PRACE NAUKOWE Akademii im. Jana Długosza w Częstochowie
Seria: CHEMIA I OCHRONA ŚRODOWISKA z. IX, 2005, ss. 77–95

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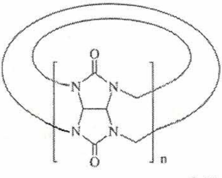
CUCURBITURILS AS MOLECULAR CONTAINERS COMPARABLE TO CYCLODEXTRINS

Abstract: In the paper cucurbiturils (CB) are presented showing their similarities and differences as compared to cyclodextrins (CD). The first part concerns host-guest complexes of CBs, then CB interlocked systems and molecular machines are described, followed by CD derivatives.

Introduction

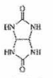
Cucurbiturils (CB) are a new class of thermally and chemically robust macrocycles consisting of 5-10 glycoluril units, the most studied among them being CB6. Cucurbiturils CB6, CB7 and CB8 have similar cavity sizes as α-, β- and γ-cyclodextrins (CDs), respectively. CBs, however, have two identical portals, contrary to CDs, in which portals (i.e. upper and lower rims) are of a different diameter.

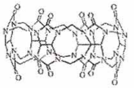


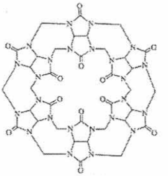
n = 5-10

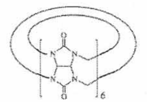
cucurbiturils

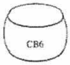
The building unit of CBs, *i.e.* glycoluril, and CB6 presented in various ways, as well as the building unit of CDs, *i.e.* α-D-glucose, along with α-CD, shown in different ways, are given below.

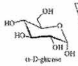

glycoluril

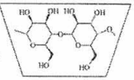


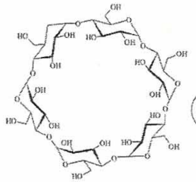

cucurbit[6]uril
CB6

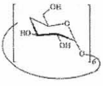





α-D-glucose






α-cyclodextrin
α-CD

In the continuation of our research concerning CDs [1-5] we present here CBs, comparing their properties to those of CDs, as the other commercially useful class of molecular containers; similarities and differences of CBs and CDs will be described.

CBs are obtained by condensation of glycolurils [6] with formaldehyde. Chemistry of CBs is developing rapidly, a great number of reports concerning this topic appears, [7-13] and has its reflection in detailed reviews. [14-16] The present paper concerns only selected, the most representative examples.

Hydrophobic cavities of CBs enable the inclusion of hydrocarbon molecules, similarly as in the case of CDs. However, unlike as in CDs, the polar carbonyl groups at the portals allow CBs to bind neutral molecules and ions *via* CT (charge transfer) and hydrogen bonding interaction.

The hollow structure of CBs and the variety of their sizes are promising for their applications as containers for inclusion or delivery of guest molecules. CBs may serve as encapsulation and delivery systems for drugs, herbicides and fragrances; they enable controlled delivery and slow release of drugs. They selectively bind gases such as O_2, CO, NO and can serve for removal of wastes from either gas or liquid streams, and of volatile organic molecules from air, offering an environmental clean-up.

CBs are promising for separation technologies, e.g. for chromatography as well as for storage and transport of volatile or unstable materials. It is important that CBs may be produced in commercially viable quanitities, with a cost comparable to that of CDs.

For example, CB6 is used in catalytical processes and in design of polyrotaxanes [17-19] and fluorescent materials, [20] it may serve for the removal of dyes from textile wastewaters; [21] CB7 has been used in the investigation of complexes. [22-24]

1. Host-guest complexes of CBs

Host-guest chemistry of CBs involves properties of their hydrophobic cavity and polar carbonyl groups surrounding the portals. CB5, which has the smallest cavity encapsulates small molecules, e.g. N_2, O_2, Ar. It strongly binds NH_4^+ and Pb^{2+} at the portals. Two NH_4^+ ions may completely seal both portals of CB5.

CB6 forms, unlike α-CD, very stable complexes with protonated diaminoalkanes $H_3^+N(CH_2)_n^+NH_3$; n = 4–7 and moderately stable complexes with protonated aromatic amines such as p-methylbenzylamine. It can also encapsulate neutral molecules, e.g. THF or benzene in aqueous solutions.

