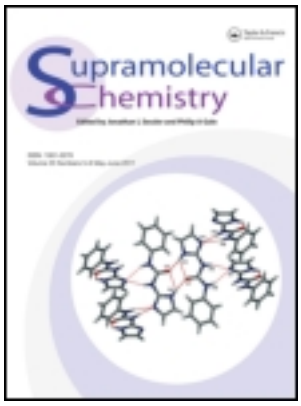

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Acetate anion-selective encapsulation in the ellipsoidal cavity of symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril

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Four symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril-based compounds have been prepared and characterised by X-ray crystallography. Their crystal structures displayed the acetate anion-selective encapsulating capability of symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril. The host–guest interaction between the symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril and the acetate anion in aqueous solution has also been observed by variable temperature ^{1}H NMR spectroscopy.

Keywords: symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril; anion encapsulation; X-ray crystallography; variable temperature ^{1}H NMR

Introduction

As a distinct branch of contemporary supramolecular chemistry, anion recognition and selective encapsulation has attracted much attention in the recent past (*1*). The main reason for this interest is that anions are relevant to biochemical systems and play important roles in synthesis, catalysis, recycling and environmental processes (*2*). Ion recognition and selective encapsulation usually requires taking into account three basic factors: size, shape and energy (*3*). However, the characteristic of anions makes the designing and synthesising of anion receptors challenge. First, anions have larger radii than isoelectronic cations, which means that anion receptors are likely to be larger than cationic receptors. Second, anionic species have a greater variety of geometries, such as spherical, linear, trigonal, tetrahedral and octahedral, than common cationic species, which requires a higher degree of design. Third, anions are strongly hydrated in an aqueous medium and any complexation process that involves anion dehydration will likely court energetic penalty.

Over the last decade, there has been intensive research into the cucurbit[*n*]uril ($n = 5–8$, 10, hereafter abbreviated as Q[*n*], Figure 1 left) (*4*), a class of organic macrocyclic cavitand, which have shown particular promise in host–guest chemistry (*5*). These unique cavitands have a central hydrophobic cavity and two identical carbonyl-fringed portals on each side and can bind various small molecules. Recently, anion encapsulation has also been demonstrated for these macrocyclic hosts (*6–8*). For example, Thuéry (*7*) synthesised a series of lanthanide complexes which show the encapsulation of perrhenate in Q[6] and Q[7]. In our previous works, we reported the selective encapsulation behaviour of Q[5] and its metal ion-based molecular capsule towards nitrate and chloride anions (*8*). We noticed that the spherical cavities of these normal Q[*n*]s are Centro symmetrical and they can accommodate a wide range of anionic species.

Recently, our research interest in this vein has been focused on Q[*n*] derivatives. In 2004, Tao group synthesised a partially substituted Q[6], the symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril (hereafter abbreviated as TMeQ[6], Figure 1 right), which exhibits better solubility in aqueous media than Q[6] (*9*).

From the structural point of view, TMeQ[6] possesses a central hydrophobic cavity and has potential anion encapsulating capability. It should be noted here, however, that the cavity of TMeQ[6] is ellipsoidal instead of spherical, which provides us new opportunity to verify the mechanism of ion-selective encapsulation we previously mentioned. With this background, we wished to address two specific questions: (1) Since the size and shape of acetate anion is similar to the cavity of TMeQ[6], can acetate anion be encapsulated into the ellipsoidal cavity of TMeQ[6]? (2) Is it possible to have spherical halide anion, such as chloride and bromide anion, residing in the ellipsoidal cavity of TMeQ[6]?

In this paper, we prepared four TMeQ[6]-based compounds and characterised their structures by X-ray crystallography, which clearly show that the acetate anion can be selectively encapsulated within the cavity of TMeQ[6]. Furthermore, we investigated the host–guest interaction between the TMeQ[6] and the acetate anion in

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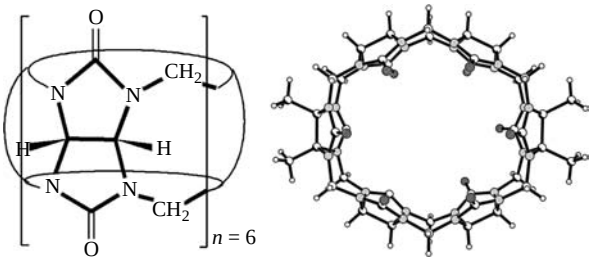

Figure 1. Molecular structure of cucurbit[6]uril (left) and X-ray crystal structure of TMeQ[6] (right).

aqueous solution by variable temperature ^{1}H NMR spectroscopy.

