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Cucurbit[5]uril, Decamethylcucurbit[5]uril and Cucurbit[6]uril. Synthesis, Solubility and Amine Complex Formation

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Abstract

A simple way to prepare cucurbit[5]uril is described. The macrocycles of the cucurbituril type are nearly insoluble in water. The solubilities of cucurbit[5]uril, decamethylcucurbit[5]uril and cucurbit[6]uril in hydrochloric acid, formic acid and acetic acid of different concentrations have been investigated. Due to the formation of complexes between cucurbit[n]urils and protons the solubility increases in aqueous acids. The macrocyclic ligands are able to form complexes with several organic compounds. Thus, the complex formation of the cucurbituril macrocycles with different amines has been studied by means of calorimetric titrations. The reaction enthalpy gives no evidence of the formation of inclusion or exclusion complexes. ^{1}H-NMR measurements show that in the case of cucurbit[5]uril and cucurbit[6]uril the organic guest compound is included within the hydrophobic cavity. Decamethylcucurbit[5]uril forms only exclusion complexes with organic amines. This was confirmed by the crystal structure of the decamethylcucurbit[5]uril-1,6-diaminohexane complex.

Introduction

The physical and chemical properties of a large number of macrocyclic ligands, for example crown ethers, cryptands, cyclodextrins and calixarenes, have been reported. An enormous number of articles concerning the synthesis, structure and the complexation behaviour of these ligands have been published. In 1905 Behrend et al. reported the synthesis of a molecule using urea, glyoxal and formaldehyde [1]. The structure and the conformation of the formed compound were unknown at that time. Much later in 1981 the macrocyclic structure of this reaction product was reported by Freeman et al. [2]. Due to the tedious IUPAC nomenclature the name "cucurbituril" (Cuc[6]) was suggested for this macrocyclic ligand. Mock reported the ability of this macrocyclic compound to form inclusion complexes with different amines [3–5]. In the meantime the complex stabilities and thermodynamic data for the reaction of cucurbituril with different alkaline and alkaline earth cations [6–8], amines [9] and other organic molecules [10–14] have been given in the literature. Further experimental results with the macrocycle cucurbituril have been discussed in review articles [15, 16].

The first hint for the synthesis of another cucurbituril derivative can be taken from the Ph.D. thesis of N.-Y. Shih [17]. However, it was not until 1992 that Stoddart et al. characterised this derivative by its crystallographic structure [18]. They described the synthesis and structure of decamethylcucurbit[5]uril (DMC[5]) in detail. Thinking of a more precise designation Stoddart suggested a new nomenclature for the cucurbituril derivatives. Thus, the number of the glycoluril units is given in brackets. The substituents at the carbon atoms are given as a prefix (see Figure 1).

Just recently the isolation of cucurbituril derivatives with a number of glycoluril units from 5 to 8 have been reported [19], which are separated from a mixture. In this paper we describe the direct synthesis of cucurbit[5]uril (Cuc[5]). Moreover the solubilities of the cucurbituril type macrocycles in aqueous acids were investigated. ^{1}H-NMR spectroscopy, calorimetric titrations and crystal structure analyses are used to analyse the complex formation between the cucurbituril derivatives and different amines.

Experimental

Elemental analyses were performed using a Carlo-Erba 1006 Analyser. The substances were purified by recrystallization from acidic solutions. They were dried in vacuum. However, not all water molecules could be removed under the experimental conditions.

The mass spectrum of decamethylcucurbit[5]uril was obtained from a glycerine matrix using the liquid-SIMS technique on an AMD 604 mass spectrometer. Using this ioniz-

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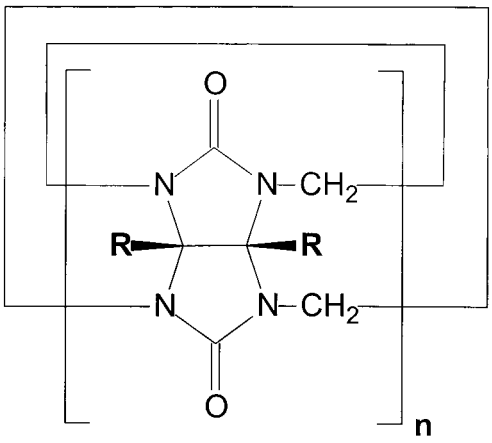

