

Full Paper

Chlorine Anion Encapsulation by Molecular Capsules Based on Cucurbit[5]uril and Decamethylcucurbit[5]uril

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Abstract: Three barrel-shaped artificial molecular capsules **1-3**, based on normal cucurbit[5]uril (Q[5]) and decamethylcucurbit[5]uril (Me₁₀Q[5]), were synthesized and structurally characterized by single-crystal X-ray diffraction. Encapsulation of a chlorine anion in the cavity of a Q[5] or Me₁₀Q[5] to form closed a molecular capsule with the coordinated metal ions or coordinated metal ions and water molecules in the crystal structures of these compounds is common. The three complexes [Pr₂(C₃₀H₃₀N₂₀O₁₀)Cl₃(H₂O)₁₃]³⁺3Cl⁻·5H₂O (**1**), [Sr₂(C₄₀H₅₀N₂₀O₁₀)(H₂O)₄Cl]³⁺3Cl⁻·2(HCl)19H₂O (**2**) and [K(C₄₀H₅₀N₂₀O₁₀)(H₂O)Cl]·[Zn(H₂O)₂Cl₂]·[ZnCl₄]²⁻·2(H₃O)⁺·8H₂O (**3**) all crystallize as isolated molecular capsules.

Keywords: Cucurbit[5]uril, decamethylcucurbit[5]uril, crystal structure, molecular capsules.

1. Introduction

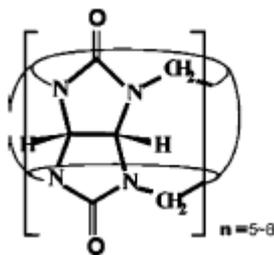
In past several decades, the coordination chemistry of cations has become well developed, while the chemistry of anion encapsulation is still in its infancy [1]. Recently, a new host-guest chemistry of anions is becoming a field of great interest [2-3]. Because anions are ubiquitous throughout biological systems [4], and they also play important roles in the areas of templation (or directed self-assembly), catalysis, environmental pollution and so on [5-6].

Many host molecules for including halide anions have been designed, synthesized and studied. The earliest macrocyclic receptor for anions, which coordinates to halide anions by a combination of electrostatic interactions and hydrogen bonds, was synthesized by Park and Simmons in 1968 [7]. More recently, calix[*n*]pyrroles and their derivatives, some imidazole derivatives and cryptands were used as receptors for halide anions through hydrogen bonds [8-12], and mercury was used as a Lewis-acidic center in a number of halide anion receptors [13].

Cucurbit[*n*=5-8]urils (Q[*n*=5-8]) are new members within the macrocyclic compound family; they are made up of glycoluril units interconnected by methylene bridges and have a macrocyclic cage rimmed by a number of carbonyl oxygens (cf. Figure 1) [14-17]. Recently some efforts have been made to introduce substitution in order to achieve ready solubility in both aqueous systems and common organic solvents, and a number of fully and partially substituted Q[*n*]s have been reported [18-23]. Decamethylcucurbit[5]uril (Me₁₀Q[5]) was the first fully substituted Q[*n*] discovered in 1992 by Stoddart and co-workers [19]. The novel structure and the capability of forming complexes with molecules and ions make the cucurbit[*n*]uril family attractive, not only as synthetic receptors but also as building blocks for supramolecular assemblies such as rotaxanes, catenanes, and molecular machines [24-30]. Nevertheless research on Q[*n*]s as receptors for anions is scarce [17, 31].

To investigate the capability of Q[*n*] inclusion anions and their potential applications, we have designed and synthesized three complexes of Q[5] and Me₁₀Q[5] in which chlorine anions are encapsulated, and herein we described this synthesis and their crystal structures.

Figure 1. Structures of the cucurbit[*n*=5-8]urils.



