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The formation of homogeneous and heterogeneous 2:1 complexes between dialkyl- and diarylammonium ions and α-cyclodextrin and cucurbit[6]uril in aqueous formic acid

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ABSTRACT

Dialkyl- and diarylammonium ions are able to form complexes with α-cyclodextrin and cucurbit[6]uril. These amines are able to complex two guest molecules simultaneously resulting in the formation of homogeneous or heterogeneous 1:2 (ratio of dialkylammonium to ligand) complexes. The stability constants and reaction enthalpies for the formation of 1:1 complexes have been measured using potentiometric and calorimetric titrations. Differences between the values obtained by these methods can be attributed to solvent composition. Only for the 1:2 complex formation with cucurbit[6]uril, the ligands influenced each other. The polar carbonyl groups at each portal of the cucurbit[6]urils interacted simultaneously with the protonated amino group resulting in an electrostatic repulsion between both molecules. No further interactions between two complexed molecules of α-cyclodextrin or cucurbit[6]uril and α-cyclodextrin were observed. The absence of polar groups in the case of α-cyclodextrin led to unaffected formation of homogeneous and even heterogeneous 1:2 complexes.

1. Introduction

The term "molecular architecture" was first used by Pauling to describe molecular structure and intermolecular reactions in living systems [1]. With the advent of supramolecular chemistry in the late 60s, quite sophisticated supramolecular assemblies featuring virtually unlimited architectural designs have emerged as well [2]. By using the template strategies based on different kinds of non-covalent interactions, some desired supramolecular architectures have been obtained ever since.

Starting with the selective complexation of alkali and alkaline earth cations [3,4], the principle of selective recognition between molecules or molecules and cations has been used for the formation of highly ordered structures like rotaxanes [5], catenanes [6], pretzelanes [7], or helicates [8]. Further investigations have led to more interesting superstructures involving a catenane made of four molecules [9] and a four-fold [2]rotaxane [10]. Even Borromean rings formed from a large number of molecules have been synthesized in the last years [11]. Without the understanding of the selective recognition between molecules [12–19], all these substances could not be synthesized unless extreme expense. Thus, the first rotaxanes have been synthesized in multiple steps with low yields using conventional methods [20]. Mechanically interlocked molecules such as rotaxanes, catenanes, and knots of interest through their topology have been employed for the construction of molecular machines in nanotechnological applications [21,22]. Reversible molecular encapsulation has been a central issue in recent studies as well [23]. Likewise, an exhaustive investigation of several kinds of self-organisation on the molecular level was published by Schmittel and Kalsani [24]. Even though the concept of multivalency has been used in supramolecular chemistry for many years, different aspects of application of multivalency in supramolecular chemistry and nanosciences have recently been the subjects of systematic research [13,25,26].

Based on their high potential ability in molecular recognition, self-assembly, and nanotechnology, the α-, β-, and γ-cyclodextrins and cucurbit[*n*]urils ($n = 5–10$) have been the subject of intensive investigation in supramolecular chemistry. The chemical structures of cucurbit[6]uril and α-cyclodextrin are shown in Fig. 1. Quite often, the cyclodextrins have been used as building blocks in supramolecular assemblies such as rotaxanes and polyrotaxanes [27–29]. The cucurbit[*n*]uril has a rigid hollow hydrophobic cavity that is able to accommodate suitable guests. This cavity is accessible through two carbonyl portal openings. The complex formation of cucurbit[*n*]uril with various guests is characterized by hydrophobic forces, van der Waals interactions, and ion-dipole interactions [30–34]. Comparable dimensions of cavity size between α-, β-, and γ-cyclodextrins (5.3–8.3 Å diameter) [35] and cucurbit[*n*]urils,