R = H	n = 6	Cucurbit[6]uril	**Cuc[6]**
R = CH_3	n = 5	Decamethylcucurbit[5]uril	**DMCuc[5]**
R = H	n = 5	Cucurbit[5]uril	**Cuc[5]**

Figure 1. Chemical structure of the different cucurbituril derivatives.

ation technique in the case of cucurbit[5]uril no signal in the mass spectrum could be observed. The mass spectrum of this compound was obtained using Time-of-Flight-SIMS (Verbundzentrum für Oberflächen und Mikrobereichsanalysen, ASTEC GmbH, Münster, Germany).

Infrared spectra were measured in solid KBr using a FTS-45 spectrometer (Biorad). The ^{1}H-NMR, NOESY and COSY spectra were recorded with a Bruker WM300 or Bruker Avance DRX 500 using D_2O, a mixture of DCl/D_2O (20 %vol.) or deuterated trifluoroacetic acid as solvents. As internal standard the sodium salt of trimethylsilyl propionic acid was used.

Synthesis of cucurbit[5]uril and decamethylcucurbit[5]uril: Glycoluril (13.4 g, 94 mmol) or dimethylglycoluril (16.0 g, 94 mmol), 37% aqueous formaldehyde solution (32 mL), concentrated hydrochloric acid (64 mL) and water (20 mL) were heated under reflux for two hours. After this time water (300 mL) was added to the clear dark solution and the resulting mixture heated for an additional hour. The solution was cooled to room temperature overnight. The precipitate was filtered off, washed three times with water, recrystallized several times from hydrochloric acid and dried in vacuum.

Yield Cuc[5]: 0.7 g (4.6%). Yield DMC[5]: 1.9 g (10.4%). Cuc[5]: ^{1}H NMR (300 MHz, DCl/D_2O): δ 4.49 (d, 10H, J = 16 Hz), δ 5.53 (d, 10 H, J = 16 Hz), δ 5.72 (s, 10 H); TOF-SIMS(pos., Ag): m/z 831 (Cuc[5] + H)$^+$, 848 (Cuc[5] + OH)$^+$, 937 (Cuc[5] + Ag)$^+$. $C_{30}H_{30}N_{20}O_{10}$ (830.7). *Calc.* C, 43.38; H, 3.64; N, 33.72; C/N, 1.29. *Exp.* C, 36.25; H, 4.92; N, 26.18; C/N, 1.38.

DMC[5]: ^{1}H NMR (500 MHz, $CF_3COOD/CDCl_3$ (1/0.37)): δ 1.92 (s, 30 H), δ 4.50 (d, 10 H, J = 16.5 Hz), δ 5.92 (d, 10 H, J = 16.5 Hz); L-SIMS (pos./matrix: glycerine): m/z 971.6 (DMC[5] + H)$^+$, 993.3 (DMC[5] + Na)$^+$, 1009.3 (DMC[5] + K)$^+$, 1103.2 (DMC[5] + Cs)$^+$ $C_{40}H_{50}N_{20}O_{10}$ (970.9). *Calc.* C, 49.48; H, 5.19; N, 28.85; C/N, 1.72. *Exp.* C, 41.87; H, 5.83; N, 26.33; C/N, 1.59. [24] C, 41.40; H, 5.80; N, 25.70.

Synthesis of cucurbit[6]uril:
A stirred mixture of glycoluril (15.0 g, 106 mmol), 37% aqueous formaldehyde solution (24 mL), concentrated sulfuric acid (14.3 mL) and water (100 mL) was heated for several hours. During this time the water was removed nearly completely from the reaction mixture. Afterwards the temperature was raised to 160–170 °C. The resulting reaction mixture was cooled to room temperature and poured into water (250 mL). A yellowish precipitate was formed, which was filtered off and dissolved in concentrated hydrochloric acid. The clear brown solution was diluted with water. A white precipitate was formed, which was washed several times with water and dried at 130 °C.

