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Hydrogen-bonded architecture based on *p*-sulfonatothiacalix[6]arene complex with dysprosium(III) cations and water molecules

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Abstract

The structure of *p*-sulfonatothiacalix[6]arene (**1**) inclusion complex with two octa-aqua dysprosium metal cations and 15 water molecules was examined by single-crystal X-ray diffraction studies. The complex showed a 2D hydrogen-bonded polymer with hydrogen bonding interactions between aquo ligands of dysprosium metal cations and sulfonate groups of thiacalixarene. In addition, it shows direct evidence for hydrogen bonding between the imbedded water and the aromatic π electrons.

In recent years, water-soluble *p*-sulfonatocalixarenes have attracted considerable attention as building blocks in the field of crystal engineering and supramolecular chemistry because there are interesting inclusion properties and a range of metal co-ordination complexes both in solution and in the solid state.[1–3] *p*-Sulfonatocalixarenes have shown a high potentiality as host molecules for hydrophobic and hydrophilic guests. Atwood et al. reported a versatility of characteristics on *p*-sulfonatocalix[4]arene as pseudo-biological system model and hydrogen bonding of water with aromatic π, which is obtained by single-crystal X-ray diffraction studies.[3] The interaction of water with aromatic π is an important work in biological system because most biological processes occur in aqueous media.

In general, the crystal structures of *p*-sulfonatocalix[4]arenes typically adopt a cone conformation, which is composed of a sandwich-like interleaved structure of organic layer and inorganic layer.[4] The X-ray crystal structures of *p*-sulfonatocalix[6]arenes, by contrast, adopt either an 'up–up' double partial cone conformation or an 'up–down' double partial cone conformation, so revealing conformational flexibility.[5–9] The properties of *p*-sulfonatocalix[6]arenes seem to be controlled by the combination or stoichiometry of organic ligand compounds and lanthanide metal cations.[7–9] On the other hand, *p*-sulfonatothiacalix[4]arene (**2**) is shown to form two different conformational structures in the solid state.[10] The X-ray crystal structure of **2**·Na·acetone complex adopts cone conformation, where there is direct co-ordination among acetone carbonyl oxygen, sulfonate groups of **2**, and sodium cations. However, in the solid state of **2**·Na·1,4-dioxane complex adopts 1,3-alternate conformation with no co-ordination between sulfonate groups of **2** and sodium cations there is co-ordination between 1,4-dioxane and sodium cations. It has been reported that changing the organic guest molecules has brought changes in the conformational structure of **2** and co-ordination state between metal cations and sulfonate groups of thiacalixarene.

Previously, we reported the synthesis of *p*-sulfonatothiacalix[6]arene (**1**) and the characterization of crystal structure of **1** complex with two penta-aqua sodium metal cations and 16 water molecules.[11] The obtained [**1**·$Na_2(H_2O)_{10}$·$16H_2O$] complex structure was revealed as the 'up–down' double partial cone conformation, which formed a supramolecular assembly as a result of the π–π staking interactions from the base of thiacalixarene to the

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nearest adjacent thiacalixarene and hydrogen bond between aquo ligands of aquated sodium metal cations and sulfonate groups of thiacalixarene. However, X-ray crystal structures of larger macrocyclic oligomer such as thiacalix[6]arene[12] are recently less researched, because the synthesis of larger macrocyclic thiacalix[6/8]arenes is more difficult than that of the smallest macrocyclic thiacalix[4]arene.[13] Furthermore, it is expected that such lanthanide metal complexes of larger macrocyclic **1** are possible to show a unique nature because it is well known that lanthanide complexes show favorable properties such as energy-transfer luminescence and magnetic characteristics.[14]

