A Novel Supramolecular Assembly Constructed by Cu/imidazole Complex with 1,2-Alternate p-Sulfonatothiacalix[4]arene

Dong-Sheng Guo and Yu Liu*

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

Received January 2, 2007; Revised Manuscript Received April 19, 2007

ABSTRACT: A novel supramolecular assembly has been prepared by p-sulfonatothiacalix[4]arene/copper(II)/imidazole through the conjoined hydrogen bonds, showing that p-sulfonatothiacalix[4]arene with 1,2-alternate conformation can bind copper(II) with a bis-tridentate coordination manner, and further displays charge-transfer behavior.

Thiacalixarenes,1 as a new family of calixarenes, represent very fascinating synthetic receptors with many potential applications in supramolecular chemistry in recent years.2 Possessing four sulfur atoms instead of the methylene bridges, thiacalixarenes possess a lot of intrinsic features differing from the methylene-bridged calixarenes, such as enlargement of the calix skeleton to provide larger cavity and more flexibility, ready oxidizability to sulfoxide and sulfone for providing new members of S bridged calixarenes, additional coordination sites to specific metal controlled by oxidation state of S, and so on.3 Because of these distinct characteristics, thiacalixarenes are regarded as a unique molecular scaffold rather than a simple substitute of the “classical” calixarenes. However, as well as calixarenes, thiacalixarenes also possess poor water solubility, which confined their uses in organic solvent. Therefore, to further explore the various properties of thiacalixarenes in aqueous solution, p-sulfonatothiacalix[4]arene (STC4A), a new analogue of water-soluble calixarenes, was prepared by Miyano et al.4 As anticipated, STC4A exhibits several extraordinary complex behaviors with not only organic molecules5 but also metal ions6 in aqueous solution, which cannot be obtained by p-sulfonatocalixarenes.

On the other hand, the solid-state supramolecular chemistry of the “classical” p-sulfonatocalixarenes have been well-studied by Atwood and Raston et al.,7 who demonstrated that the compounds can form various molecular assemblies in the presence of suitable guests. In this field, STC4A has also gained some investigations on the construction of solid-state supramolecular architectures.5b,8–10 The seminal report by Zhu et al.,8a reveals that STC4A usually prefers the cone conformation in the solid state and arranges itself in an up-down fashion to form a claylike bilayer with the hydrophobic midsections of adjacent molecules mutually aligned and engaged in intermolecular π–π stacking interactions. Furthermore, it has been validated that not only the cone conformation of STC4A can be disrupted to assume infrequent 1,2-alternate5b,9d or partial cone conformation5b but also the extended structures of STC4A can be induced to present various splendid aggregations rather than a traditional bilayer array in the presence of suitable guests (either organic molecules or metal ions). For example, the supramolecular assemblies of molecular capsules5b,c,e,5d water-filled channels,5b and hydrogen-bonded polymers5d based on STC4A have been one after the other reported by our group and others. However, among all these STC4A complexes reported before, the unique coordination ability of bridged S atoms is employed less frequently to construct the highly complex assemblies.8d,10b In fact, the coordination of bridged S atoms should be one of the most important factors to control both STC4A’s conformation and its assembled structures, which can be reflected from the relative studies of thiacalix[4]arene material.11 Therefore, exploration of the effects of the lower-rim coordination of STC4A attracts more and more attention. In the present communication, we wish to report our investigation on a dinucleating copper complex of STC4A together with imidazole ligands, in which STC4A acts as a bis-tridentate chelating ligand with its 1,2-alternate conformation.

On treatment of an aqueous solution of STC4A with a 4-fold excess of Cu(ClO4)2 and a 20-fold excess of imidazole, brown crystals of [Cu4(STC4A)(imidazole)12(H2O)11] (Chart 1) were obtained after the solution stood for several hours, Scheme 1.12 Compound 1 crystallizes in a triclinic system and the structural solution was performed in the space group P1.13 It should be noted that compound 1 has one crystallographic inversion center at its midpoint, and only half of each molecule is crystallographically independent. Therefore, in each asymmetric unit, there are half of a STC4A+, one [Cu(imidazole)]21+, two half molecules of [Cu-imidazole]2+ as counterions, and a total of 5.5 water molecules of crystallization that are disordered over 10 positions.