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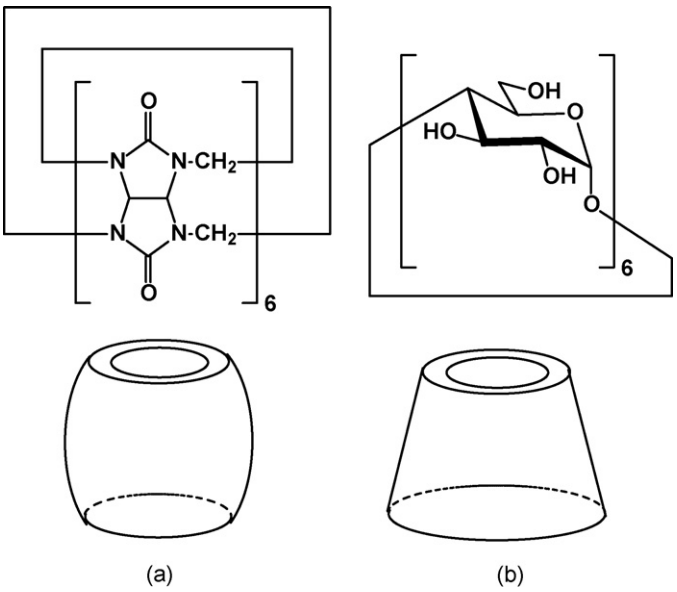


Fig. 1. Chemical structures of cucurbit[6]uril (a) and α-cyclodextrin (b).

n = 6–8 (5.8–8.8 Å diameter) [30], along with large area of applications constitute their common features. The aspects of interest in host–guest complexes of cyclodextrin and cucurbit[n]uril as host molecules with amino compounds have recently emerged in literature on the basis of their attractive properties [36–38]. Previously, it was also shown that a simple molecular architecture can be achieved by using alkylamines, α-cyclodextrin and 18-crown-6 in aqueous solution [39].

In this paper, α-cyclodextrin (α-CD) and cucurbit[6]uril (Cuc[6]) are used as host molecules for complex formation with different dialkyl- and diarylammonium ions. Up to now, in the literature only the reaction between these macrocyclic ligands and dihexylammonium has been studied and the stability constants and thermodynamic values have been reported. The formation of a 1:1:1 ternary complex between dihexylammonium, cucurbit[6]uril and β-cyclodextrin has been established using NMR experiments. In accordance with the NMR study the possible structure has been optimized by MM2 calculations [38]. However, all experimental results reported up to now are restricted to dihexylammonium. More experimental results using other dialkyl- and diarylammonium cations are necessary to enable a more basic and detailed discussion of all effects taking place during the complex formation.

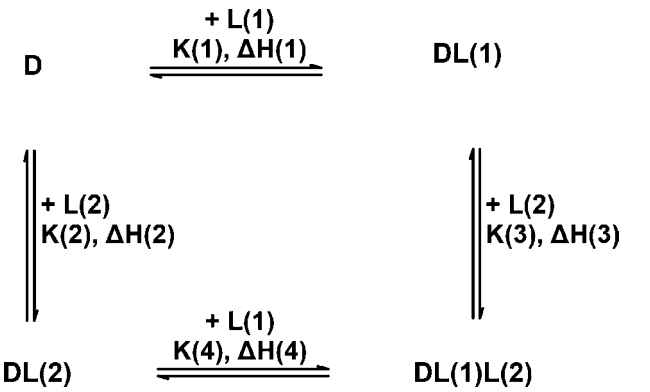
2. Experimental

2.1. Chemicals

All dialkyl- and diarylamines examined were commercial products of the highest purity available. The ligand α-cyclodextrin (α-CD, Wacker) is of the highest purity and the ligand cucurbit[6]uril (Cuc[6]) was synthesized and purified according to published procedures [40].

2.2. Measurements and calculations

Potentiometric titrations were performed using a Sirius GlpKa (Sirius Analytical Instruments Ltd., Forest Row, UK). A solution of the amine (5×10^{-4}–2×10^{-3} M) with a ten-fold excess of the macrocyclic ligands was adjusted to pH 2 using hydrochloric acid (0.5 M). This solution (20 ml) was titrated with a standard solution of KOH (0.5 M) until a pH 12 was achieved. The protonation constants and



Scheme 1. Thermodynamic cycle for the formation of heterogeneous 1:2 complexes of dialkylammonium with cuc[6] (L(1)) and α-CD (L(2)).

the stability constants were calculated directly from the experimental data using the software package Refinement Pro Version 1.114 (Sirius Analytical Instruments Ltd., Forest Row, UK). All titrations were performed at least three times. During all titrations, the ionic strength I was kept constant with KCl at I = 0.15 mol l^{-1}.

