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PAPER

Inclusion of methylviologen in symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril†

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The host–guest interaction between symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril (TMeQ[6]) and methylviologen (*N*,*N*′-dimethyl-4,4′-bipyridinium, MV) dication was investigated both in aqueous solution and in the solid state using NMR spectroscopic methods and single-crystal X-ray diffraction analysis. In the aqueous solution, TMeQ[6] forms a 1 : 1 inclusion complex with methylviologen MV^{2+}, and the chemical exchange of the MV^{2+} guest in and out of the cavity of the TMeQ[6] host was fast on the NMR time scale. In the solid state, however, the MV^{2+} guest was partially encapsulated into the TMeQ[6] host. We found that the chemical environment of the TMeQ[6] host underwent a severe change during the encapsulation process. Interestingly, electrochemical studies revealed that, unlike other cucurbiturils, TMeQ[6] has the same level of binding affinity to the charged forms (MV^{2+} and $MV^{+\bullet}$) and the fully reduced form (MV^0). These studies contribute to the fundamental understanding of the interdependence of electron-transfer processes and molecular recognition.

Introduction

Inclusion complexes have attracted considerable interest because of their potential application in the creation of rotaxanes,[1,2] catenanes,[3] and other novel molecular devices.[4] Cucurbit[*n*]urils[5,6] (*n* = 5–8, 10, hereafter abbreviated as Q[*n*]), as one type of host molecule, are receiving increasing attention for their special structure and application in constructing unique inclusion complexes. In the past decade, a large number of inclusion complexes constructed from Q[*n*] homologues and methylviologen (*N*,*N*′-dimethyl-4,4′-bipyridinium, MV) dication or its derivates have been synthesized and extensively studied.[7–11] For example, Kim and co-workers investigated the first inclusion behaviors of MV in Q[7] and Q[8]. The authors discovered that Q[7] preferred the charged forms (MV^{2+} and $MV^{+\bullet}$) to the fully reduced neutral form (MV^0) as guest, and that the $MV^{+\bullet}$ dimer was strongly stabilized in the cavity of Q[8].[7b,7c] The Kaifer group investigated the binding mode of MV^{2+} moieties with Q[7] and designed controllable molecular shuttles.[8a,f,g] These studies play a fundamental role in the understanding of the interdependence of electron-transfer processes and molecular recognition.

We were intrigued to investigate the inclusion complexes based on Q[*n*] derivatives and MV other than the first report on the MV^{2+}-MeCB6 complex.[8h] Recently, we reported the synthesis and characterization of the symmetrical α,α′,δ,δ′-tetramethyl-cucurbit[6]uril (TMeQ[6], Fig. 1).[12] TMeQ[6] possesses four methyl groups and exhibits better solubility in aqueous media than Q[6]. The four substituents give the TMeQ[6] an ellipsoidal hydrophobic cavity, rather than a round one as found in the parent Q[6], which makes it more suitable for the inclusion of guests containing aromatic rings. Noting the fact that Q[6] forms a 1 : 1 host–guest complex with MV^{2+},[11c] we hypothesized that a MV molecule would fit well into the ellipsoidal cavity of TMeQ[6]. Thus, we set out to study the inclusion behavior of MV^{2+} in the TMeQ[6] host. Herein we report the host–guest interaction between TMeQ[6] and MV^{2+} in aqueous solution and in the solid state. The electrochemical behavior of the inclusion complex was also studied.

Results and discussion

First, we studied the host–guest interactions between TMeQ[6] and MV^{2+} *via* NMR spectroscopic methods. The ^{1}H NMR spectra of MV^{2+} in the absence and presence of 0.4, 0.8 and 1.0 equiv. of TMeQ[6] in D_2O were recorded, as shown in Fig. 2. After the addition of 0.4 equiv. of TMeQ[6], the α-proton of the bipyridinium moiety and methyl protons shifted upfield by 0.35 and 0.16 ppm, respectively, from the resonances of the free MV^{2+}. In contrast, the signal of the β-proton of the bipyridinium moiety shifted downfield by 0.13 ppm. Upon the addition of more TMeQ[6] host, the ^{1}H NMR signals of the MV^{2+} guest

