The X-Ray Crystal Structures of *p*-Sulfonatocalix[6]arene Inclusion Complexes with Lanthanide Metal Ions ($M = \text{Gd}$, Ho and Er) and Water Molecules

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Three crystal structures of *p*-sulfonatocalix[6]arene (**1**) inclusion complexes with octa-aqua lanthanide metal ions ($M = \text{Gd}^{3+}$, Ho^{3+} , and Er^{3+}) have been determined by single crystal X-ray diffraction studies. Three structures show a same conformation as "up-down" double partial cone conformation. The aquated lanthanide metal ions were captured in the "up-down" cavities of thiacalixarene. In the overall their crystal structures, supramolecular assemblies are formed by hydrogen bonds and $\pi-\pi$ stacking interactions.

Key Words : calixarenes, thiacalixarenes, crystal structures, lanthanide complexes

1. Introduction

Thiacalixarenes are analogue of calixarenes, which have been attracted considerable attentions as key compounds in both of coordination chemistry and supramolecular chemistry. It have been already shown a difference of physical and chemical properties between calixarenes and thiacalixarenes.[1] In comparison with calixarenes, thiacalixarenes form the infinite coordinated complexes with metal ions because the sulfide groups of thiacalixarenes have affinity toward metal ions.[2] Therefore, many coordination complexes between thiacalixarenes and a wide range of metal ions have been synthesized and their crystal structures and unique properties such as gas adsorption and magnetization were revealed. However, such versatility occurs mainly in organic solution, because neither thiacalixarenes nor calixarenes are soluble in aqueous media. When thiacalixarenes are converted into water-soluble molecules, they must be more powerful and attractive as host molecules than those of calixarenes.[3]

Water-soluble *p*-sulfonatocalixarenes have been shown a high potentiality as host molecules for hydrophobic and hydrophilic guests.[3,4] Atwood *et al.* pioneered a new field of *p*-sulfonatocalix[4]arene chemistry as pseudo-biological system model and offered proof of hydrogen bonding between water and aromatic π , which is revealed by single-crystal X-ray diffraction studies.[4] The interaction of water with aromatic π is an important work in biological system.

In general, the crystal structures of *p*-sulfonatocalix[4]arene-complex typically adopt a cone conformation, which composed of a sandwich-like interleaved structure of organic and inorganic layer.[5] The X-ray crystal structures of *p*-sulfonatocalix[6]

arene-complex, by contract, adopt either an "up-up" double partial cone conformation or an "up-down" double partial cone conformation, which reveal conformational flexibility.[6] The properties of *p*-sulfonatocalix[6]arene-lanthanide metal complexes seem to be controlled by combination or stoichiometry of lanthanide metal ions used as guest.

Firstly, a water-soluble *p*-sulfonatocalix[4]arene (**2**) was synthesized by Iki *et al.*, which is estimated an inclusion ability toward water-miscible organic molecules such as alcohols, ketones, cyclic ethers and so on.[7] It is shown that the inclusion ability of **2** is higher than that of *p*-sulfonatocalix[4]arene. Furthermore, it is thrown up that the X-ray structures of **2** inclusion complex with sodium ion and water-miscible organic molecules have two different conformational structures, which are a cone and 1,3-alternate conformation. It is demonstrated that the adoption of these conformations would be depended on organic solvent used. The inclusion capability of *p*-sulfonatocalix[6]arene is also estimated toward ferrocenyl guests in the aqueous solutions by voltammetric study.[8]

On the other hand, we recently reported two crystal structures of **1** complexes with alkali ion and lanthanide ion.[9,10] The X-ray structure of **1** complex with two aquated sodium ions with ten and sixteen water molecules, [**1**• $\text{Na}_2(\text{H}_2\text{O})_{10} \cdot 16\text{H}_2\text{O}$], showed the "up-down" double partial cone conformation. The overall crystal structure of the complex formed a supramolecular assembly as the result of the $\pi-\pi$ stacking interactions from the base of thiacalixarene to the neighboring thiacalixarene and hydrogen bond between aquo ligands of aquated sodium ions and sulfonate groups of thiacalixarene. Also, the crystal structure of **1** complex with two aquated dysprosium ions with sixteen and fifteen water molecules, [**1**• $\text{Dy}_2(\text{H}_2\text{O})_{16} \cdot 15\text{H}_2\text{O}$], was revealed as the "up-

down" double partial cone conformation, which formed a supramolecular assembly because of the π - π staking interactions between the base of thiocalixarene and the nearest adjacent thiocalixarene and hydrogen bond between aquo ligands of aquated dysprosium ions and sulfonate groups of thiocalixarene.