The most fascinating feature in 1 is that STC4A adopts the 1,2-alternate conformation rather than its traditional cone shape as shown in Figure 1a. According to the Ugozzi–Andreatti convention,14 the actual φ and χ torsion angles values, which define the solid-state conformation of STC4A, are +79.8, −82.5; +142.5, +135.8; −79.8, +82.5; and −142.5, −135.8°. In fact, the solid-state 1,2-alternate conformation of STC4A has already been obtained by our group and others.5b,c,e,12,15 However, the present 1,2-alternate conformation of STC4A differs to some extent from the previous results. As comparison with complex of STC4A with 4,4′-dipyridinium (STC4A-4-DPD),5b not only the actual φ and χ torsion angles values of STC4A (in STC4A–4-DPD: +79.0, −85.8; +145.7, +130.2; −79.0, +85.8; and −145.7, −130.2°) but also...
The S…S approach of distal sulfonates (in I: S4–S4A, 12.561 Å; STC4A-4-DPD, 13.859 Å) are different. That is to say, the framework of STC4A in 1 is shrunken to be shorter than that in STC4A-4-DPD. It is attributed to the factors of inducing STC4A to the 1,2-alternate form being different between 1 and the STC4A-4-DPD complex. STC4A in STC4A-4-DPD assumes the 1,2-alternate form because the cone shape of STC4A cannot suitably accommodate the 4-DPD guest in its cavity. However, in 1, STC4A assumes the 1,2-alternate form, which is induced by the cooperative bis-tridentate coordination of copper cations with one bridged S atom and two lower-rim phenolic hydroxy groups. To achieve better coordination behavior, the bridged S atom needs to be more approximate to phenolic oxygen atoms (S1–O1, 3.026 Å; S1–O2, 2.944 Å), and then STC4A in 1 appears to have a more compact 1,2-alternate conformation than the others. As a result, the overturned 1,2-alternate conformation in 1 does not lead to elongated bridged S–C bonds (see Figure 1) relative to those in the cone conformation, which is also different from the STC4A-4-DPD case in which the conformational change made all the bridged S–C bonds elongated about 0.1 Å.

In addition, another interest should be concerned with the coordination behavior of STC4A with [Cu(imidazole)2]2+ (Cu1). As mentioned above, the multinuclear Cu(II) complexes of p-tert-butylthiacalix[4]arene have been reported previously. Although it also provides the bis-tridentate coordination mode to Cu(II), the cone conformation of thiacalix[4]arene is retained. Simultaneously, Zhu et al. also reported the 2D coordination polymer based on the Cu(II) tetramer with STC4A, in which STC4A acts as a multi-tridentate ligand with the conventional cone conformation. However, much differently in the present complex 1, STC4A prefers to adopt the 1,2-alternate conformation as a bis-tridentate dinucleating ligand with two Cu(II) at the anti position (Figure 1b). Herein, the additional imidazole ligands play the crucial role in manipulating the conformation of STC4A. Each Cu(II) cation is five-coordinated by a total of one S atom and two O atoms in STC4A and two N atoms in imidazoles. Therefore, the space hindrance between STC4A and imidazole ligands compels STC4A to present the uncommon 1,2-alternate conformation, which is an accessible conformation depending on the choice of metal and coligands. Moreover, the hydrogen-bonding interactions (N4A…O7, 2.901 Å, 141.0°) between sulfonate groups and NH groups of imidazoles help reinforce the stability of 1,2-alternate thiacalixarene. Upon coordination with Cu1, the bridged S–C bonds are affected slightly,
which can be seen from the almost equivalent lengths between S1−C2 (participate in coordination) and S2−C8 (do not participate in coordination) bonds. However, it is interesting that all the phenolic C−O bonds in I are shortened, although it is well-known that the coordination of O atoms may elongate the covalent bonds to some extent. This should be attributed to the deprotonation of the phenolic hydroxyls.

As investigated by Iki and co-workers,16 the pKₐ values of four phenolic hydroxyls in STC4A are 2.18, 8.45, 11.99, and 11.62, respectively. So STC4A can be utilized as divergent −4, −5, −6, −7, and −8 charged tectons upon adjusting different pH values. But the STC4A⁻ and STC4A⁻⁸ hosts are relatively difficult because they need stronger basic conditions. For complex I, the pH value of its mother liquid is at about 9. It is worth mentioning that STC4A unexpectedly presents the negative eight charge. In other words, all of the phenolic hydroxyls in STC4A are deprotonated. The deprotonations of hydroxyls may mainly be attributed to the basicity of imidazole. However, according to the pH value of the mother liquid and the pKₐ value of imidazole (pKₐ, 6.993−(1) pKₐ, 10.58(0)),17 the lower-rim phenolic hydroxyls of STC4A cannot be fully deprotonated in the present case. So it should be helped by the coordination of Cu(II) ions. In the present case, the H proton and Cu(II) ion compete for binding to the phenolic O atom and Cu(II) showed preferential binding because of its help in coordinating to other O and bridged S atoms. Also, it is possible their complexation can increase the thermodynamic acidities of phenolic hydroxyls by polarization effects.

