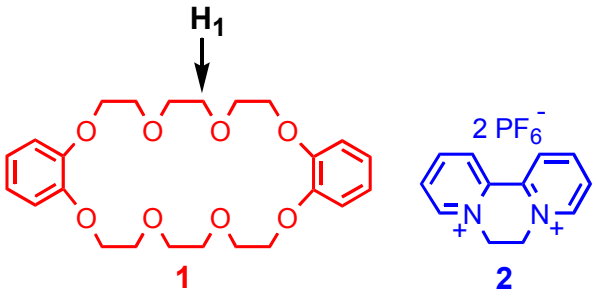
Chapter 12

An Inclusion Complex of Diquat in the Concave Cavity Provided by Two Dibenzo-24-Crown-8 Hosts

12.1. INTRODUCUTION

The chemistry of inclusion complexes has been extensively investigated by scientists all over the world with diverse objectives. Some recent examples include improvement of the solubility of fullerenes in water,[1] stabilization of a dye molecule,[2] microencapsulation of biologically active compounds,[3] drug delivery,[4] preparation of a 3D porous magnet,[5] and fabrication of a molecular elevator.[6] Dibenzo-24-crown-8 (**1**) and diquat (**2**) derivatives are commonly used hosts and guests in this field.[7,8] Though Pospisil et al. first studied the complexation between **1** and **2** in methanol in 1988,[8c-d] the complexation mechanism is still not clear up to now. Furthermore, no new complexes based on these species have been reported in the last 16 years. Here we report proton NMR and mass spectrometric characterizations and X-ray ananlysis of this complex, which was found to have a interesting conformation in the solid state.



12.2. RESULTS AND DISCUSSION

When **1** was mixed with an equivalent of **2** in CD_3COCD_3, a yellow color was observed immediately due to charge transfer interactions between the electron-rich aromatic rings of **1** and electron-poor **2**. A Job plot[9] (Fig. 1) demonstrated that the complex between **1** and **2** was of 1:1 stoichiometry in solution. The apparent assoiciation constant (K_a) of **1•2** calculated based on the proton NMR data was 2.0 (± 0.2) × 10^2 M^{-1} in acetone.†

The complex between **1** and **2** was also characterized by the electrospray ionization mass spectrometry (Fig. 2). The base peak at m/z 471.4 was assigned to [**1** + Na]$^+$. Two peaks corresponding to the 1:1 stoichiometry were found: *m*/*z* 777.5 (25%) [**1•2** - PF_6]$^+$ and 316.5 (60%) [**1•2** - $2PF_6$]$^{2+}$. Two unexpected peaks related to the 2:1 stoichiometry were also found: *m*/*z* 1225.8 (2%) [$\mathbf{1}_2$•**2** - PF_6]$^+$ and 540.7 (5%) [$\mathbf{1}_2$•**2** - $2PF_6$]$^{2+}$.

A single crystal of **2** for X-ray analysis was grown by vapor diffusion of pentane into an acetone solution of **2**.# As shown by the obtained crystal structure (Fig. 3), the two pyridinium rings of **2** are twisted with an angle of 18.5° and a centroid-centroid distance of 4.23 Å.

The complex between **1** and **2** has a 2:1 stoichiometry in the solid state as shown by its crystal structure (Fig. 4) obtained from the X-ray analysis of a single crystal grown by vapor diffusion of pentane into an equimolar solution of **1** and **2** in acetone.# $\mathbf{1}_2$•**2** is stabilized by C–H···O hydrogen bonding, face-to-face π-stacking and CH/π interactions.[13] There are totally ten hydrogen bonds between the guest **2** and the two hosts (**B-K**, Figs. 4a and 4b). Four of eight pyridinium hydrogens of diquat are involved in these hydrogen bonds (**B**-**D**, **H**, **I**). What is more important here is that all four methylene hydrogens of diquat are hydrogen bonded to the two hosts (**E**, **F**, **G**, **K**, **J**), while the methyl hydrogens of the closely related paraquat are not involved in interactions with the host in most of reported paraquat complexes.[14] One phenylene ring of each host is π-stacked to the same pyridinium ring of **2**. The two host molecules are connected by one aromatic C–H···O hydrogen bond (**L**) and an aliphatic C-H/π

interaction (**A**) to form a concave cavity for which two of six sides are open (Figs. 4c and 4d). Diquat fits this cavity very well. Complex formation has some influence on the conformation of **2** because the twist angle between the two pyridinium rings changed from 18.5° to 14.9° after the complexation but the centroid-centroid distance did not change (Figs. 3 and 4).