Herein we would like to report another three crystal structures of **1** inclusion complexes with trivalent lanthanide metal ions (M=Gd³⁺, Ho³⁺, and Er³⁺) and water molecules, which were identified as a supramolecular.

2. Experimental

X-Ray crystallography

X-Ray data for three complexes was collected using Rigaku PAXIS RAPID imaging plate diffractometer. The structures were solved by direct methods and refined full-matrix least-squares refinement on F^2 using the CrystalStructures crystallographic package. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms in the complex **I**, **II**, and **III** were determined by difference synthesis.

General procedure and crystal data:

p-Sulfonatothiocalix[6]arene (**1**) was synthesized according to literature procedure.[9]

Preparation of complex I: To solution of **1** (40.4 mg, 33 μ mol) dissolved in water (1.5 cm³) was added gadolinium chloride hexahydrate (24.8 mg, 66.7 μ mol). On standing over several days, large colorless block crystal suitable for single-crystal X-ray diffraction studies formed.

Crystal data: C₃₆H₈₂O₅₆S₁₂Gd₂, $M=2110.23$, colorless, size=0.2 $\times$ 0.15 $\times$ 0.15 mm, $a=15.568(2)$, $b=12.2974(18)$, $c=20.653(3)$ Å, $\beta=110.663(2)^\circ$, $V=3699.5(9)$ Å³, Mo-K α radiation ($\lambda=0.71075$ Å), space group $P2_1/n$ (No.14), $Z=2$, $D_{\text{calc}}=1.894$ g/cm³, $T=103$ K, $\mu(\text{MoK}\alpha)=2.235$ cm⁻¹, 34586 measured reflections, 8360 unique reflections ($R_{\text{int}}=0.050$), 6712 observed reflections ($I>2.00\sigma(I)$), 518 parameters, $R1=0.0484$, $wR2=0.1886$, GOF=0.991. CCDC reference number 675396.

Preparation of complex II: To solution of **1** (40 mg, 32 μ mol) dissolved in water (1.5 cm³) was added holmium chloride hexahydrate (24.3 mg, 64 μ mol). On standing over several days, large pink block crystal suitable for single-crystal X-ray diffraction studies formed.

Crystal data: C₃₆H₈₀O₅₅S₁₂Ho₂, $M=2107.58$, pink, size=0.25 $\times$ 0.2 $\times$ 0.2 mm, $a=15.5033(6)$, $b=12.2830(5)$, $c=20.6091(6)$ Å, $\beta=110.6200(12)^\circ$, $V=3673.1(2)$ Å³, Mo-K α radiation ($\lambda=0.71075$ Å), space group $P2_1/n$ (No.14), $Z=2$, $D_{\text{calc}}=1.905$ g/cm³, $T=103.1$ K, $\mu(\text{MoK}\alpha)=2.478$ cm⁻¹, 34194 measured reflections, 8324 unique reflections ($R_{\text{int}}=0.044$), 6794 observed reflections ($I>2.00\sigma(I)$), 518 parameters, $R1=0.0246$, $wR2=0.0406$, GOF=0.919. CCDC reference number 675397.

Preparation of complex III: To solution of **1** (20.5 mg, 16.7 μ mol) dissolved in water (1.5 cm³) was added erbium chloride hexahydrate (12.4 mg, 32.5 μ mol). On standing over several days, large pale-pink block crystal suitable for single-crystal X-ray diffraction studies formed.

Crystal data: C₃₆H₈₂O₅₆S₁₂Er₂, $M=2130.25$, pale-pink, size=0.2 $\times$ 0.2 $\times$ 0.2 mm, $a=15.5033(9)$, $b=12.2838(8)$, $c=20.5722(13)$ Å, $\beta=110.5320(19)^\circ$, $V=3668.9(4)$ Å³, Mo-K α radiation ($\lambda=0.71075$ Å), space group $P2_1/n$ (No.14), $Z=2$, $D_{\text{calc}}=1.928$ g/cm³, $T=103.1$ K, $\mu(\text{MoK}\alpha)=2.725$ cm⁻¹, 33539 measured

reflections, 8366 unique reflections ($R_{\text{int}}=0.041$), 7198 observed reflections ($I>2.00\sigma(I)$), 520 parameters, $R1=0.0244$, $wR2=0.0605$, GOF=1.001. CCDC reference number 675395.