Stability constants and thermodynamic data for the complexation were also calculated from calorimetric titrations (Tronac Model 450). A solution of the ligands (5×10^{-2}–8×10^{-2} mol l^{-1}) is added continuously to a solution of the dialkylamines or their 1:1 complexes with α-CD or Cuc[6] (3×10^{-3}–5×10^{-3} mol l^{-1}). The formation of a 1:1 complex between a ligand L(n) (n = 1 or 2) and a dialkylamine D can be described by the following equation with:

$$L(n) + D \leftrightarrow DL(n) \quad (1)$$

In the case of the formation of homogeneous 2:1 complexes, one gets:

$$L(n) + DL(n) \leftrightarrow D(L(n))_2 \quad (2)$$

and for the heterogeneous 2:1 complexes:

$$L(1) + DL(2) \leftrightarrow DL(1)L(2) \quad (3)$$

After correction of all non-chemical heat effects, the heat Q produced during titration is related to the reaction enthalpy ΔH by the following equation:

$$Q = \Delta n \cdot \Delta H \quad (4)$$

where Δn stands for the number of moles of the 1:1 or 2:1 complex formed. The mathematical treatment of the experimental data is described in detail in the literature [41–43]. Experimental data provides no evidence to stand for exchange reactions of one ligand by another. If exchange reactions take place Eq. (3) is not suitable for the calculation of Δn and a fit of the experimental data using Eq. (4) is not possible. Due to the low solubility of cucurbit[6]uril in aqueous solutions, all calorimetric titrations were performed in aqueous formic acid (50%, v/v).

The notations of the different reactions are given in Scheme 1.

3. Results and discussion

To study the influence of the solvent composition upon the reaction of α-CD with substituted ammonium ions, the reaction with

Table 1
Values of the reaction enthalpy (ΔH, in kJ/mol) for the formation of 1:1 complexes between α-CD and $(C_6H_{13})_2NH{\cdot}HCl$ at different concentrations of formic acid (v/v) and at 298.15 K.

HCOOH	0%	6.25%	12.5%	25.0%	50.0%
$-\Delta H$	3.3 ± 0.4	2.1 ± 0.2	1.9 ± 0.3	1.9 ± 0.4	2.4 ± 0.4

Table 2
Stability constants ($\log K(n)$, $K(n)$ in l/mol) and thermodynamic values ($\Delta H(n)$, $T\Delta S(n)$ (n = 1 or 2) in kJ/mol) for the formation of 1:1 complexes (DL(1); DL(2)) between dialkyl- and diarylammonium ions and the ligands cucurbit[6]uril (L(1)) and α-cyclodextrin (L(2)) at 298.15 K in aqueous formic acid (50%, v/v).

	Cuc[6]			α-CD		
Amine	$\log K(1)$	$-\Delta H(1)$	$T\Delta S$(l)	$\log K(2)$	$-\Delta H(2)$	$T\Delta S(2)$
$(C_3H_7)_2NH{\cdot}HCl$	2.59 ± 0.01[a]	33.4 ± 1.4[a]	−18.7 ± 1.5[a]	2.46 ± 0.01[a]	1.6 ± 0.2[a]	12.4 ± 0.2[a]
	2.69 ± 0.70[b]			2.91 ± 0.04[b]		
$(C_4H_9)_2NH{\cdot}HCl$	2.78 ± 0.18[a]	38.0 ± 0.9[a]	−22.2 ± 2.0[a]	2.49 ± 0.01[a]	2.1 ± 0.2[a]	12.1 ± 0.2[a]
	2.54 ± 0.1[b]			2.09 ± 0.10[b]		
$(C_5Hn)_2NH{\cdot}HCl$	3.41 ± 0.01[a]	27.3 ± 0.2[a]	−7.9 ± 0.2[a]	2.51 ± 0.01[a]	2.6 ± 0.3[a]	11.7 ± 0.3[a]
	2.93 ± 0.30[b]			2.77 ± 0.06[b]		
$(C_6Hi_3)_2NH{\cdot}HCl$	3.44 ± 0.14[a]	25.1 ± 1.7[a]	−5.6 ± 2.5[a]	2.91 ± 0.05[a]	2.7 ± 0.3[a]	13.8 ± 0.6[a]
	2.97 ± 0.07[b]			3.14 ± 0.01[b]		
	5.71[d]	24.9[d]	7.7[d]			
$(C_7Hi_5)_2NH{\cdot}HCl$	2.71 ± 0.01[a]	16.2 ± 0.3[a]	−2.7 ± 1.2	2.41 ± 0.01[a]	2.0 ± 0.3[a]	11.7 ± 0.4
	3.32 ± 0.02[b]			2.60 ± 0.07[b]		
$(Ci_8H_37)_2NH{\cdot}HCl$	–[c]	–	–	–[c]	–	–
	2.62 ± 0.40[b]			2.40 ± 0.08[b]		
$(C_6H_5)_2NH{\cdot}HCl$	–[c]	–	–	–[c]	–	–
	2.16 ± 0.16[b]			2.36 ± 0.10[b]		
$(C_6H_5CH_2)_2NH{\cdot}HCl$	2.72 ± 0.02[a]	4.1 ± 0.1[a]	11.4 ± 0.2[a]	2.38 ± 0.03[a]	2.7 ± 0.1[a]	10.8 ± 0.3[a]
	2.63 ± 0.01[b]			2.39 ± 0.09[b]		