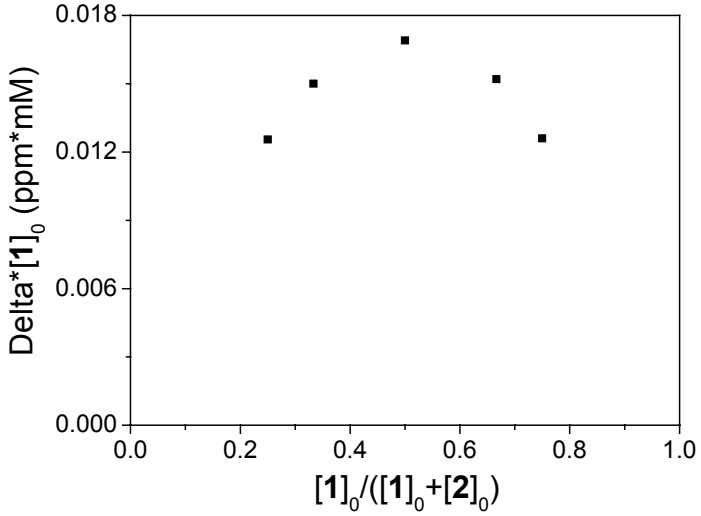


Figure 1. Job plot showing the 1:1 stoichiometry of the complex between **1** and **2** in CD_3COCD_3 solution using data for H_1 of **1**. $[\mathbf{1}]_0$ and $[\mathbf{2}]_0$ are initial concentrations of **1** and **2**. $[\mathbf{1}]_0 + [\mathbf{2}]_0 = 2.00$ mM.

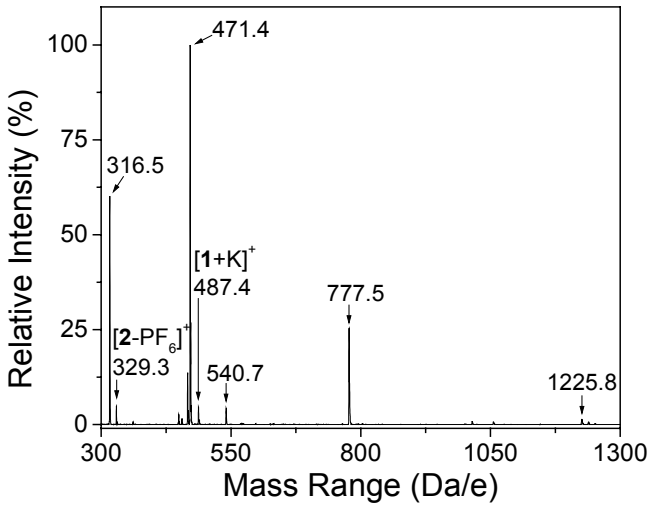


Figure 2. Electrospray mass spectrum of a solution of **1** and **2** in a mixture of acetonitrile and chloroform (4:1).

The formation of the dimer $(\mathbf{1}\bullet\mathbf{3})_2$ was confirmed by X-ray analysis of a single crystal prepared by the vapor diffusion of pentane into an acetone solution of **3** and excess **1**. **1•3** is stabilized by hydrogen bonding and face-to-face π-stacking interactions in the solid state (Fig. 3). As designed, H-bonding of the pyridyl N with the β–H of **3** (**b**) adds stability.