Yield Cuc[6]: 14.2 g (80.9 %). Cuc[6]: ^{1}H NMR (300 MHz, DCl/D_2O): δ 4.52 (d, 12 H, J = 16 Hz), δ 5.62 (d, 12 H, J = 16 Hz), δ 5.73 (s, 12 H); FAB: m/z 997.5 (Cuc[6] + H)$^+$ $C_{36}H_{36}N_{24}O)_{12}$ (996.8). *Calc.* C, 43.37; H, 3.61; N, 33.73; C/N; 1.29. *Exp.* C, 39.94; H, 4.73; N, 31.34; C/N, 1.27; [2] C, 36.66; H, 4.53; N, 30.08.

The solubilities of cucurbit[5]uril, decamethylcucurbit[5]uril and cucurbit[6]uril were determined by evaporation of saturated solutions.

Stability constants and thermodynamic values for the complexation of different ammonium ions by the cucurbituril derivatives were obtained by calorimetric titrations using a Tronac Model 450 calorimeter. The measurements were performed in aqueous formic acid (50 vol. %). Solutions of the ligands (0.03–0.08 mol/l) were added continuously to solutions of ammonium hydrochloride, hexamethylene diammoniumdichloride and anilinium hydrochloride (1–5 × 10^{-3} mol/l). The heat, Q, produced during the titration is related to the reaction enthalpy ΔH after correction of all nonchemical heat effects by the following equation:

$$Q = \Delta H \cdot \Delta n,$$

Δn is the number of moles of complexes formed. The mathematical treatment of the experimental data is described in detail in the literature [20–23]. Under these experimental conditions no evidence for the existence of other than 1:1 complexes was found.

Crystallographic studies

Crystals suitable for X-ray analyses were only obtained in the case of decamethylcucurbit[5]uril. Solid decamethylcucurbit[5]uril (2.0 g, 2.06 mmol) was added to a solution of 1,6-diaminohexane (0.24 g, 2.06 mmol) in 10 mL water. The solid dissolved rapidly. Crystals were obtained after slow evaporation of the solvent during a period of five weeks. All attempts to prepare crystals with cucurbit[5]uril failed. Only transparent films were obtained.

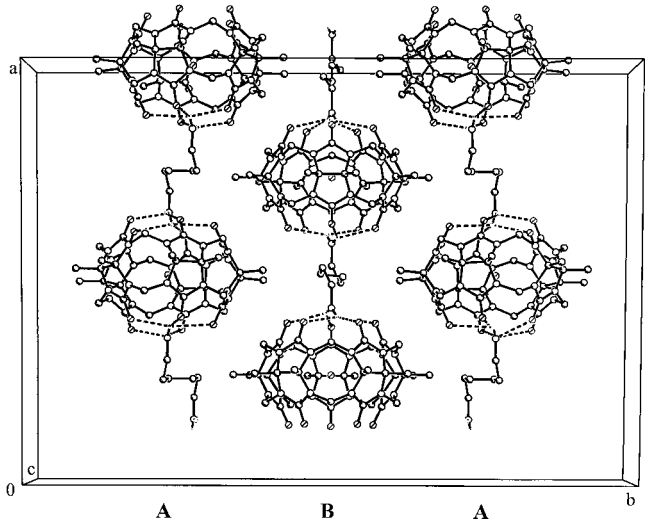

Figure 2. Crystal structure of the 1,6-diaminohexane DMC[5] exclusion-complex.

DMC[5] + 1,6-diaminohexane + 11.5 H_2O. *Calc.* C, 42.69; H, 6.93; N, 23.81; $C_{46}H_{89}N_{22}O_{21.5}$: *exp.* C, 41.96; H, 6.26; N, 23.13.

The crystal structure, see Figure 2, of the complex between decamethylcucurbit[5]uril and 1,6-diaminohexane was measured using a STOE-IPDS diffractometer. Graphite-crystal monochromator, MO-Kα-radiation, λ = 0.71069 Å; $C_{46}H_{66}N_{22}O_{10}\cdot 11{,}5\ H_2O$, M_r = 1293.3, crystal 0.5 × 0.42 × 0.08 mm^3, colourless lamina, space group C2/m, monoclinic, a = 25.366(5), b = 36.456(7), c = 14.625(3) Å, β = 98.95(3)°, V = 13360(5) $Å^3$, Z = 8, ρ_{cal} = 1.216 g cm^{-3}, 13552 reflections collected, 7232 symmetrically independent reflections, 4418 of them observed ($I > 2\sigma(I)$), R = 0.1077, wR2 (all data) = 0.3210, 795 parameter.