Experimental section

General

Chemicals, such as NaOAc, KOAc, KCl and KBr, and solvents employed were commercially available and used as received without further purification. TMeQ[6] was prepared by the published procedures (*9*). The C, H and N microanalyses were carried out with a PE 240C elemental analyser. The solid-state circular dichroism (CD) spectra were recorded on a Jasco J-810 spectropolarimeter with KBr pellets. The variable temperature 1H NMR spectra were recorded on a Varian INOVA-500 spectrometer.

Crystal structure determination

Diffraction intensity data were collected on a Bruker Apex-2000 CCD diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) with $\omega/2\theta$ scan mode. Lorentz polarisation and absorption corrections were applied. Structural solution and full-matrix least-squares refinement based on F^2 were carried out with the SHELXS-*97* program package and the SHELXL-97 program package, respectively (*10*). All the non-hydrogen atoms were refined anisotropically. The carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. For all compounds, no hydrogen atoms were given for all water molecules because it was not possible to accurately locate them, and that their absence does not affect the validity of the part of the structure of interest. CCDC 768593, 768594, 790382 and 790383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Pertinent crystallographic data and refinement parameters for the four coordination compounds 1–4 are summarised in Table 1.

Preparation of compounds

Compound **1** was synthesised as follows: TMeQ[6] (0.1044 g, 0.1 mmol) and potassium acetate (0.02 g, 0.2 mmol) were dissolved in 5.0 ml water with stirring at room temperature. After heated for about 10 min, the solution was filtered. Colourless prismatic crystals of **1** were obtained within 5 days in 70% yield. Anal. Calcd (Found) for $C_{42}H_{67}KN_{24}O_{24}$ (**1**): C, 37.89 (37.62), N, 25.25 (25.11), H, 5.07 (5.18). Compounds **2** and **3** were prepared in a similar way as illustrated for **1** except that KOAc was replaced by NaOAc (0.016 g, 0.2 mmol) or KCl (0.015 g, 0.2 mmol). Yield for **2**: 70%. Yield for **3**: 60%.

Table 1. Crystal data as well as details of data collection and refinement for compounds **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{42}H_{67}KN_{24}O_{24}$	$C_{42}H_{67}NaN_{24}O_{24}$	$C_{40}H_{58}K_3Cl_3N_{24}O_{19}$	$C_{40}H_{60}K_2BrClN_{24}O_{20}$
Formula weight	1331.30	1315.19	1402.75	1390.67
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_1$	*Fddd*	*Fddd*
a/Å	13.380(3)	13.386(5)	22.096(2)	22.216(15)
b/Å	16.380(3)	16.536(6)	31.349(3)	33.00(3)
c/Å	13.890(3)	14.109(5)	32.870(3)	31.676(18)
β°	106.02(3)	106.786(6)		
Volume [Å ^{3}]	2926.0(10)	2989.9(19)	22768(4)	23223(24)
Z	2	2	16	16
D_{calcd} [mg/m^3]	1.513	1.461	1.637	1.591
F(000)	1400	1380	11616	11485
reflns measured	16297	20810	45770	38363
Unique reflns	7985	9746	5423	5497
R(int)	0.0717	0.1188	0.0464	0.0810
R_1/wR_2 [$I > 2\sigma(I)$]	0.0717/0.1523	0.1142/0.2701	0.1191/0.3070	0.1068/0.2969
R_1/wR_2 (all data)	0.1271/ 0.1670	0.2435/0.3436	0.1273/0.3152	0.1571/0.3421
Goodness-of-fit on F^2	1.013	1.071	1.116	1.108
Flack parameter	0.09(11)	0.0(17)		

