



Host–guest inclusion complexes of viologen derivative and tetramethylcucurbit[6]uril with multiple interaction models

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ABSTRACT

A novel supramolecular complex formed by *N,N'*-diethyl viologen (EV^{2+}) and symmetrical tetramethylcucurbit[6]uril (TMeQ[6]) was described both in solution and in the solid state by ^1H NMR, UV spectroscopy and Single-crystal structure analysis. In the solid state, EV^{2+} and TMeQ[6] formed two types of inclusion models in the self-assembled complex, a pseudorotaxane of a *N,N'*-diethyl viologen threading into the cavity of TMeQ[6] and a dumbbell-like structure of a *N,N'*-diethyl viologen shouldering two TMeQ[6] molecules, and the two types of complexes assembled to 1D supramolecular chain through hydrogen bonding.

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1. Introduction

Viologen compounds, particularly those derivatives with two N-substitutions, are special guest molecules in the cucurbit[*n*]uril chemistry [1–11]. These guests contain multiple functional groups that can develop strong intermolecular interactions with the host cucurbit[*n*]urils and form switch-type rotaxanes with multiple modes of host–guest interactions, which can be controlled chemically, photochemically, or electrochemically [12–16]. The unique charge-transfer properties of viologen compounds can enhance the stability of the host–guest inclusion complex and form trimolecular inclusion complexes. These axle compounds play an important role in the study of the chemistry of interlocked molecules of cucurbit[*n*]uril hosts.

Cucurbit[*n*]urils are commonly composed of *n* glycoluril units linked by 2*n* methylene to form a hydrophobic hollow cavity with two rimmed polar carbonyl openings. The sizes of the cavity and the opening of cucurbit[*n*]urils increase as the *n* increases. The remarkable macrocyclic structures and novel properties of cucurbit[*n*]urils attracted much attention recently [17–23]. The homologues of cucurbituril (Q[6]) [24] with larger cavity and opening, such as cucurbit[7]uril (Q[7]), cucurbit[8]uril (Q[8]), and the largest cucurbit[10]uril (Q[10]) were disclosed since 2000 [17–23,25–27]. A number of host–guest inclusion complexes with novel structures, properties and functions have been reported by research groups around the world and these works are summarised in recent reviews [28–33]. Recently, the cucurbit[*n*]uril family has grown further with more derivatives, congeners, and

analogues being prepared [34–39]. Sindelar and co-workers studied the complex between methylviologen and hexamethylated cucurbit[6]uril, in which alkyl chain and one aromatic ring is included inside the hexamethylated cucurbit[6]uril [40]. We have developed a method for controlled synthesis of symmetrical and unsymmetrical partially substituted cucurbit[*n*]urils with the C-shaped methylene-bridged glycoluril dimer. Amongst them, the symmetrical tetramethylcucurbit[6]uril (TMeQ[6]) was the first reported partially substituted cucurbit[*n*]urils [41]. Novel building blocks in the chemistry of interlocked molecules have attracted much attention due to their aesthetic appeal and potential applications. Moreover, many unique assembled molecular systems that exhibit reversible structural changes in response to chemical (acid, base, ions), electrochemical or photochemical stimuli were reported [12–16]. Here, we report a novel structure system consisting of viologen derivatives with aliphatic substitutions and TMeQ[6] both in solution and in the solid state, the association constant of the complex was determined using ^1H NMR spectroscopy, electronic absorption spectroscopy, and Single-crystal structure analysis of the inclusion complex reveals that *N,N'*-diethyl viologen (EV^{2+}) and TMeQ[6] formed two different self-assembled complexes, a pseudorotaxane of a *N,N'*-diethyl viologen threading into the cavity of TMeQ[6] and a dumbbell-like structure of a *N,N'*-diethyl viologen shouldering two TMeQ[6] molecules.

2. Experimental section

2.1. General

TMeQ[6] was prepared and purified according to the method established in our laboratories. EV^{2+} was from Aldrich and used

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without further purification. Titration ^1H spectra were recorded on 400 MHz Varian Inova spectrometers. UV–visible (UV–vis) absorption spectra of the host–guest complexes were recorded on an Agilent 8453 spectrophotometer at room temperature.

2.2. Preparation of single crystals of $\text{TMeQ[6]}-\text{EV}^{2+}$

EV^{2+} (0.10 g, 0.30 mmol) was dissolved in H_2O (50 ml), and to this solution TMeQ[6] (0.24 g, 0.20 mmol) was added. The mixture was heated to dissolve the host and guest and then filtered. The filtrate was set aside for 3 weeks which resulted in the deposit of colourless crystals of $\text{TMeQ[6]}-\text{EV}^{2+}$ (30% yield based on TMeQ[6]).

