Self-assembly of a three-dimensional supramolecular structure based on carboxyl-bridged tetrameric water clusters

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A self-assembled, tetrameric water cluster stabilised by carboxyl-bridging has been characterised by X-ray diffraction studies and thermogravimetric analysis. Every water cluster is connected strongly *via* hydrogen bonds to four carboxyl oxygens of a terephthalate anion. The water rings are stable at room temperature, but when thermally decomposed, the water loss is irreversible.

Keywords: water cluster, carboxyl-bridges, hydrogen bonds, thermogravimetric analysis

The present upsurge in studying water clusters is aimed not only at understanding the "anomalous" behaviour of bulk water, but also in probing its possible roles in the stabilisation and functioning of biomolecules[1] and in designing new materials.[2] The investigation of hydrogen-bonded water clusters $(H_2O)_n$ may provide clues to understanding the interactions of water aggregates and their surroundings.[3]

Benzimidazole (BIZ) is a typical hydrogen-bond building block, which has a potential hydrogen bond donor site as well as an acceptor site. Its derivatives are ubiquitous in biological structure and function as well as catalytic mechanisms of ribonuclease and other phosphoesterases. Therefore supramolecular chemistry, including BIZ and its derivatives, has attracted much attention.[4-7]

1,3-Bis(benzimidazolyl)benzene, a N-heterocycle that can be conveniently synthesised by condensing *o*-phenylenediamine and isophthalic acid under the influence of microwaves, is a good synthon for investigating the nature of the hydrogen bonding interaction between the N–H group and H_2O, as well as the COOH group.[8] Furthermore, the unprotonated N atom of the ligand is also a good candidate for research on O–H...N hydrogen bonds.

Attempting to understand the behaviour of water in the structure of crystals has prompted extensive investigation in recent years. Some discrete water clusters $(H_2O)_n$, (where $n = 2$–10, 12 and 16) in various crystal hosts at room temperature are known,[9-15] but to our knowledge, terephthalate anion-bridged water clusters have not been reported. We present here the preparation, crystal structure, and thermogravimetric analysis of tetrameric water clusters in a co-crystal formed by terephthalate and 1,3-bis(benzimidazolyl)benzene, $(C_{20}N_4H_{15})_2\,(C_8O_4H_4)\cdot 4H_2O$ (**1**) (tp = terephthalate, bbb = 1,3-bis(benzimidazolyl)benzene). In the adduct **1**, 1-D water chains constructed by a tetrameric water cluster and tp have been observed, in which the water chains assemble into a 3-D network through O–H...O and N–H...O hydrogen-bond interactions.

Results and discussion

The crystal lattice of **1** belongs to the triclinic system with a space group *P*-1. Tp with bbb formed binary co-crystalline salts leading to the stoichiometry $(bbb)_2\,(tp)\cdot 4H_2O$, as shown in Fig. 1. Proton transfer occurs between one molecule of the tp and the bbb. The asymmetric unit in the co-crystal consists of one molecule of 1,3-bis(benzimidazolyl)benzene, a molecule of terephthalate and two molecules of lattice water molecules. It can be seen from Fig. 1 that bbb and tp are held together by hydrogen bonds, where the amide proton on bbb serves as donor and the carbonyl group on tp as acceptor. Furthermore, the bbb and the lattice water molecules are held together by two hydrogen bonds; one where the amide proton on bbb serves as donor and oxygen on a lattice water molecule as acceptor, and a second hydrogen bond where another lattice water molecule serves as the donor and the benzimidazole nitrogen in bbb as the acceptor. The dihedral angle between the aromatic planes of tp^{-1} and bbb^{+} is 54.5°, and the dihedral angle between the aromatic plane of tp^{-1} and the midazole plane of bbb^{+} is 48.9°, the dihedral angle between the benzimidazole and the aromatic planes of protonated bbp is 12.2°.

The most interesting result is the observation of a novel one-dimensional supramolecular water chain. Fig. 2 displays