CB7 forms complexes with larger guest molecules, for example with protonated adamantylamine, with viologen and with ferrocene. The cavity of CB8 is larger, it can encapsulate cyclen, cyclam, or two different guests, e.g. viologen with 2,6-dihydroxynaphthalene.[14]

The carbonyl portals of CBs bind guests by hydrogen bonding as well as by charge-dipole interaction and are able to coordinate metal ions. However, CDs bind guests mainly *via* hydrogen bonding through their hydroxyl groups. CBs preferentially bind positively charged guests, while CDs favor neutral guest molecules.

The mechanism of the inclusion of cyclohexylmethylammonium ion **1** into the CB6 cavity has been investigated in aqueous solution, in the presence of cations [25-27]. So, there are two binding partners – the organic ammonium guest and the inorganic cation.

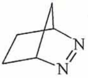
In the study of guest inclusion into CBs cavities in the presence of salts it was observed that the complexation of metal ions at the portals, which is often necessary to enhance solubility, can lead to ternary complexes consisting of host, included guest and associated metal ion. It is suggested that the ions act as "lids" sealing portals.

CBs show two distinct supramolecular interactions: a hydrophobic effect, favoring inclusion of organic residues and ion-dipole interactions at the carbonyl-fringed portals, which promote binding of either cationic sites of organic guests (ammonium salts) or of inorganic cations. Cations may serve as "lids" sealing the portal. An uncharged guest may enter the cavity directly, but an organic ammonium cation at first coordinates with the portal to form an association complex, and then the organic moiety enters the cavity.

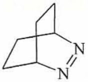
Many molecular containers such as CDs and calixarenes allow a fast exchange of the guest, due to their large portals. Carcerands and hemicarcerands, however, have high barriers toward guest exchange; often an elevated temperature is necessary for their surmounting. This phenomenon, called a constrictive binding is found also in CBs, since their portals are tight, they have diameter of only ca 4 Å. The complexation of CB6 is much slower than that of CDs or calixarenes which have large portals; its kinetics resembles that of complexation of carcerands.

CB6 includes **1** to give CB6·**1** in which the chair conformation of **1** with the equatorial methylammonium group is retained. The methylene group of **1** protrudes from the CB cavity, and the ammonium ion interacts with portal carbonyl groups. The cyclohexyl group is deeply immersed in the CB6 cavity[25].

1

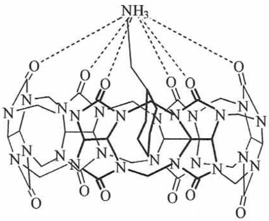


DBH



DBO

DABCO



CB6·**1**

CB6 includes also 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) in D_2O/ 0.2 M Na_2SO_4. It is interesting that CB6 encapsulates DBH only in the presence of sodium, but not with the heavier alkali ions; this observation confirms the important influence of the metal cation on the complexation process. CB6 does not form inclusion complexes with larger guests, such as 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) or 1,4-diazabicyclo[2.2.2]octane (DABCO).

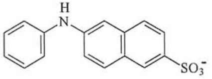
The above described host-guest complexation processes occurring in the presence of metal ions are promising for use of CBs for binding of metals, e.g. in the removal of contaminants from water.

CB7 forms the fluorescent inclusion complex with DBO. This complex has a very long-lived emission and may serve as an enhancer in time-resolved fluorescence-based assays, e.g. for screening the enzyme activity by using DBO -labeled peptides [28].

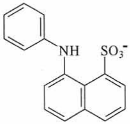
Complex stabilities and thermodynamic data for the complexation of CB6 with amino acids, such as L-alanine, L-valine, L-phenylalanine, 6-amino hexanoic acid, 8-amino octanoic acid, 11-amino undecanoic acid and with dipeptides, such as glycyl-glycine, glycyl-L-valine, glycyl-L-leucine and glycyl-L-phenylalanine have been determined by calorimetric titrations in aqueous solution [26].

Complexes of CB6 with amino acids are formed by ion–dipole interactions between carbonyl groups of CB6 and the protonated amino groups of the amino acids. Complexes of CB6 and α-CD with dipeptides are characterized by hydrophobic interactions, and in the case of CB6 also by additional ion-dipole interactions. Stabilities of complexes formed by CB6 and α-CD have comparable values.

It was observed the fluorescence enhancement of 2-anilinonaphthalene-6-sulfonic acid (2,6-ANS) **2** and 1-anilinonaphthalene-8-sulfonic acid (1,8-ANS) **3** when they are complexed with CB7.