The crystal structures of $\text{TMeQ[6]}-\text{EV}^{2+}$ was determined with a Bruker SMART Apex-II CCD diffractometer with graphite-monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 223 K in the range $1.33 \leq \theta \leq 26.00$ for $\text{TMeQ[6]}-\text{EV}^{2+}$. The structures were solved by direct methods and refined using full-matrix least squares on F^2 (SHELXTL, Bruker, 2000). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$. Crystal data for $\text{TMeQ[6]}-\text{EV}^{2+}$: triclinic, space group $P-1$, $a = 15.398(13)$, $b = 16.552(14)$, $c = 22.17(3) \text{ \AA}$, $\alpha = 107.914(15)$, $\beta = 108.623(15)$, $\gamma = 96.654(11)$, $V = 4948(8) \text{ \AA}^3$, $Z = 1$, $\rho_{\text{calcd}} = 1.521 \text{ g cm}^{-3}$, $\mu = 0.128 \text{ mm}^{-1}$, $R_1 = 0.1579$ for 5206 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.4370$ for 17980 unique reflections. CCDC 641138 contain the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Description of ^1H NMR and UV spectroscopy of the inclusion complex

In our previous work, we have demonstrated that a partially methyl substituted cucurbituril (TMeQ[6]), which had an ellipsoid configuration, was soluble in neutral water [40]. We studied the interactions of Q[6] , TMeQ[6] and Q[7] with viologen and methyl viologen (MV^{2+}) and found that Q[6] cannot encapsulate the nucleus of viologen. However, TMeQ[6] was found to be able to encapsulate these two guests due to its ellipsoid configuration that has an extended dimension [42–45]. In this work, we investigated the $\text{TMeQ[6]}-\text{EV}^{2+}$ system and expect TMeQ[6] should interact with the aromatic nucleus of EV^{2+} viologen. The ^1H NMR spectra of EV^{2+} in the absence and presence of 1.0, 2.5 equiv. of TMeQ[6] and the neat TMeQ[6] in neutral D_2O solution are shown in Figure 1, in which not only the protons of aromatic nucleus of EV^{2+} , but also the protons of the substituted ethyl groups experienced up-field shift with increasing proportions of TMeQ[6] , the chemical shift change of the β -protons of aromatic nucleus ($\sim 0.6 \text{ ppm}$) is significantly larger than the chemical shift changes of the α -protons of aromatic nucleus ($\sim 0.2 \text{ ppm}$) or the ethyl protons (0.1–0.2 ppm), these shifts in their direction and magnitude suggest that the host TMeQ[6] shuttle between two terminal ethyl units through aromatic part or the guest EV^{2+} thread through the cavity of TMeQ[6] with a fast ingress and egress exchange ratio.

To better understand the interaction between TMeQ[6] and EV^{2+} , we carried out UV titration experiments. As shown in Figure 2, the UV spectrum of the EV^{2+} has peak with λ_{max} value of 260 nm. As the concentration of TMeQ[6] is increased in a solution containing a fixed concentration of EV^{2+} , a slow decrease in absorbance is observed. According to the mole ratio method, the experimental data of the absorbance (A) versus the ratio of the number of moles of TMeQ[6] host to EV^{2+} guest can be fitted to 1:1 host–guest

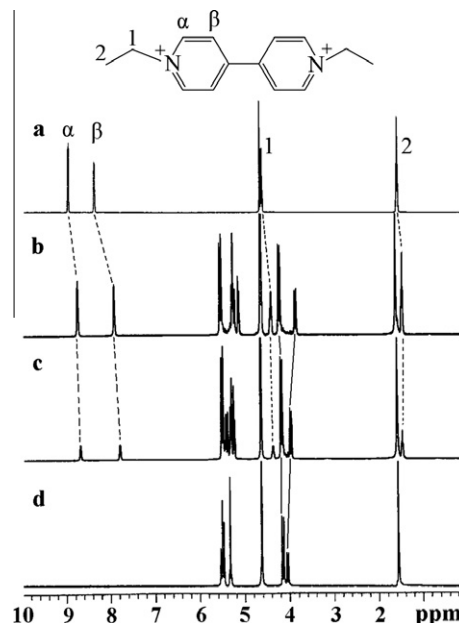


Figure 1. ^1H NMR spectra (400 MHz, D_2O) of EV^{2+} in the absence (a) and in the presence of 1.0 (b), 2.5 (c), equiv. of TMeQ[6] and the neat TMeQ[6] (d).

inclusion model. In addition, continuous variation Job's plot was constructed (Figure 2c), which shows the UV spectrum data fit well to the same 1:1 stoichiometry of the host–guest inclusion complex. For this 1:1 inclusion complex, the UV spectra data yield an equilibrium association constant of $(5.18 \pm 0.55) \times 10^4 \text{ M}^{-1}$.