The hydrogen atoms have been brought into position geometrically (riding model). The carbon atoms of two 1,6-diaminohexane molecules are disordered at the mirror plane. They have been calculated to chemically meaningful positions by restraints. 18 partly occupied positions for water molecules with a checksum of 11.5 have been identified. No local hydrogen positions for improvement are used.

The crystallographic data were deposited as "supplementary publication No. CCDC-116335" at Cambridge Crystallographic Data Centre. They can be ordered free using the following address: CCDC, 12 Union Road, Cambridge CB21EZ, Great Britain (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Results and discussion

The reaction conditions known from the literature using hot, concentrated sulfuric acid are only suitable for the formation of cucurbit[6]uril [1, 2, 6]. Our attempts to synthesize any cucurbituril derivatives using these experimental conditions failed. By variation of the reaction conditions Kim et al. were able to synthesize a mixture of different cucurbituril derivatives [19]. Using hydrochloric acid instead of sulfuric acid and dimethylglycoluril Stoddart et al. obtained decamethycucurbit[5]uril [18].

Starting this synthetic procedure with glycoluril leads to a white substance. The characterization of this product however, is difficult. The ^{1}H-NMR-spectra of this new compound and of cucurbit[6]uril are more or less identical. There are only tiny differences in the chemical environment of the protons in cucurbit[5]uril or cucurbit[6]uril. The higher ring tension in the 5-membered macrocycle effects a shift of the proton signals. Small differences (<0.1 ppm) are observed, see Figure 3.

IR-spectra of cucurbit[5]uril and cucurbit[6]uril do not show significant differences. The elemental analyses of cucurbit[6]uril, decamethylcucurbit[5]uril and the new compound cucurbit[5]uril are not in accordance with the expected theoretical values. In the case of cucurbit[6]uril the differences between the calculated and experimental values can be attributed to the water content of this ligand [23]. The C/N ratio is independent of the number of water molecules bound to the macrocyclic compound. Differences between the C/N ratio calculated and experimentally obtained are negligible for cucurbit[6]uril. The composition of decamethylcucurbit[5]uril differs from the theoretical values, however the experimental results reported by Stoddart [24] and our work agree very well. Up to now no reason is known for the discrepancies between the calculated and experimentally obtained composition of the cucurbit[5]uril-type macrocycles. From the literature it is known that the experimental results of the elemental analyses of some calixarenes are not in accordance with the calculated values [25–27]. Nevertheless the existence of both cucurbit[5]uril derivatives is well established by their mass and ^{1}H-NMR spectra. In contrast satisfactory results of elemental analyses of cucurbit[5]uril have been reported by Kim et al. [19].

The solubilities of the cucurbituril derivatives in different aqueous acids are summarized in Tables 1–3. With increasing acid concentration the solubilities of cucurbit[5]uril and cucurbit[6]uril increase. The values pass through a maximum and decrease at high acid concentrations. The formation of complexes with protons is responsible for the increase in solubility. At high acid concentrations the proton concentration in solution decreases due to incomplete acid dissociation. In the case of decamethylcucurbit[5]uril a decrease in solubility of the proton complex at low acid concentrations is observed. Obviously the interactions between this ligand and protons result in a weakening of the interactions between the complex and solvent molecules. The same observation is made in the presence of some salts [28]. However at higher acid concentrations the solubility increases as expected. In concentrated hydrochloric acid decomposition of cucurbit[5]uril and decamethylcucurbit[5]uril is observed.

