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Formation of different polymeric water clusters via organic anionic templates: More carboxylate groups used, more water molecules gathered

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ABSTRACT

Two sandwich-like frameworks with Ag(I) and mixed ligands, $[Ag_3(bpp)_3(ctc)\cdot 16H_2O]_n$ (**1**) and $[Ag_3(bpe)_3(btc)\cdot 12H_2O]_n$ (**2**) (where bpp = 1,3-bis(4-pyridyl)propane, H_3ctc = 1,3,5-cyclohexanetricarboxylic acid, bpe = 1,2-bis(4-pyridyl)ethane, and H_3btc = 1,2,4-benzenetricarboxylic acid), have been synthesized and structurally characterized. Fully deprotonated tricarboxylate ctc^{3-} in **1** or btc^{3-} in **2**, serves as anionic template driving more water molecules to aggregate into different morphologies of polymeric clusters. In **1**, the hydrogen-bonding association of sixteen lattice water molecules leads to the formation of 2D layered water, which is composed of three kinds of units including planar $(H_2O)_4$, ladder-like $(H_2O)_8$ and windmill-shaped $(H_2O)_{20}$ cluster. One novel 1D double-comb-like water aggregate constructed from alternating $(H_2O)_{22}$ cluster and water dimmer exists in **2**. The present observations suggest that anionic templates with more carboxylate groups have high tendency of being hydrated and make polymeric clusters possible.

Great interest has been focused on the rapidly expanding field of hydrogen-bonded water clusters or networks based on the fundamental importance of water in many biological, chemical and physical processes [1,2]. With the development of water clusters, they have been classified as two classes: discrete clusters (small water clusters) and polymeric clusters. Small water clusters are the subject of considerable theoretical and experimental interest as they are the first step toward understanding the anomalous properties (high boiling and melting points, high dielectric constant) of bulk water [3,4]. Growth of larger clusters and how the small clusters link to form a large network, which is the bridge between clusters and bulk water, is still a challenging scientific endeavor [5,6]. On the other hand, as a branch of water chemistry, anion–water aggregations are important in understanding the behavior of anions in water-based biological systems [7,8]. As we know, more examples are mainly focusing on inorganic anion–water aggregations [9–12], such as $[(NO_3)_4(H_2O)_6]^{4-}$, $[Cl(H_2O)_4]^-$, $[Cl_2(H_2O)_6]^{2-}$ and $[Br_2(H_2O)_6]^{2-}$, whereas organic anion–water aggregations have been largely unexplored. Thereinto, organic carboxylate anionic species with the abundance of hydrogen-bond sites may offer suitable hydrophilic environments where water clusters can exist.

In a continuation of our investigations of water clusters and carboxylic anion clusters in the lattices of crystal hosts [13,14], two strategies have been employed for the formation of different water morphologies. One strategy is the simple employment of different relative orientations of carboxylate groups situated in the aromatic ring as anionic templates [13]. In the other strategy, we choose suc^{2-} (H_2suc = succinic acid) as anionic template and modulate the $-(CH_2)_n-$ (n = 3 and 2) spacer lengths of bis(pyridyl) ligands motifs, leading to the formation of water clusters with different morphologies [14]. In this communication, we report two sandwich-like frameworks, $[Ag_3(bpp)_3(ctc)\cdot 16H_2O]_n$ (**1**) and $[Ag_3(bpe)_3(btc)\cdot 12H_2O]_n$ (**2**) (bpp = 1,3-bis(4-pyridyl)propane, H_3ctc = 1,3,5-cyclohexanetricarboxylic acid, bpe = 1,2-bis(4-pyridyl) ethane H_3btc = 1,2,4-benzenetricarboxylic acid), encapsulating an infinite 2D-layered water and 1D double-comb-like water aggregate, respectively. Attractively, in the two complexes, we will show another strategy obtaining different polymeric water clusters, i.e., more hydrophilic carboxylate groups employed, more water molecules gathered [13–16].