[a] From calorimetric titration in formic acid (50%, v/v).
[b] From pH-metric titrations in aqueous solution (I = 0.15 mol l^{-1} KCl).
[c] Solubility not high enough for calorimetric titrations.
[d] Ref. [38] in aqueous NaCl solution (0.05 M; pH 3).

dihexylammonium has been measured at different solvent compositions in aqueous formic acid. The results are given in Table 1. In the concentration range of formic acid, the solvent composition has no influence upon the measured values of the reaction enthalpy.

Due to the relative low solubility of cucurbit[6]uril in aqueous solution and to the higher solubility in aqueous formic acid [40], all calorimetric titrations have been performed in aqueous formic acid (50%, v/v). In addition, potentiometric titrations have been employed to measure the formation of the 1:1 complexes in pure aqueous solution for comparison. The stability constants and the reaction enthalpies and entropies for the formation of 1:1 complexes between dialkyl- and diarylamines and α-CD or Cuc[6] are summarized in Table 2.

The stability constants obtained from calorimetric and potentiometric titrations are of the same order of magnitude. Surprisingly, no pronounced influence of the solvent composition upon the values of the stability constants is observable. The stability constants in the case of the ammonium complexes with α-CD and Cuc[6] are rather similar, although the potentiometric titrations are performed in KCl solution (0.15 mol l^{-1}) and the calorimetric titrations in aqueous formic acid (50%). However the stability constant reported in the literature for the 1:1 complex formation of dihexylamine hydrochloride with cucurbit[6]uril is two orders of magnitude higher than the values found in our study. This difference may be caused by salt effects as they have been observed for the complexation of cyclohexylamine hydrochloride and hexylamine hydrochloride with Cuc[6] [44]. This explanation is supported by the fact that the stability constants and thermodynamic values for the reaction of α-CD with hexylamine hydrochloride ($\log K$ = 2.59; ΔH = −17.5 kJ/mol [38]) are identical (within experimental errors) with the results previously reported by the authors ($\log K$ = 2.51; ΔH = −19.5 kJ/mol [39]). Obviously, complexation reactions with Cuc[6] are very sensitive with respect to medium effects.

The formation of Cuc[6] complexes with dialkylammonium ions is favoured by enthalpic and disfavoured by entropic factors. Between the positive charged amino and the six carbonyl groups at one portal of Cuc[6], ion-dipole interactions occur that entail strong enthalpic contributions. The restriction of the conformational mobility is not compensated by the release of water molecules from the solvated dialkylammonium ions and Cuc[6]. As a result negative values of the reaction entropies are observed. The formation of the corresponding complexes with α-CD is mainly favoured by entropic factors. The values of the reaction enthalpy are small. Contributions to the experimental reaction enthalpy are the release of structured water molecules from the dialkylammonium ions and the release of "high energy" water molecules from the cyclodextrin cavity [45,46]. Obviously the strong solvated ammonium groups are located outside the cavity and prevent optimal interactions between the alkyl chains and the interior of the cavity. Thus, no influence of the length of the alkyl chain upon the values of the reaction enthalpy is observed. The release of water molecules from the cavity is mainly responsible for the observed positive values of the reaction entropy. These results are in accordance with the results reported for the complex formation between α-CD and alkylamines and their hydrochlorides [37].

