

两种部分甲基取代瓜环配合物的晶体结构

陈文建¹ 曾金萍¹ 张云黔¹ 祝黔江¹ 薛赛凤¹ 陶 朱^{*,1} 卫 钢^{*,2}

(¹ 贵州省大环化学及超分子化学重点实验室, 贵阳 550025)

(²CSIRO Materials Science and Engineering, P.O. Box 218, Lindfield, NSW 2070, Australia)

摘要: 本文报道了 2 种新的部分甲基取代瓜环配合物的晶体结构, 利用 X-射线单晶衍射技术表征了 2 种配合物的结构, 在 CdCl₂ 溶液中, 1,2,4,5-八甲基六元瓜环选择性的包结客体分子 1,2-(2,2'-bisbenzimidazolyl)ethane dichloride, 形成 2:1 的哑铃型主客体包结配合物; 而 1,2,4-六甲基五元瓜环(HMeQ[5])与钠离子配位形成包结一个水分子的“分子胶囊”, “分子胶囊”之间通过氢键自组装形成一维的超分子长链。

关键词: 部分甲基取代瓜环; 1,2,4,5-八甲基取代六元瓜环; 1,2,4-六甲基取代五元瓜环; 晶体结构

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Crystal Structures of Two Partially Methyl-Substituted Cucurbit[n]urils

CHEN Wen-Jian¹ ZENG Jin-Ping¹ ZHANG Yun-Qian¹

ZHU Qian-Jiang¹ XUE Sai-Feng¹ TAO Zhu^{*,1} WEI Gang^{*,2}

(¹Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025)

(²CSIRO Materials Science and Engineering, P.O. Box 218, Lindfield, NSW 2070, Australia)

Abstract: Two partial methyl-substituted cucurbit[n]urils were characterized by single-crystal X-ray diffractions. A new methyl-substituted cucurbituril, 1,2,4,5-octamethylcucurbit[6]uril (OMeQ[6]) was separated by the formation of the inclusion complexes of OMeQ[6] with 1,2-(2,2'-bisbenzimidazolyl)ethane dichloride (SBE) in the presence of CdCl₂, and a 1,2,4-hexamethylcucurbit[5]uril (HMeQ[5]) coordination to sodium ion was also obtained. In the crystal structure of compound $\{(\text{SBE}@2\text{OMeQ}[6])^{2+}[\text{Cd}_2(\mu\text{-Cl})_2(\text{Cl}_2)_2(\text{H}_2\text{O})_2]^{2-}\}$ (**1**), the OMeQ[6] host selectively included the benzimidazolyl moiety of the guest SBE through the hydrophobic cavity interaction and the ion-dipole interaction of the cation N⁺ with the carbonyl oxygens of the host, and formed a dumbbell shape host-guest inclusion complex with a ratio of 2:1. In the crystal structure of the complex $\{[\text{Na}(\text{H}_2\text{O})\text{HMeQ}[5]]^+(\text{NO}_3)^-(5\text{H}_2\text{O})\}$ (**2**), a molecular capsule included one water molecule was formed, and the capsules assembled one-dimensional supramolecular chain through the hydrogen bonding. CCDC: 760759, **1**; 760758, **2**.

Key words: partial methyl-substituted cucurbit[n]urils; 1,2,4,5-octamethylcucurbit[6]uril; 1,2,4-hexamethylcucurbit[5]uril; crystal structures

Recent year, our group reported a series of partial methyl-substituted cucurbit[n]urils. The first partial methyl-substituted cucurbit [n]urils, 1,4-tetramethylcu-

cucurbit[6]uril (TMeQ[6]), was synthesised by using diether of dimethyl glycoluril and the dimer of the unsubstituted glycoluril^[1]. This partial methyl-substitu-

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*通讯联系人。E-mail: gzutao@263.net, gang.wei@csiro.au