2,6-ANS

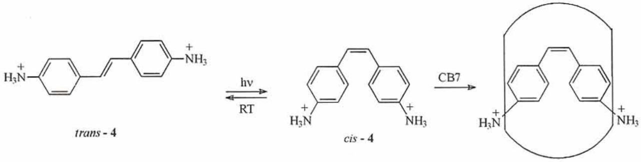
2


1,8-ANS

3

CB7 forms 1:1 host-guest complex with **2** in which the phenyl moiety of **2** is immersed into CB7 cavity. However, in the case of **3** the host-guest system does not exist, instead the 2:1 complex of CB7 with **3** is formed, in which **3** is sandwiched between the outer surfaces of two CB7 molecules [29].

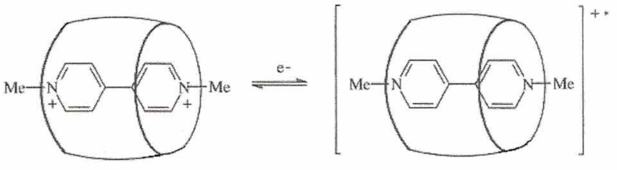
CBs can stabilize unstable compounds by encapsulation. As an example may serve *cis*-diprotonated diaminostilbene **4**; it is formed from *trans*-**4** by UV irradiation, and in the dark slowly returns to the *trans* form. However, when *cis*-**4** is encapsulated in CB7, its conversion into the *trans* form is impossible [14].



trans - **4**

cis - **4**

CB7 forms with viologen and its derivatives host-guest complexes in which viologens and their cation radicals are guests [24]. Such **5a,b** complexes for viologen are shown below.



5a

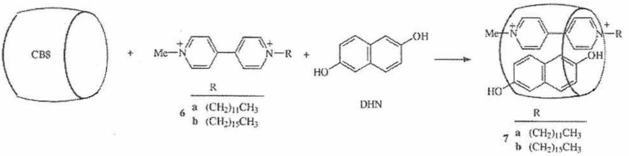
5b

It was found that CB7, unlike β-CD, prefers charged species, e.g. dication MV^{2+} and cation radical $MV^{+\bullet}$ over the neutral MV^{o} as a guest [30]. CB8 forms a 1:1 host-guest complex with MV^{2+} in spite that its cavity is large enough to encapsulate two MV^{2+} molecules.

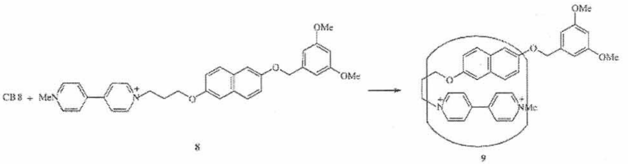
The sonication of CB8, a viologen with a long alkyl chain **6a,b** and 2,6-dihydroxynaphthalene (DHN) in H_2O affords stable ternary complexes **7a,b**.[31] These complexes are held by CT interaction between the electron-deficient and electron-rich guest molecules, accomodated inside the hydrophobic CB8 cavity.

They form large vesicles (an average diameter for **7b** is 870 nm), as it was confirmed by TEM and SEM images (TEM=transmission electron microscope; SEM = scanning electron microscope). The vesicles are robust; when dried on a solid surface they maintain their spherical shape.

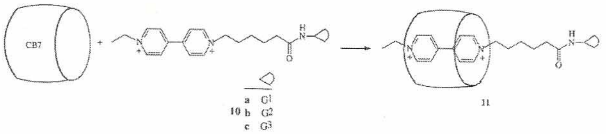
Since viologen and DHN are redox active, the reduction of viologen or oxidation of DHN results in the loss of charge transfer interaction between two guests, followed by the destruction of the host-guest system. This behavior has been confirmed by the oxidation of DHN with ceric ammonium nitrate (CAN) to naphthoquinone; in this case the vesicles collapse [31].

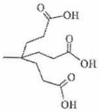


The complexation of CB8 with a guest molecule **8**, containing both an electron donor and an electron acceptor moieties has been investigated. The formed complex **9** has a folded structure; its intramolecular CT interaction has been host induced [32].

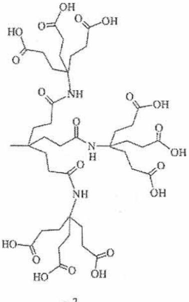


The host-guest interaction of CB7 with Newkome type viologen dendrimers **10a-c** affords complexes **11** [33]. The viologen dendrimers **10a-c** are water soluble. The binding constants of CB7 with **10a** and **10b** are higher than in the case of **10c** due to steric reasons.