3. Results and Discussion

3.1. The X-ray structure of *p*-sulfonatothiocalix[6]arene with aquated gadolinium metal ions and water molecules

Slow evaporation of 1:2 molar ratios of **1** and gadolinium (III) chloride afforded a crystalline complex, **I**, which was characterized by single-crystal X-ray diffraction studies. Complex **I** crystallizes in the space group $P2_1/n$, and had an overall composition [*p*-sulfonatothiocalix[6]arene⁶⁻] {Gd(H₂O)₈³⁺}₂(H₂O)₁₆] as shown in Figure 1. Charge neutrality dictates the thiocalixarene is in the hexa-anion form. It was found that same charges between complex **I** and [**1**•Dy₂(H₂O)₁₆•15H₂O] complex. In the solid state of the complex **I**, the results of X-ray diffraction analysis shows 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...O distances of 2.283 and 2.714 Å, respectively, as shown in Figure 2. The complex has no coordination between sulfonate groups of thiocalixarene and gadolinium metal centers. However, it seems

Figure 1 The X-ray structure of complex **I** showing the "up-down" double partial cone conformation. The carbons, oxygens, sulfurs, dysprosiums, and hydrogens in the complex **I** are in gray, red, yellow, blue, and white, respectively.

Figure 2 The structure of complex **I** showing intramolecular hydrogen bonding interactions between imbedded water molecules and aquated gadolinium ions in the "up-down" cavities of thiocalixarene (blue, and green dotted lines, respectively).

that two aquated gadolinium ions are incorporated in the "up-down" cavities of thiacalixarene. Two captured aquated gadolinium ions are stabilized by hydrogen bonding between aquo ligands of aquated gadolinium ions and oxygens of the sulfonate groups in the cavity of thiacalixarene with the Gd-OH $\cdots$ OS distances ranging from 1.958 to 2.135 Å, respectively. In addition, each of these gadolinium ions has eight aquo ligands with the Gd-O distances ranging from 2.348 to 2.417 Å, respectively. Eight included water molecules and two aquated gadolinium ions form an intricate hydrogen bonded networks in the "up-down" cavity of thiacalixarene at the O $\cdots$ H-O distances ranging from 1.720 to 1.925 Å. Hydrogen bond consists of one of the phenolic hydroxyl group and one of the imbedded water molecule at a distance of 1.884 Å. Furthermore, there are OH-aromatic π hydrogen bonding between the imbedded water molecule and an aromatic moiety of thiacalixarene with a centroid $\cdots$ H distance at 2.518 Å and the centroid $\cdots$ H-O angle of 151°. The H-O-H angle is 112°. There are the hydrogen bonding interactions among host **1**, aquated gadolinium ions and water molecules. The interaction can be classified in three groups: interactions between inside and outside water molecules, aquo ligands of gadolinium ions and **1**. The complex forms hydrogen bonded networks by intermediations of aquated gadolinium ions between organic layer and inorganic layer. The extended structure of complex **I**, which forms 2D hydrogen bonded polymers by interactions between aquated gadolinium ions and neighboring sulfonate groups of thiacalixarene at GdO $\cdots$ OS distances ranging from 2.684 to 2.984 Å, respectively, as shown in Figures 3 and 4. 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 in the two positions with aromatic centroid $\cdots$ centroid distances of 3.707 and 3.724 Å. In the same layers of thiacalixarenes at the base, hydrogen bonding is recognized between two phenolic hydroxyl groups and a sulfonate group of the nearest adjacent thiacalixarene with distances of

Figure 3 The extended structure of complex **I** showing hydrogen bonding and π - π stacking interactions between mixed layers of thiacalixarene (green, and orange dotted lines, respectively).

2.189 and 3.465 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 gadolinium ion and sulfonate groups of thiacalixarene, a formation of water molecule networks as shown in Figure 5.

3.2. The X-ray structure of *p*-sulfonatothiocalix[6]arene with aquated holmium ions and water molecules

Slow evaporation of 1:2 molar ratios of **1** and holmium (III) chloride afforded a crystalline complex, **II**. The complex crystallizes in the monoclinic space group $P2_1/n$ with an overall composition $[\{p\text{-sulfonatothiocalix[6]arene}^{6-}\}\{\text{Ho}(\text{H}_2\text{O})_8^{3+}\}_2(\text{H}_2\text{O})_{15}]$ as shown

Figure 4 The extended structure of complex **I** showing hydrogen bonding interactions between same layers of thiacalixarene (green dotted line).