To satisfy the charged balance of STC4A⁻⁸, we need additional positively charged cations besides the two Cu(I) cations coordinated by STC4A. In complex I, there are two [Cu(imidazole)₂(H₂O)]⁺² cations (Cu₂ and Cu₃) restricted in the crystal lattice as counterions. Unlike Cu1 with coordination number five, Cu2 and Cu3 counternions are six-coordinated by four imidazole ligands and two additional water molecules. For the further extended structure of I, because of the conventional cone shape of STC4A disrupted, its typical bilayer array is no long maintained. The noncovalent interactions (π-stacking and hydrogen bonding) between calixarenes do not appear any more. The STC4A molecules are held apart from each other by either counterions or water molecules. Primarily, the 1,2-alternate STC4As are linked together to form a monodimensional chain structure by solvent water molecules (O10−O2, 2.833 Å; O10−O8, 2.844 Å), as shown in Figure 2a. Moreover, the chains extend along the crystallographic b direction through the joining of Cu2 counternions (O9−O3, 2.853 Å; O9−O6, 2.716 Å) to present the bidimensional layer array at the a×b plane (Figure 2b). By viewing from the crystallographic a direction, the complexed layer structures are separated by Cu3 counternions (Figure 2c).

In summary, a novel 1,2-alternate conformation of STC4A induced by bis-tridentate coordination of copper ions has been observed, and complex I then presents the overall packing structure of hydrogen-bonded polymers. The present results inspired us to prepare the lower-rim coordinated complexes of calixarenes with metal ions through the cooperative coordination of suitable ligands, which can also achieve the research goal of building spectacular supramolecular architectures. Differently from most previous reports that mainly concern the contributions of upper-rim sulfonate groups and cavities of calixarenes upon complexation with guests, this research provides a new project to not only manipulate the conformation of sulfonatocalixes but also further overcome their bilayer arrays.

Acknowledgment. This work was supported by the 973 Program (2006CB932900), the NNSFC (20673061 and 20402008) and Special Fund for Doctoral Program from the Ministry of Education of China (20050055004), which are gratefully acknowledged.

Supporting Information Available: X-ray crystallographic data as a CIF file (CCDC reference 631451). This material is available free of charge via the Internet at http://pubs.acs.org.

References


(12) To a solution of p-sulfonatoolithiatic acid [4] (148.0 mg, 0.19 mmol) in 10 mL of deionized water was added Cu(ClO4)2·6H2O (148.2 mg, 0.4 mmol) and then imidazole (136.2 mg, 2.0 mmol). After being heated for a moment, the brown solution was allowed to stand for several hours. The crystalline compound suitable for X-ray structural analysis was then obtained as brown blocks with a yield of 72.8 mg (35%).

(13) The X-ray intensity data for compound I were collected on a standard Siemens SMART CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator at T = 293–2 K. The structure was solved by using direct methods and refined employing full-matrix least squares on F2 (Siemens, SHELXTL-97). Crystal data for I: C26H24Cu2N2O2S4, M, = 2078.10, triclinic, space group P1, a = 11.426(4) Å, b = 13.704(4) Å, c = 14.625(5) Å, α = 110.958(5)°, β = 94.824(5)°, γ = 93.25(2)(5)°, Z = 1, V = 2126.1–(11) Å³, D, = 1.626 g/cm³, μ = 1.276 mm, θ(max) = 26.44°, F(000) = 1066, crystal dimensions 0.30 × 0.25 × 0.20 mm, reflections collected/unique, 12187/8576 (R(int) = 0.0402), final R indices [I > 2σ(I)] Rp = 0.0633, wR = 0.1403, R indices (all data) Rp = 0.1348, wR = 0.1741, goodness-of-fit on F² = 1.00. Some oxygen atoms of the sulfonate groups (O3, O4, O5, O8) were disordered and refined in two positions with equal occupancies. Anal. Calcd. for I: C, 34.68; H, 3.78; N, 16.18; S, 12.34. Found: C, 35.21; H, 3.64; N, 16.47; S, 12.55.


