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Formation of Host-Guest Complexes of 3-(aminomethyl)pyridine HCl Salt and Tetramethylcucurbit[6]uril

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The structure of complex of 3-(aminomethyl)pyridine hydrochloride ($AMPY^+$, guest) and symmetrical tetramethyl substituted cucurbit[6]uril (TMeQ[6], host) has been studied by single crystal X-ray diffraction. UV-vis spectra titration has been employed and the moderate association constants 9.51×10^5 L/mol has been obtained with the interaction models in a ratio of 1:1 between guest and host.

Key Words: Cucurbituril, Single crystal X-ray diffraction, Host-guest interaction, Inclusion complex, Supramolecular.

INTRODUCTION

Since the structure of the first cucurbituril, a cyclic oligomer of glycoluril linked by 12 methylene bridges was determined by Mock and co-workers[1]. Considerable interest has emerged inspired by this novel receptor and the supramolecular of cucurbit[*n*]uril(Q[n]) has expanded dramatically with the discovery of cucurbituril(Q[6]) and its homologues (Q[5], Q[7], Q[8] and Q[10])[2]. However, the poor solubility and low reactivity of the unsubstituted Qs in the commonly used solvents limited the research of Q[n] chemistry. With the development of the research in this field, large number of substituted cucurbiturils with good solubility in neutral water or organic solvent have been discovered[3], such as decamethylcucurbit[5]uril ($Me_{10}Q[5]$), fully alkyl-substituted cucurbiturils[4] and the partially substituted cucurbiturils[3,5,6].

In this work, the symmetrical tetramethylcucurbit[6]uril (TMeQ[6]) was selected as a host molecule and an organic cation, 3-(aminomethyl)pyridyl hydrochloride ($AMPY^+$) was selected as a guest molecule. We have studied on the interactions of TMeQ[6] and $AMPY^+$ with single crystal X-ray diffraction determination and UV-vis spectra.

EXPERIMENTAL

Hydrochloric acid, acetone, 3-(aminomethyl)pyridine were of reagent grade and used without further purification. TMeQ[6] was prepared and purified according

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to the published procedures[4]. The guest was prepared by dissolving 3-(aminomethyl)-pyridine in concentrate HCl followed by crystallization with acetone, collected by filtration and dried in air.

To a solution of TMeQ[6] (0.41g, 0.40 mmol) in 20 mL water, $AMPY^+$ (0.067 g, 0.37 mmol) was added dropwise with stirring at 35 °C for 1 h. The solution was deposited by acetone, then filtered and the filtrate was allowed to stand at room temperature for a month. Colourless X-ray quality crystals of the compound were obtained from the solution with a yield of 30 %.

The single crystal X-ray diffraction data of the host-guest inclusion complex was collected on a Bruker Apex-2000 CCD diffractometer using graphite mono-chromated MoKα radiation (λ = 0.71073 Å) with ω scan mode. Structural solution and full matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packagerespectively[7,8]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically.

Absorption spectra of the host-guest complexes were recorded on a an Agilent 8453 instrument at 25 °C.

RESULTS AND DISCUSSION

Crystallographic analysis revealed that an $AMPY^+$ molecule was encapsulated inside the cavity of a TMeQ[6] to form a host-guest inclusion complex. The crystal structure showed that the TMeQ[6]@$AMPY^+$ complex belonged to single bevel-crystal system and its space group was C2/m, a = 14.789(6)Å, b = 18.832(7) Å, c = 12.743(4) Å; α = 90.00(0)°, β = 97.04(2)°, γ = 90.00(0)°, V = 3522(2) nm^3, Z = 5, F_{000} = 3300, R_1 = 0.1070, Rw = 0.3110. The Fig. 1 showed the character of the inclusion complex crystal structure by side view and top view.

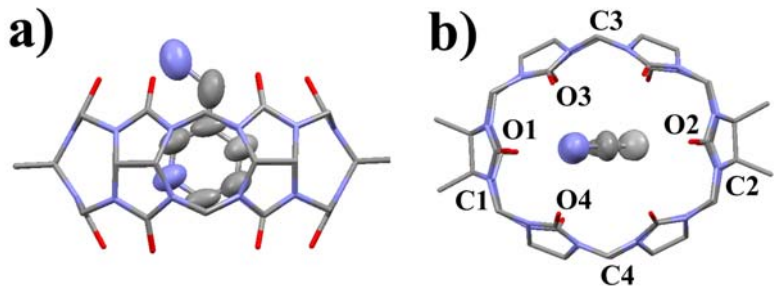

Fig. 1. Structure of the title complex. a): side view; b): top view

The crystal structure revealed the inclusion complex of TMeQ[6]@$AMPY^+$ to be in a 1:1 ratio of host: guest. The protonated aminomethyl group on the pyridine ring is detected at outside portal of the host and one pyridine ring of the guest inserts deeply into the cavity of the host (Fig. 1). A hydrogen bond of 2.89 Å has been observed between O1 and the amino proton on included guest. Furthermore, the distortions of the TMeQ[6] were observed obviously, because the guest $AMPY^+$

inserted itself into the cavity of Q[6] in the certain orientation. For example, the distance between O1 and O2 (7.463 Å) is 1.763 Å longer than the long axis diameter distance of TMeQ[6], the distance between O3 and O4 (5.714 Å) is 2.014 Å longer than the short diameter axis distance. However, the distances were same to TMeQ[6] between C1 and C2, also C3 and C4[5].