第一作者: 陈文建, 男, 28 岁, 硕士研究生; 研究方向: 应用有机化学。

ted Q[6] showed surprising water solubility, which allowed us to investigate host-guest chemistry in neutral water. The most significant feature of the TMeQ[6] is not circular but ellipsoid with D_{2h} symmetry. More recent, the crystal structure of 1,3,5-hexamethylcucurbit[6]uril (*m*-HMeQ[6])^[2] was obtained after it was first reported by Day and coworkers^[3]. A tetramethylcucurbit[6]uril isomer, 1,2-tetra methylcucurbit[6]uril (*o*-TMeQ[6]) was prepared by using the similar synthesis process to the conditions for the synthesis of TMeQ[6], and was separated by the formation of the inclusion complexes of *o*-TMeQ[6] with 1,6-(2,2'-bisbenzimidazolyl) hexane dichloride (SBH), and the water solubility was even better than TMeQ[6] due to the lower symmetric feature^[4]. Another hexamethylcucurbit[6]uril (HMeQ[6]), which was first synthesized by using 3a-methyl-glycoluril as the building block, was characterized by the single crystal X-ray diffraction in 2008^[5]. In the methyl-substituted cucurbit[5]urils homologues, the permethylated cucurbit[5]uril (Me10Q[5]) was first reported by Flinn and coworkers in 1992^[6]. This methyl-substituted Q[5] was structurally identified even 8 years earlier than the normal cucurbituril homologues (Q[*n* = 5, 7, 8, 10]) were reported^[7-9]. However, the partial methyl-substituted cucurbit[5]urils, such as the dimethyl-cucurbit[5]uril (DMeQ[5])^[10], pentamethyl-substitutedQ[5] (PMeQ[5])^[5], 1,3-tetramethylcucurbit[5]uril (1,3-TMeQ[5])^[11], 1,2,4-hexamethylcucurbit[5]uril

(1,2,4-HMeQ[5])^[11] and nonylmethylcucurbit[5]uril (NMeQ[5])^[11], exhibited some interesting properties. First, we found that an unsymmetrical partially substituted cucurbit[*n*]uril is more water soluble than a symmetrical one. *ab initio* calculations suggested that the water solubility of a normal cucurbit[*n*]uril or substituted cucurbit[*n*]uril relates with its dipole. The larger the dipole of a cucurbit[*n*]uril, the more water soluble the cucurbit[*n*]uril is. The dipole of a cucurbit[*n*]uril is dependent upon its molecular symmetry and the substituted group. Recent works in our laboratory revealed that it was a common feature of alkyl-substituted cucurbit[5]urils, including the partial methyl-substituted cucurbit[5]urils, to coordinate directly with metal ions and to form various alkyl-substitutedQ[5]-based metal-organic frame works (MOFs) with novel structures^[10].

In this work, A new partial methyl-substituted cucurbiturils, 1,2,4,5-octamethylcucurbit[6]uril (OMeQ[6]) was separated by the formation of the inclusion complexes of OMeQ[6] with 1,2-(2,2'-bis benzimidazolyl)ethane dichloride (SBE) in the presence of CdCl₂. A complex of sodium ion with 1,2,4-hexamethylcucurbit[5]uril (HMeQ[5]), which was synthesised by using diether of dimethyl glycoluril and the unsubstituted glycouril was also obtained. Their structures were characterized by single-crystal X-ray diffractions (Fig.1).