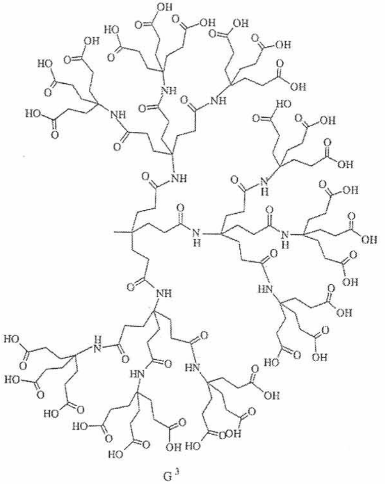




G^1

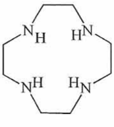


G^2

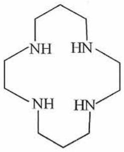


G^3

Host-guest systems of CB[8] with cyclen and with cyclam have been obtained. They can be metalated by Cu(II) and Zn(II) ions; these metal ions are complexed within cyclen or cyclam molecules. For example, the reaction of CB8 and cyclen tetrahydrochloride gives 1:1 host-guest system; four Cl^- anions are localized outside CB8. The metalation of this host-guest system with $Cu(NO_3)_2$ affords crystalline species in which Cu^{2+} ion is encapsulated inside the cyclen molecule [34].



cyclen



cyclam

One should mention here the gyroscane, *i.e.* CB10 encapsulating CB5; the name gyroscane originates from the independent rotation of CB5 inside CB10, resembling that of a gyroscope [35].

Other complexes of CBs

Numerous complexes of CBs with metal ions are known. They are formed due to the presence of carbonyl groups directed towards the centre of each portal and are held by ion–dipole and by hydrophobic interactions.

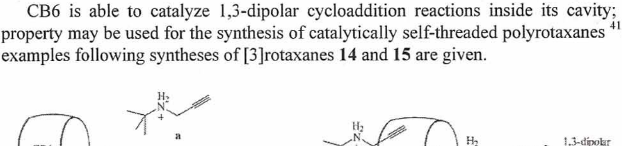
The complexation of CB6 with lanthanide ions La (III), Ce (III), Pr (III), Nd (III), Sm (III), Eu (III), Gd (III), Tb (III), Dy (III), Ho (III), Er (III), Tm (III), Yb (III) and Lu (III) has been studied in water and in aqueous formic acid [36].

Stability constants of complexes of CB5 and CB6 with Co(II), Ni(II), Cu(II), Pb(II), Zn(II), Cd(II), Cr(III) and Fe (III) have been determined in aqueous solution [37]. It was found that the measurement of the total organic carbon content can be used for the determination of stability constants of the above complexes. Among the metals investigated the most stable complex proved to be that of CB6 with Cd(II).

Crystalline adducts of CB6 with seleno bridged triangular cluster $Mo_3Se_4(aq)^{4+}$ have been obtained in HCl solution; depending on HCl concentration, 2M and 6M, the adducts $\{[Mo_3Se_4Cl(H_2O)_8]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_6 \cdot 16H_2O$ and $(H_3O)_2[Mo_3Se_4Cl_5(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12}) \cdot 15H_2O$ where $(C_{36}H_{36}N_{24}O_{12})$ is CB6, respectively, are formed [38].

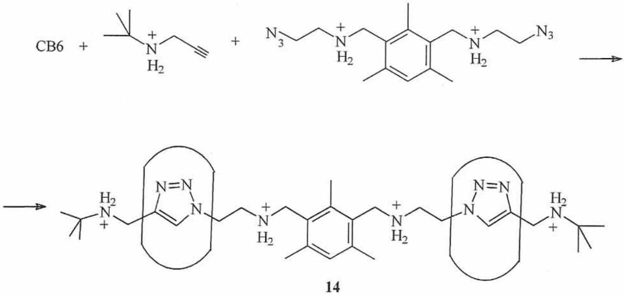
CB6 reacts with clusters $[W_3S_4(H_2O)_6Cl_3]^+$ and $[W_3(SbCl_3)S_4(H_2O)_6Cl_3]^+$ to give cluster·CB (2:1) adducts in which two CB6 portals are closed by two cluster cations [39].

CBs may mediate chemical reactions, *e.g.* cycloadditions. The following highly stereoselective (2+2) photocycloaddition of *trans*-diprotonated diaminostilbene **4** occurs in the cavity of CB8. When the aqueous solution of CB8 and *trans*-**4** is UV irradiated, the host-guest complex **12** is formed; subsequent removal of CB8 affords the cycloadduct **13** [40].



