



Original article

Dimensional effects of organic anion templates in modulating the assembly of water clusters in cucurbit[6]uril supramolecular systems



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ABSTRACT

Two new supramolecular architectures $\{(\text{HC}_2\text{O}_4)_2^{2-}[\text{C}_6\text{H}_{18}\text{N}_2^{2+} \subset \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}]\} \cdot 12\text{H}_2\text{O}$ (**1**) and $\{(\text{C}_6\text{H}_5\text{SO}_3)_2^{2-}[\text{C}_6\text{H}_{18}\text{N}_2^{2+} \subset \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}]\} \cdot 12\text{H}_2\text{O}$ (**2**) were synthesized and characterized by single-crystal X-ray diffraction, thermogravimetric analysis and X-ray powder diffraction. Compound **1** contains infinite two dimensional (2D) L18(8)14(8)8(4) type anion–water aggregates $[(\text{HC}_2\text{O}_4)_4(\text{H}_2\text{O})_{22}]^{4-}$ and results in the construction of sandwich-like three dimensional (3D) networks. In compound **2**, honeycomb-like three dimensional (3D) networks are fabricated by one dimensional (1D) “W”-like T5(0)A2 type anion–water clusters $[(\text{C}_6\text{H}_5\text{SO}_3)(\text{H}_2\text{O})_6]^-$. These results indicate that anionic groups play a crucial role in modulating the structures of water clusters with their spatial structure and binding sites. In these two structures, the majority of interactions are O...H and H...H interactions on the Hirshfeld surface, which means that hydrogen bonding and hydrophobic interactions are the dominate drive forces in forming these supramolecular systems.

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1. Introduction

Hydrogen-bonded water clusters or networks have attracted significant attention because water clusters can act as promising models for the study of water and water clusters in biological, chemical, and physical processes [1–4]. Growing larger clusters and controlling the linkage mode of small clusters to form large networks, which is the bridge between water clusters and bulk water, is still a challenging scientific endeavour [5,6].

Anion–water aggregation is an important branch of water chemistry. The negative charges and rich binding sites on anions greatly facilitate the formation of hydrogen bonds among water molecules. The water clusters with the participation of anions have larger numbers of water molecules and more interesting spatial structures, which is important in understanding the behaviour of anions in water-based biological systems [7,8]. According to the literature, extensive research efforts have been devoted to inorganic anion–water aggregation [9–15]. However, organic anion–water aggregates and their influences to the formation of water clusters have rarely been explored.

Water clusters need certain frames to support their structures, including coordination compounds and organic compounds

[16,17]. Compared to metal–organic complexes, organic frames have their own advantages in simulating biological systems. The stability of the water clusters contributes significantly to the investigation of biological molecules and stereochemistry. These networks also play an important role in the self-assembly process involving an intricate array of hydrogen-bonding interactions in the organism, which could insert, exchange and co-constitute the structures with biomolecules [18,19]. However, water clusters have not been extensively studied in a wide range of organic compounds systems, in particular, for supramolecular assembly systems.

Cucurbit[6]uril (CB[6]) is a unique macrocyclic host molecule, in which the hydrophobic cavity can provide a potential inclusion site for nonpolar units such as aliphatic chains and aromatic rings [20,21]. The polar carbonyl groups at the portals allow CB[6] to bind cations and charged molecules through charge-dipole and hydrogen-bonding interactions [22,23]. CB[6] is often utilized for the construction of supramolecular architectures, such as (pseudo)rotaxanes, polyrotaxanes and molecular necklaces [24–29]. In our previous studies, the construction of $[\text{Br}(\text{H}_2\text{O})_3]^-$ [30] and $[(\text{COO})_2(\text{H}_2\text{O})_{10}]^{2-}$ [31] in CB supramolecular systems were successfully constructed. In this study, the CB[6] supramolecular system was selected as frames to support water clusters. Therefore, consider that organic carboxylate anionic species with abundant hydrogen bonding sites may offer suitable hydrophilic environments beneficial for the existence of water clusters, organic

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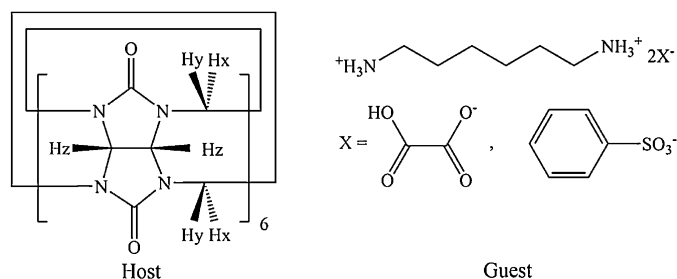


Fig. 1. The structure of host cucurbit[6]uril and the guests hexamethylene diamine salts.

carboxylate anions were added as templates to study the factors of spatial structures of water clusters.