As known from the literature cucurbit[6]uril forms very stable complexes with different aromatic and aliphatic amine compounds and ammonium ions in acid solutions [3–5, 7, 9]. Two isomeric structures of the complex are possible. The first complex rapidly formed is the association complex, where the charged ammonium group of the guest substance

Table 1. Solubility (in g/l) of cucurbit[5]uril in aqueous acids at 25 °C

HCl		HCOOH		CH_3COOH	
Concentration weight (%)	Solubility (g/l)	Concentration weight (%)	Solubility (g/l)	Concentration weight (%)	Solubility (g/l)
3.2	0.765 ± 0.002	11.9	1.319 ± 0.010	10.4	0.575 ± 0.025
6.5	1.454 ± 0.003	23.4	3.592 ± 0.011	20.8	0.725 ± 0.025
9.6	3.304 ± 0.041	34.3	7.757 ± 0.124	31.0	0.875 ± 0.024
12.8	3.885 ± 0.044	44.9	8.466 ± 0.001	41.2	1.100 ± 0.010
16.0	–*	55.0	10.971 ± 0.023	51.2	1.125 ± 0.005
		64.7	8.317 ± 0.064	61.2	1.275 ± 0.025
		74.0	–*	71.0	0.940 ± 0.100
				80.8	0.725 ± 0.025
				90.4	0.230 ± 0.023

*Decomposition.

Table 2. Solubility (in g/l) of decamethylcucurbit[5]uril in aqueous acids at 25 °C

HCl		HCOOH		CH_3COOH	
Concentration weight (%)	Solubility (g/l)	Concentration weight (%)	Solubility (g/l)	Concentration weight (%)	Solubility (g/l)
0	7.981 ± 0.394	11.9	19.860 ± 0.157	10.4	21.030 ± 0.020
3.2	0.427 ± 0.011	23.4	36.520 ± 0.315	20.8	25.020 ± 0.040
6.4	0.859 ± 0.008	34.3	48.624 ± 0.851	31.0	27.030 ± 0.140
9.6	1.629 ± 0.004	44.9	61.290 ± 0.297	41.2	28.560 ± 0.090
12.8	3.465 ± 0.277	55.0	102.578 ± 0.613	51.2	27.680 ± 0.090
16.0	6.679 ± 1.064	64.7	147.345 ± 0.765	61.2	25.175 ± 0.085
19.2	11.706 ± 0.554	74.0	–*	71.0	19.255 ± 0.015
22.4	–*			80.8	11.695 ± 0.055
				90.4	3.525 ± 0.025
				100.0	0.635 ± 0.025

*Decomposition.

Table 3. Solubility (in g/l) of cucurbit[6]uril in aqueous acids at 25 °C

HCl		HCOOH*		CH_3COOH	
Concentration weight (%)	Solubility (g/l)	Concentration weight (%)	Solubility (g/l)	Concentration weight (%)	Solubility (g/l)
1.6	0.720 ± 0.020	6.0	0.080 ± 0.030	5.2	0.150 ± 0.030
3.2	1.670 ± 0.010	11.9	0.380 ± 0.050	10.4	0.190 ± 0.020
6.4	3.560 ± 0.060	17.7	0.550 ± 0.090	20.8	0.260 ± 0.030
9.6	15.720 ± 2.100	23.4	1.170 ± 0.200	31.0	0.410 ± 0.050
12.8	29.260 ± 0.500	34.3	6.440 ± 0.400	41.2	0.600 ± 0.080
16.0	53.280 ± 0.200	44.9	29.100 ± 0.300	51.2	0.690 ± 0.130
19.2	92.570 ± 0.500	55.0	60.350 ± 0.600	61.2	1.660 ± 0.040
22.4	159.160 ± 2.400	64.7	112.540 ± 8.000	71.0	1.040 ± 0.050
25.6	255.480 ± 0.500	74.0	90.110 ± 7.000	80.8	0.760 ± 0.080
28.8	323.190 ± 12.500	83.0	70.020 ± 5.000	90.4	0.090 ± 0.050
32.0	223.260 ± 17.800	91.7	22.500 ± 1.300	100.0	0.030 ± 0.010
		100.0	5.520 ± 0.300		

*[8].

