Supramolecular assembly based on *p*-sulfonatothiacalix[6]arene with sodium and water molecules†

Manabu Yamada,[a] Yoshihiko Kondo,[a] Kazuhiko Akimoto,[b] Chizuko Kabuto[c] and Fumio Hamada*[a]

Received (in Durham, UK) 8th May 2007, Accepted 28th August 2007
First published as an Advance Article on the web 4th September 2007
DOI: 10.1039/b706891c

A water-soluble *p*-sulfonatothiacalix[6]arene (1) has been prepared in high yield and the inclusion complex with hydrated sodium cations and water has been investigated by X-ray crystal analysis. Host 1 formed a complex with two hydrated sodium cations with ten and sixteen water molecules.

Introduction

Thiacalixarenes are analogues of calixarenes, composed of benzene rings linked *via* sulfide bridges, and have been attracting much attention because of their increased versatility over calixarenes.[1] Such versatility occurs mainly in organic solution,[2] because neither thiacalixarenes nor calixarenes are soluble in aqueous media. When thiacalixarenes are converted into water-soluble molecules, however, they become more powerful and useful as hosts because most biological processes occur in aqueous solution.[3] From this point of view, Iki *et al.* reported the synthesis of water-soluble *p*-sulfonatothiacalix[4]arene (**2**),[4] which shows removal of halogenated organic substances[5] and inclusion behavior toward water-miscible organic molecules[6] in water. In the solid state of **2** adoption of either a cone conformation or 1,3-alternate conformation occurs by changing the organic solvent molecules.[6] Later, Kunsági-Máté *et al.* reported that inclusion complexes of **2** and *p*-sulfonatocalix[6]arene (**3**) with C_{60} fullerene showed 2 : 1 and 1 : 1 stoichiometry, respectively.[7] On the other hand, many articles focused on only thiacalix[4]arene because the synthesis of thiacalix[6/8]arenes is not as easy as that of thiacalix[4]arene. Recently, Kondo and Hamada reported an improved method for the synthesis of thiacalix[6/8]arenes, however, the synthetic yields are still low.[8] It seemed to be of interest to study water-soluble thiacalix[6/8]arenes, because a couple of papers showed a difference of physical and chemical properties between thiacalix[4]arene and thiacalix[6/8]arenes.[8]

Herein we would like to present a preliminary results of water-soluble *p*-sulfonatothiacalix[6]arene (**1**). Treatment of *p*-*tert*-butylthiacalix[6]arene with conc. H_2SO_4 followed by salting out with NaCl affords an adduct [$\mathbf{1}\cdot Na_2(H_2O)_{10}\cdot 16H_2O$] as pale-brown crystals (monoclinic, space group *C*2/*c*). The most favourable reaction conditions were determined as reaction temperature and reaction time of 100 °C and 3 h, respectively (see ESI†).

In general, *p*-sulfonatocalix[4]arenes typically show a cone conformation in the solid state.[9] By contrast, the X-ray crystal structure of **3** adopts either the "up–up" double partial cone conformation or the "up–down" double partial cone conformation, so revealing conformational flexibility.[10–14] Atwood *et al.* reported the X-ray crystal structure of **3**, which shows an "up–down" double partial cone conformation,[10] in which intramolecular hydrogen bonds between the three phenolic oxygen atoms and the two remaining hydrogen atoms were observed. Furthermore, Asfari *et al.* also reported that the X-ray structure of **3** with rubidium and caesium complexes adopt an "up–down" double partial cone conformation.[11] In the solid state of **1**, the results of a single-crystal X-ray diffraction study shows the "up–down" double partial cone conformation having an inversion center, which was stabilized by intramolecular hydrogen bonds between three undissociated phenolic hydroxyl atoms. Basically, the X-ray crystal structure of **1** seems to be similar to that of **3**.[10–12] The corresponding O···O separations are O1···O2 (2.854 Å), O2···O3 (2.950 Å). It is observed that host **1** interacts with sixteen water molecules and two hydrated Na^+ as shown in Fig. 1. Binding behavior of water molecules with **1** can be classified in three groups: interactions between sulfonate group, phenolic oxygen and sulfide of **1**. There are hydrogen bonds between four water molecules and sulfide and phenolic oxygen of **1**, in which water molecule 1 binds with phenolic oxygens 1 and 2, with W1···O1 and W1···O2 distances of 2.902 and 3.275 Å, and water molecule 2 binds with phenolic oxygens 1 and sulfide 1, with W2···O1 and W2···S1 distances of 2.473 and 3.386 Å, respectively, as shown in Fig. 1. Additionally, X-ray crystal analysis reveals that another two water molecules are incorporated in the cavity of **1**, where there are hydrogen and aromatic π hydrogen bonds between the water molecules and **1** as shown in Fig. 2. Water molecule 3 (W3) interacts with sulfonate group and/or aromatic units of **1**, at distances of 3.762 and 3.530 Å, respectively. Water molecule 4 (W4) was more stabilized because there is a hydrogen bond between this water molecule and the sulfonate

