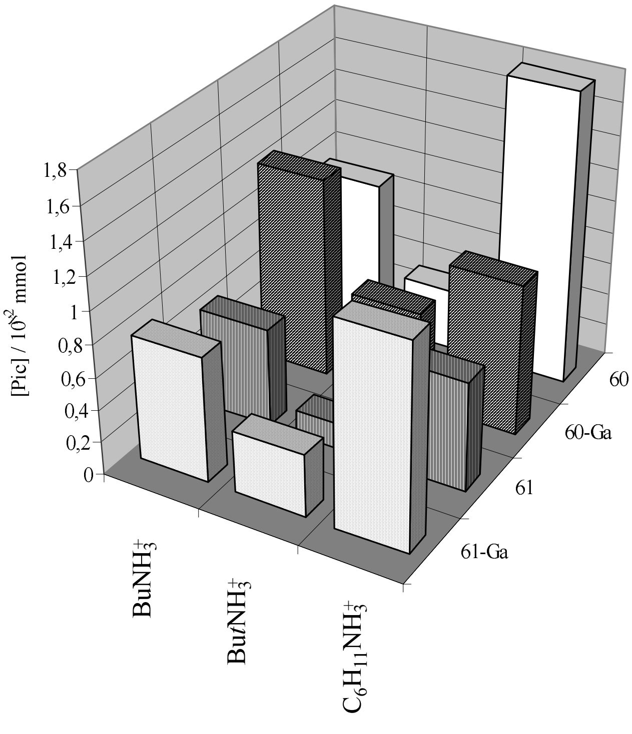


Fig. 12. Extraction (%) of primary ammonium cations by ligands **62** and **63**.

Table 2. Thermodynamic parameters and association constants of complexes of oxacalixarenes **64** and **66** with ammonium ions[a]

Complexes	**64**·PheOMe	**64**·PhgOMe[a]	**64**·1-(1-naphthylethyl)[b]	**64**·1-phenylethyl	**66**·PheOMe
$\Delta H^{\#}$, kJ mol^{-1}	–42	–12	–23	–10	–1.4
$\Delta S^{\#}$, J mol^{-1} deg	–120	–26	–60	–14	1.4
K_{ass} (293 K), l mol^{-1}	16.4	6.0	9.3	12.1	2.1

[a] Perchlorates of (*S*)-isomers were used. [b] Solvent THF-d_8–$CDCl_3$, in other cases THF-d_8.

factor. The extraction of butylammonium cations is enhanced in the presence of Ga^{3+} cation suggesting the cooperative character of the molecular recognition. Ohkanda *et al.* [49] reported that the complex of ligand **62** with cation $BuNH_3^+$ had 1:1 composition and that in the complex existed interactions $C=O\cdots HN^+$ and $ArO\cdots HN^+$. As to ion $C_6H_{11}NH_3^+$, its extraction with ligand **62** decreased in the presence of cation Ga^{3+}. This observation is in conformity to the difference in the association constant of the complex in the absence (K_{ass} 4375) and in the presence (K_{ass} 2833) of ion Ga^{3+}. It was believed that the complex of Ga^{3+} ions with ligand **62** ensured building up of a rigid cavity favorable for selective recognition of ammonium ions.

Ionophore properties of rigid molecules **64** and **65** with respect to metal and ammonium cations were investigated in [50, 51]. The rigidity of molecules was achieved by "*capping*" the lower rim of oxacalixarenes. The complexing with ligand **64** was studied by dynamic NMR and mass spectrometry [51]. For comparison was used a "*non-capped*" triether **66**. The results are presented in Table 2.

Ionophore properties of oxacalixarene **65** were studied by extraction from the water phase into CH_2Cl_2 [50]. For comparison a related oxacalixarene **67** was used. The results are presented in Fig. 13 and Table 3.

The data obtained show that compounds **65** and **67** thanks to their C_3-symmetry possess a high affinity to the butylammonium ion and excellent extraction qualities.

Table 3. Association constants ($K_{ass}\cdot 10^{-4}$ l·mol^{-1}) and free energies of binding ($\Delta G^{\#}$, kJ mol^{-1}) of "host" molecules **65** and **67** with cations in CH_2Cl_2–THF, 99:1, at 27°C

Cation	**65**		**67**		$\Delta\Delta G^{\#}$ [$\Delta G^{\#}$ (**65**) – $\Delta G^{\#}$ (**67**)]
	K_{ass}	$\Delta G^{\#}$	K_{ass}	$\Delta G^{\#}$	
Na^+	5.27	–26.47	2.48	–24.64	–1.83
K^+	6.71	–27.06	2.28	–24.43	–2.63
Cs^+	5.76	–26.69	1.61	–23.59	–3.10
Ag^+	5.03	–26.36	2.77	–24.91	–1.45
$BuNH_3^+$	7.64	–27.38	2.21	–24.36	–3.02

Therewith "capped" oxacalixarene **65** is more sensitive to metal cations than the "open" compound **67** probably due to the lower rate of dissociation of complex [(**65**)·metal]. The high affinity of compound **65** to K^+ ions may be rationalized as follows. The C=O groups in ligand **65** are directed to the outside of the cavity thus decreasing the electrostatic repulsion. When binding the metal cation they turn into the inside in order to take part in the complex formation alongside the phenol oxygen atoms. The ionophore cavity formed by three OCH_2COOCH_2 groups proved to be favorable by size for K^+ cation and too large for ion Li^+.

The NMR-titration was applied to a study of a model of ligand **65** complexing with primary ammonium ions $BuNH_3^+$, $EtNH_3^+$, and $MeNH_3^+$, [50]. The special interest of this study lies in the fact of the presence of $BuNH_3^+$ structural units in biologically important systems. The resuts obtained suggested [50] that in the arising complexes the $EtNH_3^+$, ion is located deep in cavity of ligand **65,** the $MeNH_3^+$, ion is on the edge of the cavity, and the alkyl chain length of the $BuNH_3^+$, ion is already sufficient for "*protruding*" from the calixarene cavity. In the complex of $BuNH_3^+$, with oxacalixarene **65** the protons of NH_3 group interact with three C=O groups and phenol oxygens, whereas the butyl chain is located in the cavity formed by benzene rings.

The ionophore features of conformationally rigid oxacalixarenes **68** and **69** with methoxy groups on the lower rim and capped by *symm*-tri-(methyloxy- or methylthia-)benzene "cap" on the upper rim [52]. For comparison tri-O-methyl derivative **3** was used. The results are presented in Fig. 14.

A high selectivity of compound **68** to ions Cs^+ comparable to that of "classic" calixarene ionophores was revealed [53–55]. Note that oxacalixarene **69** with CH_2SCH_2 moieties on the upper rim of the molecule (instead of CH_2OCH_2 present in compound **68**) did not at all extract alkali metal cations [52].

Pseudo-C_2-symmetric compound *anti*-**70** with two butyloxy and one methoxy group on the lower rim of the

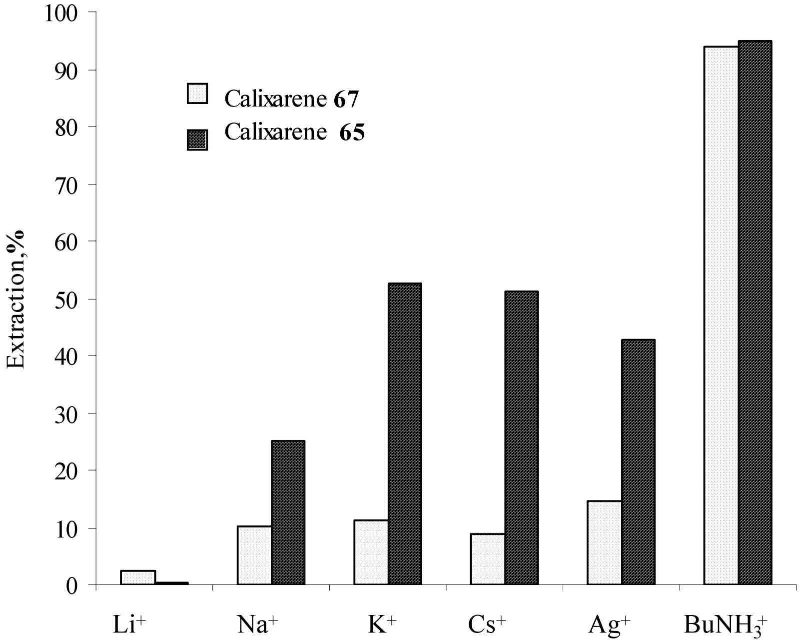
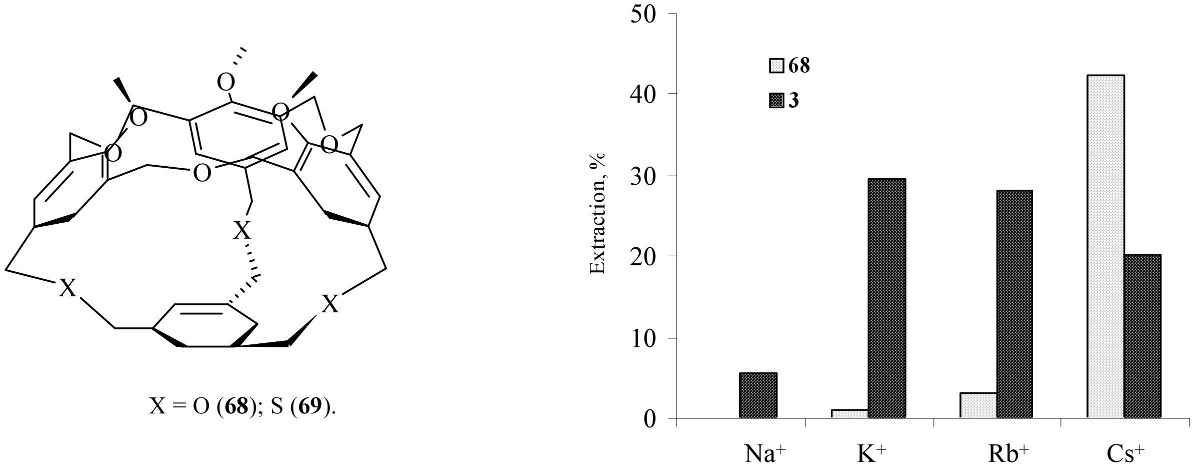