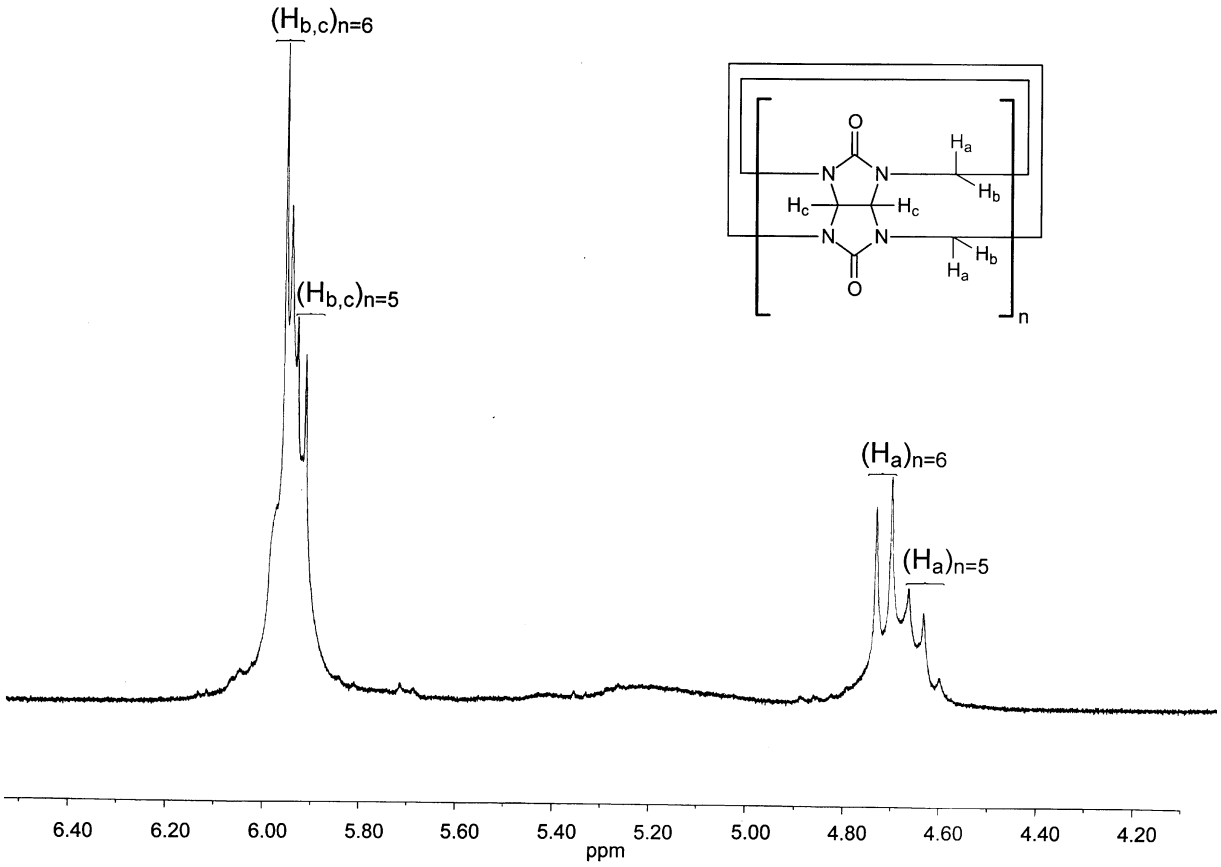

Figure 3. 500 MHz ^{1}H-NMR spectra of a mixture of Cuc[5] and Cuc[6] in DCl (20 vol. %).

binds to the carbonyl groups of one portal of cucurbit[6]uril. The organic molecule part still extends into the solvent (exclusion complex). Another possibility is an inclusion complex, whereby the ammonium group also binds to the carbonyl groups but the aliphatic or aromatic parts of the guest molecule occupy the hydrophobic cavity of the ligand (inclusion complex) [7]. NMR data reported by Mock confirm the formation of inclusion complexes between cucurbit[6]uril and different amines. The lone pairs of the carbonyl groups interact with the ammonium groups of the included molecule. Some stability constants and thermodynamic data for the complexation of aliphatic amines (ammonium hydrochloride, hexamethylene diammoniumdichloride) and the aromatic amine anilinium hydrochloride with the cucurbituril derivatives are given in Table 4. The value of the complex formation enthalpy of cucurbit[6]uril with hexamethylene diammoniumdichloride is conspicuously high. Obviously the hexamethylene diammoniumdichloride has the optimum size to fit into the cavity of the ligand. Interactions between the ligand carbonyl groups and the guest R-NH_3^+ groups reinforce the stability of the complex.