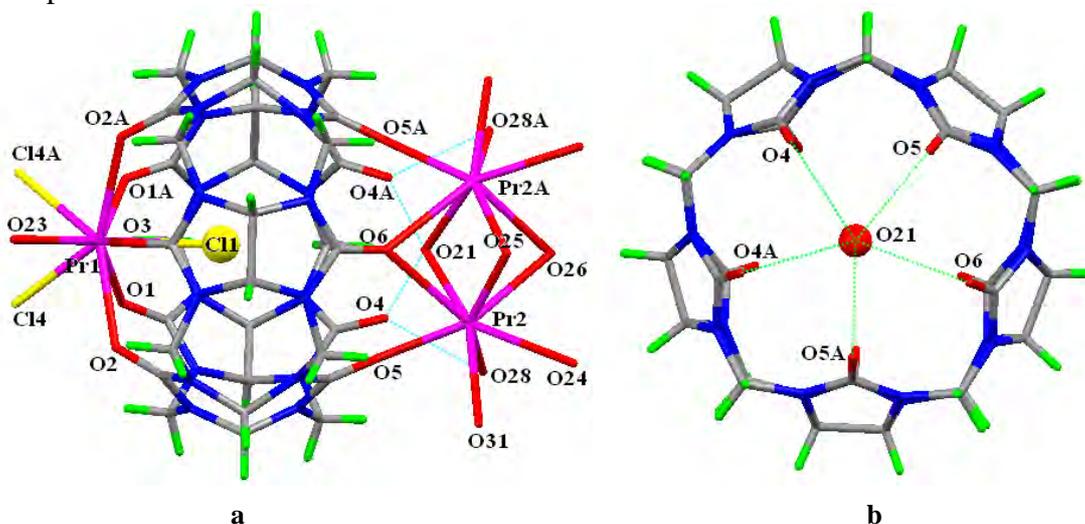
2. Results and Discussion

2.1 Crystal structure of [Pr₂(C₃₀H₃₀N₂₀O₁₀)Cl₃(H₂O)₁₃]³⁺·3Cl⁻·5H₂O (1)

In the X-ray crystals structure of Q[5] complexes with praseodymium, two praseodymium ions (Pr1 and Pr2) are coordinated to the two portals of a Q[5] molecule because the carbonyl oxygens at the Q[5] portal can provide metal ion binding sites. The Pr1 cation is nona-coordinated by five carbonyl oxygens (O1, O1A, O2, O2A and O3) with bond lengths of 2.529(4), 2.529(4), 2.577(4), 2.577(4), and 2.509(5) Å, respectively, one water molecule (O23) with a bond length of 2.530(7), and three chlorine anions (Cl1, Cl4 and Cl4A), with bond lengths of 2.766(2), 2.546(4) and 2.546(4) Å, respectively. Thus, the Pr1 cation plays a role of a lid on a Q[5] portal, while the coordinated chlorine Cl1 is encapsulated in the cavity of the Q[5]. The Pr2 atom is disordered over two positions (represented by Pr2 and Pr2A in Figure 2a). The Pr2 or Pr2A cation is octa-coordinated by two carbonyl oxygens (O5 and O6) with bond lengths of 2.358(5) and 2.774(5) Å, respectively, and six

water molecules (O21, O24, O25, O26, O28 and O31), with bond lengths of 2.509(4), 2.608(8), 2.164(6), 2.768(7), 2.612(11), and 2.333(3) Å (Figure 2a). Among these coordinated atoms or water molecules, the O21 water molecule plays an important role as a lid on the other portal of the Q[5] molecule, and the distances of this water molecule to the five carbonyl oxygens (O4, O4A, O5, O5A and O6) are 2.870, 2.870, 2.830, 2.830 and 2.881 Å (Figure 2b). Thus, the Cl1 chlorine anion coordinated to the Pr1 cation is encapsulated in the Q[5] cavity and forms a molecular capsule (Figure 2).