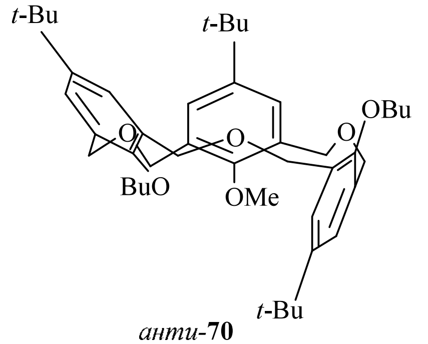
Fig. 13. Extraction (%) of metal cations and butylammonium by calixarenes **65** and **67**.



X = O (**68**); S (**69**).

Fig. 14. Extraction (%) of alkali metal cations into CH_2Cl_2 at 25°C with calixarenea **3** and **68**.

molecule built up on the C_3-symmetric skeleton of oxacalixarene **2** proved to be very efficient in chiral recognition of optically active primary alkylammonium ions [56]. The K_{ass} of the complexes of ligand *anti*-**70** with ethyl esters of α-amino acids and 1-arylethylamines are given in Table 4, and the process of binding RNH^+ ions is presented on Scheme 8.

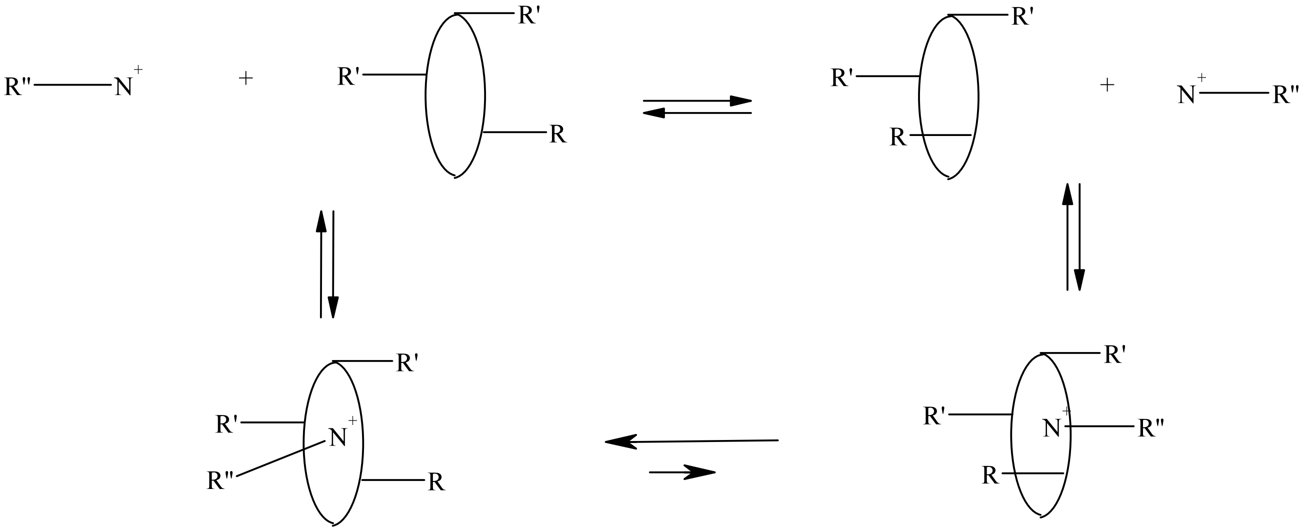


анти-**70**

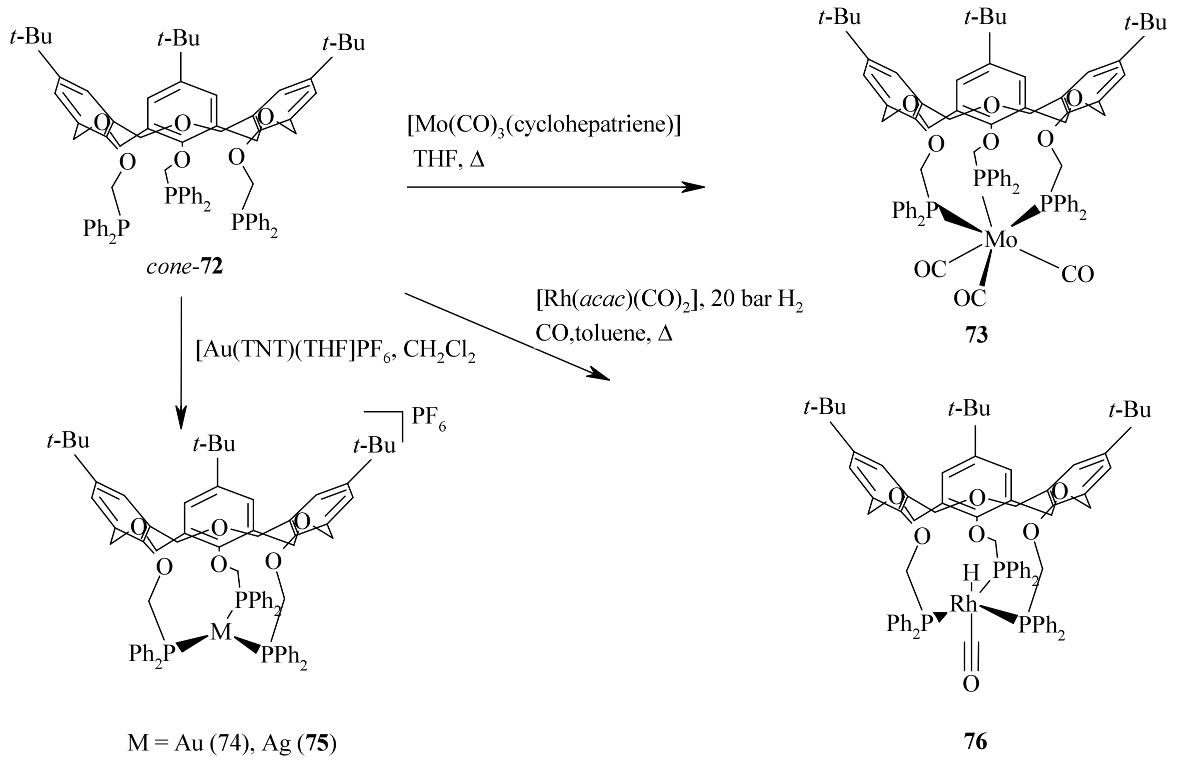
Table 4. Association constants (K_{ass}, l mol^{-1}) of *anti*-**70** complexes with α-amino acids ethyl esters picrates and 1-arylethylamines in $CHCl_3$–THF, 99:1, 25°C

Picrate of	(+)-*anti*-**70**	(–)-*anti*-**70**	K_{ass}(large)/ K_{ass}(small)
L-alanine ethyl ester	4500	3200	1.4
L-phenylalanine ethyl ester	1200	180	6.7
(R)-1-phenylethyl-amine	2200	3000	1.4
(R)-1-naphthylethyl-amine	2000	2400	1.2

Scheme 8.



Scheme 9.



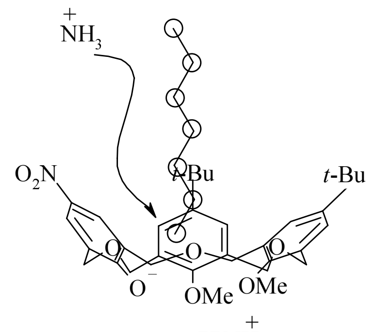
The above data indicate that the K_{ass} for L-amino acids is larger at the use of ligand (–)-*anti*-compared to the (+)-*anti*-isomer **70**. The highest degree of the chiral recognition (enantiomer excess of 74%) was observed with L-phenylalanine ethyl ester picrate.