Herein we would like to report the X-ray diffraction analysis of larger macrocyclic oligomer **1** inclusion complex with dysprosium metal cations and water molecules, and present a supramolecular formation among **1**, water molecules, and aquated dysprosium metal cations. Slow evaporation of 1:2 molar ratio of **1** and dysprosium(III) chloride afforded a crystalline complex as [**1**$\cdot$$Dy_2(H_2O)_{16}\cdot 15H_2O$], that is [{*p*-sulfonatothiacalix[6]arene^{6-}}{$Dy(H_2O)_8{}^{3+}$}$_2$ $(H_2O)_{15}$], which was characterized by single-crystal X-ray diffraction studies (monoclinic, space group $P2_1/n$).[15] Although all hydrogen atoms of water molecules were clearly visible in this complex, their positions could not be refined. However, the thiacalixarene of [**1**$\cdot$$Na_2(H_2O)_{10}\cdot 16H_2O$] which is [{*p*-sulfonatothiacalix[6]arene^{2-}}{$Na(H_2O)^{5+}$}$_2${H_2O}$_{16}$], shows different charges of [**1**$\cdot$$Dy_2(H_2O)_{16}\cdot 15H_2O$], because the calixarene is versatile in taking on different charges by the valencies of their metal cations examined. In the solid state of [**1**$\cdot$$Dy_2$ $(H_2O)_{16}\cdot 15H_2O$] complex, the results of X-ray diffraction analysis show to adopt the 'up–down' double partial cone conformation having an inversion center, which is stabilized by intramolecular hydrogen bonding among three phenolic hydroxyl groups with the OH$\cdots$O distances of 2.413 and 2.734 Å, respectively, as shown in Figures 1 and 2.The complex has no co-ordination between sulfonate groups of thiacalixarene and dysprosium metal centers. However, it seems that two aquated dysprosium metal cations are captured in the 'up–down' cavity of thiacalixarene. Two captured aquated dysprosium metal cations are stabilized by hydrogen bonding between aquo ligands of aquated dysprosium metal cations and oxygens of the sulfonate groups in the cavity of thiacalixarene with the DyO$\cdots$OS distances ranging from 2.791 to 2.981 Å, respectively. In addition, each of these dysprosium cations has eight aquo ligands with the Dy–O distances ranging from 2.321 to 2.395 Å, respectively. To the best of our knowledge, this is uncommon for binary systems of *p*-sulfonatocalix[6]arene complex with transition or lanthanide metals. Eight included water molecules form intricate hydrogen-bonded networks in the 'up–down' cavity of thiacalixarene at the O$\cdots$H–O distances ranging from 1.707 to 2.303 Å, as shown in Figure 2. Hydrogen bond consists of one phenolic hydroxyl group and one imbedded water molecule at a distance of 1.966 Å. Furthermore, there is OH-aromatic π hydrogen bonding between the imbedded water molecule and an aromatic moiety of thiacalixarene with a centroid$\cdots$H distance at 2.502 Å and the centroid$\cdots$H–O angle of 144°. The H–O–H angle is 117°. In detail, as shown in Figure 3, there is an interaction among host **1**, aquated dysprosium metal cations and water molecules. Thus, hydrogen bonding can be classified into three groups: interactions between inside and outside water molecules, aquated dysprosium metal cations and **1**. The complex forms hydrogen-bonded networks by intermediations of aquated dysprosium cations between organic layer and inorganic layer. The extended structure of [**1**$\cdot$$Dy_2(H_2O)_{16}\cdot 15H_2O$], which forms 2D hydrogen-bonded

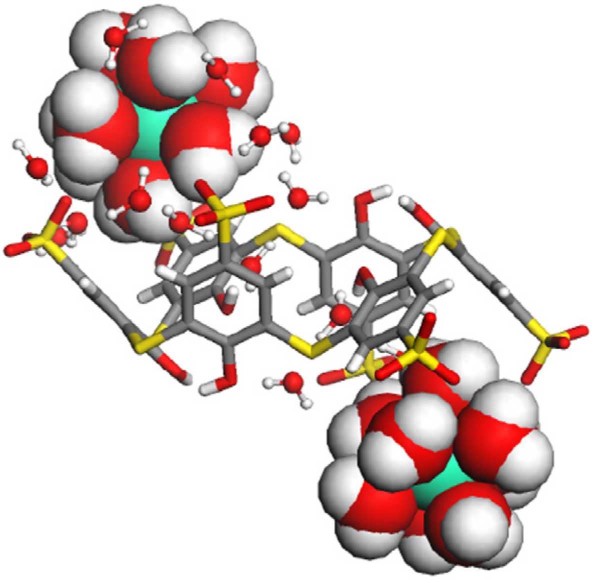

Fig. 1. The X-ray structure of [**1**$\cdot$$Dy_2(H_2O)_{16}\cdot 15H_2O$] complex showing the 'up–down' double partial cone conformation. The carbons, oxygens, sulfurs, dysprosiums, and hydrogens in [**1**$\cdot$$Dy_2(H_2O)_{16}\cdot 15H_2O$] are in gray, red, yellow, green, and white, respectively.