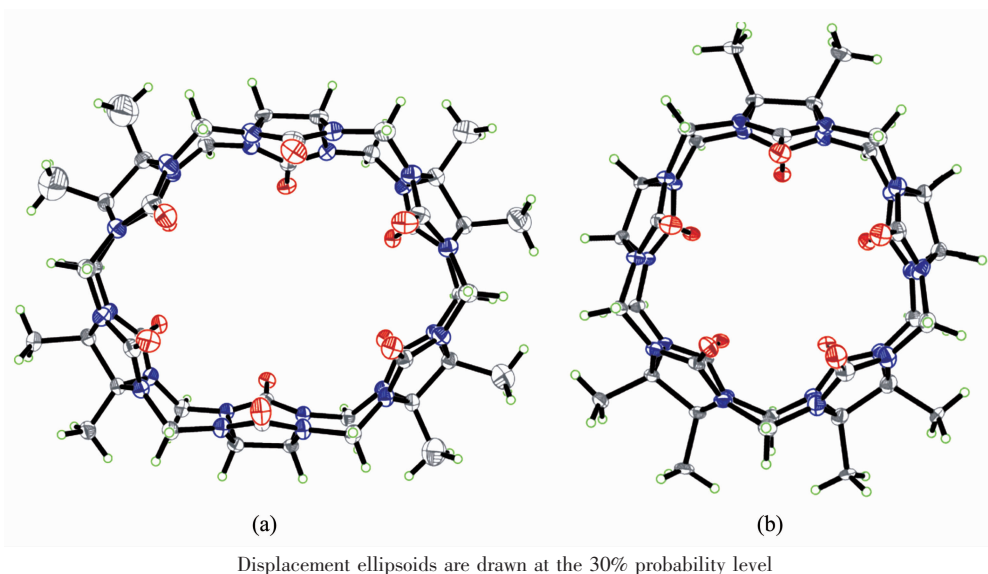


Fig.1 ORTEP diagram of two partial methyl-substituted cucurbit[*n*]urils: (a) OMeQ[6]; (b) HMeQ[5]

1 Experimental

1.1 General materials

Starting materials were purchased from commercial suppliers and used without further purification, and sodium nitrate and cadmium chloride were of reagent grade and used without further purification. The host 1,2,4-hexamethylcucurbit[5]uril (HMeQ[5]) was prepared by procedures reported previously^[11]. The guest 1,2-(2,2'-bis-benzimidazolyl)-ethane dichloride (SBE) and 1,6-(2,2'-bis-benzimidazolyl)hexane dichloride (SBH) were synthesized as the literature method^[12].

1.2 Synthesis of 1,2,4,5-octamethylcucurbit[6]uril (OMeQ[6])

To synthesize OMeQ[6], dimethyl- glycoluril (3.40 g, 20 mmol) and polyformaldehyde (2.70 g, 90 mmol) were added in a round bottom flask. To the mixture, 37% concentrated hydrochloric acid (60 mL) was added. The mixture was stirred at room temperature for 30 min until the solid was dissolved completely. To the mixture, unsubstituted glycouril (1.42 g, 10 mmol) was added while the solution was heated up to 50 °C. The solution was heated up to 100 °C for five hours and then allowed to cool to room temperature. The acidic solvent was removed by rotary evaporation and then diluted with water (100 mL) and filtered. Dioxane (5 mL) was added to the filtrate and the resulting solution was left to stand overnight. Light brown crystals were collected and dissolved in HCl (10 mol·L⁻¹, 50 mL), followed by evaporation of the acidic solvent in vacuo. This process was repeated three times to remove the dioxane. Finally, the residue was dissolved with water (20 mL) and poured into acetone (200 mL) to produce a white solid. The precipitate was collected by filtration and dried to afford the product (1.12 g, 20.3%).

1.3 Preparation of {(SBE@2OMeQ[6])²⁺[Cd₂(μ-Cl)₂Cl₄(H₂O)₂]²⁻} (1)

To prepare crystals of the related methyl-substitu-

ted cucurbit[n]urils, water was used as the solvent due to their water solubility. Thus, the single crystals of OMeQ[6] adduct with SBE and CdCl₂ was obtained by dissolving OMeQ[6] (0.5 g, 0.5 mmol) in a solution of CdCl₂ (0.3 g, 2 mmol) and SBE (0.16 g, 0.5 mmol) in water (15 mL). The solution was mixed thoroughly and filtered to remove insoluble impurity. The filtrate was left at room temperature and colorless X-ray quality crystals were obtained by slow evaporation of this mixture solution in several weeks.

1.4 Preparation of {[Na(H₂O)HMeQ[5]]⁺(NO₃)⁻5H₂O} (2)

The single crystals of HMeQ[5] adduct with NaNO₃ was obtained by dissolving HMeQ[5] (0.45 g, 0.5 mmol) in a solution of NaNO₃ (0.17 g, 2 mmol) in water (10 mL). The solution was mixed thoroughly and allowed to stand at room temperature and colorless X-ray quality crystals formed after several days. Anal. Calcd. for C₃₆H₅₂N₂₁O₁₉Na (%): C, 39.08; H, 4.74; N, 26.60. Found(%): C, 39.55; H, 4.65; N, 27.06.

1.5 X-ray crystallography

The crystal data of the two compounds {(SBE@2OMeQ[6])²⁺[Cd₂(μ-Cl)₂Cl₄(H₂O)₂]²⁻} (1) and [Na(H₂O)HMeQ[5]]⁺(NO₃)⁻5H₂O (2) were collected on a SMART Apex II CCD diffractometer with graphite monochromated Mo Kα radiation (λ=0.071 073 nm) in the ω scan mode. Lorentz polarization and absorption corrections were applied. Structural solution and full matrix least-squares refinement based on F² were performed with the SHELXS-97 and SHELXL-97 program package^[13-14], respectively. All the non-hydrogen atoms were refined anisotropically. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data, data collection conditions, and refinement parameters for compounds 1, 2 are listed in Table 1.