Complexes **1** and **2** were synthesized using one-pot methodology by ultrasonic treatment of a mixture of Ag_2O with bpp, H_3ctc or bpe, and H_3btc [17]. Single-crystal X-ray diffraction analysis revealed that complex **1** crystallizes in the triclinic space group *P*-1 [18]. The asymmetric unit of **1** consists of three Ag(I) ions, three bpp ligands, one ctc anion and sixteen lattice water molecules (Fig. 1). All the Ag(I) ions are similarly located in linear coordination geometries completed by bpp ligands. The Ag–N bond lengths fall in the ranges of 2.132(9)–2.153(11) Å (Table S1) and are well-matched to those observed in similar complexes [13,14,19]. Each flexible bpp ligand adopts a *TT* (*T* = *trans*) conformation with average N···N separation of 9.226 Å and bridges two different Ag(I) ions, yielding 1D sinusoidal cationic chains. The adjacent polymeric strands are stacked along the *b* direction in such a way that the Ag(I) ions are close to a pyridyl ring (Ag···Py, ~3.378 Å) (Fig. S1). The closest Ag···Ag is 3.804 Å, which is notably longer than the sum of the van der Waals radii of two Ag(I) ions (3.44 Å) [20] indicating that there is no Ag···Ag interaction in **1**.

In **1**, H_3ctc molecule is fully deprotonated to generate ctc^{3-} anion during the process of reaction. Each ctc^{3-} anion serves as a counter-

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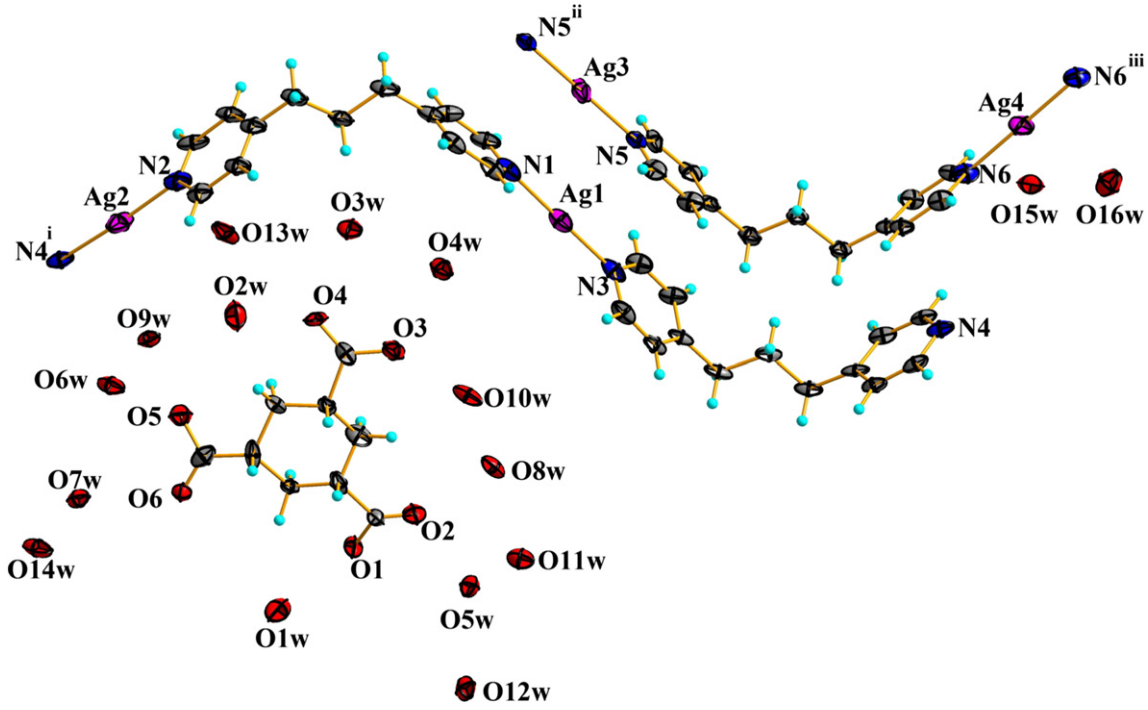