Figure 5 Packing diagram of the bi-layer in complex **I** showing interactions among thiacalixarene layers, aquated gadolinium metal cations and water molecules in parallel with *ac* plain.

in Figure 6. It was found that same charges between complex **I** and complex **II**. In the solid state of **II**, the complex shows to adopt the same conformation of **I** having an inversion center, which is stabilized by intramolecular hydrogen bonding among three phenolic hydroxyl groups with the OH...O distances of 2.461 and 2.781 Å, respectively, as shown in Figure 7. It seems that two aquated holmium ions are captured in the "up-down" cavity of thiocalixarene. The aquated holmium ions are stabilized by hydrogen bonding between aquo ligands of aquated holmium ions and oxygens of the sulfonate groups in the cavity of thiocalixarene with the Ho-OH...OS distances ranging from 2.076 to 2.126 Å, respectively. In addition, each of these holmium ions has eight aquo ligands with the Ho-O distances ranging from 2.310 to 2.386 Å, respectively. Eight included water molecules and two aquated holmium ions form an intricate hydrogen bonded networks in the "up-down" cavity of thiocalixarene at the O...H-O distances ranging from 1.621 to 1.971 Å. Hydrogen bond consists of one phenolic hydroxyl group and one imbedded water molecule at a distance of 1.931 Å. Furthermore, there are OH-aromatic π hydrogen bonding between the imbedded water molecule and an aromatic moiety of thiocalixarene with a centroid...H distance at 2.461 Å and the centroid...H-O angle of 161°. The H-O-H angle

Figure 6 The X-ray structure of complex **II** showing the "up-down" double partial cone conformation. The carbons, oxygens, sulfurs, holmiums, and hydrogens in the complex **II** are in gray, red, yellow, pink, and white, respectively.

Figure 7 The structure of complex **II** showing intramolecular hydrogen bonding interactions between imbedded water molecules and aquated holmium ions in the "up-down" cavities of thiocalixarene (blue, and green dotted lines, respectively).

is 104°. The complex forms hydrogen bonded networks by intermediations of aquated holmium ions between organic layer and inorganic layer. The extended structure of complex **II**, which forms 2D hydrogen bonded polymers by interactions between aquated holmium ions and neighboring sulfonate groups of thiocalixarene at HoO...OS distances ranging from 2.718 to 2.987

Figure 8 The extended structure of complex **II** showing hydrogen bonding and $\pi-\pi$ stacking interactions between mixed layers of thiocalixarene (blue, and orange dotted lines, respectively).

Figure 9 The extended structure of complex **II** showing hydrogen bonding interactions between same layers of thiocalixarene (blue dotted line).

Å, respectively, as shown in Figures 8 and 9. 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, the thiacalixarene assemblies with each layer compose of $\pi-\pi$ stacking interactions between the base thiacalixarenes and the nearest adjacent thiacalixarenes in the two positions with aromatic centroid...centroid distances of 3.694 and 3.696 Å. In the same layers of thiacalixarenes at the base, hydrogen bonding is recognized between two phenolic hydroxyl groups and a sulfonate group of the nearest adjacent thiacalixarene with distances of 3.231 and 3.292 Å. The overall crystal structure of the complex is comprised of organic and inorganic layers, which formed supramolecular assemblies because of the $\pi-\pi$ stacking, hydrogen bonding interactions, and a formation of water molecule networks in parallel with *ac* plain as shown in Figure 10.

3.3. The X-ray structure of *p*-sulfonatothiacalix[6]arene with aquated erbium metal ions and water molecules

Slow evaporation of 1:2 molar ratios of **1** and erbium (III) chloride afforded a crystalline complex as **III**. The crystals are in a monoclinic cell and the structure solution was performed in the space group $P2_1/n$, and had an overall composition [*p*-

sulfonatothiacalix[6]arene⁶⁻] $\{\text{Er}(\text{H}_2\text{O})_8^{3+}\}_2(\text{H}_2\text{O})_{16}$ as shown in Figure 11. It was found that same charges between complex **I**, **II**, and **III**. In the solid state of **III**, the "up-down" double partial cone conformation effectively has two pseudo cavities, and optimizes hydrogen bonding among three phenolic hydroxyl groups with the OH...O distances of 2.297 and 2.765 Å, respectively, as shown in Figure 12. It seems that two aquated erbium ions are captured in the "up-down" cavity of thiacalixarene, and are stabilized by hydrogen bond between aquo ligands of aquated erbium ions and oxygens of the sulfonate groups in the cavity of thiacalixarene with the Er-OH...OS distances ranging from 1.936 to 2.019 Å, respectively. Two erbium ions are attached eight water molecules with the Er-O distances ranging from 2.301 to 2.367 Å, respectively. In addition, eight imbedded water molecules form an