3.2. Description of crystal structures of the inclusion complex

In the crystal structure of $\text{TMeQ[6]}-\text{EV}^{2+}$, two kinds of host–guest inclusion complexes were observed. In the first complex (Figure 3a), the EV^{2+} molecule inserted itself into the cavity of TMeQ[6] like a pseudorotaxane (1:1 host: guest). A distortion of both portals of TMeQ[6] is required for containing the pyridyl rings of the guest. The distance between the portal oxygen O13 and O16 was up to 8.013 \AA , which is longer than that of the normal $\sim 6.9 \text{ \AA}$ distance in Q[6] . However, this distortion can be compensated by the stronger hydrophobic forces between the aromatic nucleus of the guest and the inner surface of the cavity of the host. In addition, there were interactions between the positively charged nitrogens of the guests EV^{2+} and the carbonyl oxygens at the portals of the host in this complex. The distances of the charged nitrogen N38 to O14, O15, O17 and O18 were between 3.292 and 3.645 \AA ; the distances of N38 to O13, O16 were 3.997 and 4.066 \AA , respectively. Moreover, the proton H53A, H53B and H54A, H54B were located in the shielding region of the guest aromatic nucleus, consistent with the ^1H NMR spectra of the $\text{TMeQ[6]}-\text{EV}^{2+}$ system, in which the corresponding protons were upfield shifted (Figure 1b and c). In the second type of complex (Figure 3b), the two ethyl groups of a EV^{2+} molecule inserted into the cavities of two TMeQ[6] s to form a dumbbell-like structure with a 2:1 host to guest ratio. Obviously, the distortion of the host TMeQ[6] is much smaller in the first complex due to the inclusion of a small species in the cavity. The formation of such dumbbell-like assembly is attributed to the strong interactions between the positively charged nitrogens of the guests EV^{2+} and the carbonyl groups at the portals of TMeQ[6] in this complex. The distances of the charged nitrogen N37 to the O7–O12 were between 3.279 and 4.150 \AA . And the torsions of the substituted ethyl group with the pyridyl ring plane were 84.69° in the first complex and 21.30° in the second complex.

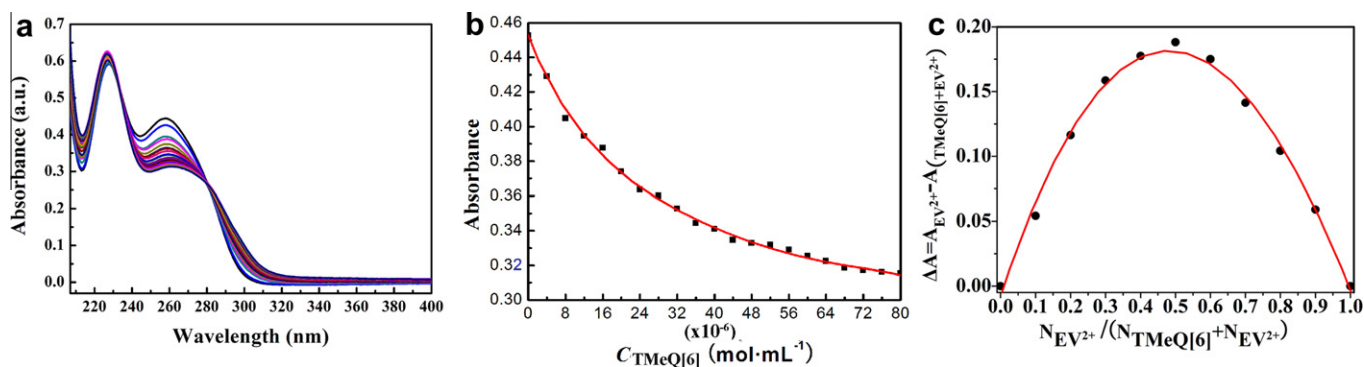


Figure 2. (a) UV titration of EV^{2+} with increasing TMeQ[6], (b) absorbance (A) versus the concentration of TMeQ[6] curve at 260 nm and (c) continuous variation Job's plot for TMeQ[6] and EV^{2+} on the basis of UV spectra.

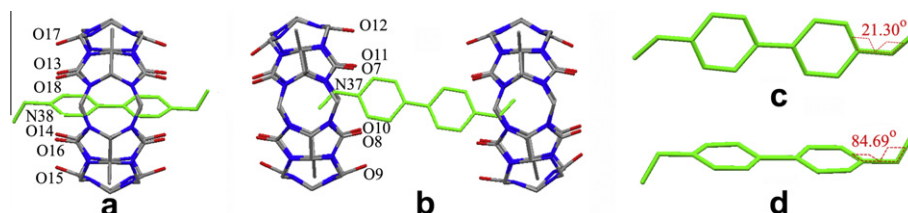


Figure 3. The EV^{2+} and TMeQ[6] formed two types of inclusion models in the self-assembled complex, (a) pseudorotaxane interaction model and (b) dumbbell interaction model, the two different included EV^{2+} guests (c and d), hydrogen atoms are omitted for clarity.