Figure 2. a) X-ray crystal structure of **1** (Symmetry code: (A) $x, -y+1/2, z$). Dashed lines indicate hydrogen bonding interactions. b) The water molecule O21 as a lid on the other portal of the Q[5]. Pr cations, Cl anions and water molecules are all omitted for clarity, except for O21.



2.2. Crystal structure of the complex $[Sr_2(C_{40}H_{50}N_{20}O_{10}) \cdot (H_2O)_4 \cdot Cl]^{3+} \cdot 3Cl^- \cdot 2(HCl) \cdot 19H_2O$ (**2**)

Crystals of the fully methyl substituted cucurbit[5]uril Me₁₀Q[5] with SrCl₂ were prepared and the crystal structure showed that two Sr²⁺ cations are located at the center of both portals of a Me₁₀Q[5] molecule. Each strontium ion is octa-coordinated by five carbonyl oxygens. The bond lengths of the Sr1 cation with O1, O2, O3, O4 and O5 are 2.522(3), 2.574(3), 2.574(3), 2.510(4), and 2.592(3) Å, respectively; the coordination unit also has two water molecules (O21 and O24) with bond lengths of 2.547(4) and 2.663(4) Å, respectively, and one chlorine anion (Cl1) with a bond length of 3.270 (2) Å. The two lids on each portal of the Me₁₀Q[5] are coordinated to the chlorine anion, which is located in the center of the Me₁₀Q[5] cavity. Thus, a typical molecular capsule is formed with a Me₁₀Q[5] shell capping two coordinated Sr²⁺ cations (Figure 3).

2.3. Crystal structure of the complex



Crystals of the fully methyl substituted cucurbit[5]uril Me₁₀Q[5] with KCl and ZnCl₂ solution were prepared in 2 M HCl. In the unit cell of the X-ray crystals structure of **3**, three metal ions – K1, Zn1 and Zn2 – are coordinated. The K1 cation is hepta-coordinated by five carbonyl oxygens (O1, O2, O3,

O4 and O5), with bond lengths of 2.437(7), 2.449(7), 2.587(8), 2.539(8) and 2.481(7) Å, respectively, by one water molecule (O17), with a bond length of 2.273(10), and one chlorine anion (Cl1), with a bond length of 2.677(4) Å. Like the complex **1**, the K1 cation plays a role of a lid on a Me₁₀Q[5] portal, while the coordinated chlorine Cl1 is encapsulated in the cavity of the Me₁₀Q[5].

Figure 3. X-ray crystal structure of **2**. Solvated water molecules and anions are omitted for clarity.

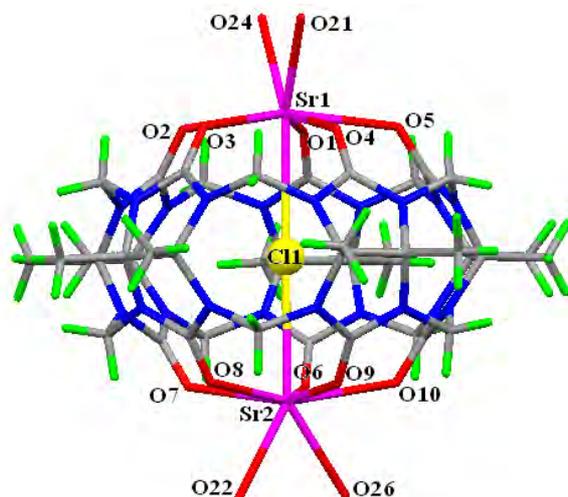
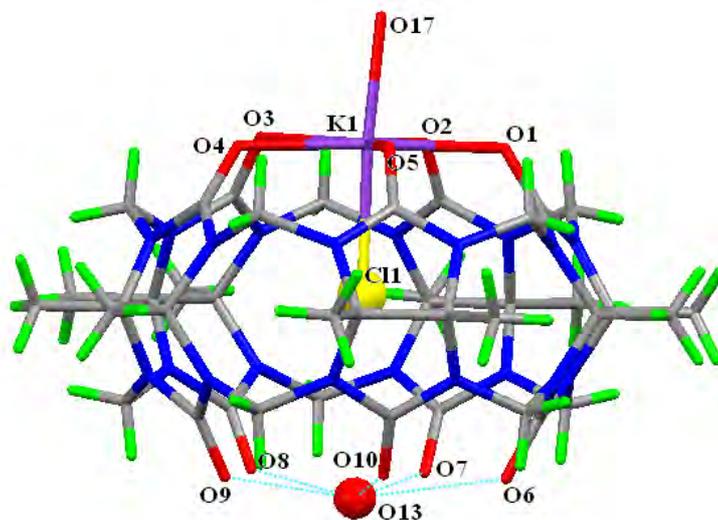