Triphosphorylated oxacalixarene *cone*-**71** is an active agent for transfer of rare-earth metal cations from the water phase to CH_2Cl_2 [57]. Extraction percent of cations Y, La, Pr, Nd, Sm, Eu, and Gd proved to be considerably higher than at the use of the corresponding derivatives of "classic" czlix[4]arene [58]. The highest selectivity was attained for the elements possessing ion radii close to that of Pr. Ligand *cone*-**72** turned out to be an ideal compound for building up C_3-symmetric metal complexes **73–76** (Scheme 9).

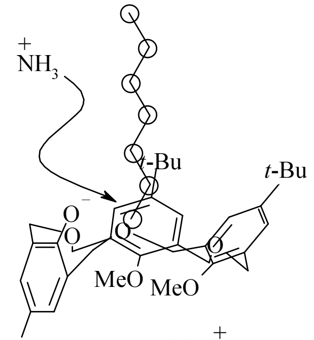
It was demonstrated that in complex **73** the metal center was situated below the cavity of the molecule.

In the preparation of cation complexes with Au (**74**) and Ag (**75**) the salt $AgBF_4$ was used; the metal center in these complexes was found to be placed across the entrance to the cavity. The synthesized complex with rhodium **76** is worth special attention: There the bond Rh–H is directed inside the cavity, and thus the H atom occurs very close to the CH_2 group of the $ArCH_2O$ moiety and to the protons of PCH_2 fragment.

In [59] complexing with hexylamine was studied of a flexible dimethyl ether of *p*-nitrooxacalixarene **77** selectively modified at the upper and lower rims. The macrocycle contained a single *p*-nitrophenol fragment. The association constants of the complex at 25°C were determined in various solvents by means of UV-*vis* titration [60, 61] [251±2 ($CHCl_3$), 1116±6 (MeOH), 133±1 (THF), 627±17 (CH_3CN), > 10^5 (DMSO)]. The structure of the complex was estimated from the ^1H spectra. The data obtained confirmed the assumption [59] that from the two possible forms existed the complex where the "guest" amine was included into the inner cavity of the *cone*-conformer of the calixarene.



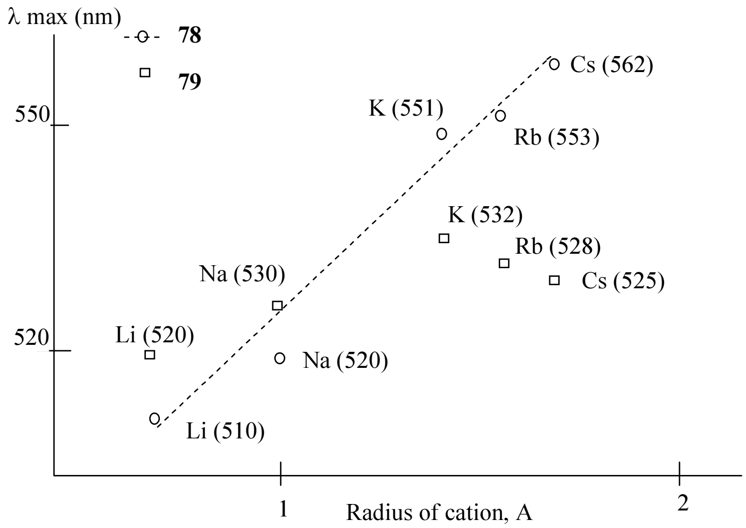
cone - **77**·$\overset{+}{N}H_3$

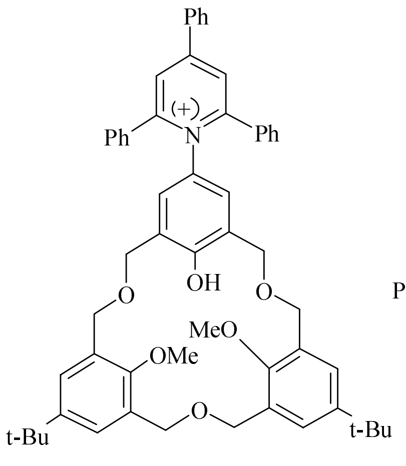


paco - **77**·$\overset{+}{N}H_3$

Proceeding from oxacalixarene **77** a chromogenic receptor **78** was synthesized containing a fragment of a pyridinium N-phenolate dye (Reichardt dye E_T1) [62]. It was shown that the presence of a phenol group capable of ionization makes possible to regard compound **78** as a chemical switch changing color at complex formation with alkali metal cations and various amines [62]. The absorption maxima in the UV spectra of the corresponding complexes of compound **78** as a function of cations radii are presented on Fig. 15 compared to the complexes with the dye $E_T1\cdot HCl$ **79**.

The data obtained unambiguously evidence that the dye can enhance the color due to the presence of the homooxacalix[3]arene template.





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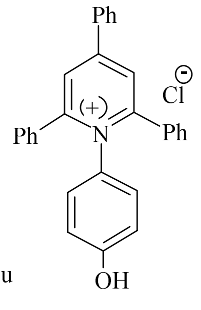

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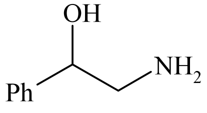
Fig. 15. Absorption maxima in UV spectra of of complexes with compounds **78** and **79** as a function of cations radii.



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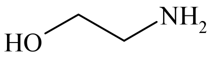

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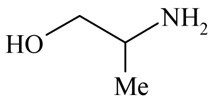

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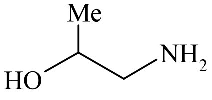


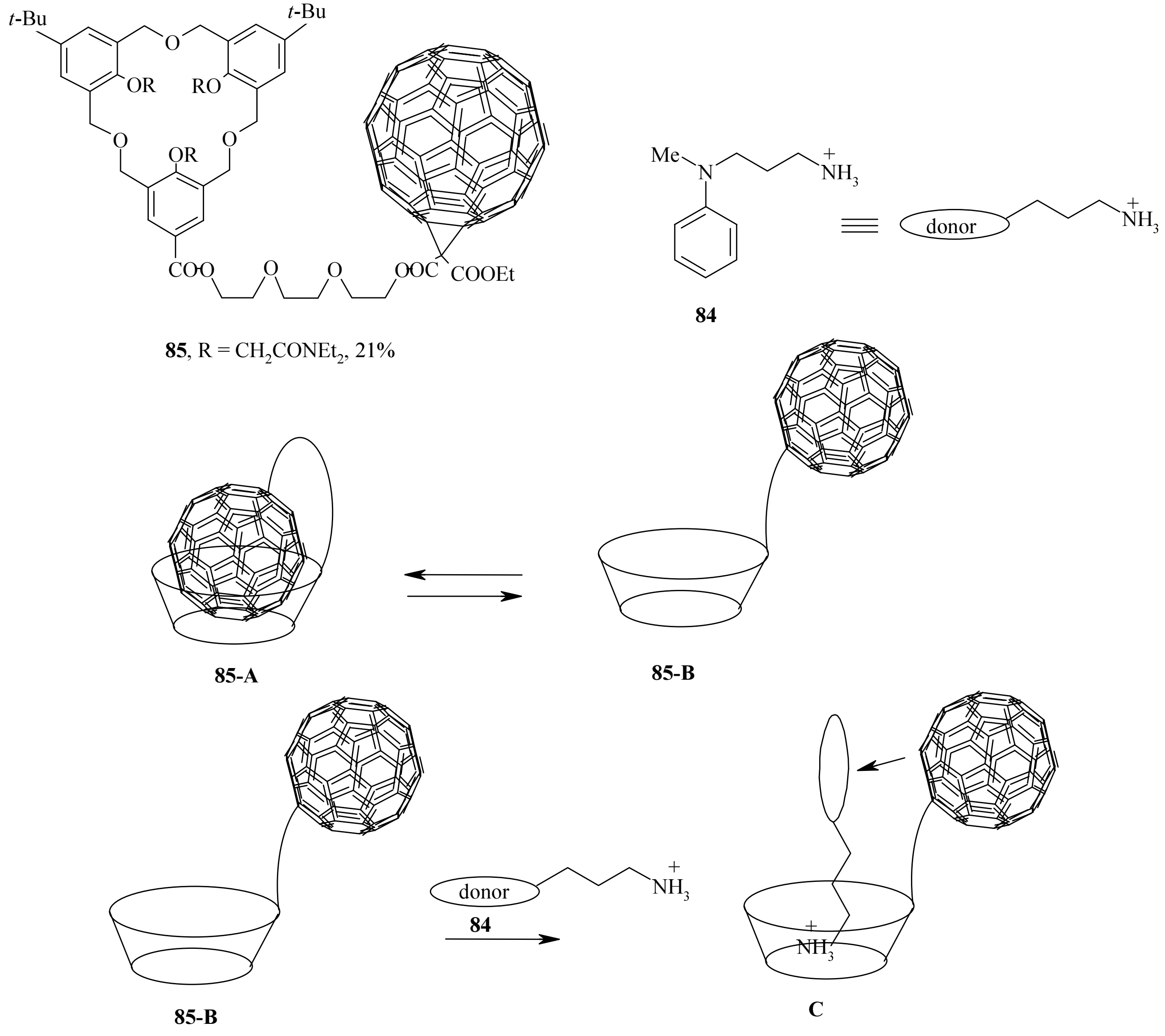
83

In complexing with amines the structure of the latter significantly (and sometimes decidedly) affected the change in the color. It was found that the use as “guest” of 2-amino-1-phenylethanol **80** did not result in the color strengthening although it was observed in the case of other amines **(81–83)** with a similar skeleton.