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[a] *Department of Materials-process & Applied Chemistry for Environments, Faculty of Engineering and Resource Science, Akita University, Akita 010-8502, Japan. E-mail: hamada@ipc.akita-u.ac.jp; Fax: +81 18 837 0404; Tel: +81 18 889 2440*
[b] *Electronic Materials Research Laboratories, Nissan chemical Industries, Ltd, 635 Sasakura, Fuchu-Machi, Toyama 939-2792, Japan*
[c] *Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan*

† Electronic supplementary information (ESI) available: Experimental section for general procedures. See DOI: 10.1039/b706891c

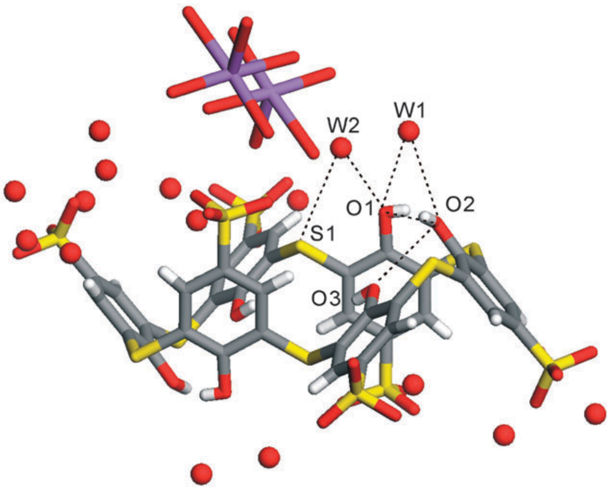

Fig. 1 Overall crystal structure of [**1** · $Na_2(H_2O)_{10}$ · $16H_2O$] showing the three "up", three "down" sulfonate group arrangement of the double partial cone conformation. The carbon, oxygen, sulfur, sodium and hydrogen atoms in [**1** · $Na_2(H_2O)_{10}$ · $16H_2O$] are gray, red, yellow, purple and white, respectively.

group of upper rim, and sulfide group and hydroxyl group of lower rim of **1**, with distances of 2.884, 3.448 and 3.426 Å, respectively.

Two water molecules located in the cavity of **1** bind together *via* a hydrogen bond with a distance of 2.823 Å. Host **1** binds together through π–π stacking interaction with a distance of 3.940 Å, which results in the formation of a sheet structure as shown in Fig. 3. There exist two hydrated Na^+ with ten water molecules, a $[Na_2(H_2O)_{10}]^{2+}$ dimer with octahedral Na and two bridging aquo ligands,[15] which were included in the layer derived from host **1** as shown in Fig. 4. X-Ray crystal analysis reveals that the Na^+ is coordinated with five water molecules, Na–O distances ranging from 2.407 to 2.460 Å. Moreover, it was observed that a water molecule with hydrated Na^+, hydrated a neighboring Na^+ at 2.435 Å. The hydrated water with Na^+ binds a sulfonate group of the host **1** *via* a hydrogen bond with NaO···OS distances ranging from 2.814 to 3.213 Å

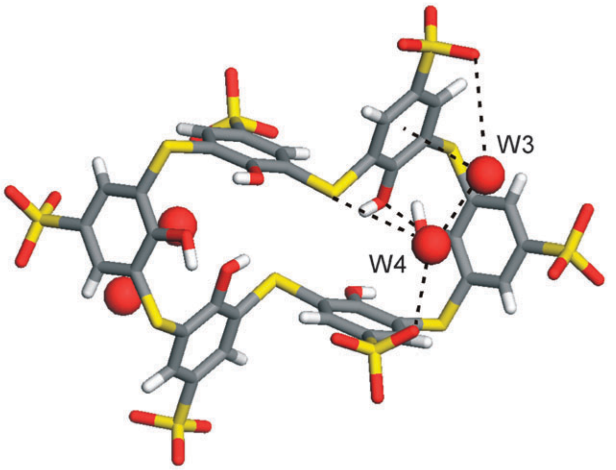

Fig. 2 Included water molecules structure in the "up–down" cavities of having the double partial cone conformation **1** (hydrated sodium cations, and non-included water molecules omitted for clarity). The carbon, oxygen, sulfur and hydrogen atoms in **1** are gray, red, yellow and white, respectively.