CCDC: 760759, 1; CCDC: 760758, 2.

Table 1 Crystallographic data for complexes 1~2

Complex	1	2
Empirical formula	C ₁₀₄ H ₁₂₄ N ₅₂ O ₂₆ Cd ₂ Cl ₆	C ₃₆ H ₅₂ N ₂₁ O ₁₉ Na
Formula weight	2 956.05	1 087.96
Crystal system	Triclinic	Triclinic

Continued Table 1

Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.289 68(7)	1.114 75(10)
b / nm	1.526 60(8)	1.140 07(10)
c / nm	2.030 21(11)	2.094 45(18)
α / (°)	82.375(2)	103.301(3)
β / (°)	83.399(2)	95.845(3)
γ / (°)	66.642(2)	96.505(3)
V / nm ³	3.628 6(3)	2.551 1(4)
Z	1	2
D_c / (g·cm ⁻³)	1.353	1.416
T / K	223(2)	223(2)
μ / mm ⁻¹	0.484	0.122
Unique reflns	13 792	9 597
Obsd reflns	8 971	6 567
Params	875	713
R_{int}	0.047 5	0.052 9
R ($I > 2\sigma(I)$) ^a	0.059 6	0.091 9
wR ($I > 2\sigma(I)$) ^b	0.165 7	0.272 6
R (all data)	0.084 2	0.117 5
wR (all data)	0.180 8	0.292 6
GOF on F^2	0.974	1.047

^a Conventional R on F_{obs} : $\sum ||F_o| - |F_c|| / \sum |F_o|$;^b Weighted R on $|F_{obs}|^2$: $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

2 Results and discussion

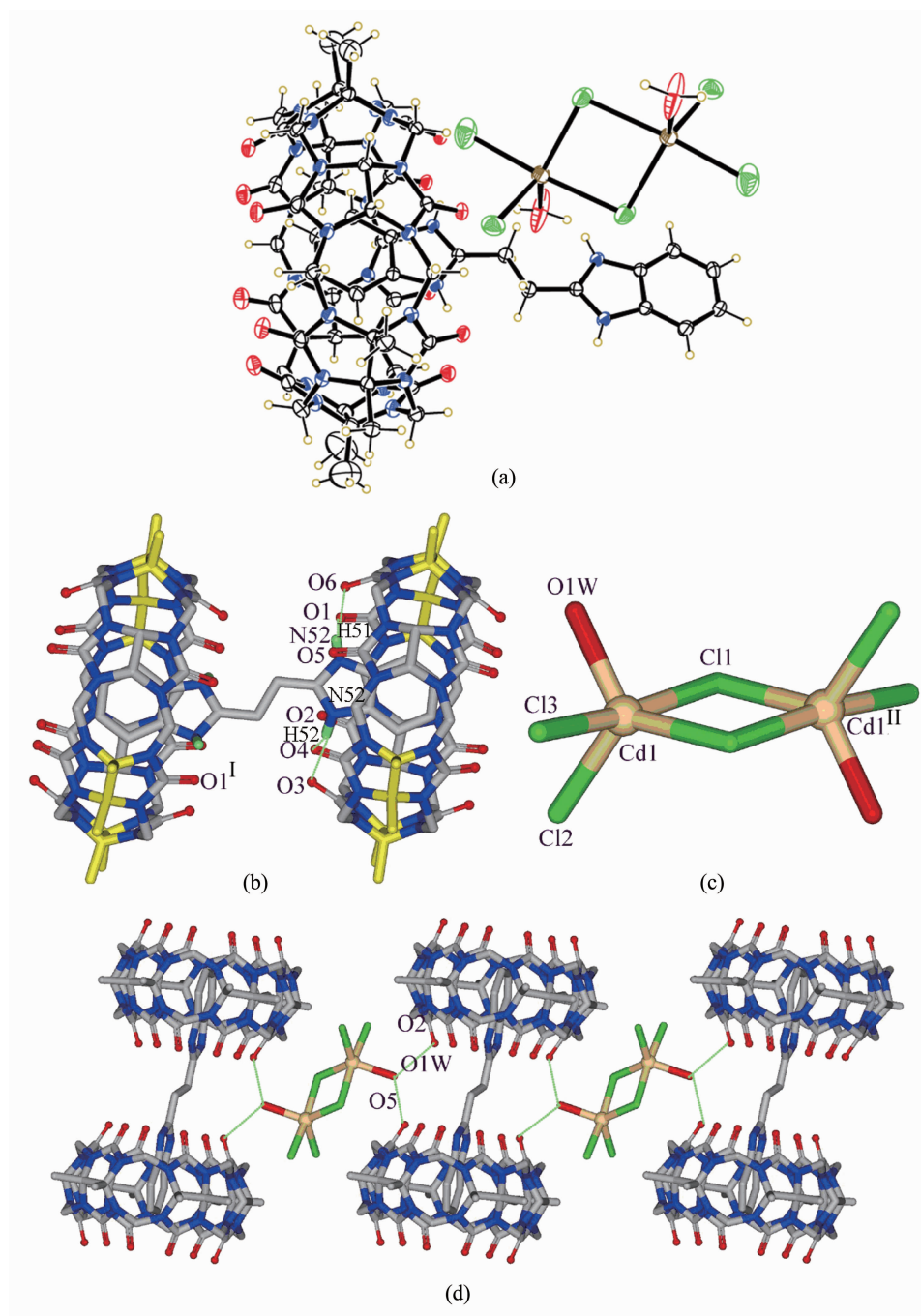
The X-ray structures of the HMeQ[5] show that its macrocyclic cavity and with D_{1h} symmetry with two identical portals surrounded by carbonyl groups, and OMeQ[6] with D_{2h} symmetry. Unlike the normal cucurbituril and its homologues (Q[5], Q[7], Q[8] and Q[10]), the macrocycle of HMeQ[5] and OMeQ[6] are not circular and their structures are easy to be deformed.