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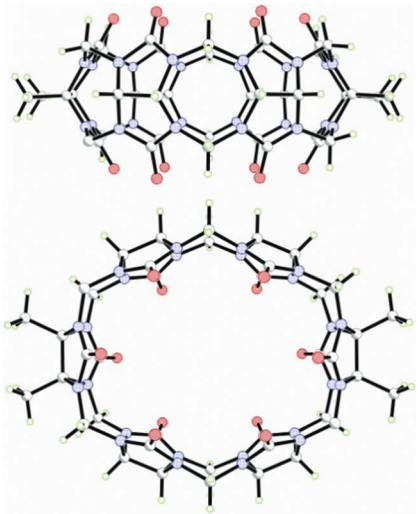

Fig. 1 X-Ray crystal structure of TMeQ[6] in side view and top view.

shifted upfield or downfield gradually. As the ratio of TMeQ[6] to the guest increased up to 1.0, the α-proton of the bipyridinium moiety and methyl protons of the guest experienced an upfield shift of 0.66 and 0.25 ppm, respectively, while the β-proton shifted 0.35 ppm downfield (Fig. 2e). These chemical shifts indicated that the methyl group and part of the bipyridinium moiety of the MV^{2+} were engulfed in the cavity of TMeQ[6], while the other part of the bipyridinium moiety of MV^{2+} was located outside the portal of the TMeQ[6]. On the other hand, even with a guest/host ratio higher than two, only one set of signals was observed for the MV^{2+} guest, suggesting that the apparent signals were actually average signals of the free and included guests, and that the intermolecular host exchange rate between the free guest and the TMeQ[6]-complexed guest is fast on the NMR time scale.

To better understand the interaction between TMeQ[6] and MV^{2+}, ^{1}H NMR titration experiments were constructed. According to the experimental data and the mole ratio method,[13] we obtained the curve of the shifts of the NMR-signals (α-proton) *versus* the equivalence of TMeQ[6] (Fig. 3), which suggests the formation of a 1 : 1 host–guest inclusion complex between the TMeQ[6] host and the MV^{2+} guest in aqueous solution. For this 1 : 1 inclusion complex, the experimental data yield a binding constant of 4.0×10^2 M^{-1}, which is much smaller than that recorded in the literature.[8h]

The guest protons are frequently shifted on NMR spectra because of shielding or deshielding effects of the host, especially in cucurbituril chemistry. However, to the best of our knowledge, Q[*n*] host protons have never been reported to undergo chemical shifts. In the present system, remarkable chemical shifts were observed for TMeQ[6] host protons in the inclusion complex TMeQ[6]·MV^{2+} (Fig. 2e). For the TMeQ[6] host protons, the H1, H2 and H7 resonances experienced downfield shifts of about 0.17, 0.18 and 0.16 ppm, respectively, while the H3, H4, H5 and H6 resonances experienced upfield shifts of about 0.10, 0.16, 0.18 and 0.17 ppm, respectively. These data indicated that the chemical environment of the TMeQ[6] host underwent changes after including the MV^{2+} guest. In fact, the asymmetric displacement of the guest in the cavity, with one ring out of the cavity and one inside, gives different chemical shifts (splitting of resonances) for the TMeQ[6] host protons.

To understand the interaction between TMeQ[6] and MV^{2+} in the solid state, we next determined the X-ray crystal structure of