Fig. 1. ORTEP diagram depicting the building unit of crystal structure in **1** (35% thermal probability ellipsoids). Symmetry codes: (i) $x, y, z-1$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x+1, -y+2, -z+2$.

anion to balance the polymeric host charge, while not participating in the primary coordination of any Ag(I) centers. The fact that the coordination ability of nitrogen ligands (bpp) is stronger than that of the carboxylic acid functional groups of ctc^{3-} in this case can be appropriately explained by the Pearson HSAB theory [21]. As shown in Fig. 2a, ctc^{3-} as anionic template induces sixteen independent water molecules into a position favorable for the formation of hydrogen-bonded-driven 2D water–ctc anionic layer $\{[(ctc)\cdot 16H_2O]^{3-}\}_n$. Of particular interest, the complicated water layers are not continuous and contain large circular holes defined by 22 molecules of water. The ctc^{3-} anions located in

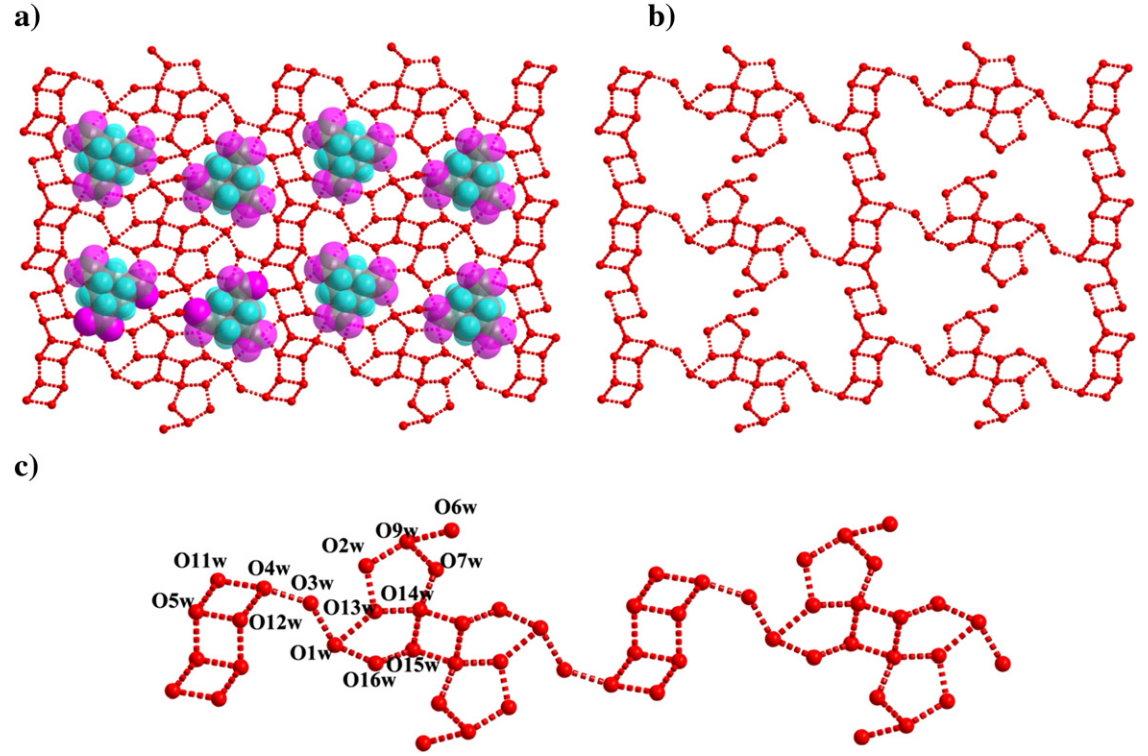

Fig. 2. (a) View showing the 2-D anionic $\{[(ctc)\cdot 16H_2O]^{3-}\}_n$ layer of **1** in which hydrogen bonds are indicated by dashed lines, (b) 2D water layer, (c) 1D water aggregate composed of ladder-like $(H_2O)_8$ and windmill-shaped $(H_2O)_{20}$ cluster.