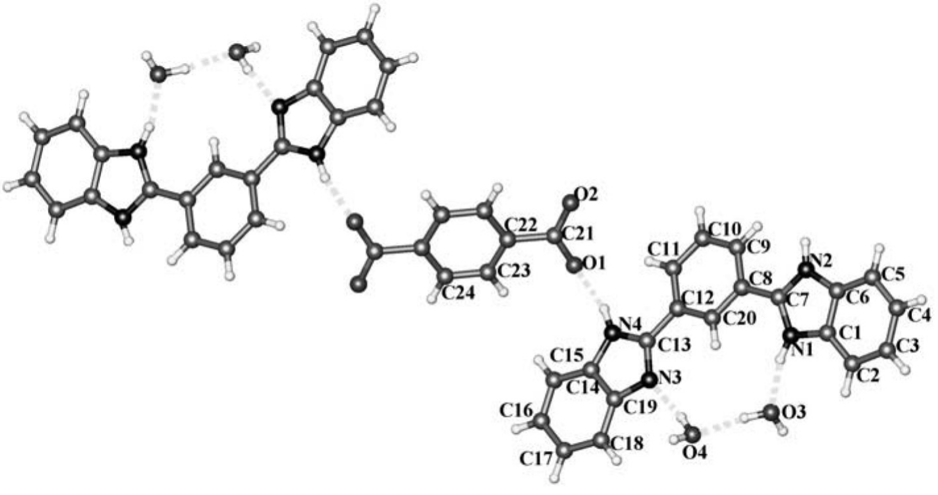

Fig. 1 Diagram of **1** with atomic labelling scheme.

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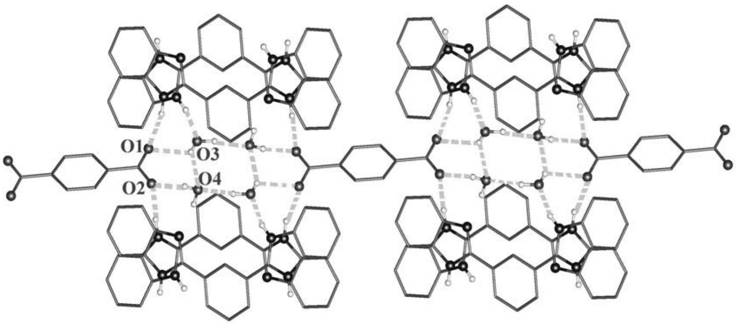

Fig. 2 1D chain formed through multiple O–H…O hydrogen bonds in the crystal structure of **1**.

Table 1 Crystal data and structure refinement parameters for **1**

Empirical formula	$C_{48}H_{42}N_8O_8$
Crystal size (mm^3)	0.32 x 0.26 x 0.19
Molecular mass	858.90
Crystal system	Triclinic
Space group	*P*-1
a (Å)	7.9422(3)
b (Å)	9.2534(3)
c (Å)	14.5539(4)
α (°)	88.9470(10)
β (°)	79.1290(10)
γ (°)	72.6560(10)
V (Å^3)	1001.83(6)
Z	1
T (K)	153(2)
*D*calcd (g cm^{-3})	1.424
F(000)	450
Reflections collected	9927
Independent reflections	4551
GoF	1.059
R^1, wR^2 [$I > 2\sigma(I)$]	$R^1 = 0.0363$, $wR^2 = 0.1057$
R^1, wR^2 (all data)	$R^1 = 0.0551$, $wR^2 = 0.1285$

the environment of the water chain, which consists of tetramer water clusters and tp, the tetramer is formed by two type of water molecule, O3, O4, both acting as hydrogen acceptor and as donor; O1 and O2 from the tp act as hydrogen-bond acceptors to bond with O3 and O4, respectively. O3 is in tetrahedral geometry, which is constructed by two hydrogen bonds in the cyclic tetramer, one hydrogen bond with the carboxyl oxygen, and a bond to the nitrogen of bbb. O4 has to two hydrogen bonds in the cyclic tetramer and one hydrogen bond with the carboxyl oxygen. Thus the carboxyl-bridged water chains are formed *via* four kinds of hydrogen bonding, O(3)–H(3AO)...O(4), O(3)–H(3BO)...O(4)#3, O(3)–H(3BO)...O(1)#4 and O(4)–H(4BO)...O(2)#5, (#3: $-x+1, -y, -z+1$; #4: $-x+1, -y+1, -z+1$; #5: $x, y-1, z$). The average O···O distance in the water clusters is 2.779 Å, which is slightly shorter than those observed in liquid water (2.854 Å) and comparable to those in the ice II phase(2.77–2.84 Å).[16] The presence of the amino group of 1,3-bis(benzimidazolyl)benzene and the nitrogen atom in the molecules leads to the formation of an extensive 3-D supramolecular structure, which is constructed *via* the N(2)–H(2N)...O(2)#2 and N(1)–H(1N)...O(3) (#2 $-x$, $-y+2$, $-z+1$) interactions.

In summary, we have prepared a tetrameric carboxyl-bridged water cluster, which acts as a glue to stabilise the host structure. The precise structural data of the water cluster and crystal host in **1** may be helpful in improving our understanding of the contribution of water clusters to the stability and function of biological assemblies, as well as the anomalous properties of water.