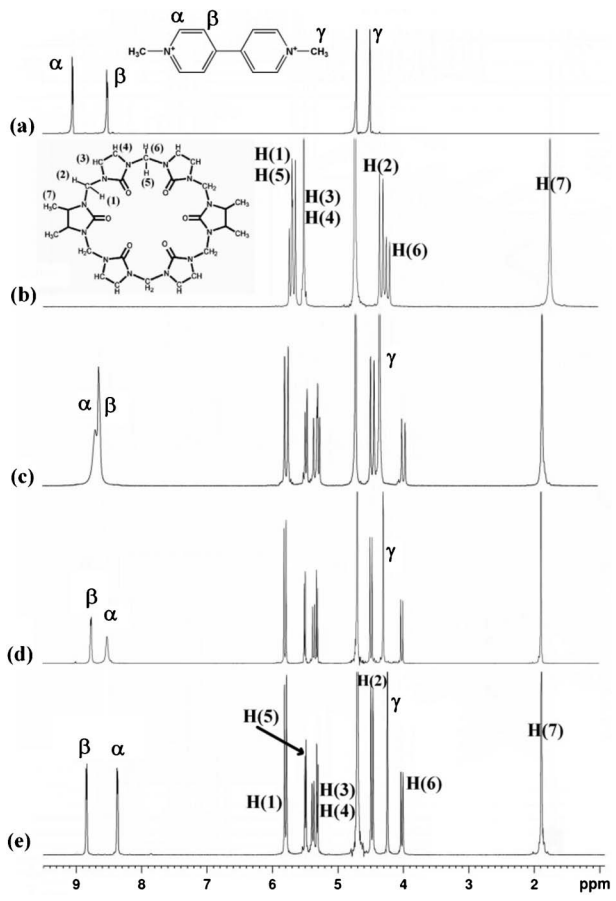

Fig. 2 ^{1}H NMR spectra of 2.3 mg MV^{2+} in the absence (a) and presence of 0.4 (c), 0.8 (d), and 1.0 (e) equiv. of TMeQ[6] in 0.50 ml D_2O at 20 °C. (b) shows the ^{1}H NMR spectrum of TMeQ[6] in 0.50 ml D_2O at 20 °C.

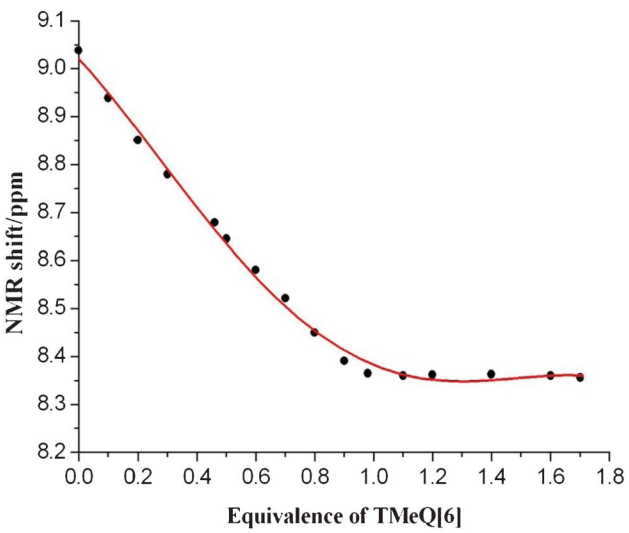

Fig. 3 ^{1}H NMR (500 MHz, D_2O) titration curve of MV^{2+} by addition of TMeQ[6] in aqueous solution.

the inclusion complex TMeQ[6]·MV^{2+}. Slow evaporation of an aqueous solution of the host and the guest in 1 : 1 ratio produced good quality single crystals of the inclusion complex TMeQ[6]·MV^{2+}, which crystallized in the triclinic system with the $P\bar{1}$ space group. The single-crystal X-ray structure of the inclusion complex TMeQ[6]·MV^{2+} revealed a unique binding mode between MV^{2+} and TMeQ[6] in the solid state. As shown in Fig. 4, half of the MV^{2+} guest (including one pyridinium ring and one neighboring methyl group) is located inside the cavity of the TMeQ[6] host while the other half of the MV^{2+} guest remains outside of the portal. The inclusion complex TMeQ[6]·MV^{2+} is strong similar to its counterpart, the complex MV^{2+}-MeCB6 reported by Sindelar and coworkers.[8h] However, some subtle differences exist. The MV^{2+} guest in the MV^{2+}-MeCB6 complex possesses a normal D_{2h} molecular point group, while in TMeQ[6]·MV^{2+}, the MV^{2+} guest experiences a slight deformation.

As depicted in Fig. 4, there might be two driving forces causing the assembly of such an inclusion complex. Short-distance C–H···O hydrogen bonds between methyne protons on the pyridinium ring of the guest and carbonyls on portals of the TMeQ[6] appear to be the major driving force. Another driving force that must be taken into account is the hydrophobic interactions of the TMeQ[6] cavity. However, hydrophobic interactions are dominant for the host–guest interaction between TMeQ[6] and MV^{2+} in solution.