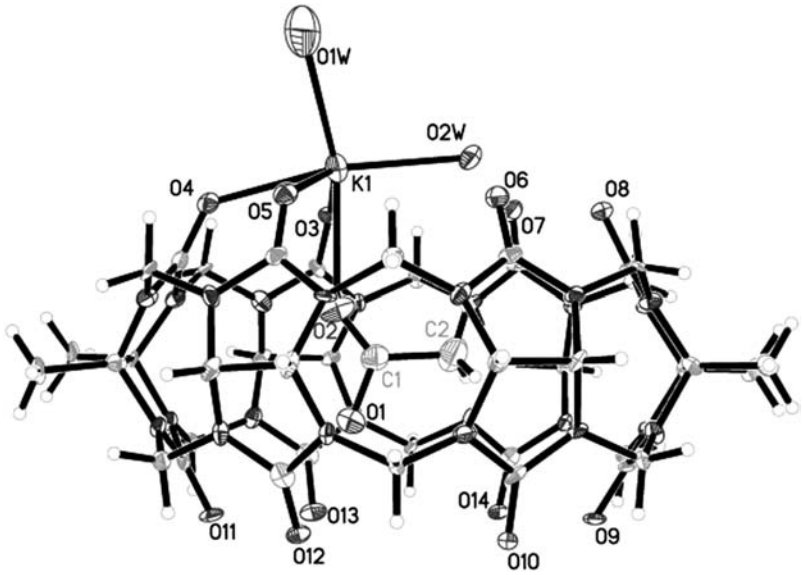

Figure 2. ORTEP diagram of **1**; displacement ellipsoids are drawn at the 30% probability level; solvent water molecules are omitted for clarity.

Anal. Calcd (Found): for $C_{42}H_{65}NaN_{24}O_{23}$ (**2**): C, 38.36 (38.78), N, 25.56 (25.75), H, 5.14 (5.16) and for $C_{40}H_{58}K_3Cl_3N_{24}O_{19}$ (**3**): C, 34.25 (33.87), N, 23.97 (23.77), H, 4.17 (4.36).

Compound **4** was synthesised as follows: KCl (0.008 g, 0.1 mmol) and KBr (0.012 g, 0.1 mmol) were dissolved in distilled water (5 ml), and to this solution TMeQ[6] (0.1044 g, 0.1 mmol) was added. The mixture was stirred and heated at 60°C for about 10 min. Slow evaporation of the filtered solution over a period of a month provided colourless crystals. Yield: 60%. Anal. Calcd (Found) for $C_{40}H_{60}K_2BrClN_{24}O_{20}$ (**4**): C, 34.55 (34.37), N, 24.17 (24.25), H, 4.35 (4.56).

Results and discussion

Discription of the crystal structures

The reaction of TMeQ[6] with sodium acetate and potassium acetate, respectively, generates two host–guest compounds, $\{[K^+(H_2O)_2][C_2H_3O_2^-@(C_{40}H_{44}N_{24}O_{12})]\}\cdot 8H_2O$ (**1**) and $\{[Na^+(H_2O)_2][C_2H_3O_2^-@(C_{40}H_{44}N_{24}O_{12})]\}\cdot 7H_2O$ (**2**). Compound **1** consists of 1 potassium cation, 1 TMeQ[6], 1 acetate anion and 10 water molecules. Single-crystal structure analysis reveals that the potassium ion 'lean' towards the portal of TMeQ[6], being coordinated to only three carbonyl oxygen atoms (O3, O4, O5) at the portal (Figure 2). Obviously, the main reason is that TMeQ[6] is too large for all six donors of one portal to be bound to one potassium ion. The coordination sphere of K1 is completed by two water molecules (O1w and O2w) outside the TMeQ[6] cavity and one oxygen atoms of the acetate anion inside. The average $K—O_{carbonyl}$ bond length of 2.728 Å is slightly smaller than that of 2.799 Å in the potassium complex of Q[6] previously reported (*11*). Selected bond lengths (Å) for **1** are shown in Table 2. Most notably, the acetate anion is located in the centre of the TMeQ[6] cavity to form a molecular capsule open on one side, which unambiguously confirms that TMeQ[6] is capable of encapsulating the acetate anion. Obviously, the orientation of the acetate anion in TMeQ[6] cavity is attributed to the shape complementarities and dipole–quadrupole interactions (*12*). In the crystal structure of compound **1**, the host–guest complex is isolated and these isolated molecular capsules are surrounded by water molecules and they interact with each other to form a complicated hydrogen-bonding network.

Compounds **2** and **1** crystallise with the same monoclinic $P2_1$ space group. The observed absolute structure (Flack) parameters of these two compounds are 0.09(11) and 0.0(17). However, investigation using solid-state CD spectroscopy in a KBr pellet showed that both compounds **1** and **2** were CD-silent. Their X-ray crystallography reveals that they are isomorphous. They have the same distorted TMeQ[6] crust and accommodated the

Table 2. Selected bond lengths (Å) for compounds **1** and **2**.