2.1 Crystal structure of $\{(SBE@2OMeQ[6])^{2+}[Cd_2(\mu-Cl)_2Cl_4(OH_2)_2]^{2-}\}$ (1)

The X-ray crystal structure of the compound **1** revealed that the OMeQ[6] host selectively included the benzimidazolyl moiety of the guest through the hydrophobic cavity interaction and the ion-dipole interaction of the cation N^+ with the carbonyl oxygens of the host, and formed a symmetric dumbbell shape host-guest inclusion complex (Fig.2a) with a 2:1 host:guest ratio. The NH on the included benzimidazolyl moiety (N51-H51 and N52-H52) formed hydrogen bonds with

the portal oxygen atoms O3, O4 and O1, O5, O6 of the OMeQ[6] with bond distances of 0.273 7 (N51-O3), 0.288 7 (N51-O4), 0.284 1 (N52-O1), 0.304 5 (N52-O5) and 0.273 7 (N52-O6) nm respectively.

In the compound **1**, the Cd^{2+} did not directly coordinated with the portal oxygen atom of the OMeQ [6], and formed a cluster $[Cd_2(\mu-Cl)_2Cl_4(OH_2)_2]^{2-}$ as shown in Fig.2b. Each of two Cd^{2+} ions in the cluster is five-coordinated to four Cl^- atoms ($Cl1$, $Cl1'$, $Cl2$ and $Cl3$) and one water molecule ($O1W$). The related bond distances and angles in the cluster are 0.261 6 (Cd1- $Cl1$), 0.255 7 (Cd1- $Cl1'$), 0.244 9 (Cd1- $Cl2$), 0.251 7 (Cd1- $Cl3$), 0.226 0 (Cd1- $O1W$) nm and 100.21° ($Cl1$ -Cd1- $Cl3$), 85.36° ($Cl1$ -Cd1- $Cl1'$), 92.36° ($Cl2$ -Cd1- $Cl1'$), 87.36° ($Cl2$ -Cd1- $Cl3$), 83.64° ($Cl1$ -Cd1- $O1W$), 120.92° ($Cl3$ -Cd1- $Cl1'$), 130.18° ($Cl1'$ -Cd1- $O1W$), 92.21° ($Cl2$ -Cd1- $O1W$), 108.84° ($Cl3$ -Cd1- $O1W$). The coordination geometry of the Cd^{2+} was best described as an anamorphic square-wimble of pentahedral structure. The two cadmium atoms ($Cd1$) were linked by two