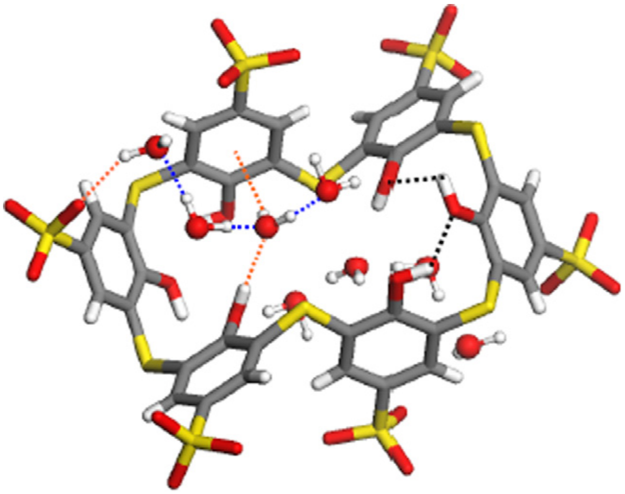

Fig. 2. Imbedded water molecules showing intramolecular hydrogen bonding interactions in the 'up–down' cavities of thiacalixarene (blue, orange, and black dotted lines, respectively).

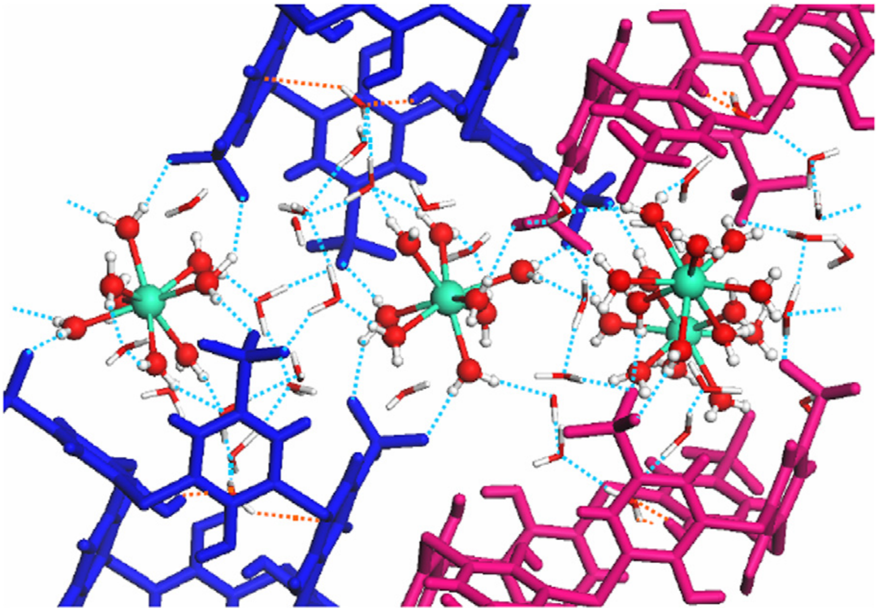

Fig. 3. Hydrogen-bonded networks formed by interactions among water, aquated dysprosium cations and host **1** (blue, orange dotted lines, respectively).

polymer by interactions between aquated dysprosium metal cations and neighboring sulfonate groups of thiacalixarene at DyO···OS distances ranging from 2.713 to 2.981 Å, respectively, is shown in Figures 4 and 5. In addition, organic layers of thiacalixarene are confirmed to be involving thiacalixarene unit in two different directions, but both molecular structures indicate same conformation. In the two mixed layers of thiacalixarenes, π–π stacking interactions are recognized between the base thiacalixarenes and the nearest adjacent thiacalixarenes with an aromatic centroid···centroid distance of 3.673 Å. In the same layers of thiacalixarenes at the base, hydrogen bonding is recognized between two hydroxyl groups and a sulfonate group of the nearest adjacent thiacalixarene with distances of 2.825 and 3.467 Å. As mentioned above, overall crystal structure of the complex is comprised of organic and inorganic layers, which formed supramolecular assemblies because of the π–π stacking and hydrogen bonding interactions between the base thiacalixarene and the nearest adjacent thiacalixarene, hydrogen bonding interactions between aquo ligands of aquated dysprosium cation and sulfonate groups of thiacalixarene, and a formation of water molecule networks in parallel with *ac* plain as shown in Figure 6.