The stability constants and the thermodynamic parameters for the formation of homogenous 1:2 complexes between one dialkyl- or diarylammonium ion and two molecules of Cuc[6] or α-CD are given in Tables 3 and 4, respectively.

All values of the stability constants and reaction enthalpies for the complex formation with the second Cuc[6] ligand are smaller when compared with the results for the formation of the 1:1 complex. The six carbonyl groups at one portal of the Cuc[6] molecule interact with the protonated amino group and, as a result, the second Cuc[6] molecule is not able to achieve identical interactions due to the repulsion between the carbonyl groups of the two ligands.

Table 3
Stability constants ($\log K(DL(1)_2)$, $K(DL(1)_2)$ in l/mol) and thermodynamic values ($\Delta H(DL(1)_2)$, $T\Delta S(DL(1)_2)$ in kJ/mol) for the formation of homogeneous 1:2 complexes ($D(L(1))_2$) between the 1:1 complexes of cucurbituril and dialkyl- and diarylammonium ions (DL(1) and cucurbit[6]uril (L(1)) at 298.15 K in aqueous formic acid (50%, v/v).

Complex	$\log K(DL(1)_2)$	$-\Delta H(DL(1)_2)$	$T\Delta S(DL(1)_2)$
$(C_3H_7)_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.29 ± 0.04	26.0 ± 0.9	−13.0 ± 1.1
$(C_4H_9)_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.38 ± 0.05	12.6 ± 1.14	0.9 ± 1.7
$(C_5H_{11})_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.39 ± 0.08	14.5 ± 1.0	−0.9 ± 1.4
$(C_6H_{13})_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.39 ± 0.04	18.3 ± 0.2	−4.7 ± 0.4
$(C_7H_{15})_2NH{\cdot}HCl{\cdot}Cuc[6]$	–[a]	–[a]	–[a]
$(C_{18}H_{37})_2NH{\cdot}HCl{\cdot}Cuc[6]$	–[a]	–[a]	–[a]
$(C_6H_5)_2NH{\cdot}HCl{\cdot}Cuc[6]$	–[a]	–[a]	–[a]
$(C_6H_5CH_2)_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.23 ± 0.05	1.9 ± 0.6	10.8 ± 0.9

[a] Solubility not high enough or value of the reaction enthalpy too small.

Table 4
Stability constants ($\log K(DL(2)_2)$, $K(DL(2)_2)$ in l/mol) and thermodynamic values ($\Delta H(DL(2)_2)$, $T\Delta S(DL(2)_2)$ in kJ/mol) for the formation of homogeneous 1:2 complexes ($D(L(2))_2$) between the 1:1 complexes of α-CD (DL(2)) and dialkyl- and diarylammonium ions and α-CD (L(2)) at 298.15 K in aqueous formic acid (50%, v/v).

Complex	$\log K(DL(2)_2)$	$\Delta H(DL(2)_2)$	$T\Delta S(DL(2)_2)$
$(C_3H_7)_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.49 ± 0.03	1.2 ± 0.1	13.0 ± 0.2
$(C_4H_9)_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.29 ± 0.02	0.5 ± 0.1	12.5 ± 0.2
$(C_5H_{11})_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.45 ± 0.04	2.5 ± 02	11.4 ± 0.5
$(C_6H_{13})_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.46 ± 0.02	2.4 ± 0.4	11.6 ± 0.5
$(C_7H_{15})_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.39 ± 0.01	3.4 ± 0.4	10.2 ± 0.4
$(C_{18}H_{37})_2NH{\cdot}HCl{\cdot}\alpha$-CD	–[a]	–[a]	–[a]
$(C_6H_5)_2NH{\cdot}HCl{\cdot}\alpha$-CD	–[a]	–[a]	–[a]
$(C_6H_5CH_2)_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.43 ± 0.03	0.5 ± 0.2	13.3 ± 0.4

[a] Solubility not high enough.