Symmetry codes (b, c): ^I $-x+1, -y+1, -z$; ^{II} $-x+1, -y+2, -z$

Fig.2 (a) ORTEP diagram (displacement ellipsoids are drawn at the 30% probability level) and (b) crystal structure of the “dumbbell” shape like host-guest inclusion complex of {(SBE@2OMeQ[6])²⁺; (c) the [Cd₂(μ-Cl)₂Cl₄(OH₂)₂]²⁻ cluster; (d) connection between the “dumbbell” of (SBE@2OMeQ[6])²⁺ and the [Cd₂(μ-Cl)₂Cl₄(OH₂)₂]²⁻ cluster and the “dumbbells” chain linked by the Cd-Cl clusters with carbon-bound hydrogen atoms omitted (Dashed lines indicate hydrogen bonding interactions)

bridging Cl⁻ (Cl1 and Cl1'), and were separated by 0.3802 nm.

Although the Cd²⁺ did not directly coordinated with the portal oxygen atom of the OMeQ[6], the Cd-Cl

cluster [Cd₂(μ-Cl)₂Cl₄(OH₂)₂]²⁻ plays an important role in the formation of a “(SBE@2OMeQ[6])²⁺ dumbbell” supra-molecular chain in which the Cd-Cl cluster [Cd₂(μ-Cl)₂Cl₄(OH₂)₂]²⁻ links two neighboring “(SBE@

2OMeQ[6]²⁺ dumbbells” through hydrogen bonding (Fig.2c). The two coordinated water molecules (O1W) in a cluster interacts two portal oxygen atoms (O5 and O2) belonging to the two OMeQ[6]s in the two neighboring dumbbells. The related bond distances are 0.276 6 (O1W-O2), 0.273 6 (O1W-O5) nm.

2.2 Crystal structure of [Na(H₂O)HMeQ[5]⁺ (NO₃)-5H₂O (2)

HMeQ[5], similar to the 1,2,4-tricyclohexanocucurbit[5]uril (1,2,4-TriCyH Q[5]), has a tendency to coordinate directly with potassium ions and form a 10-membered “bracelet”^[10], it promoted us to find the

similar coordination of this ligand with other metal ions. The compound **2** contains a complex of HMeQ[5] with sodium ion. Fig.3a shows the crystal structure of a molecular capsule of the host HMeQ[5] which is lidded by two sodium ions (Na1 and Na2 with a 50% occupancy for each) includes one water molecule O5W. The Na⁺ ions (Na1 or Na2) coordinated to six O atoms, the five carbonyl oxygens of a HMeQ[5] portal (O1, O2, O3, O4, O5 for Na1 ion and O6, O7, O8, O9, O10 for Na2 ion), and one water molecule O2W and O4W respectively. The average distance between the lidded cation Na1 and carbonyl oxygens of HMeQ[5] is 0.288 4