Herein, we report the crystal structure of two supramolecular architectures using CB[6] as the host and hexamethylene diamine salt as the guest (Fig. 1), namely $\{[(\text{HC}_2\text{O}_4)_2]^{2-}[\text{C}_6\text{H}_{18}\text{N}_2^{2+} \subset \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}]\} \cdot 12\text{H}_2\text{O}$ (**1**) and $\{[(\text{C}_6\text{H}_5\text{SO}_3)_2]^{2-}[\text{C}_6\text{H}_{18}\text{N}_2^{2+} \subset \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}]\} \cdot 12\text{H}_2\text{O}$ (**2**), which involved hydrogen oxalate and benzenesulfonate as anionic templates. Two dimensional infinite L18(8)14(8)8(4) type anion–water aggregates $[(\text{HC}_2\text{O}_4)_4(\text{H}_2\text{O})_{22}]^{4-}$ and one dimensional “W”-like T5(0)A2 type anion–water clusters $[(\text{C}_6\text{H}_5\text{SO}_3)(\text{H}_2\text{O})_6]^-$ were encapsulated in these two supramolecular compounds. Hexamethylene diamine salt was used in each supramolecular compound in order to avoid the interruption caused by different guests in the structures. The two new anion–water clusters can help to delineate the effect of the space structure of anions and the positions of oxygen atoms on water clusters in CB’s supramolecular systems. The effect of intermolecular interactions on the architectures was also analyzed by Hirshfeld surface analyses. The stability and the process of dehydration and rehydration of water clusters were profiled by thermogravimetric analysis (TGA) curves and X-ray powder diffraction (XRD).

2. Experimental

2.1. Synthesis of the pseudorotaxane **1** and **2**

CB[6] was prepared according to the literatures [18,20]. A mixture of CB[6] (1.20 g, 1.20 mmol) and 1,6-hexyl-di(ammonium hydrogen oxalate) (0.296 g, 1.0 mmol) in 50 mL water was heated at 105 °C for 12 h. After stirring at room temperature overnight, the mixture was filtered and heated at 80 °C in the reactor for 1 day. X-ray quality white crystals of pseudorotaxane **1** were obtained after slowly cooled to room temperature with the yield of 73%. ^1H NMR (400 MHz, D_2O): δ 0.453–0.524 (m, 4H, H1), 0.650 (s, 4H, H2), 2.740–2.764 (m, 4H, H3), 4.325–4.354 (d, 12H, $J = 11.6$ Hz, Hx), 5.617 (s, 12H, Hz), 5.760–5.779 (d, 12H, $J = 7.6$ Hz, Hy); IR (KBr, cm^{-1}): 3003, 2362, 1736, 1624, 1471; ESI-MS: m/z : 1113.3 $[\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12} + \text{C}_6\text{H}_{18}\text{N}_2\text{H}]^+$.

The synthesis of pseudorotaxane **2** is similar to **1**. A mixture of CB[6] (1.20 g, 1.20 mmol) and 1,6-hexyl-di(ammonium benzenesulfonate) (0.434 g, 1.0 mmol) in water (50 mL) was heated at 110 °C for 24 h. After stirring at room temperature overnight, the residue was filtered off. The mixture was heated at 80 °C in the reactor for 1 day and then slowly cooled to room temperature to get X-ray quality white crystals of pseudorotaxane **2** with the yield of 65%. ^1H NMR (400 MHz, D_2O): δ 0.48–0.52 (m, 4H, H1), 0.65 (m, 4H, H2), 2.92–2.95 (t, 4H, H3), 4.35–4.39 (d, 12H, $J^2 = 7.6$ Hz, Hx), 5.61 (s, 12H, Hz), 5.71–5.74 (d, 12H, Hy), 7.80 (m, 2H, Ha), 7.53–7.62 (m, 3H, Hb, Hc); IR (KBr, cm^{-1}): 2927, 1732, 1473; ESI-MS: m/z : 1272.2 $[\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12} + \text{C}_6\text{H}_5\text{SO}_3 + \text{C}_6\text{H}_{18}\text{N}_2]^+$.