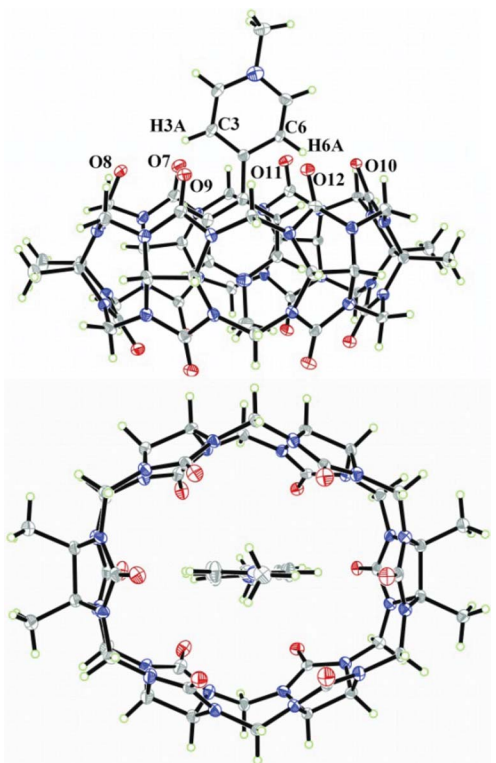

Fig. 4 ORTEP diagram of the inclusion complex TMeQ[6]·MV^{2+} (asymmetric unit) in side view and top view; displacement ellipsoids are drawn at the 30% probability level. The distances of hydrogen atoms of MV^{2+} and carbonyl groups of TMeQ[6]: H3A···O7 2.671 Å, H3A···O8 2.406 Å, H3A···O9 2.989 Å, H6A···O10 1.874 Å, H6A···O11 2.778 Å, H6A···O12 2.719 Å. Solvate water molecules and chloride anions are omitted for clarity.

Finally, the electrochemical behavior of MV^{2+} in the presence of TMeQ[6] was investigated. To better understand the host–guest interaction between TMeQ[6] and MV^{2+} in aqueous solution, we carried out electrochemistry experiments to give cyclic voltammograms. Fig. 5 shows the current–potential curves of 0.1 mM MV^{2+} in the absence (dotted line) and presence of 1.0 equiv. (solid line) of TMeQ[6]. As anticipated, MV^{2+} undergoes two reversible one-electron reductions in the absence of TMeQ[6]. In the presence of 1.0 equiv. of TMeQ[6], a pronounced decrease in the current levels is observed, which further confirmed the formation of the host–guest inclusion complex between TMeQ[6] and MV^{2+}. The decrease of current also suggests the smaller diffusion coefficient of the host–guest inclusion complex compared to free MV^{2+}.

It is interesting to note that TMeQ[6] little affects the half-wave potentials ($E_{1/2}$) for both the first reduction and the second reduction. It was generally accepted that the shift in half-wave potentials ($E_{1/2}$) reflects relative binding affinities of the guest of different redox states to the host.[7b] The observed unaffected half-wave potentials ($E_{1/2}$) of MV^{2+} in the presence of TMeQ[6] is worth noting. TMeQ[6] could have the same level of binding affinity to the charged species (including the initial, dication MV^{2+} and the cation radical $MV^{+\bullet}$) and the fully reduced, neutral species (MV^0). To the best of our knowledge this would be the first macrocycle exhibiting the same binding affinities to a guest of different redox states. Previously, Q[7] induced pronounced shifts in both reduction waves in the cyclic voltammogram of MV^{2+}, which indicates that Q[7] prefers the MV dication (MV^{2+}) and the cation radical $MV^{+\bullet}$ to the fully reduced neutral species (MV^0) as guest.[7b] It was proposed that the ion–dipole interaction between the positive charge of the guest and the portal oxygen atoms of Q[7] contributed to the formation of the host–guest inclusion complex. In the case of TMeQ[6], the carbonyl groups at the elliptical portal of TMeQ[6] may not be able to provide effective binding sites, leading to a less effective ion–dipole interaction between the carbonyl groups of TMeQ[6] and the positive charge of the guest. We believe that, in our case, the hydrophobic effect of the TMeQ[6] cavity is the