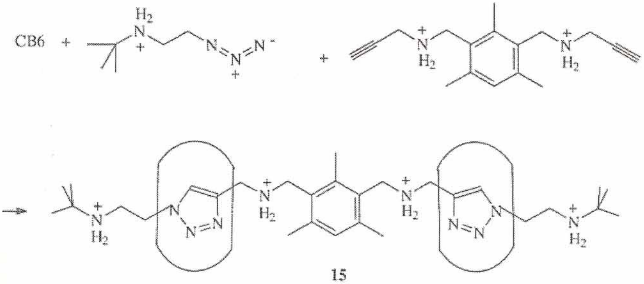
CB6 is able to catalyze 1,3-dipolar cycloaddition reactions inside its cavity; this property may be used for the synthesis of catalytically self-threaded polyrotaxanes [41]. As examples following syntheses of [3]rotaxanes **14** and **15** are given.

Synthesis of [3]rotaxane **14**:



14

Synthesis of [3]rotaxane **15**:

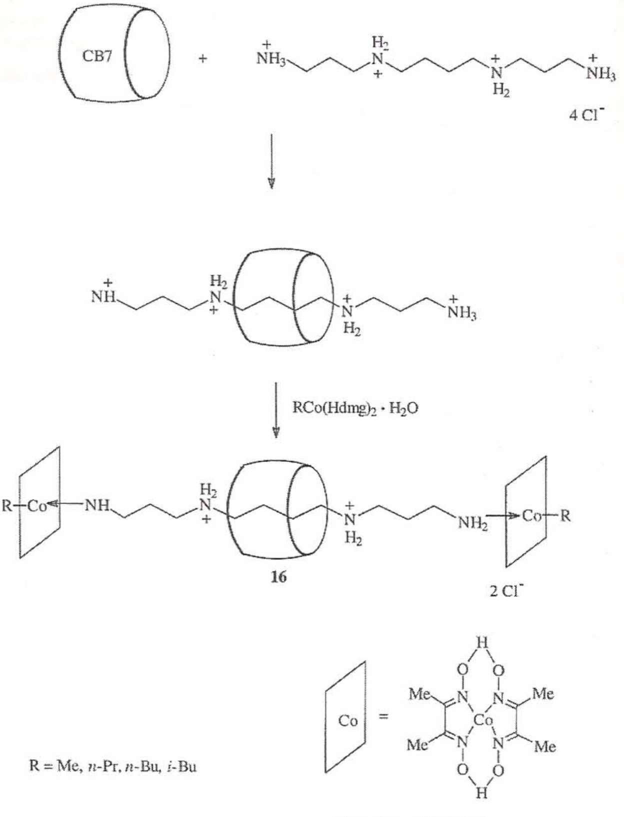


15

The subsequent dethreading of [n]semi- or [n]pseudorotaxanes allows to isolate regioselectively pure 1,3-disubstituted triazoles.

2. CB interlocked systems

CBs are components of interlocked species, such as rotaxanes and molecular necklaces. An example of CB-based rotaxane in which metal complexes serve as stoppers is **16** obtained as shown below [42]. These rotaxanes have been studied as coenzyme B_{12} models.

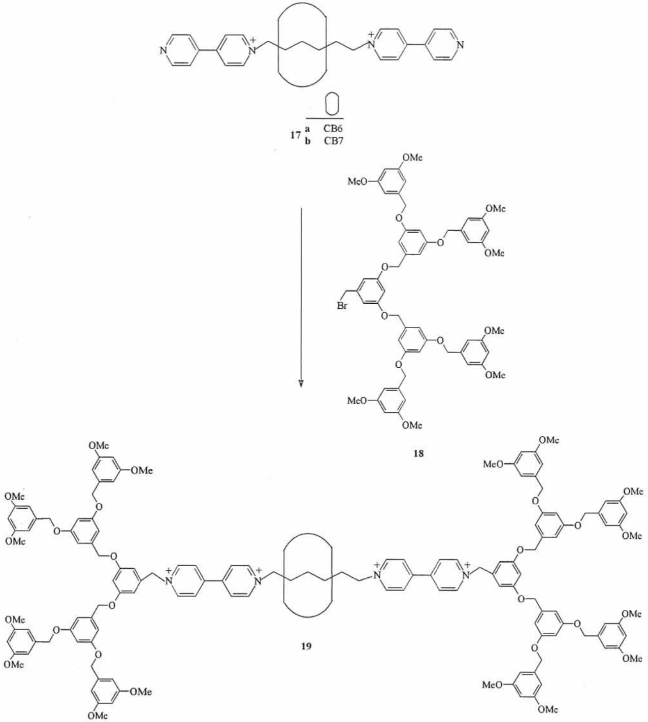


16

R = Me, *n*-Pr, *n*-Bu, *i*-Bu

cobaloxime = $Co(Hdmg)_2$

Reaction of pseudorotaxanes **17a,b** with Fréchet dendron **18** leads to rotaxanes **19** containing Fréchet dendrons as stoppers [15].