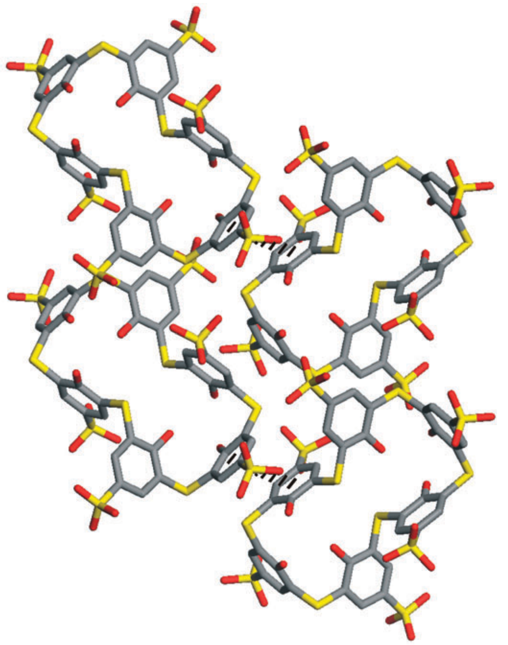

Fig. 3 Sheet structure and π–π stacking interactions in **1** parallel with the *bc* plane (hydrogens, hydrated sodium cations, included water molecules and non-included water molecules omitted for clarity). The carbon, oxygen, sulfur and hydrogen atoms in **1** are gray, red, yellow and white, respectively.

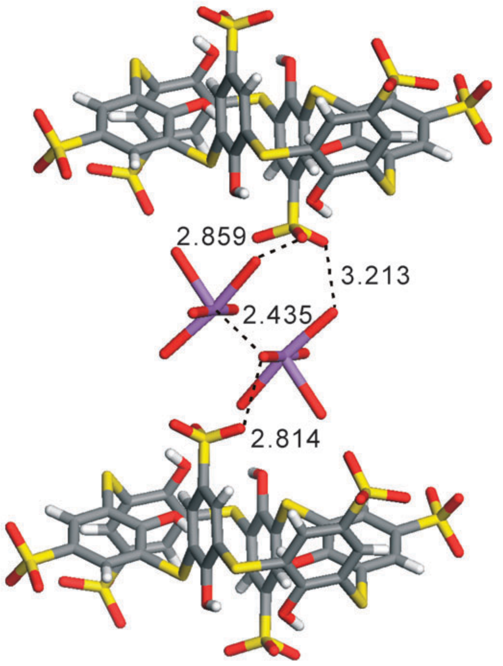

Fig. 4 Interaction between sulfonate groups of **1** and hydrated sodium along the *c*-axis (included water molecules and non-included water molecules omitted for clarity). The carbon, oxygen, sulfur, sodium and hydrogen atoms in **1** are gray, red, yellow, purple and white, respectively.

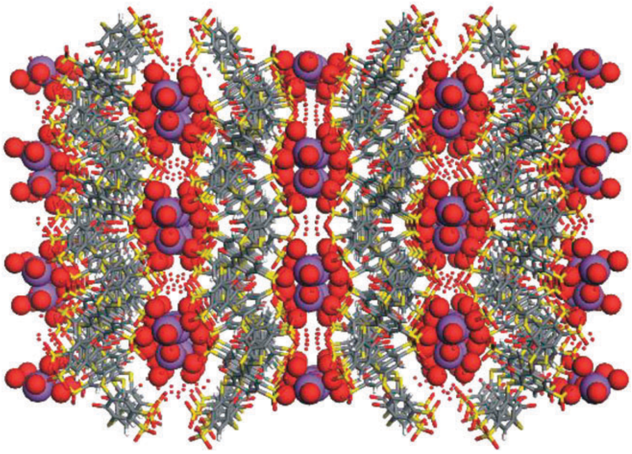

Fig. 5 Supramolecular assembly based on **1** with hydrated sodium ions and water molecules parallel with the *ab* plane. The hydrated sodium cations are shown as a CPK model. The carbon, oxygen, sulfur, sodium and hydrogen atoms in **1** are gray, red, yellow, purple, and white, respectively.