The other ΔH values reported in Table 4 are of the same order of magnitude. In the case of decamethylcucurbit[5]uril positive values of ΔH are observed. The complex formation is only favoured by entropic contributions. Thus, the thermodynamic parameters give no information what complex species is formed, either inclusion or exclusion.

Table 4. Stability constants (log K; K in l/mol) and thermodynamic values ΔH and $T\Delta S$ (in kJ/mol) for the complexation of different amines by cucurbit[5]uril, decamethylcucurbit[5]uril and cucurbit[6]uril in aqueous formic acid (50 vol. %) at 25 °C

Ligand	Ammonium ion	log K	$-\Delta H$	$T\Delta S$
Cuc[5]	NH_4^+	–[c]	9.8 ± 0.6	–
	C_5H_{11}–NH_3^+	–[c]	3.2 ± 0.5	–
	^+H_3N-C_6H_{12}–NH_3^+	–[c]	1.4 ± 0.2	–
DMC[5]	NH_4^+	3.20 ± 0.18	-2.0 ± 0.1	20.1 ± 1.0
	C_5H_{11}–NH_3^+	–[c]	4.5 ± 1.1	–
	^+H_3N–C_6H_{12}–NH_3^+	4.31 ± 0.21	-2.3 ± 0.2	22.0 ± 1.2
Cuc[6]	NH_4^+	2.69 ± 0.03	3.9 ± 0.4	11.4 ± 0.6
	C_5H_{11}–NH_3^+	–[c]	<1.0	–
	^+H_3N–C_6H_{12}–NH_3^+	>5	29.8 ± 0.6	–

[c] Not calculable from the thermogram.

^{1}H-NMR spectroscopic experiments show the inclusion complex formation between cucurbit[6]uril and aromatic and aliphatic amines [29]. Due to the different chemical environment caused by the shielding macrocycle the proton signals of the complexed amine are shifted and broadened. The cavity of cucurbit[5]uril is too small to include the aromatic molecule part of anilinium hydrochloride. Only aliphatic amines are complexed within the hydrophobic cavity. ^{1}H-NMR measurements with cucurbit[5]uril and hexylamine give an indication for the formation of an in-