2.2. Single crystal X-ray crystallography

Single-crystal X-ray diffraction data were measured on a Bruker SMART APEX II CCD diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 173(2) K. The structures were solved by the direct method using the (SHELXL-97) and refined against F^2 in anisotropic approximation (SHELXL-97). The crystallographic data, data collection conditions and refinement parameters for compounds **1** and **2** are listed in Table 1.

3. Results and discussion

3.1. Structure descriptions

The single crystal X-ray analysis of pseudorotaxane **1** reveals the guest molecule hexamethylene diamine cation is threaded into the cavity of CB[6] by intermolecular interactions and two HC_2O_4^- anions serve as counter ions to balance the charge. In the crystal structure, the supramolecular architecture contains 3D sandwich-like networks constructed by alternating $\text{C}_6\text{H}_{18}\text{N}_2 \subset \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}$ units and anion–water clusters (Fig. 2).

Sandwich-like supramolecular networks exhibit remarkable features involving 2D infinite L18(8)14(8)8(4) type anion–water aggregates $[(\text{HC}_2\text{O}_4)_4(\text{H}_2\text{O})_{22}]^{4-}$ in compound **1** along the *boc* layer. HC_2O_4^- acts as a anionic template and induces six independent water molecules into the positions favourable for the formation of a 2D $\text{H}_2\text{O} - \text{HC}_2\text{O}_4^-$ anion layer $\{[(\text{HC}_2\text{O}_4)_4(\text{H}_2\text{O})_{22}]^{4-}\}_n$ by hydrogen bonds (Fig. 2a and b). Interestingly, the complicated water layers contain large holes defined by 12 water molecules. The HC_2O_4^- anions were located at the edges of the circular holes and act as bridges to link different $(\text{H}_2\text{O})_6$ water clusters through hydrogen bonds between the individual $(\text{H}_2\text{O})_6$ water clusters and the oxalate groups. Each HC_2O_4^- anion supplies three O atoms (O7, O9, and O10) and binds four lattice water molecules (O14W, O11W, O12W, and O14'W) through four hydrogen bonds (O–O: in the range of 2.561–2.992 Å). The O···O distance in the $(\text{H}_2\text{O})_6$ water cluster is in the range of 2.655–2.852 Å with an average value of 2.745 Å, which is extremely close to the distance of 2.74 Å in ice I_c [32], and 2.76 Å in ice I_h [33].

The 2D layer of anion–water aggregates consists of one 18-, one 14- membered macrocycles and two 8-membered small rings as loops. The 18-membered ring consists of two HC_2O_4^- anions and ten water molecules while the 14-membered ring consists of two HC_2O_4^- anions and eight water molecules. The 18-membered ring shares four water molecules (O11W, O14W, O15W, and O16W) with the 14-membered ring as the shared edge. Both rings are arranged alternately in a ladder-like conformation along the *c* axis. 8-membered rings are connected with each other through HC_2O_4^- anions to form a necklace-like structure. Ladder-like and necklace-like conformations share common edges comprising HC_2O_4^- anion and two water molecules (O11W, and O12W). The 2D anion–water layers are stacked one by one in parallel along *a* axis.

Pseudorotaxane $\text{C}_6\text{H}_{18}\text{N}_2^{2+} \subset \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}$ act as pillars and connect the 2D anion–water layers through eight hydrogen bonds (Fig. 2c). One CB[6] is connected to four lattice water molecules (O12W, O13W, O15W, and O16W) present in one anion–water layer, and four lattice water molecules (O12'W, O13'W, O15'W, and O16'W) in another anion–water layer. Pseudorotaxanes $\text{C}_6\text{H}_{18}\text{N}_2^{2+} \subset \text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}$ are stacked in tubular style with the distance of repeating unit of 12.746 Å and inserted into the anion–water layers along *c* axis. The average distance between two neighbouring supramolecular tubes at the same layer is 10.081 Å and the distance between the consecutive tubes layer is 13.160 Å. Alternating anion–water layer and tube layer form 3D sandwich-like supramolecular networks (Fig. 2d).

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