In conclusion, we succeeded in the synthesis of *p*-sulfonatothiacalix[6]arene inclusion complex with aquated

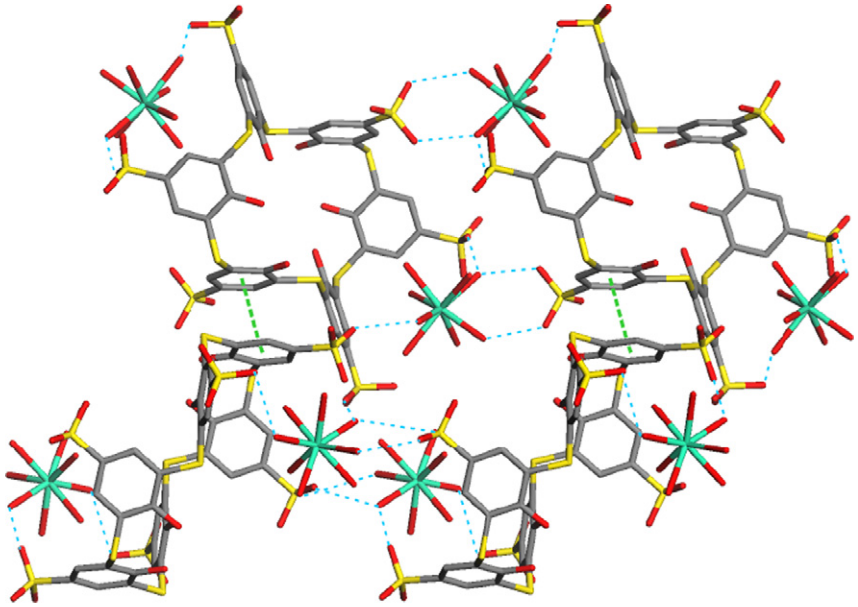

Fig. 4. Extended structure of [**1**·$Dy_2(H_2O)_{16}$·$15H_2O$] complex showing hydrogen bonding and π–π stacking interactions between the two mixed layers of thiacalixarenes (green and blue dotted lines, respectively).

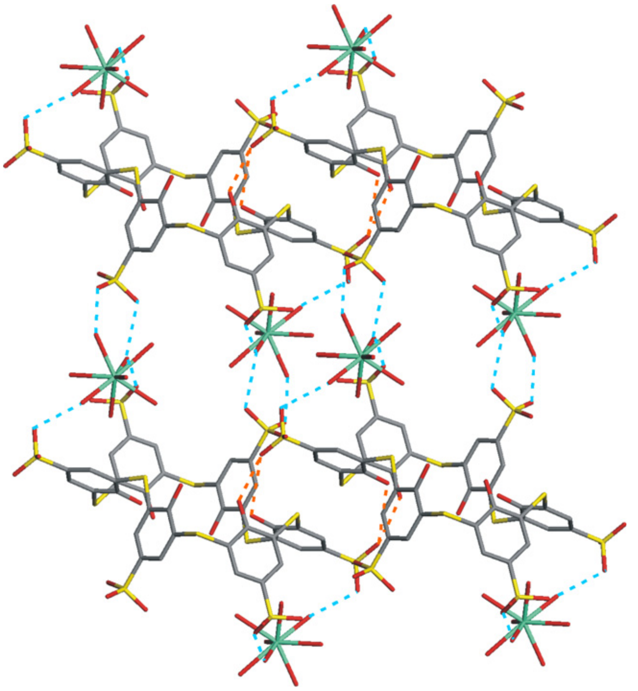

Fig. 5. Extended structure of [**1**·$Dy_2(H_2O)_{16}$·$15H_2O$] complex showing hydrogen bonding interactions between the same layers of thiacalixarenes (orange and blue dotted lines, respectively).