Figure 10 Packing diagram of the bi-layer in complex **II** showing interactions among thiacalixarene layers, aquated holmium ions and water molecules in parallel with *ac* plain.

Figure 11 The X-ray structure of complex **III** showing the "up-down" double partial cone conformation. The carbons, oxygens, sulfurs, erbiums, and hydrogens in the complex **III** are in gray, red, yellow, green, and white, respectively.

Figure 12 The structure of complex **III** showing intramolecular hydrogen bonding interactions between imbedded water molecules and aquated erbium ions in the "up-down" cavities of thiacalixarene (blue dotted line).

Figure 13 The extended structure of complex **III** showing hydrogen bonding and $\pi-\pi$ stacking interactions between mixed layers of thiacalixarene (blue, and orange dotted lines, respectively).

intricate hydrogen bonded networks in the "up-down" cavity of thiacalixarene at the O $\cdots$ H-O distances ranging from 2.297 to 2.765 Å. Hydrogen bond consists of between one of the phenolic hydroxyl group and one of the imbedded water molecule at a distance of 1.997 Å. Furthermore, OH-aromatic π hydrogen bonding is recognized between the imbedded water molecule and an aromatic moiety of thiacalixarene with a centroid $\cdots$ H distance at 2.526 Å and the centroid $\cdots$ H-O angle of 154°. The H-O-H angle is 106°. The extended structure of complex **III**, which forms a 2D hydrogen bonded polymer by interactions between the aquated erbium ions and neighboring sulfonate groups of thiacalixarene at GdO $\cdots$ OS distances ranging from 2.715 to 2.9814 Å, respectively, as shown in Figures 13 and 14. In addition, organic layers of thiacalixarene are confirmed to be involving thiacalixarene unit in two different directions, but both molecular

Figure 14 The extended structure of complex **III** showing hydrogen bonding interactions between same layers of thiacalixarene (blue dotted line).

Figure 15 Packing diagram of the bi-layer in complex **III** showing interactions among thiacalixarene layers, aquated erbium ions and water molecules in parallel with *ac* plane

structures indicate same conformation. In the two mixed layers of thiacalixarenes, $\pi-\pi$ stacking interactions are recognized from the base thiacalixarenes to the nearest adjacent thiacalixarenes in the two positions with aromatic centroid $\cdots$ centroid distances of 3.713 and 3.788 Å. In the same layers of thiacalixarenes at the base, hydrogen bonding is recognized between two phenolic hydroxyl groups and a sulfonate group of the nearest adjacent thiacalixarene with distances of 2.832 and 3.477 Å. The overall crystal structure of **III** is comprised of organic and inorganic layers, which formed supramolecular assemblies because there are the $\pi-\pi$ stacking, hydrogen bonding, and a formation of water molecule networks as shown in Figure 15.

4. Conclusion

In conclusion, we succeeded in the synthesis of **1** inclusion complexes with aquated lanthanide metal ions (Gd³⁺, Ho³⁺, and Er³⁺) and water molecules, which are the complexes **I**, **II**, and **III**. It was found that these complexes appear to be similar to the conformational structure of [1•Dy₂(H₂O)₁₆•15H₂O] complex. In addition, these complexes show a same behavior because the ion radii of gadolinium, holmium, and erbium are as large as that of dysprosium. However, the overall structures of these complexes show to form a different structure of [1•Na₂(H₂O)₁₀•16H₂O] complex. This suggests that the thiacalixarene could recognize each of aquated metal ions because the structures of thiacalixarenes have more flexible than those of calixarenes. Therefore, the molecular structure of **1** can alternate size to fit the lanthanide ions. Furthermore, a fashion of coordination between sulfonate groups of **1** and metal centers might be affected by the ion radii of metals examined. We are investigating lanthanide metal complexes with **1**, and further studies on this system are in progress.

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