1		**2**	
K(1)—O(1W)	2.946(14)	Na(1)—O(1W)	2.93(3)
K(1)—O(2W)	2.642(6)	Na(1)—O(2W)	2.665(14)
K(1)—O(2)	2.733(8)	Na(1)—O(1)	2.72(2)
K(1)—O(5)	2.747(6)	Na(1)—O(5)	2.830(13)
K(1)—O(3)	2.866(7)	Na(1)—O(3)	2.851(16)
K(1)—O(4)	2.570(6)	Na(1)—O(4)	2.564(12)

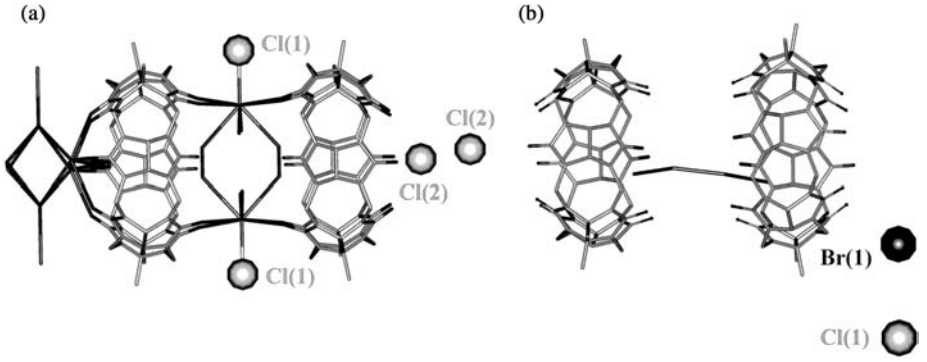

Figure 3. X-ray crystal structure of compounds **3** and **4**; solvate water molecules are omitted for clarity.

same acetate anion. Moreover, the oxygen atoms of their acetate anion all point towards the Lewis acidic metal atom. The Na − $O_{carbonyl}$ and Na − O_{water} bond lengths of 2.564(12) − 2.851(16) and 2.665(14) − 2.93(3) Å (Table 2) are much larger than those of 2.274 – 2.461 and 2.294 – 2.397 Å in $[(C_{36}H_{36}N_{24}O_{12})Na_4(H_2O)_{10}\cdot C_4H_8O_2](SO_4)_2\cdot 10H_2O$ (*13*).

To better understand the three fundamental factors (size, shape and energy) controlling anion-selective encapsulation, we investigated two contrastive compounds, $\{KCl(H_2O)_3(C_{40}H_{44}N_{24}O_{12})[K^+(H_2O)_2]_2\}\cdot 2Cl^-$ (**3**) and $\{[K^+(H_2O)]_2\cdot(C_{40}H_{44}N_{24}O_{12})\}\cdot Br^-\cdot Cl^-\cdot 6H_2O$ (**4**), the reaction products of TMeQ[6] with KCl and KBr. It should be mentioned that compounds **3** and **4** are not isomorphous, although they both crystallise in the same orthorhombic system with the same *Fddd* space group. Their X-ray crystal structures (Figure 3) clearly show that the free spherical chloride and bromide anion reside outside the ellipsoidal cavity of TMeQ[6], whereas the ellipsoidal cavity of TMeQ[6] is empty. The high water solubility of the halides and the shape mismatch between TMeQ[6] and the halides are most likely the main reasons for this phenomenon.

Solution behaviour by variable temperature ^{1}H NMR spectroscopy

As for the investigation of the host–guest interaction between TMeQ[6] and acetate anion in the aqueous solution, variable temperature ^{1}H NMR measurements were carried out. TMeQ[6] (0.0053 g, 0.005 mmol) and potassium acetate (0.002 g, 0.01 mmol) were added to an NMR tube and they dissolved completely in D_2O (0.55 ml). Typical ^{1}H NMR spectra of this mixture at different temperatures are shown in Figure 4. At 293 K, the ^{1}H NMR spectra clearly show that the methyl of the acetate anion is in different magnetic environments. The protons resonances on methyl of the acetate anion are shifted by about 0.1 ppm to higher field, which indicates that the acetate anion is buried into the cavity of TMeQ[6] and the acetate anion readily forms a stable host–guest complex with TMeQ[6] in the aqueous solution. On the other hand, the existence of two sets of signals for acetate anion, one for included acetate anion and the other for free, implies that the exchange between the two is slow on the NMR timescale.