dysprosium metal cations and water molecules. In comparison with [**1**·$Na_2(H_2O)_{10}$·$16H_2O$] complex, the results of X-ray crystal analysis of [**1**·$Dy_2(H_2O)_{16}$·$15H_2O$] appears to be similar to the molecular structure of [**1**·$Na_2(H_2O)_{10}$·$16H_2O$] complex. However, two complexes show a different behavior because the ion radius of dysprosium is smaller than that of sodium. It was suggested that host **1** could recognize each of the aquated metal cations. It was found that aquated dysprosium cations were captured in the 'up–down' thiacalixarene cavity because the molecular structure of **1** can alternate size to fit the aquated dysprosium cations. This suggests that thicalixarenes have more flexibility than calixarenes because there are sulfide groups at the bridged moieties. Iki et al. reported a greater flexibility of thiacalixarenes than that of calixarenes.[16] Therefore, it seems that a fashion of co-ordination between sulfonate groups of **1** and metal centers might be affected by the ion radius of metals examined. It seems that interactions between host **1** and water are important evidence of biological system because it was demonstrated in biomolecules such as proteins and enzymes.[3] We are investigating metal complexes with host **1**, and further studies on this system are in progress.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.01.049.

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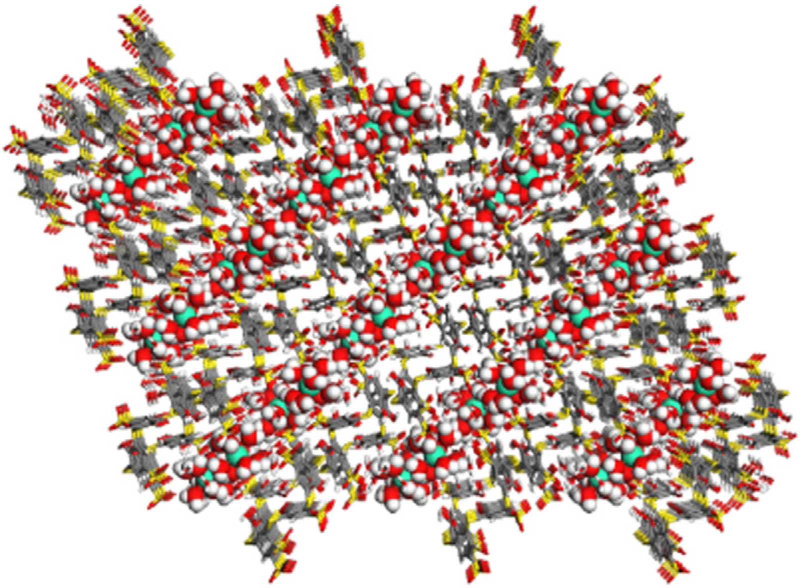

Fig. 6. Packing diagram of the bi-layer in [**1**·$Dy_2(H_2O)_{16}$·$15H_2O$] complex showing interactions among thiacalixarene, aquated dysprosium metal cations, and water molecules in parallel with *ac* plain.

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15. *Preparation of* $[\mathbf{1}\cdot Dy_2(H_2O)_{16}\cdot 15H_2O]$: To a solution of **1** (40 mg, 32 μmol) dissolved in distilled water (3 cm^3) was added dysprosium chloride (17.2 mg, 64 μmol). On standing over several days, large colorless block crystal suitable for single-crystal X-ray diffraction studies formed, 9.8 mg, 15%. IR (KBr): ν 3384 (O–H), 1151, 1045 (SO_3) cm^{-1}.

    Crystal data for $[\mathbf{1}\cdot \mathrm{Dy_2(H_2O)_{16}\cdot 15H_2O}]$: $C_{36}H_{80}O_{55}S_{12}Dy_2$, $M = 2102.72$, colorless, size $= 0.2 \times 0.2 \times 0.2$ mm, $a = 15.5071(5)$, $b = 12.2820(4)$, $c = 20.5764(8)$ Å, $V = 3670.7(2)$ Å^3, $\beta = 110.5027(11)°$, Mo Kα radiation ($\lambda = 0.71069$ Å), space group $P2_1/n$ (No. 14), monoclinic, $Z = 2$, $D_{calcd} = 1.902$ g/cm^3, $T = 103$ K, μ(Mo Kα) = 24.782 cm^{-1}, 34,972 measured reflections, 8373 unique reflections ($R_{int} = 0.040$), 7445 observed reflections ($I > 2.00\sigma(I)$), 479 parameters, $R_1 = 0.0256$, $wR_2 = 0.0583$, GOF = 1.05. CCDC reference number 662801.
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