Table 5
Stability constants ($\log K(4)$, $K(4)$ in l/mol) and thermodynamic values ($\Delta H(4)$, $T\Delta S(4)$ in kJ/mol) for the formation of heterogeneous 1:2 complexes (D(L1)(L2)) between the 1:1 complexes of α-CD and dialkyl- and diarylammonium ions (DL(2))and Cuc[6] (L(1)) at 298.15 K in aqueous formic acid (50%, v/v).

Complex	$\log K(4)$	$-\Delta H(4)$	$T\Delta S(4)$
$(C_3H_7)_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.49 ± 0.04	38.1 ± 0.6	−24.0 ± 0.9
$(C_4H_9)_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.69 ± 0.04	36.9 ± 0.6	−21.6 ± 0.8
$(C_5H_{11})_2NH{\cdot}HCl{\cdot}\alpha$-CD	3.21 ± 0.04	28.6 ± 0.1	−10.4 ± 0.4
$(C_6H_{13})_2NH{\cdot}HCl{\cdot}\alpha$-CD	3.34 ± 0.14	27.2 ± 0.3	−8.2 ± 1.1
$(C_7H_{15})_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.97 ± 0.02	9.8 ± 0.4	7.1 ± 0.5
$(C_{18}H_{37})_2NH{\cdot}HCl{\cdot}\alpha$-CD	–[a]	–[a]	–[a]
$(C_6H_5)_2NH{\cdot}HCl{\cdot}\alpha$-CD	–[a]	–[a]	–[a]
$(C_6H_5CH_2)_2NH{\cdot}HCl{\cdot}\alpha$-CD	2.43 ± 0.02	6.9 ± 0.2	6.9 ± 0.3

[a] solubility not high enough.

Table 6
Stability constants ($\log K(3)$, $K(3)$ in l/mol) and thermodynamic values ($\Delta H(3)$, $T\Delta S(3)$ in kJ/mol) for the formation of heterogeneous 1:2 complexes (DL(1)L(2)) between the 1:1 complexes of Cuc[6] (DL(1)) and dialkyl- and diarylammonium ions and α-CD (L(2)) at 298.15 K in aqueous formic acid (50%, v/v).

Complex	$\log K(3)$	$-\Delta H(3)$	$T\Delta S(3)$
$(C_3H_7)_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.40 ± 0.05	2.7 ± 0.8	10.9 ± 1.1
$(C_4H_9)_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.43 ± 0.03	2.1 ± 0.1	11.7 ± 0.3
$(C_5H_{11})_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.50 ± 0.02	2.2 ± 0.2	12.0 ± 0.3
$(C_6H_{13})_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.45 ± 0.06	4.3 ± 0.5	9.6 ± 0.9
	2.90[a]	20.5[a]	−3.9[a]
$(C_7H_{15})_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.38 ± 0.02	3.5 ± 0.5	10.0 ± 1.6
$(C_{18}H_{37})_2NH{\cdot}HCl{\cdot}Cuc[6]$	–[b]	–[b]	–[b]
$(C_6H_5)_2NH{\cdot}HCl{\cdot}Cuc[6]$	–[b]	–[b]	–[b]
$(C_6H_5CH_2)_2NH{\cdot}HCl{\cdot}Cuc[6]$	2.51 ± 0.02	3.4 ± 0.1	10.9 ± 0.2

[a] Ref. [38] in aqueous NaCl solution (0.05 M; pH 3).
[b] Solubility not high enough.

Table 7
Calculated differences of the thermodynamic data for the reaction of dialkyl- and diarylamines with Cuc[6], and α-CD, according to Scheme 1, using the experimental data from Tables 2, 5 and 6.