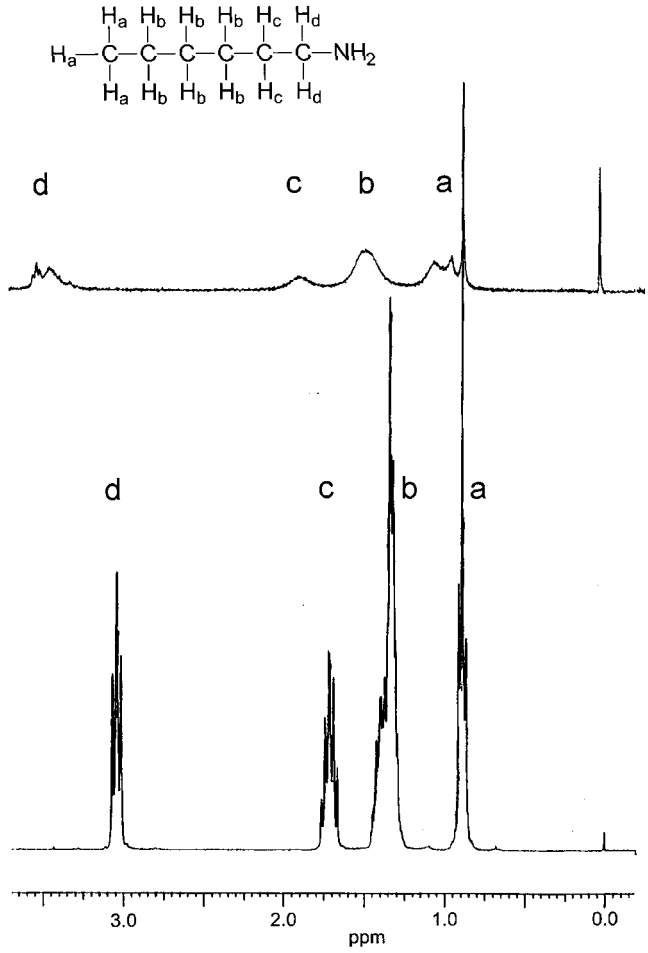

Figure 4. 300 MHz ^{1}H-NMR spectra of hexylamine (bottom) and a mixture of Cuc[5] and hexylamine (top) in DCl (20 vol. %).

clusion complex, see Figure 4. The observed shifts of the aliphatic protons may also be caused by draping of the alkyl chain over the outside of the host. However, under these circumstances the complex formation should be disfavored by entropic contributions due to the high steric requirements. This interpretation is not confirmed by the thermodynamic data in Table 4.

^{1}H-NMR measurements and NOESY experiments give no indication of the inclusion complex formation of amines and decamethylcucurbit[5]uril. These results are confirmed by the crystal structure of decamethylcucurbit[5]uril and 1,6-diaminohexane, see Figure 2.

The structure of the coordination complex between 1,6-diaminohexane and decamethylcucurbit[5]uril determined crystallographically shows hydrogen bonds between the protons of the amino groups and the carbonyl oxygen atoms. In chain A, which is oriented parallel to the crystallographic *a*-axis, decamethylcucurbit[5]uril and diaminohexane both have C_2-symmetry. On the mirror level of the unit cell (space group C2/m) the molecules of chain B are oriented to the space vector (1 0 1). Decamethylcucurbit[5]uril here possesses σ-symmetry. The two symmetrically independent 1,6-diaminohexane molecules have C_2-symmetry. Their position on the mirror level causes a disorder in the orientation. The nitrogen atoms within these linear structures have a position near to the centre of the portals built by the carbonyl oxygen atoms (2.776(9)–2.948(6) Å. N–H···O – bridging bonds (2.01(1)–2.50(1) Å; 104.6(7)–145.2(6)°) are present.

The solid state structure of decamethylcucurbit[5]uril differs only slightly from D_{5h}-symmetry. The symmetry elements determined crystallographically agree with the C_2 and σ_d operations of the point-group D_{5h}. The NCN-angle in the bridging methylene groups is increased due to the ring tension from 109° to 113.1(6)–115.5(9)° (114-116° [2]). The N–C(O)–N-angles are 108.1(7)-110.7(7)° (103-114° [2]). All atoms on the equatorial plane are coplanar within a deviation of 0.02 Å. The angle of inclination between the two planes of the symmetrically independent decamethylcucurbit[5]uril molecules is 8.76(8)°.

11.5 water molecules in 18 layers are detected in the asymmetric units. One molecule of crystal water is located in the centre of the cavity of decamethylcucurbit[5]uril. The deviation from the equatorial layer is 0.00 or 0.12(3) Å.

Conclusions

Cucurbit[6]uril, cucurbit[5]uril and decamethylcucurbit[5]uril are rigid molecules with hydrophobic cavities. They are barely soluble in water. The formation of protonated complexes increases their solubility in acid solutions. Cucurbit[6]uril and cucurbit[5]uril are able to complex organic molecules within their hydrophobic cavities. Stability constants and complex formation enthalpies of some aliphatic and aromatic ammonium salts have been measured by calorimetric titrations. Cucurbit[6]uril forms inclusion complexes with aliphatic and aromatic amines. However, only aliphatic amines are included in the cavity of cucurbit[5]uril. Only exclusion complex formation could be observed for the reaction of amines and decamethylcucurbit[5]uril.

Cucurbit[6]uril forms significantly stable complexes with aliphatic diamines and spermine as known from the literature. Voluminous stopper groups can be attached to the terminal amine groups of the complexed amines to form [2]rotaxanes [30, 31]. The formation of amine complexes with cucurbit[5]uril enables the synthesis of comparable rotaxanes. These results will be reported separately [32].

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