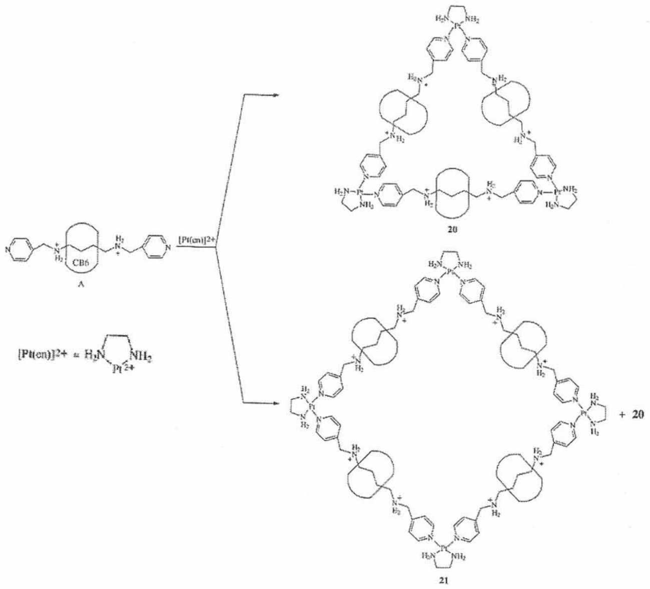


17 **a** CB6
b CB7

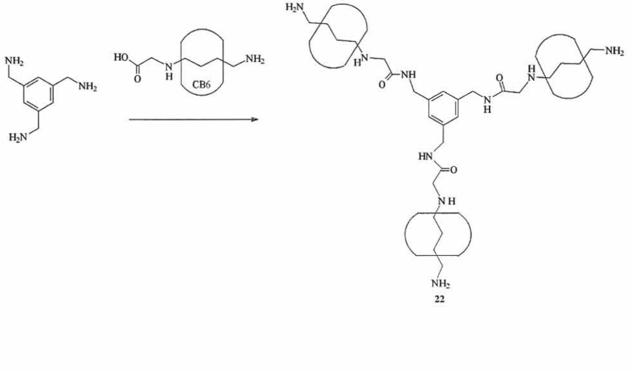
18

19

Examples of molecular necklaces are **20** and **21** synthesized as shown below [43].

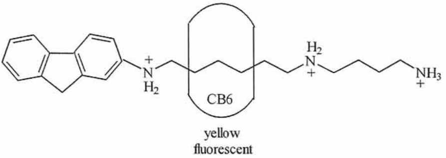


An example of a dendritic CB6 pseudorotaxane is **22**, obtained as follows[15].

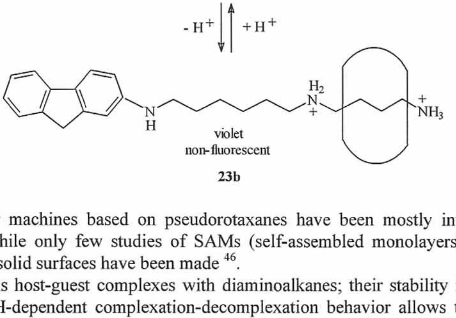


3. CB molecular switches and machines

Rotaxanes in which the position of the ring can be changed by external stimuli such as temperature, pH, redox reactions, photo- or electrochemical processes are promising for the construction of molecular switches and machines. An example of a molecular switch containing CB6 is **23**, changing its color and fluorescence intensity with pH[44].



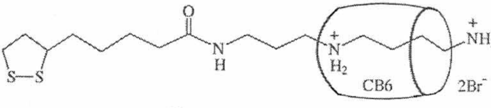
23a



23b

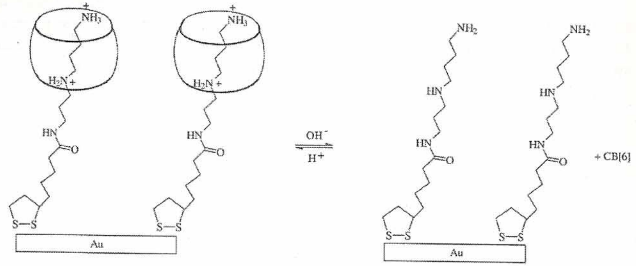
Molecular machines based on pseudorotaxanes have been mostly investigated in solution[45] while only few studies of SAMs (self-assembled monolayers) of pseudorotaxanes on solid surfaces have been made[46].