This phenomenon is apparently caused by the reduced acidity of the OH group in compound **80** (as compared to oxyamines **81–83**) and by a possibility to form intramolecular hydrogen bonds between OH and NH$_2$ groups. As a result the reaction of phenol groups of the “host” molecules **78** with NH$_2$ groups of the “guest” molecule **80** gets blocked by the net of the hydrogen bonds, and no change in color was observed [62].

The complexing of oxacalixarenes with ammonium ions was applied to constructing a new class of efficient

Scheme 10.



“*electron-transfer*” systems [63]. It was shown that on adding a solution of 3-(*N*-methylamino)propylammonium **84** in $CDCl_3$ to calixfullerene **85** where the calixarene part was connected to C_{60}-fullerene by a flexible triethylene glycol bridge the inclusion of the ammonium fragment into the cavity of oxacalixarene and the cation–π interaction resulted in formation of a donor-acceptor pair. According to ^1H NMR spectra the initial calixfullerene **85** is a mixture of **A** and **B** conformers; on addition of “guest” **84** the amount of conformer **A** is reduced. Into the reaction with the “guest” the conformer **B** is involved providing a donor-acceptor pair **C** (Scheme 10).

The selective action of a pulse laser light on the reaction product **C** induced formation of calixfullerene anion-radical Cal-$C_{60}^{-\cdot}$ with a quantum yield of 0.95. As a result of the intramolecular *e* transfer the dissociation of an excited triplet “*exciplex*” in the system calix-C_{60}/ammonium-aniline (AA) gave rise simultaneously to an ammonium-aniline cation-radical.

$$(\text{Cal-C}_{60}\cdots\text{AA}) \rightarrow {}^3(\text{Cal-C}_{60}\cdots\text{AA})^* \rightarrow (\text{Cal-C}_{60}{}^{-\cdot}\cdots\text{AA}^{+\cdot})$$

$$\rightarrow \text{Cal-C}_{60}{}^{-\cdot} + \text{AA}^{+\cdot}.$$

The lifetime of the forming ion-radicals is over 1 ms.

To conclude this section the studies should be mentioned considering the possibility to use oxacalixarenes in biological analysis [64] and in imitation of biological objects [65].

Among important problems dopamine analysis should be mentioned in the presence of the other catecholamines (adrenalin, noradrenalin) and inorganic cations K^+ and Na^+. It was demonstrated in 1999 [64] that this goal could be successfully achieved applying oxacalixarene **49** with butyloxy groups on the lower rim of the molecule. The selectivity was studied of poly(vinyl chloride) membranes modified with derivative **49**, esters of *p*-H-calix[6]arene [RO = $OCH_2COOC_{10}H_{21}$ (**86**) and $OCH_2COOC_2H_5$], and dibenzo[18]crown ether. As “guests” were applied the following ammonium salts RNH_3^+: first set, R = $CH_3(CH_2)_7$, $Ph(CH_2)_2$, $PhCH_2$, 1-adamantyl, $(CH_3)_3C$; second set, dopamine **87,** noradrenalin **88**, adrenalin **89**, cations K^+ and Na^+. The data for liquid poly(vinyl chloride) membranes modified with oxacalixarene **49** and “classic” calix[6]arene **86** are presented on Fig. 16.

The data presented demonstrate an excellent activity of membranes modified with oxacalixarene **49** triether with respect to dopamine as compared to adrenalin and noradrenalin, and also K^+ and Na^+ cations.

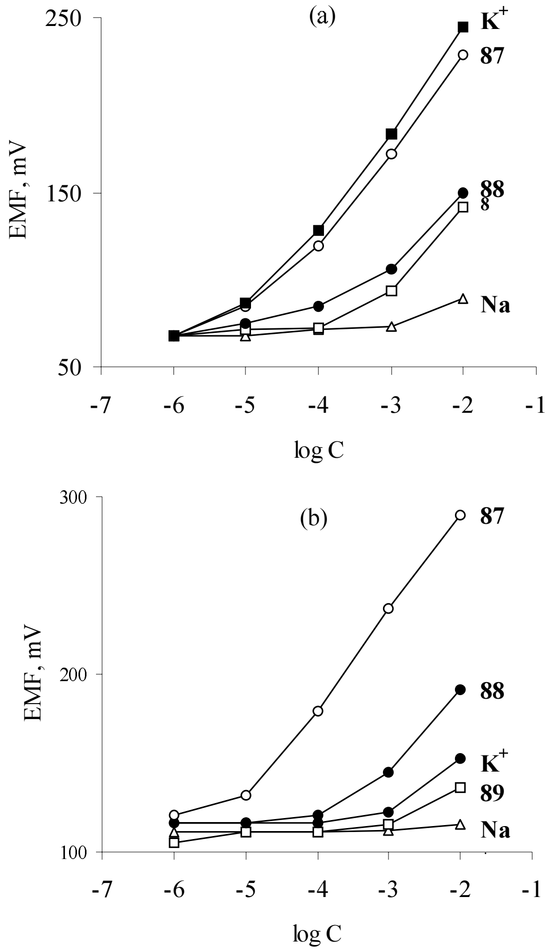


Fig. 16. Dependence of potential of poly(vinyl chloride) membranes modified with calixarenes **86** (*a*) and **49** (*b*) on the “guests” (**87–89**) and inorganic cations K^+ q Na^+ concentration at pH 5.0.

The transport of K^+ and Na^+ cations through the channels of the phospholipid membranes is well known to be crucially important for many biological processes, especially for transfer of nervous impulses [66, 67]. The inner surface of the channels of selective conical biological filters is covered with a succession of rings formed of O atoms of carbonyl groups from the amino acids rests. It proved to be possible to imitate successfully their structure and operation using diethylamido derivative of trioxacalixarene **51** [65] where oxygen atoms of phenol and carbonyl groups formed a three-dimensional cavity involving a double ring of six oxygen donors. The “belt” of *p-tert*-butylaryl groups ensures the hydrophoby of the conical entrance to the donor center.

The reaction of calixarene **51** with $NaPF_6$ in H_2O–MeOH mixture afforded complex **90** $\{[Na_2(\mathbf{51})](PF_6)_2 \cdot H_2O \cdot 2MeOH\}$ that was characterized by X-ray

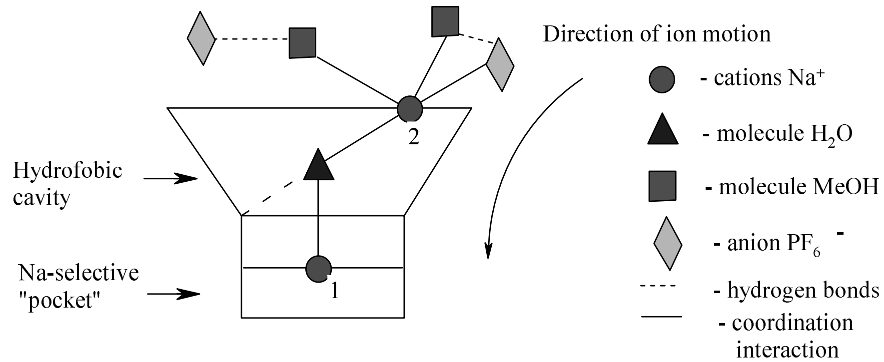


Fig. 17. Diagram representing the key structural fragments of complexa **90**.

diffraction analysis [65]. This study revealed that one cation Na$^+$(*1*) was firmly incapsulated into a Na-selective "*pocket*" formed by phenol and carbonyl oxygen atoms whereas the second ion Na$^+$(*2*) at the entrance of the conical hydrophobic cavity served as a salt bridge in an additional cavity built of anions PF_6^-. Both ions Na$^+$(*1*) and Na$^+$(*2*) are connected by a water molecule [the distance Na$^+$(*1*)–OH_2 is 2.437(5) , the distance Na$^+$(*2*)–OH_2 is 2.277(5)]. The water molecule is located in the center of the conical cavity and is capable of interaction also with the ether oxygens of the ligand (Fig.17).