Interestingly, we found that all the protons of the TMeQ[6] host and the acetate anion guest move downfield gradually with increasing temperature. Moreover, we found that the integration of the proton signals of the included acetate anion increases, whereas that of the proton signals of the free acetate anion decreases with increase in temperature. We, therefore, conclude that the binding constant of the host–guest complex is accompanied by the temperature, and the binding constant of the host–guest complex at high temperature is larger than that at low temperature. In principle, if the exchange of included and free guest is slow on NMR timescale, then the binding constant may be approximately evaluated by simple integration of the NMR signals for bound and unbound host or guest (*1b*). For the present host–guest complex, however, it is difficult to figure out the binding constant from the integrations of the free and included acetate anion because the proton signals of the included acetate anion and those of the methyl of TMeQ[6] partially overlap each other.

Conclusions

In summary, we have presented crystallographic reports of four TMeQ[6]-based compounds, in which TMeQ[6] displays an impressive ability to selectively encapsulate anion of appropriate size and shape within its ellipsoidal cavity. The acetate anion-encapsulating capability of TMeQ[6] was further confirmed by variable temperature ^{1}H NMR spectroscopy. There might be several reasons for the selective encapsulation of TMeQ[6] to acetate anion. First, size and shape complementarity of TMeQ[6] and the acetate anion is clearly crucial in determining selectivity. In the present case, the stretched trigonal shape of the

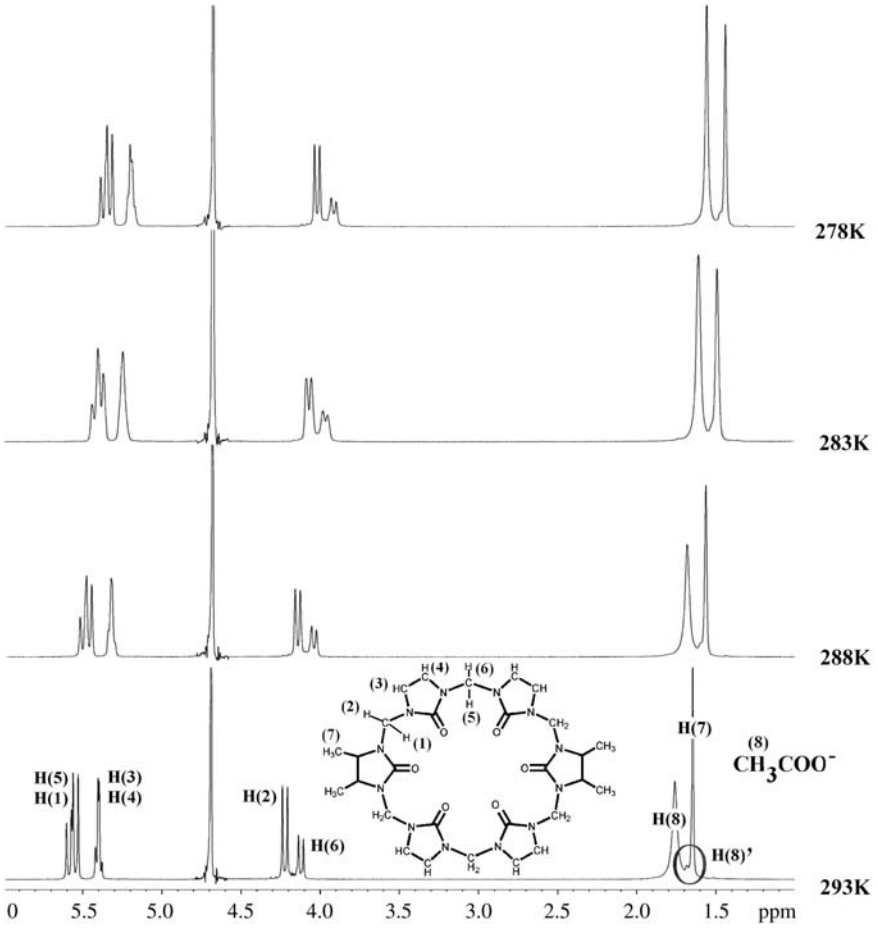

Figure 4. Variable temperature ^{1}H NMR spectra of the host–guest interaction between TMeQ[6] and acetate anion. H(8) is the methyl on non-included acetate, H(8)′ is from the methyl on cavity-included acetate.

acetate anion and the ellipsoidal cavity of TMeQ[6] are complementary to each other. Second, the hydrophobic effect of the TMeQ[6] cavity drives the formation of the host–guest inclusion complex. Note that the acetate anion is not only an anion but also an organic guest. This work not only contributes to the fundamental understanding of the mechanism of anion-selective encapsulation, but also may provide useful information for designing other hosts.

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