CB6 forms host-guest complexes with diaminoalkanes; their stability is pH-dependent. This pH-dependent complexation-decomplexation behavior allows to synthesize pseudorotaxane-based molecular machines working in solution[12].



24

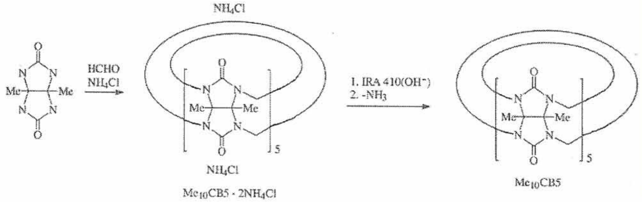
In order to design a molecular machine working on gold surface, the pseudorotaxane **24** was used. This species is composed of the CB6 ring and a thread. The thread possesses a diaminobutane unit as a station for CB6 and a 1,2-dithiolane group as an anchoring point towards a gold surface. Immersion of a gold substrate in water containing **24** leads to the formation of SAM. By soaking SAM in the NaOH solution the dethreading of CB6 takes place, and in the presence of NH_4Cl the rethreading occurs; due to this reversible process the pseudorotaxane acts as a molecular machine [47].



4. CB derivatives

CB derivatives are **a**) decamethylCB5, **b**) cyclohexane$_5$CB5 with cyclohexane$_6$CB6, and **c**) diphenylCB6, as well as **d**) perhydroxyCBs.

a) Synthesis of decamethylCB5, *i.e*Me_{10}CB5, or abbreviated MeCB5 from glycoluril proceeds as follows:



25

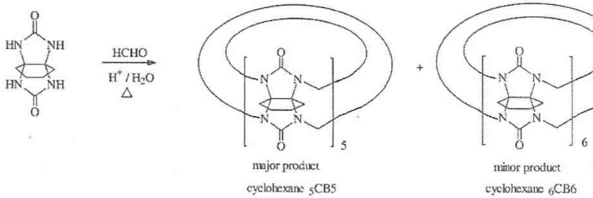
The adduct **25** is a complex MeCB5·2NH_4Cl containing two NH_4Cl lids at portals. The NH_4Cl lids may be removed from **25** by converting it into the hydroxide using Amberlite IRA 410 ion-exchange resin (OH^- form), and then heating in vacuo to expel NH_3.

MeCB5 binds metal ions, showing very high affinity for Pb^{2+} ion. Complexes of MeCB5 with NH_4^+ or metal ions may encapsulate gases in solution, but they are inactive in the solid state. However, when the lids (NH_4^+ or metal ions) are removed, then MeCB5 behaves as a molecular sieve in the solid state [48].

Gases such as N_2, O_2, Ar, N_2O, NO, CO and CO_2 may be absorbed and released by MeCB5 repeatedly. It should be pointed out that gases are encapsulated in the molecular cavity of MeCB5 and not in the lattice space as in zeolites.

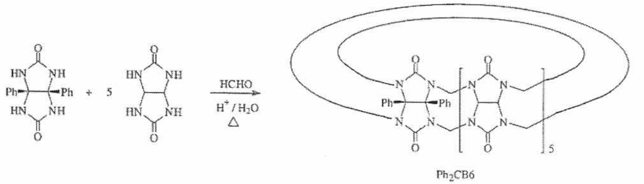
Due to these properties MeCB5 finds practical applications for the decrease of the level of CO_2, N_2O and NO in air, and it can be qualitavely regenerated by re-crystallization. For example, the high level of CO_2 (5%) in air may be decreased (to 0.01%) in 1 hour by circulating the air through a powder of MeCB5 (the fresh air has 0.035% CO_2).

b) The reaction of cyclohexaneglycoluril and formaldehyde leads to cyclohexane$_5$CB5 and cyclohexane$_6$CB6. It should be pointed out that they are soluble in common solvents such as water, methanol, DMF and DMSO [49].