Coordination sphere of ion Na$^+$(*2*) involves a water molecule, two molecules of the other solvent (MeOH), PF_6^- anion, an oxygen atom from the ether bridge of calixarene, and finally, a cation-p interaction with one of aryl rings is detected [the distance Na$^+$(*2*)–C is 3.026(6) E]. This environment is a good illustration of the desolvation process that should occur in biological systems when the alkali metal cation enters the selective conical filter. The water molecule acts as molecular "bracket" that pulls the second metal cation to follow the first along the ionic channel.

The study [65] was extended by investigation of possibility of complex formation between oxacalixarene **51** and $HgCl_2$ in order to get additional data for providing an understanding of the high neurotoxicity of Hg^{2+} derivatives [68]. Nowadays the mechanism of this influence is not fully understood, but it is often suggested that the mercury derivatives affect the transport of cations Na$^+$, K$^+$, and Ca^{2+} along the channels of the biological membranes [69–72].

It turned out that diethylamido derivative **51** with $HgCl_2$ afforded a dimeric complex [**51**·$HgCl_2$]$_2$ whose structure was studied by X-ray diffraction analysis. The molecule of oxacalixarene in the crystal structure of the complex takes a "herringbone" position, and the fragments of $HgCl_2$ are included in between (Fig. 18).

The coordination sphere of each Hg atom involves two bonds Hg–Cl, one weak interaction Hg–Cl, and two interactions with substituents at the lower rim of the oxacalixarene (ether O and carbonyl O atom of the diethylacetamide fragment). The most important distances are as follows:

Hg–Cl (terminal)	2.318 Å	Hg–O (amide)	2.549 Å
Hg–Cl (bridging)	2.331Å	Hg–O (ether)	2.705 Å
Hg···Cl (bridging)	3.136 Å	Hg–Ar (centroid)	3.875 Å
Hg···Hg	4.077 Å		

The results obtained show that the inorganic mercury is not attracted by the π-electrons-reach funnel of the oxacalixarene, and therefore the ions Hg^{2+} *in vivo* should not go to the ionic channels whose aromatic fragments are among the components ensuring the selectivity of cations transport [68].

3. RECEPTOR PROPERTIES OF HOMOOXACALIX[*n*]ARENES DERIVATIVES ($n > 3$)

Gutsche *et al.* [27] were the first to isolate and characterize monooxacalix[4]arene **91**. They also reported that the compound tended to form complexes (1:1) with small molecules, like $CHCl_3$ and CH_2Cl_2. In

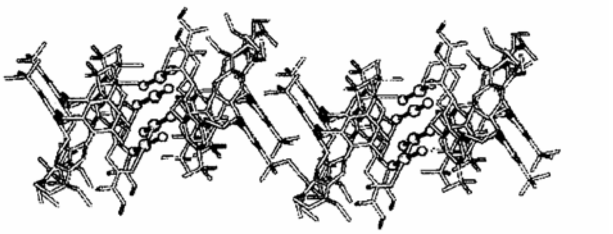
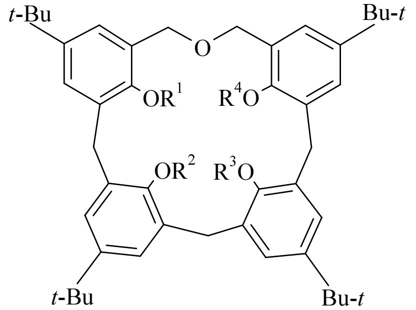


Fig. 18. Packing of oxacalixarene **51** complex with $HgCl_2$.



91, $R^1 = R^2 = R^3 = R^4 = H$;
92, $R^1 = R^2 = R^3 = R^4 = 2\text{-}CH_2Py$;
93, $R^1 = Me$, $R^2 = R^3 = R^4 = 2\text{-}CH_2Py$

1991 complexes were prepared of monooxacalix[4]arene **91** with Eu^{3+} (in solid state) and Yb^{3+} cations (in C_6D_6) [35]. The complexes have a similar composition: $\{[Me_2(L\text{-}3H)_2(DMSO)_2]\cdot 2CH_3COCH_3\}$ where Me is the metal, L is the ligand. X-ray diffraction study of the Eu^{3+} complex revealed the presence of binuclear species; heptacoordinate metal ion was located in the cup of the ligand. The metal coordination involved not only the O atoms of the phenol fragments but also the bridging ether oxygen and the oxygen from the DMSO molecule included into the complex. Three of the four OH groups of the ligand are deprotonated. It is worth mentioning that the complex contains a second neutral molecule, that of acetone, selectively "chosen" from the mixture acetone–CH_3CN used in the course of the complex synthesis.

The extraction activity of *cone*-tetrapyridylmonooxacalix[4]arene **92** with respect to cations of alkali, alkaline-earth, transition and heavy metals was investigated (metal picrates, H_2O/CH_2Cl_2) [73]. A very high activity was revealed for transfer of cations Ag^+ (*E* 90%) and relatively high one for cations Hg^{2+} and Pb^{2+} (*E* 70 and 40% respectively).

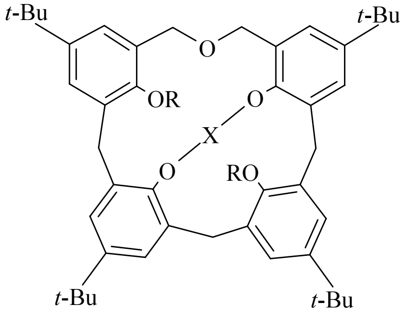
The binding properties of monooxacalix[4]arene **93** selectively modified at the lower rim were studied [74] with respect to alkali and alkaline-earth metal cations. The comparison with tetraethylacetate of a "classic" *p-tert*-butylcalix[4]arene **55** was performed [75, 76]. The extraction percent of picrates from the water phase into CH_2Cl_2, the transfer rate through a liquid membrane of CH_2Cl_2, and stability constants of the complexes in MeOH at 25°C were estimated. The data obtained showed that compound **93** in contrast to "classic" calix[4]arene **55** is a good transfer agent for alkali metal cations and a selective transfer agent for the ion Ba^{2+}.

The ionophore properties of calixcrowns **94–96** with respect to alkali and alkaline-earth metal cations were described in [77]. The extraction results are presented on Fig. 19.

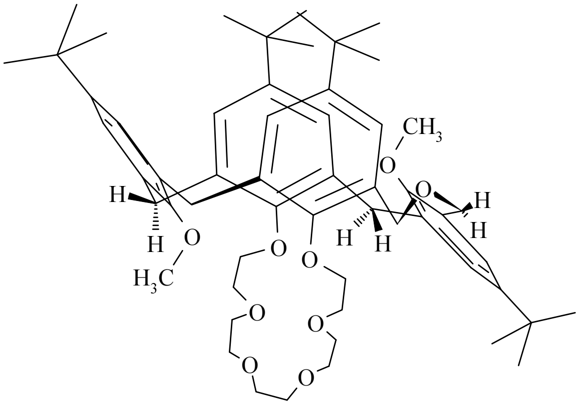
The high activity of compound **96** is believed to originate from its *paco* conformation [77] that is less polar and less solvated that the corresponding *cone* conformation [78], and therefore the captured cations may be involved not only in the interaction with the crown ether moiety, but also with one of the aromatic rings (cation-π interaction) [79].

The found extraction activity toward the alkaline-earth cations was low in all the compounds studied (*E* did not exceed 6%).

As to the cations transfer through the liquid membrane of CH_2Cl_2, the calixcrowns **94–96** are good transfer agents and display a selectivity with respect to ions Ba^{2+}. Calixarene **96** was the best transfer agent for all cations



94, $X = (CH_2CH_2O)_3CH_2CH_2$, R = H;
95, $X = (CH_2CH_2O)_4CH_2CH_2$, R = H;
96, $X = (CH_2CH_2O)_4CH_2CH_2$, $R = CH_3$



paco-**96**

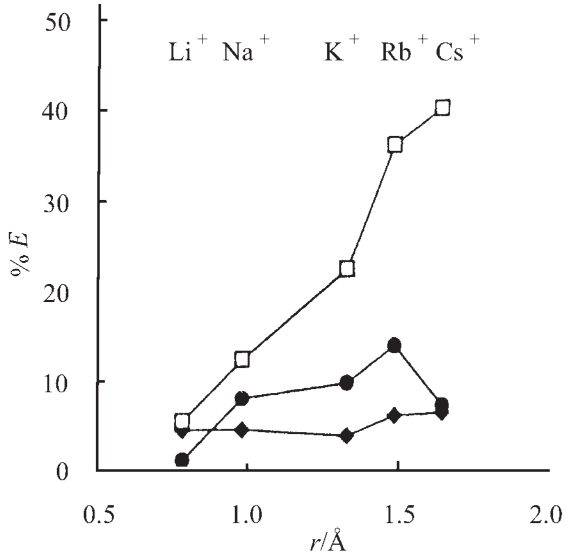
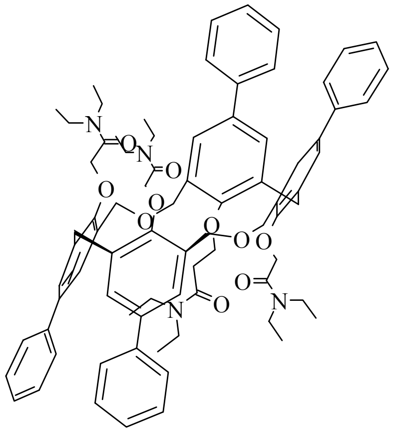


Fig. 19. Extraction degree of alkalimetal pictures as a function of the cation radius for compounds: *cone*-**94** (●), *cone*-**95** (◆) and *paco*-**96** (☐).