Thermogravimetric analysis

Adduct **1** is air stable and can retain its structural integrity at room temperature for a considerable length of time. Thermogravimetric analysis (TGA) was conducted to determine the thermal stability of the crystalline material. As shown in Fig. 3, a weight loss of 8.35% in the temperature range 50–135 °C is close to the theoretical value of 8.40% for the loss of the lattice water. The TG curve of adduct **1** exhibits a continuous weight loss stage in the temperature range 135–380 °C, corresponding to the expulsion of all base and acid components.

Experimental

The ligand 1,3-bis(benzimidazolyl)benzene was synthesised according to the procedure reported by Chawla *et al.*[17] Other reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were carried out on a Perkin-Elmer 240 elemental analyser. Thermogravimetric analysis (TGA) was performed with a Netzsch STA-499C thermoanalyser under N_2 (30–600 °C range) at a heating rate of 10 °C/min. The X-ray diffraction intensity data for the adduct was collected using Mo *Ka* radiation (κ = 0.71073Å) on a Rigaku R-axis Spide diffractometer in the h scan mode at 153(2) ^{0}K. Structure solution and refinement were carried out using the programmes SHELXS 97[18] and SHELXL97.[19] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic data for the adduct are summarised in Table 1. Hydrogen bonds are listed in Table 2.

$(C_{20}N_4H_{15})_2\ (C_8O_4H_4)\cdot 4H_2O$: Crystals were synthesised from terephthalic acid (0.021 g, 0.125 mmol), 1,3-bis(benzimidazolyl)

Table 2 Hydrogen bonds for **1** (Å and deg)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)–H(1N)...O(3)	0.878(9)	1.727(12)	2.5809(17)	163(2)
N(2)–H(2N)...O(2)#2	0.879(9)	1.849(10)	2.7262(16)	177(2)
N(4)–H(4N)...O(1)	0.872(9)	1.917(11)	2.7692(16)	165.3(18)
O(3)–H(3AO)...O(4)	0.875(9)	1.766(10)	2.6374(19)	174(2)
O(3)–H(3BO)...O(4)#3	0.843(10)	2.19(2)	2.9202(19)	146(3)
O(3)–H(3BO)...O(1)#4	0.843(10)	2.39(3)	2.9648(18)	126(3)
O(4)–H(4AO)...N(3)	0.849(10)	1.937(10)	2.7798(17)	172(2)
O(4)–H(4BO)...O(2)#5	0.849(10)	1.894(11)	2.7313(18)	169(3)
O(4)–H(4BO)...O(1)#5	0.849(10)	2.63(2)	3.1918(17)	125(2)

Symmetry transformations used to generate equivalent atoms:
#1 $-x+1, -y+2, -z$; #3 $-x+1, -y, -z+1$; #4 $-x+1, -y+1, -z+1$; #5 $x, y-1, z$.

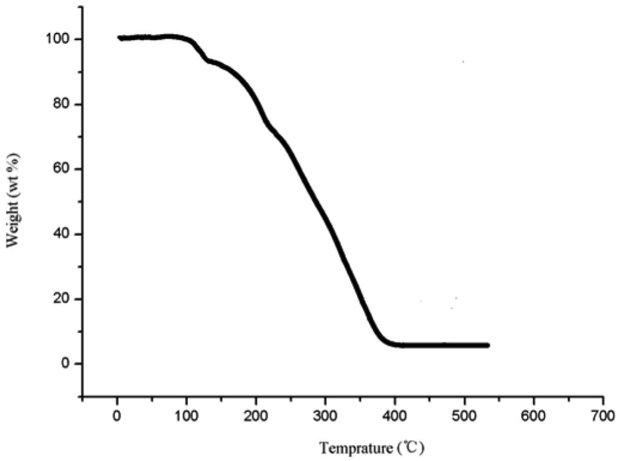

Fig. 3 The TG curve of adduct **1**.

benzene (0.039 g, 0.125 mmol) and water (15 ml), which were placed in a 23 ml Teflon-lined stainless steel Parr bomb. The bomb was heated at 433 K for 5 days and cooled to room temperature at 5 K h^{-1}. Pale yellow block crystals were obtained in 15% yield based on the initial terephthalic acid used. Anal. Calcd for $C_{48}H_{42}N_8O_8$: C, 67.12; H, 4.93; N, 13.05. Found: C, 67.08; H, 4.95; N, 13.02%.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as CCDC-691661. The author would like to thank the Huangshi Institute of Technology (grant No.07yjz07A) for financial support.

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