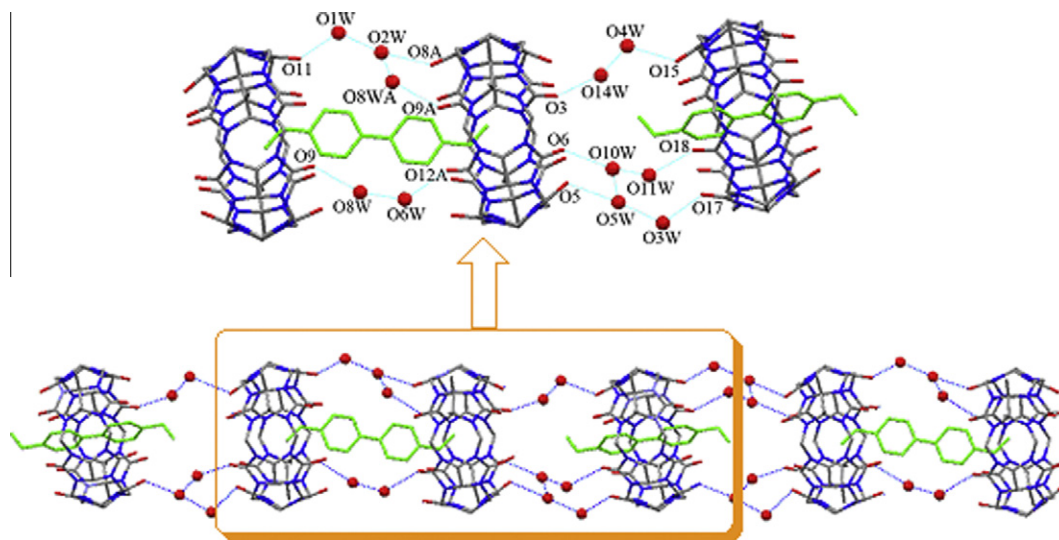


Figure 4. 1D assembled supramolecular chain consisting of alternating pseudorotaxane block and dumbbell block through hydrogen bonding in the crystal structure (hydrogen atoms are omitted for clarity).

The two interaction models of TMeQ[6] and EV^{2+} along with the guest in the crystal structure have been discussed individually. Now we like to examine the interactions between these two types of complexes. As shown in Figure 4, there is no direct interaction between two different guests or the guest in the pseudorotaxane structure of TMeQ[6]- EV^{2+} with the next equilibrium of the two interaction models in the system was reversible. But, a great deal of hydrogen bonds were observed between the two TMeQ[6] in different complexes. The carbonyl oxygen of one complex formed hydrogen bonds with water molecules and those water molecules formed hydrogen bonds with the carbonyl oxygen of another complex. Hydrogen bonding bridges, such as $\text{O3}\cdots\text{O14W}\cdots\text{O4W}\cdots\text{O15}$; $\text{O6}\cdots\text{O10W}\cdots\text{O11W}\cdots\text{O18}$; $\text{O5}\cdots\text{O5W}\cdots\text{O3W}\cdots\text{O17}$ were observed with bond lengths between 2.746 and 2.924 Å. Moreover,

additional hydrogen bonds, such as $\text{O11}\cdots\text{O1W}\cdots\text{O2W}\cdots\text{O8A}$ and $\text{O9}\cdots\text{O8W}\cdots\text{O6W}\cdots\text{O12A}$, were observed between the two TMeQ[6] molecules in the dumbbell structure with bond lengths between 2.670 and 2.823 Å. These hydrogen bonds strengthen the dumbbell-like structure further. Thus, one dimensional supramolecular chains consisting of alternating pseudorotaxane block and dumbbell block are formed through hydrogen bonding.

4. Conclusions

In summary, through the ^1H NMR and UV spectroscopy, we have demonstrated solution structure of TMeQ[6]- EV^{2+} system in which the TMeQ[6] host can accommodate the EV^{2+} cationic guest

to form inclusion complex with a 1:1 ratio of host to guest. The X-ray crystal structures of the inclusion complex clearly show a novel structure system in which two types of inclusion models (dumbbell-like structure and pseudorotaxane structure) of EV^{2+} and TMeQ[6] were found, the major driving force for the assembly of these complexes is presumably ion–dipole interaction between the TMeQ[6] portals and the EV^{2+} cation. The present work shows that the interaction model of a certain host–guest system could be different in the solution state and in the solid state.

Acknowledgments

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