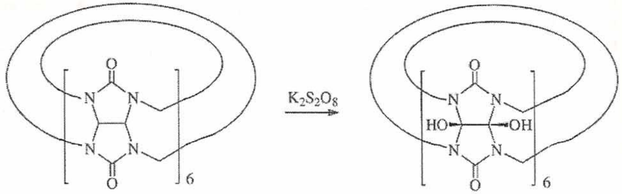
Cyclohexane$_6$CB6 forms in water at pH7 a stable 1:1 host-guest complex with acetylcholine while it does not interact with choline. Therefore cyclohexane$_6$CB6 behaves like an artificial receptor which can differentiate acetylcholine from choline, this fact being of interest for its application in neuroscience.

c) DiphenylCB6, *i.e.* = Ph_2CB6, promising in view of its functionalization in the phenyl rings [50] has been obtained as follows [50].



d) The synthesis of cucurbituril derivatives *via* direct functionalization has been made[51].

It was observed that CB6 reacts with $K_2S_2O_8$ to give perhydroxyCB6, *i.e.* $(HO)_{12}$CB6 as a potassium complex. This CB derivative is soluble in DMSO and moderately soluble in DMF.



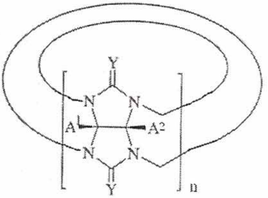
CB6 $(HO)_{12}CB6$

In the same way CB homologues (CBn, n = 5, 7 and 8) have been functionalized to give $(HO)_{2n}CBn$ (n = 5,7,8). Reactions proceed easily; the obtained perhydroxyCBs may be further functionalized, *e.g.* to give esters, ethers or thioethers.

The CB derivatives bearing different functional groups are promising for use in various fields, such as transport, drug delivery, catalysis; they may serve in the design of sensors, artificial ion channels and nanomaterials.

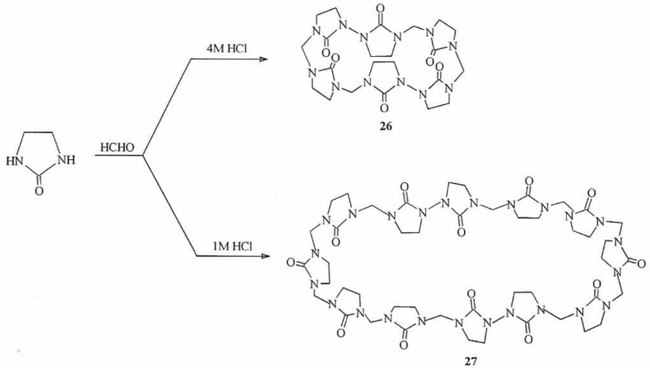
The functionalization of perhydroxyCB derivatives leads to derivatives soluble in common solvents, promising for application in drugs, cosmetics, agrochemicals and in the wastewater treatment [52].

Following derivatives of CBs and of their analogues have been obtained.

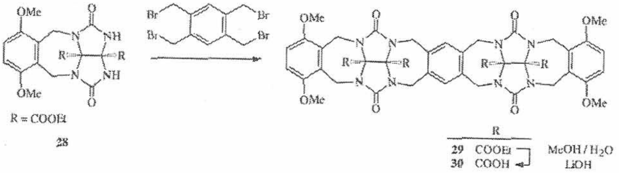


A^1, A^2 = OH, (un)substituted, C_{1-30} alkoxy,
C_1-C_{30} alkenyloxy, C_{2-30} carbonylalkoxy,
C_1-C_{30} thioalkoxy, C_{1-30} aminoalkoxy
$A^1 = A^2 = H$; Y = O,S,NH; n = 4-20

One should mention here also hemiCBs and acyclic CBs. In order to synthesize hemiCBs, reactions of ethylene urea with formaldehyde in 4M and 1M HCl have been made, affording hemiCB6 and hemiCB12, respectively, the former being a receptor molecule, *e.g.* for propargyl alcohol, and the latter acting as a gelating agent [53].



The reaction of glycoluril derivative **28** with tetrakis(bromomethyl)benzene proceeds *via* the ester **29** to give acyclic cucurbituril **30**. It was established that **30** binds diols, diacids and diamines [54].



Concluding remarks

Since the number of reports concerning cucurbiturils is enormous, in the above review only selected examples have been presented.

This area of chemistry develops rapidly in recent years [55], interesting properties of cucurbiturils being promising for their applications in various fields.

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KUKURBITURILE JAKO MOLEKULARNE RECEPTORY PODOBNE DO CYKLODEKSTRYN

Streszczenie: W artykule przedstawiono kukurbiturile w porównaniu z cyklodekstrynami. W pierwszej części omówiono układy typu gość-gospodarz, następnie molekularne przełączniki i maszyny, a w końcowej części scharakteryzowano pochodne kukurbiturili.