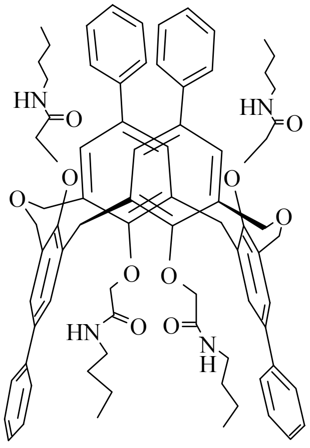
(Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}), compound **95** showed the fastest transfer rate for ions Cs^+ (3.7 μmol h^{-1}), and calixcrown **94** was the most selective agent for transfer of ions Ba^{2+} ($Ba^{2+}/Sr^{2+} = 23$; $Ba^{2+}/Ca^{2=} = 23$; $Ba^{2+}/Mg^{2+} = 13$).

The extraction activity of tetraamides **97** and **98** and tetrathioamides **99** and **100** of dioxacalix[4]arene with respect to metal cations was measured; it turned out that cations Pb^{2+} were selectively bound by tetraamide 1,2-*alt*-**97** (*E* 86.55%), and cations Ag^{2+} by tetrathioamides 1,2-*alt*-**99** and 1,2-*alt*-**100** (*E* 158.64 and 179.04% respectively) [80].

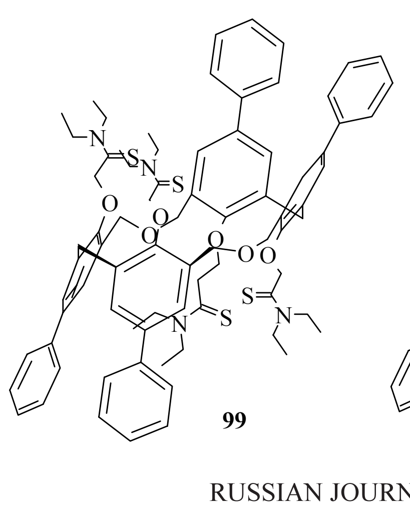
In going from *N,N*-diethyltetraamide **97** to corresponding 1,2-*alt*-*N,N*-dipentyl derivative **102** the selectivity of cation Pb^{2+} binding is conserved (*E* 96.6%), whereas the extraction activity of monopentyl derivative **101** with respect to cations Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Pb^{2+} was very low both for 1,2-*alt*- and 1,3-*alt*-conformation [81]. The low complexing activity of compound **101** was as-



1,2-alt- **97, 101, 102**
$R^1 = R^2 = Et$ (**97**), C_5H_{11} (**102**);
$R^1 = H$, $R^2 = C_5H_{11}$ (**101**)



1,3-alt-**98, 101**
R = Bu (**98**), C_5H_{11} (**101**)



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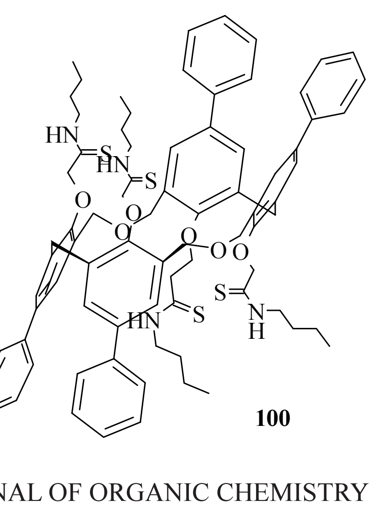


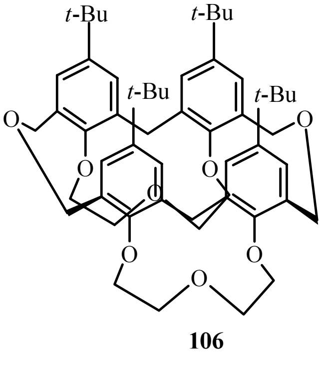
100

cribed to the existence of hydrogen bonds between NH groups and oxygen atoms of the phenoxy groups.

Trioxacalix[3]- and dioxacalix-[4]arene derivatives having free COOH groups on the lower rim of the molecules **103** and **104** formed stable complexes in CH_3OH with lanthanides (cations Pr^{3+}, Eu^{3+}, and Yb^{3+}) and with an actinide (ion Th^{4+}) [82, 83]. The complexes stability was measured by potentiometric procedure; that of the complex Th^{4+} ion was greater than the stability of lanthanides complexes. The dominant role of electrostatic interactions in the binding process was demonstrated. The selectivity of complexing was measured for Yb/Eu on ligand **103** and for Th/Na on compound **104** [82].

In [43] was reported on the complexing of mono- and dioxacalix-[4]arenes **91** and **105** with cyclic and acyclic quaternary alkylammonium iodides. The association constants and free energies of formation were determined in $CDCl_3$ at 30°C for the arising complexes. For the monooxacalixarene **91** complexes the values of K_{ass}, l mol^{-1} ($-\Delta G^\#$, kcal mol^{-1}) lie within the limits 11–13 (1.44–1.54); for the complexes of dioxacalixarene **105** within 8–16 (1.2–1.66). The maximal values correspond to the complex of calixarene **91** with the trimethylammonium iodide and to the complex of calixarene **105** with *N*-methyl-1-azabicyclo[2.2.2]octylammonium iodide.

Outstanding complexing ability was found in dioxacalix[4]arene **106** modified at the lower rim by polyoxaethylene bridges towards quaternary ammonium salts in $CDCl_3$ and other organic solvents [24]. The $-\Delta G^\#$ values (kcal mol^{-1}) for complexes of calixarene **106** with tetramethylammonium acetate and picrate, *N*-methylpyridinium and *N*-methylpyrrolidinium iodides were 3.3, 4.3, 2.3, and 2.5 respectively. Apparently the efficient complex formation is due to acquiring by the ligand of a conformation with a parallel position of the polyoxaethylene bridges thus providing an inner cavity in a good agreement with the tetramethylammonium ion [84].



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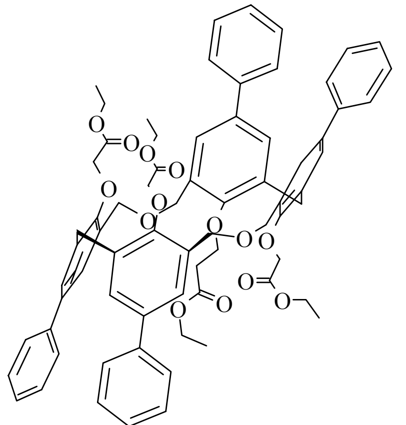

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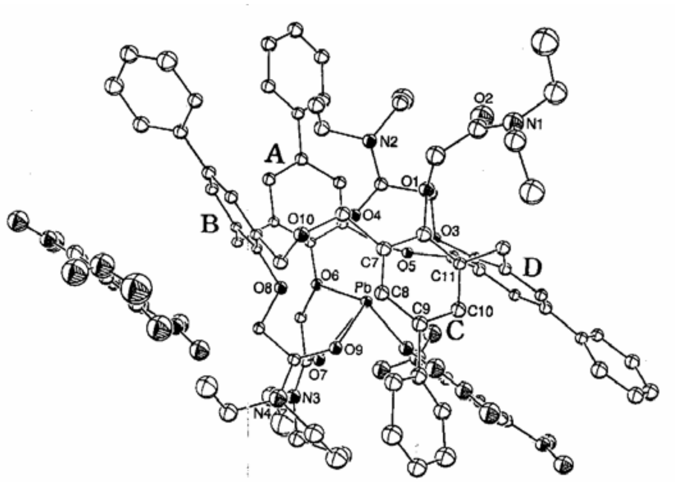
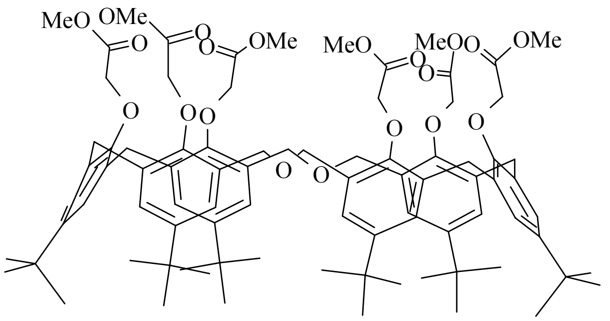


Fig. 20. Crystal structure of ligand **97** complex with lead pictures.