Figure 4. X-ray crystal structure of **3**, anions and solvated water molecules and anions are omitted for clarity, except for O13.



However, the Zn1 and Zn2 atoms are tetra-coordinated by four chlorine anions (Cl2, Cl3, Cl5 and Cl6) and two chlorine anions (Cl4 and Cl7) and two water molecules (O11 and O12), respectively. The experiments revealed that the Zn²⁺ transition metal cations were not involved in direct coordination to Me₁₀Q[5]. A possible explanation for this result is that the Zn²⁺ ion diameter is not effectively coordinated to the carbonyl oxygens of the portals of the Me₁₀Q[5]. It is common that cucurbituril (Q[6]) displays rather weak ligation towards transition metals (as opposed to s and f-elements), and does not replace water, as in Cr(H₂O)₆³⁺, Ni(H₂O)₆³⁺, Al(H₂O)₆³⁺, In(H₂O)₆³⁺, which remain uncoordinated [32]. At other portal of the Me₁₀Q[5], a water molecule (O13) is coordinated to the five

carbonyl oxygens (O6, O7, O8, O9 and O10) of the remaining portal of the Me₁₀Q[5] and play a role of another Me₁₀Q[5] lid. The distances of O13 to O6-O10 are 2.722, 2.646, 2.592, 2.645 and 2.627 Å respectively. Thus, a typical molecular capsule is formed with a Me₁₀Q[5] shell capping a coordinated K⁺ cation and a coordinated water molecule (Figure 4).

As has been mentioned, all three coordinated compounds encapsulate anions to form molecular capsules. The major reason for formation of these molecular capsules is electrostatic interactions. The carbonyl groups at the portal of Q[5] or Me₁₀Q[5] can provide metal ion binding sites, and when a metal ion is chelated to the carbonyl oxygen, the molecular capsule shell offers a high affinity environment for an anion, such as Cl⁻. The strong electrostatic interactions attract anions entering the cavity of the Q[5]s and lead to the formation of open or closed molecular capsules that encapsulate an anion. In the present cases of the simultaneous encapsulation of chlorine anions, the driving force appears to be electrostatic interactions. In addition, hydrophobic effect of the cavity of the Q[5]s must be taken into account, and complementarily between the receptor and the anion is clearly crucial in determining selectivity.

3. Experimental

3.1 General

Chemicals, such as zinc chloride, potassium chloride, strontium chloride, hydrochloric acid and praseodymium oxide were of commercial quality and used without further purification. Q[5] and Me₁₀Q[5] were prepared and purified according to the published procedures or procedures developed in our laboratory [16, 33]. Elemental analysis was carried out on a EURO EA-3000 element analyzer.

3.2. Synthesis

3.2.1. Preparation of [Pr₂(C₃₀H₃₀N₂₀O₁₀)Cl₃·(H₂O)₁₃]³⁺·3Cl⁻·5H₂O (**1**)

To a solution of Q[5] (0.42 g, 0.51 mmol) in HCl (3 M), Pr₂O₃ (0.83 g, 2.5 mmol) was added. The solution was heated in boiling water for 30 min and cooled to room temperature. Then the solution was filtered and the filtrate was left standing for about three months to give green crystals. Anal. Calcd. for C₃₀H₆₇Cl₆N₂₀O_{28.50}Pr₂: C, 21.71; H, 4.04; N, 16.89. Found: C, 21.74; H, 4.01; N, 16.79.