Amine	$\Delta(\log K_i)$	$\Delta(\Delta H_i)$	$\Delta(T\Delta S_i)$
$(C_3H_7)_2NH{\cdot}HCl$	0.04 ± 0.11	3.6 ± 3.0	3.8 ± 3.7
$(C_4H_9)_2NH{\cdot}HCl{\cdot}$	0.03 ± 0.26	−1.1 ± 1.8	−1.0 ± 3.3
$(C_5H_{11})_2NH{\cdot}HCl$	0.19 ± 0.08	−1.7 ± 0.8	2.8 ± 1.2
$(C_6H_{13})_2NH{\cdot}HCl$	−0.36 ± 0.39	−1.6 ± 1.4	−1.6 ± 5.1
$(C_6H_5CH_2)_2NH{\cdot}HCl$	−0.42 ± 0.09	2.1 ± 0.5	4.6 ± 1.0

As such, the sterical requirements for the second Cuc[6] molecule are also lower compared with the first one. Thus, the values of the reaction entropies are smaller. Only for the complex formation with dibenzylammonium the situation is different. The values of the reaction enthalpies and entropies for the formation of the 1:1 and 1:2 are small and nearly identical. Obviously, only minor ion-dipole interactions between the ammonium ion and the donor groups of Cuc[6] take place during the complex formation.

The stability constants and thermodynamic values for the formation of 1:1 and 1:2 complexes between dialkyl- and diarylammonium ions and α-CD are identical within the experimental error. The ligand α-CD does not have any interactions with the ammonium group. As a result both ligands can arrange in a way that no repulsions between them occur.

The heterogeneous 1:2 complexes of dialkyl- and diarylammonium are formed with one molecule Cuc[6] and one molecule α-CD. A schematic drawing of such complex is shown in Fig. 2. All individual measured reactions resulting in the mixed 1:2 complexes can be arranged in a thermodynamic cycle, see Scheme 1. Such a cycle enables to check the accuracy of the experimental results for each individual reaction step. In the absence of additional reactions not mentioned in Scheme 1 one gets:

$$\Delta(\log K) = \log K(1) + \log K(3) - \log K(4) - \log K(2) = 0 \quad (1)$$

Identical correlations are valid for the reaction enthalpies and entropies. Using the experimental data from Tables 2, 5 and 6, the differences of the thermodynamic data are calculated and summarized in Table 7. No systematic aberration is observed. As expected, the differences are small and close to zero.

Using Scheme 1 it is possible to detect qualitatively any cooperative effects during the formation of the heterogeneous 1:2 complexes. The thermodynamic values $K(1)$, $\Delta H(1)$ and $T\Delta S(1)$ with $K(4)$, $\Delta H(4)$ and $T\Delta S(4)$, see Tables 2 and 5, are identical within the experimental error. The same results are obtained for the comparison of the values of $K(2)$, $\Delta H(2)$ and $T\Delta S(2)$ with $K(3)$, $\Delta H(3)$ and $T\Delta S(3)$. From the comparison of these results, one can conclude that the formation of the 1:1 complexes with Cuc[6] or α-CD has no influence upon the formation of the heterogeneous 1:2 complexes. Within the experimental error of the acquired thermodynamic data, no contribution resulting from additional interactions between Cuc[6] and α-CD can be assessed statistically significant.

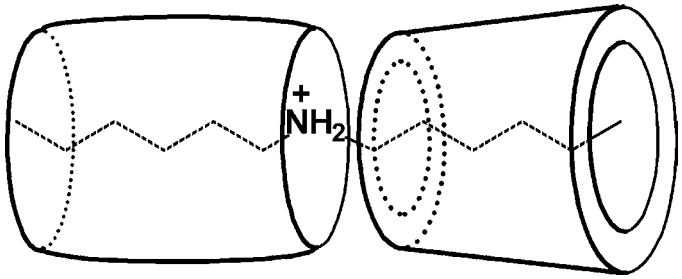


Fig. 2. Schematic presentation of a mixed 2:1 complex of dihexylammonium with one molecule of cucurbituril and cyclodextrin.

Both macrocyclic ligands Cuc[6] and α-CD are able to form homogeneous and heterogeneous 1:2 complexes with dialkyl- and diarylammonium cations. Only in the case of the homogeneous 1:2 complexes with Cuc[6], an interaction between both ligands is evident. The polar carbonyl groups at each portal of Cuc[6] and their simultaneous interactions with the protonated amino groups are responsible for this effect. The hydroxyl groups located at both rims of α-CD are able to form hydrogen bonds with the protonated amino groups. Thus, no repulsion between both ligands occurs. Taking advantage of the different interactions of both ligands with guest molecules it becomes possible to synthesize mixed rotaxanes, catenanes, and other molecular assemblies where the location of these ligands is predetermined by the molecular structure of the guest molecule.

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