The complexing activity with respect to cations of alkali, alkaline-earth, and transition metals of dioxacalix[4]arene **97** tetraamide with phenyl substituents in the *para*-positions of the aromatic rings was investigated [85]. The comparison was carried out with the corresponding tetraethylacetate of dioxacalix[4]arene **107**. The data obtained showed the high activity of tetraamide **97** toward ions Pb^{2+} (*E* 37.59%); the arising complex was of 1:1 composition. *E* for cation Pb^{2+} with tetraethylacetate **107** was only 0.83%. The evaportion of a solution of Pb^{2+} picrate and ligand **97** in CH_2Cl_2–MeOH furnished a crystal of complex [(**97**)·Pb(Pic)$_2$], whose X-ray diffraction analysis demonstrated that the ligand in the complex was in the 1,4-*alt* conformation. The Pb^{2+} cation is linked to two oxygen atoms of the CO groups belonging to two neighboring amide substituents and to the ester oxygen atom in one of them. The metal ion is located over the center of one among the aromatic rings of the ligand due to cation-π interaction (Fig. 20).



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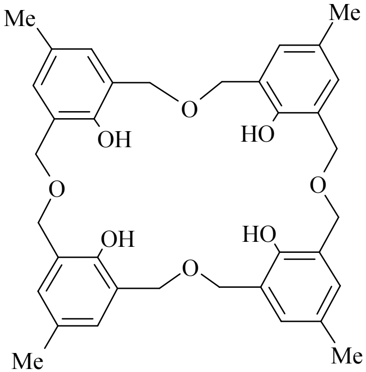
A preliminary study of complex formation with alkali metal cations was carried out with completely esterified dioxacalix[6]arene **108.** The complex formation with Li^+ and Na^+ions was observed, but K^+, Rb^+, and Cs^+ ions did not interact with the ligand [86]. The low extractive power of compound **108** was apparently due to the two large size of the macroring. The formation of a complex with the smallest Li^+ cation may be understood on assumption that ligand **108** operats as two-site receptor composed of two homooxacalix[3]arene subunits connected by ether linkers.

In 2001 dioxouranium complexes of five homooxacalixarenes **105, 109–112** distinguished by the number of phenol fragments and ether bridges in a macrocyle were prepared and characterized [87–89]. It proved that the composition and structure of the complexes depended on the structure of the original ligand.

Complex of dioxacalix[4]arene **105** with the uranyl cation was prepared from calixarene **105** and $UO_2(NO_3)_2 \cdot 6H_2O$ in a mixture MeCN–$CHCl_3$, 1:1, in the presence of Et_3N. Its composition corresponds to the for-



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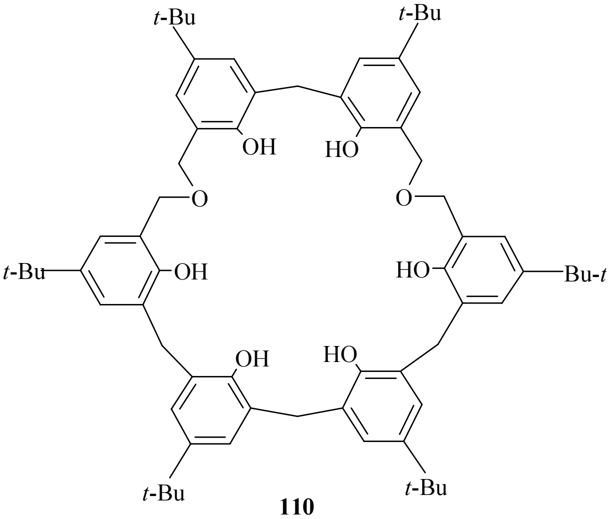

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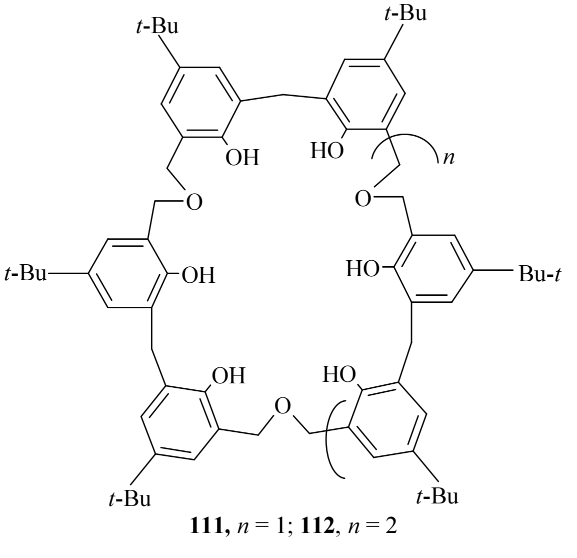


111, $n = 1$; **112**, $n = 2$

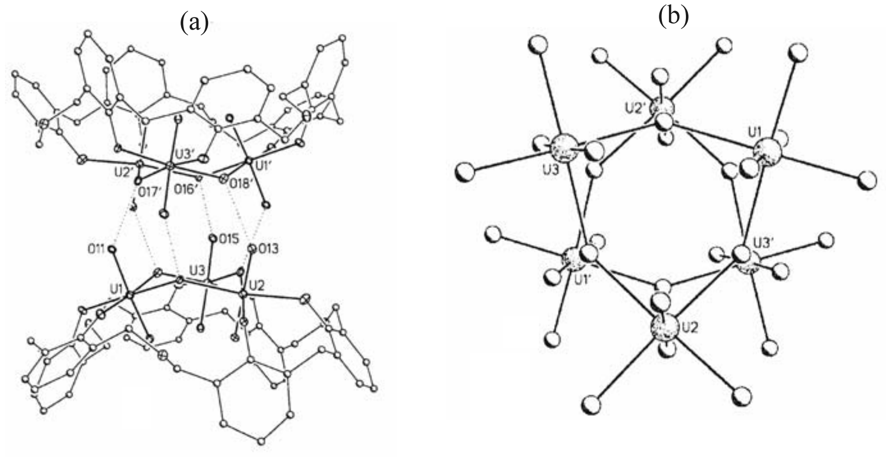


Fig. 21. Hexauranate claster resulting from autocomplementary character of two units $[(UO_2)_3(\mathbf{111}\text{-}6H)(OH)_3]^{3-}$ due to hydrogen bonds (a); appearance of the hehauranate claster (b).