3.2.2. Preparation of [Sr₂(C₄₀H₅₀N₂₀O₁₀)·(H₂O)₄·Cl]³⁺·3Cl⁻·2(HCl)·19H₂O (**2**)

SrCl₂ (0.53 g, 2.5 mmol) was dissolved in a solution of Me₁₀Q[5] (0.77 g, 0.50 mmol) in HCl (3 M), after stirring for 10 min and heating for 30 min. Colorless crystals of **2** separated after two weeks. Anal. Calcd. for C₄₀H₉₆N₂₀O₃₃Sr₂Cl₂: C, 27.07; H, 5.42; N, 15.79. Found: C, 27.12; H, 5.38; N, 15.72.

3.2.3. Preparation of [K(C₄₀H₅₀N₂₀O₁₀)(H₂O)·Cl]·(ZnCl₄)[Zn(H₂O)₂·Cl₂]²⁻·2(H₃O)⁺·8(H₂O) (**3**)

KCl (0.29 g, 3.9 mmol) and ZnCl₂ (0.51 g, 3.9 mmol) was added to a solution of Me₁₀Q[5] (0.77g, 0.5 mmol) in HCl (3 M) and kept at room temperature in an open beaker. X-ray quality colorless crystals

of **3** separated after two weeks. Anal. Calcd. for $C_{40}H_{78}N_{20}O_{23}KZn_2Cl_7$: C, 29.54; H, 4.80; N, 17.23. Found: C, 29.59; H, 4.78; N, 17.16.

3.3. Crystal Structure Determination

The data were collected on a Bruker Apex-II CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with ω and ϕ scan mode. Lorentz polarization and absorption corrections were applied. Structural solution and full matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages [34-35], respectively. All the non-hydrogen atoms were refined anisotropically. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystallographic data, data collection and refinement parameters for compounds **1-3** are given in Table 1.

Table 1. Crystallographic data for complexes.

Complex	1	2	3
Empirical formula	$C_{30}H_{67}N_{20}O_{28.5}Pr_2Cl_6$	$C_{40}H_{96}N_{20}O_{33}Sr_2Cl_2$	$C_{40}H_{78}N_{20}O_{23}KZn_2Cl_7$
Formula weight	1658.26	1772.94	1624.99
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	P nma	P -1	P 21/n
a, \AA	15.6055(13)	16.100(4)	15.4926(11)
b, \AA	17.8941(13)	16.105(4)	25.7015(18)
c, \AA	20.3494(16)	16.465(4)	17.5866(12)
α , deg	90	65.370(3)	90.00
β , deg	90	80.916(3)	114.2380(10)
γ , deg	90	65.687(3)	90.00
V, \AA^3	5682.5(8)	3536.0(16)	6385.4(8)
Z	4	2	4
Dcalcd, g cm^{-3}	1.895	1.622	1.661
T, K	22	223	223
μ , mm^{-1}	2.080	1.834	1.199
unique reflns	5246	12139	11198
obsd reflns	4484	7836	6264
params	421	910	834
Rint	0.0508	0.056	0.0866
$R[I > 2\sigma(I)]^a$	0.0522	0.0616	0.1135
$wR[I > 2\sigma(I)]^b$	0.1450	0.1699	0.3021
R(all data)	0.0619	0.1099	0.1753
WR(all data)	0.1531	0.1927	0.3312
GOF on F^2	1.080	1.031	1.039

^a Conventional R on $Fhkl$: $\sum||F_o| - |F_c||/\sum|F_o|$. ^b Weighted R on $|Fhkl|^2$: $\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition Nos. CCDC 647406, 648721

and 648722. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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