Crystallographic analysis discussed above revealed that TMeQ[6] can include the pyridine moiety of the HCl salt of the guest and formed inclusion complexes with a host-guest ratio of 1:1. The absorption spectrophotometric analysis has been employed to quantitatively define the interaction between TMeQ[6] and the guest $AMPY^+$. Inclusion ratio and binding constant of $AMPY^+$ and TMeQ[6] have been measured with UV-Vis spectra titration and the results are exhibited in Fig. 2, which shows the variation in the UV spectra obtained with aqueous solutions containing a fixed concentration of $AMPY^+$ (2.5×10^{-4} mol L^{-1}) and variable concentrations of TMeQ[6]. Generally, TMeQ[6] shows no absorbance above ~210 nm, but the absorption bands of guest exhibit a progressive violet-shift as the ratio of $C_{TMeQ[6]}/C_{AMPY^+}$ is gradually increased, while the maximum absorbance of $AMPY^+$ at λ = 259 nm (A_{259}, $\varepsilon = 2.32 \times 10^3$ L mol^{-1} cm^{-1}) become progressively lower with increasing concentration of host from 5.00×10^{-4} mol L^{-1} to 5.00×10^{-4} mol L^{-1} and the maximum absorbance is violet-shifted to λ = 257 nm. The sharp isosbestic points at λ = 268 nm is consistent with a simple interaction between TMeQ[6] and $AMPY^+$.

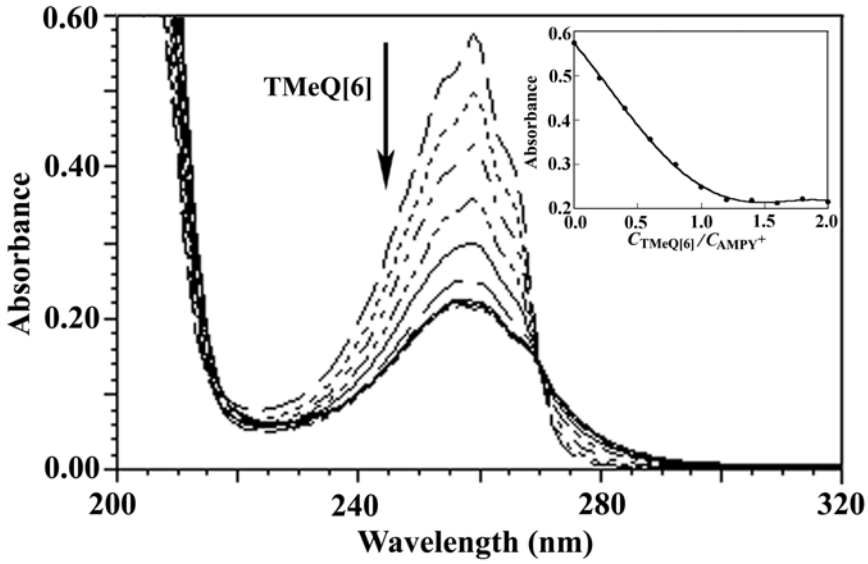

Fig. 2. Absorption spectra changes of the mixtures of guest-host and curve-fitting analysis for the inclusion complexes. Inset: related A *vs.* $C_{TMeQ[6]}/C_{AMPY^+}$ curve at 259 nm

The absorbance (A) *vs.* ratio of moles of the host TMeQ[6] and guest $AMPY^+$ ($C_{TMeQ[6]}/C_{AMPY^+}$) data can be fitted to a 1:1 binding model for the TMeQ[6]@$AMPY^+$ system at λ_{max} = 257 nm. This behaviour is consistent with the results from the crystallographic analysis. The corresponding association constant (K_a) was found to be 9.51×10^5 L/mol (R > 0.99) with nonlinear least square fitting according to curve fitting[9].

Conclusion

The interaction of a substituted cucurbituril, TMeQ[6], with $AMPY^+$ have been studied by single crystal X-ray diffraction and electron absorption spectroscopy. The formation of a 1:1 inclusion complex has been confirmed by crystal structure and a moderate association constant has been obtained with UV-vis spectroscopy. Present study suggested that the host TMeQ[6] had selectivity for the guest molecules that were readily included in the cavity of TMeQ[6]. The shell structure TMeQ[6] was affected by the guest and the distortion of the shell structure was dependent upon not only the interactions with the included guest, but also the interactions between the guest and the portal carbonyl oxygens.

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