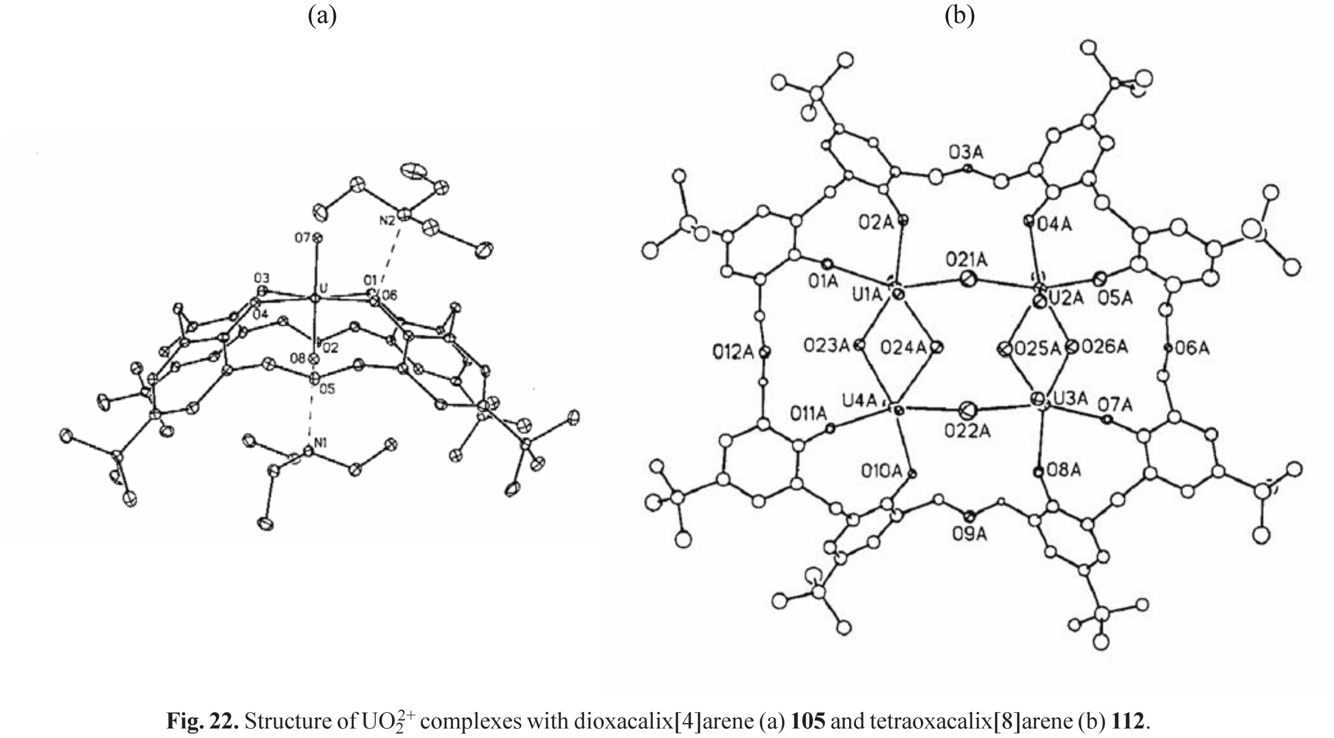


Fig. 22. Structure of UO_2^{2+} complexes with dioxacalix[4]arene (a) **105** and tetraoxacalix[8]arene (b) **112**.

mula $[UO_2(\mathbf{105}\text{-}4H)]^{2-}(HNEt_3^+)_2 \cdot CHCl_3 \cdot CH_3CN$ [87]. The conformation of the macrocycle changes in the course of complex formation, and the cation gets localized in the center of the lower rim and i.e.connected to four deprotonated oxygen atoms [mean distance U–O 2.28(3) Å] [87].

Tetraoxacalix[4]arene **109** formed complex $[C_5H_5N][(UO_2)_2(\mathbf{109}\text{-}4H)(OH)(H_2O)] \cdot 2.5\ C_5H_5N$ with two UO_2 moieties coordinated by the phenoxide and ether oxygen atoms [88]. In a complex of dioxacalix[6]arene **110** $[HNEt_3]_2[UO_2(\mathbf{110}\text{-}4H)] \cdot 3CH_3CN$ the UO_2 moiety is fixed by four phenoxide oxygen atoms [88].

Uranate complexes were obtained from trioxacalix[6]arene **111 [89]** whose size corresponded approximately to the dimensions of "classic" *p-tert*-butylcalix[9]arene [80]. From the uranyl nitrate hexahydrate and the selected ligand (L) two complexes were obtained with an identical anionic part $[(UO_2)_3(L\text{-}6H)(OH)_3]^{3-}$ a and a cationic part depending on the solvent used. The calixarene fragments of the complexes were in a distorted *cone*-conformation. The bridging O atoms do not partake in the uranate center coordination. The most interesting is the discovery of the "self-complementarity" of the two units in each of the trinuclear complexes obtained. As a result a supramolecular system is formed: a hexauranate claster surrounded by two divergent macrocycles connected by six hydrogen bonds OH···O (oxo) of the length 2.79(5) Å (Fig. 21a). The claster possessed the S_3-symmetry, and the U atoms were located in the apexes of a trigonal antiprism (Fig. 21a). Before the publication of [89] no such self-complementarity phenomenon was known in the coordination chemistry of uranium.

Finally, the complex of the largest ligand, tetraoxacalix[8]arene **112**, includes four UO_2 fragments $\{[HNEt_3]_2[(UO_2)_4(\mathbf{112}\text{-}8H)(OH)_2(H_2O)_4]\cdot 1.5\ NEt_3\cdot 2.5\ H_2O\}$ and possesses a unique structure [88]. It represents a tetrauranate cluster containing both double and single oxygen bridges between uranium atoms coordinated only by deprotonated phenol fragments (Fig. 22).

As regards the complex formation with neutral molecules, it was reported in [90] on formation of a solvate of dioxacalix[4]arene **105** with one molecule of $CHCl_3$ and one molecule of THF. Here the calixarene was in a *cone*-like conformation stabilized by intramolecular hydrogen bonds involving both phenol and ether oxygen atoms. Two molecules of the solvent are located in each of the two parts of the crown (Fig. 23).

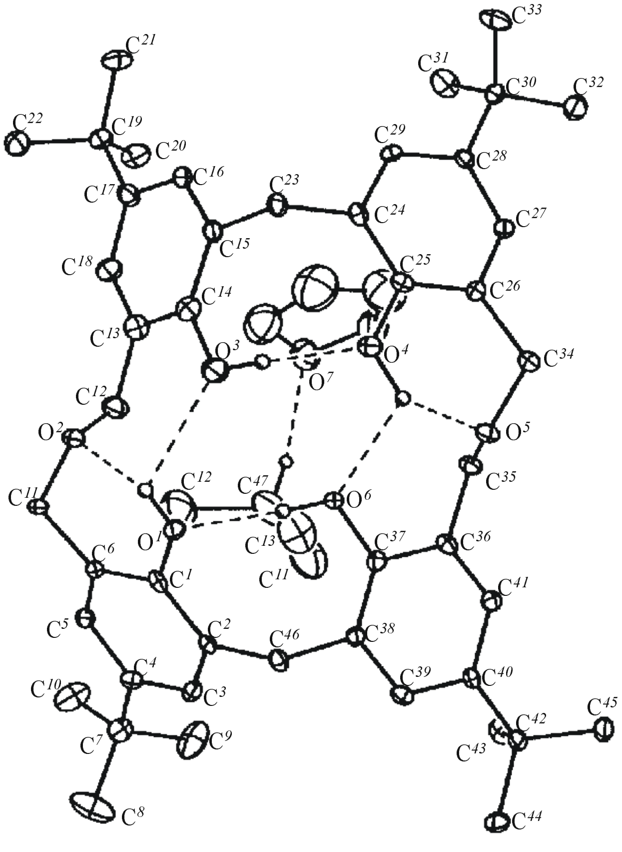
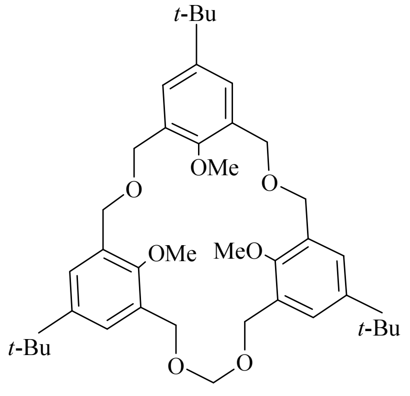


Fig. 23. Dioxacalix[4]arene **105** soluate structure with molecules $CHCl_3$ and THF.

Complex [**105**·$2CH_3CN$] [79] exists in a highly distorted *cone*-conformation fixed by the intramolecular hydrogen bonds between phenol and ether groups. The depth of the cavity was sufficient to include two molecules of CH_3CN. The conformation of complex [**105**·$2.5C_5H_5N$] [87] is similar to that of the complex with CH_3CN but differs in surrounding of the ether O^5 atom resulting in slight expansion of the macrocycle.

4. RECEPTOR PROPERTIES OF HOMOOXACALIXARENE ANALOGS

Analogs of oxacalixarenes, heptahomotetraoxacalix[3]arenes and hexahomotrioxacalix[3]naphthalenes, were first synthesized in 2001. Their receptor activity was tested at once. The extraction (%) of alkali metal cations from the water phase into CH_2Cl_2 with the help of calixarene **113** was as follows: 1.3 (Li^+), 3.3 (Na^+), 7.2 (K^+), 8.5 (Rb^+), and 9.5 (Cs^+) [91].



113

The complexing of C_{60}-fullerene with oxacalixnaphthalenes **25** and **26** was described in Section **1**. A preliminary study of the receptor properties of these compounds [92] with respect to ions Ag^+ and alkali metal cations showed their weak activity and stronger affinity of derivative **26** to cations K^+ and Cs^+.

CONCLUSION

The extremely high intensity of research in the field of calix[*n*]arene chemistry within the last two decades in all industrially developed countries suggests that an independent field of supramolecular chemistry came into existence. The unique features of calixarenes possessing a developed hydrophobic cavity and capable of versatile modification, in particular, conformational, ensures the feasibility of their application to preparation of highly efficient and selective receptors for metal cations, anions, and neutral molecules.

Most recently heterocalixarenes are extensively involved into studies [93]. The presence of a heteroatom instead of a CH_2 bridge affects the size of the calixarene cavity, the symmetry of the molecule, its receptor properties, and becomes an additional "recognition" center. In a recently published review [94] we showed that the application of thiacalix[*n*]arenas are extremely promising for building up new types of selective receptors, especially for metal cations. The present review demonstrates that the research in this field using oxacalix[*n*]arene is important and necessary. The reported data on complex formation with fullerene and ammonium salts is a spectacular confirmation of the above statement.

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