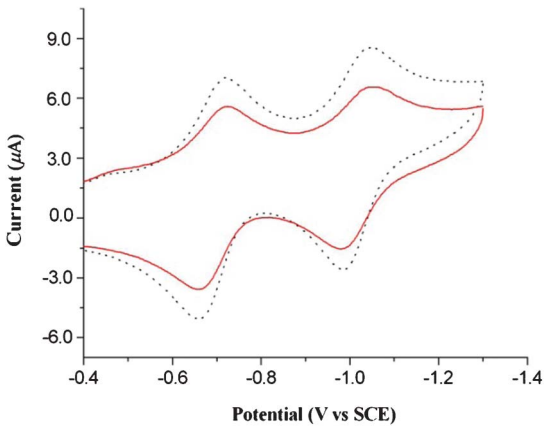

Fig. 5 Cyclic voltammograms (0.1 V s^{-1}) of 0.1 mM MV^{2+} in the absence (dotted line) and presence of 1.0 equiv. (solid line) of TMeQ[6]. SCE, saturated calomel electrode.

exclusive driving force for the formation of the host–guest inclusion complex. Hence, TMeQ[6] as host displays the same level of binding affinity to the charged and neutral guests.

Conclusions

To close, we have investigated the host–guest interactions between TMeQ[6] and MV^{2+} both in aqueous solution and in the solid state using NMR spectroscopic methods and the X-ray diffraction analysis. The host–guest inclusion behavior of MV^{2+} in TMeQ[6] in aqueous solution is distinctly different from that in the solid state. Moreover, the chemical environment of the TMeQ[6] host underwent a substantial change during the encapsulation process. Electrochemical experiments indicated that TMeQ[6] had the same binding affinity to the charged forms (MV^{2+} and $MV^{+\bullet}$) and the fully reduced form (MV^0). This observation not only contributes to a deeper understanding of the interactions between redox guests and macrocycle hosts, but also helps in the design and construction of novel molecular machines. We are actively pursuing such opportunities.

Experimental section

Materials and methods

MV dichloride was purchased from Aldrich, and TMeQ[6] was synthesized according to literature methods.[12a] ^{1}H NMR and 2D NOESY spectra were recorded at 20 °C on a Varian INOVA-500 spectrometer. C, H, and N microanalyses were carried out with a PE 240C elemental analyzer.

Electrochemical experiments

Electrochemical measurements were performed on a CHI 852 C electrochemical workstation (Co., CHI, USA) interfaced with a personal computer. A three-electrode system consisting of a saturated calomel electrode as reference electrode, a platinum wire as counter electrode, and a freshly polished glassy carbon (diameter 2 mm) as working electrode was used in a single compartment cell. The experiments were conducted in 0.2 M NaCl medium solutions prepared with purified water. The potentials vary from 0 V to −1.3 V, scan rate 0.1 V s^{-1}, quiet time 2 s. All solutions were purged with purified nitrogen to remove dissolved oxygen before the electrochemical measurements.

Synthesis of the inclusion complex TMeQ[6]·MV^{2+}

MV dichloride ($C_{12}H_{14}N_2Cl_2 \cdot 10H_2O$, 0.029 g, 0.1 mmol) was dissolved in H_2O (5 ml), and to this solution TMeQ[6] (0.1044 g, 0.10 mmol) was added. The mixture was stirred and heated at 50 °C for 10 min and then filtered. Slow evaporation of the filtrate over a period of about two weeks provided rhombic colorless crystals. Yield: 20%. Anal. calcd for TMeQ[6]·MV^{2+}: C, 39.08; H, 5.68; N, 22.78. Found: C, 39.01; H, 5.73; N, 22.72%.

Crystal structure determination

Diffraction data for the inclusion complex TMeQ[6]·MV^{2+} were collected at 173 K with a Bruker SMART Apex-II CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by using the multiscan program SADABS. Structural solution and full matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package,[14] respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. For the inclusion complex TMeQ[6]·MV^{2+}, no hydrogen atoms are given for all isolated water molecules since it is difficult and unnecessary.

Crystal data for the inclusion complex TMeQ[6]·MV^{2+}. $C_{52}H_{90}N_{26}O_{28}Cl_2$, M_r = 1598.40, triclinic, space group $P\bar{1}$, a = 11.9780(10) Å, b = 12.7819(11) Å, c = 24.262(2) Å, α = 104.128(3)°, β = 93.847(3)°, γ = 91.500(3)°, V = 3590.5(5) Å^3, Z = 2, D_c = 1.478 g cm^{-3}, F(000) = 1684, GoF = 1.006, R_1 = 0.1170 ($I > 2\sigma(I)$), wR_2 = 0.3566 (all data). CCDC 836463.†

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