as shown in Fig. 4. Iki *et al*. reported the X-ray structure of a **2** · Na · acetone complex, in which there are direct coordination interactions among acetone carbonyl oxygen, sulfonate groups of **2** and Na^+.[6] However, in the solid state of the **2** · Na · 1,4-dioxane complex there is no coordination between sulfonate groups of **2** and sodium cations, indicating the coordination of between 1,4-dioxane and sodium cations.[6] On the other hand, it was shown that there is no coordination between Na^+ and sulfonate groups of **1**, which means that Na^+ exists in the channels formed by interaction of **1** and water molecules.

Fig. 5 shows the supramolecular assembly of sulfonate groups of **1** with water molecules of sodium cations and water molecules, which is comprised of organic and inorganic layers parallel with the *ab* plane. The complexes formed a supramolecular assembly as a result of a π–π stacking interaction among **1** in the organic layer and hydrogen bonds between coordinated water molecules of hydrated Na^+ and sulfonate groups of **1** in the inorganic layer. Organic and inorganic hybrid materials are of current interest because of their novel properties and potential for rational design of their structure and functionality.[16,17] It was interesting that a hydrated structure such as **1** was constructed, because the folding, structure, mobility, function and properties of biomolecules such as proteins and nucleic acids and biological multimolecular assemblies such as membranes all depend on the aqueous environment.[18] We are investigating metal complexes with host **1**, and have succeeded in preparing a complex with lanthanum chloride. Further studies on this system are in progress.

Experimental

Synthesis of [$\mathbf{1} \cdot Na_2(H_2O)_{10} \cdot 16H_2O$]

A mixture of *p*-*tert*-butylthiacalix[6]arene (1.0 g, 0.925 mmol) and conc. H_2SO_4 (10 mL) was heated at 100 °C for 3 h. After cooling, the precipitate was recovered by filtration. The precipitate was washed with a small amount of conc. H_2SO_4, and then the precipitate was heated and dissolved in water (60 mL), and insoluble material was removed by filtration. A white precipitate was obtained from the mother-liquor upon addition of NaCl (salting out). The solution was heated and dissolved, and upon cooling to room temperature, pale-brown crystals of [$\mathbf{1} \cdot Na_2(H_2O)_{10} \cdot 16H_2O$] were obtained: yield: 0.43 g (38%); IR (KBr) ν 3433 (O–H), 1197, 1043 (SO_3) cm^{-1}; ^1H NMR (300 MHz, D_2O) δ 7.415 (s, 12H, Ar–H); ^{13}C NMR (75 MHz, CH_3CN, D_2O) δ 122.448, 131.502, 136.571, 157.768 (Ar).

X-Ray crystallography

X-Ray crystal data for **1** were collected using a Rigaku PAXIS RAPID imaging plate diffractometer. The structure was solved by direct methods using SHELXS-97[19] and refined by full-matrix least-squares on F^2 using the SHELXL-97[20] program. The non-hydrogen atoms were refined anisotropically. Several oxygens of the sulfonate groups in structure **1** and water molecules were disordered. The hydrogens of water molecules in the structure **1** were not refined.

Crystal data. $C_{36}H_{76}O_{50}S_{12}Na_2$, M = 1739.67, brown, crystal dimensions 0.50 × 0.20 × 0.10 mm, monoclinic, space group $C2/c$ (no. 15), a = 27.7660(14), b = 11.5247(6), c = 21.2342(10), β = 94.895(2)°, V = 6770.1(6) Å^3, Z = 4, Mo-Kα radiation (λ = 0.71069 Å), D_c = 1.707 g cm^{-3}, T = 163 K, μ(Mo-Kα) = 5.137 cm^{-1}, 29 912 measured reflections, 7743 unique reflections (R_{int} = 0.081), 5989 observed reflections ($I > 2.00\sigma(I)$), 485 parameters, R = 0.1034, wR = 0.2714, refined against $|F|$, GOF = 1.128. CCDC reference number 631426. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706891c

Acknowledgements

This work was supported by Grant Industrial Technology Research (Financial support to young researchers) in 2006 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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