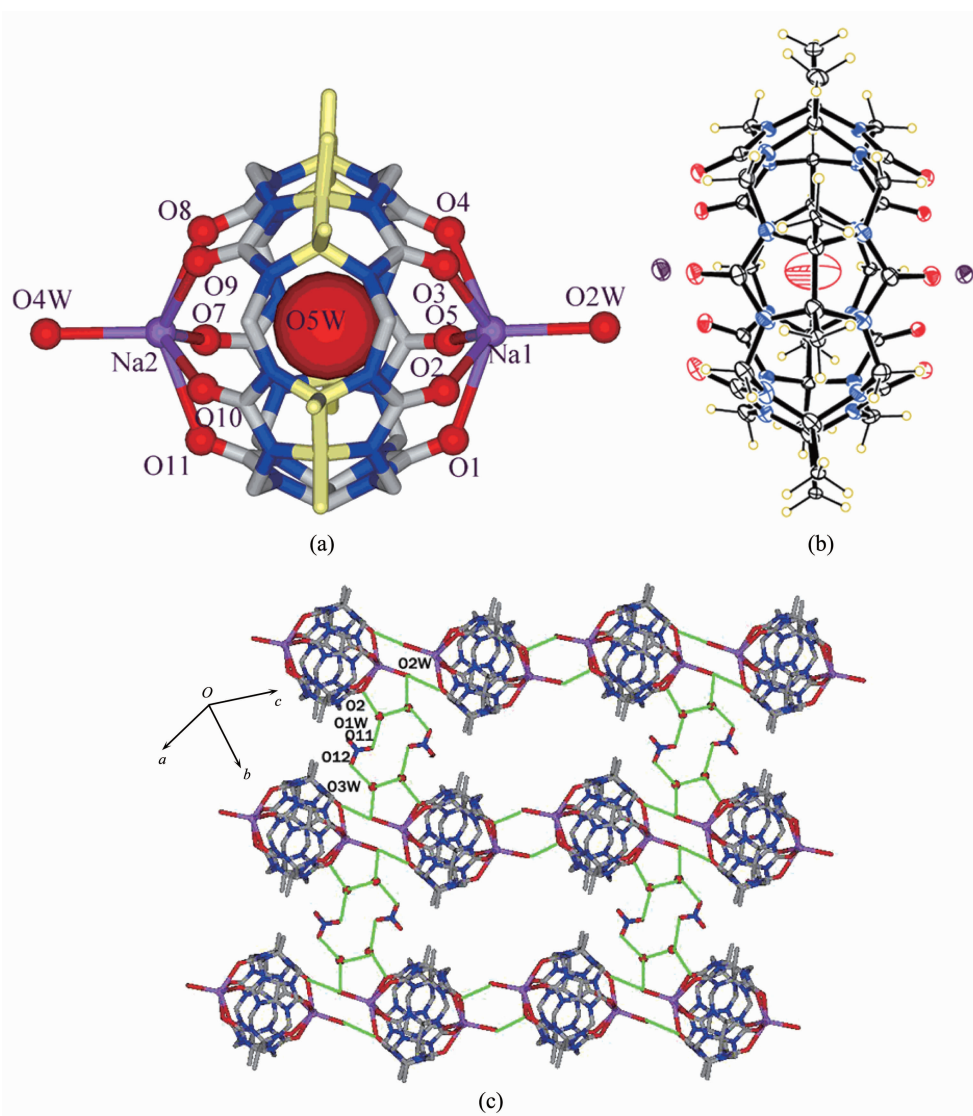


Fig.3 (a) Crystal structure and (b) corresponding ORTEP diagram (displacement ellipsoids are drawn at the 30% probability level) of the molecular capsule in the complex **2**; (c) the supramolecular layer constructed of the one dimensional chains connected by the hydrogen bonding nets (Dashed lines indicate hydrogen bonding interactions)

nm, and another lidded cation Na²⁺ and carbonyl oxygens of HMeQ[5] is 0.290 7 nm, while the distances between the lidded ions Na⁺ and the coordinated water are 0.283 7 nm (Na1-O2W) and 0.283 8 nm (Na2-O4W) respectively. Although no direct coordination exists between the lidded sodium ion with the carbonyl oxygen of the neighboring molecular capsules, the interaction of the coordinated water molecule O2W or O4W with the portal oxygen atom O1 or O9 leads to the formation of a one dimensional supramolecular chain constructed of HMeQ[5] molecular capsules through the hydrogen bonding (Fig.3b). A hydrogen bonding net plays a role of connection of the two neighboring supramolecular chains. The hydrogen bonding net consists of two nitrate anions, four water molecules (O1W, O3W), two carbonyl oxygens (O2) and also two coordinated water molecules (O2W). Thus, a supramolecular layer constructed of HMeQ[5]-based supramolecular chains can be formed through the hydrogen bonding nets (Fig.3c).

3 Conclusion

Generally, it is difficult to separate the homologues of the SQ[n]s. Using 1, ω -(2,2'-bisbenzimidazolyl)alkane as a ligand could form a certain inclusion complex in presence of SQ[n]s. The formation of the inclusion complexes of OMeQ[6] with 1,2-(2,2'-bisbenzimidazolyl) ethane dichloride (SBE) in the presence of CdCl₂ is a typical example. The partial alkyl-substituted Q[5]s have a strong tendency to coordinate directly with potassium ions and form some novel potassium-alkyl-substituted Q[5]s networks or frameworks based on the

6 or 10-membered “bracelets”. However, the complexation of HMeQ[5] with sodium ion showed no such special structures in the experimental condition in this work.

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