Dimer formation is driven by dipole-dipole and face-to-face π-stacking interactions (Fig. 4). The pyridine ring of **1** is electron-poor due to the electron-withdrawing effectsof the two carbonyl substituents and hydrogen bonding of its nitrogen atom with a β-pyridinium hydrogen of the electron-poor guest **3**. Therefore, the relatively electron-rich phenyl ring of **1** forms a dipole with the pyridine ring. In dimer two dipoles are arranged in opposite directions to allow π-π interactions between donor-acceptor pairs. The centroid-centroid distances and ring plane/ring plane dihedral angle for these face-to-face π-stacking interactions are smaller than the above discussed interactions between the electron-rich phenylene rings of **1** and the electron-poor pyridinium rings of **3**. This demonstrates that the face-to-face π-stacking interactions here are strong.

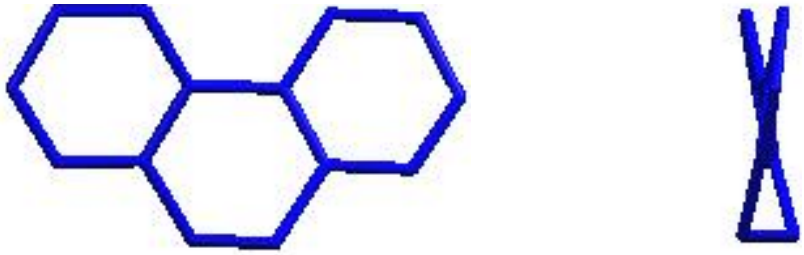


Figure 3. Two views of the solid-state structure of **2** as determined by X-ray crystallography. Two PF_6 counter ions and hydrogens have been omitted for clarity. The angle and centroid-centroid distance between two pyridinium rings of **2** (deg and Å): 18.5 and 4.23.

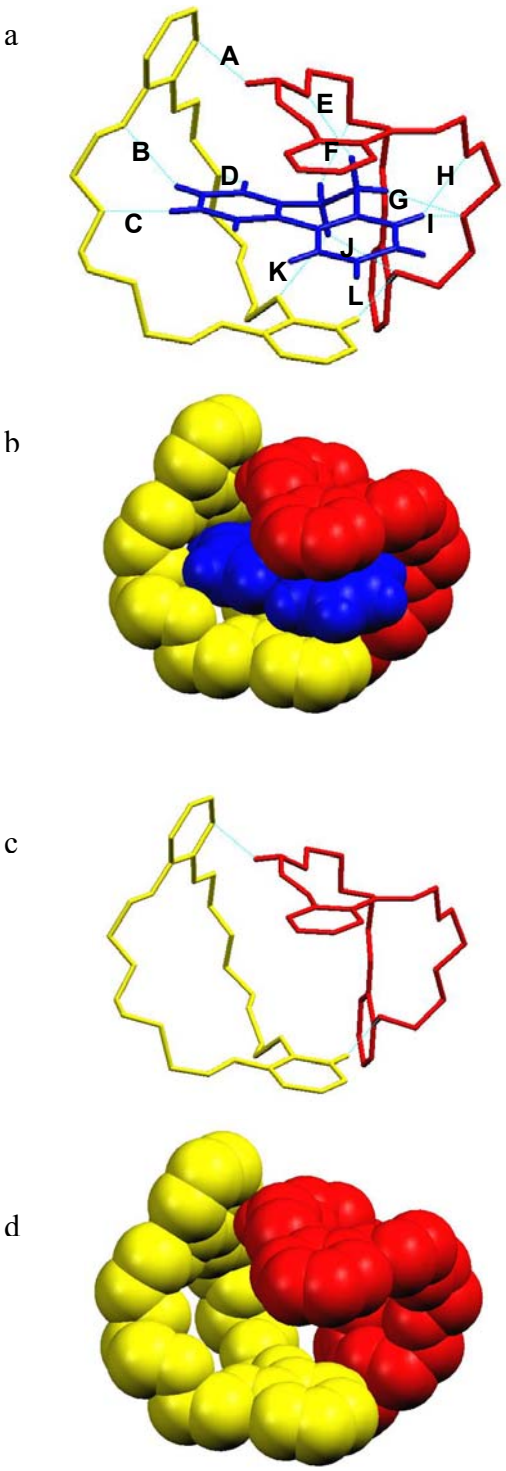


Figure 4. Stick (a) and space-filling (b) representations of the X-ray structure of $\mathbf{1}_2$•**2** and stick (c) and space-filling (d) representations of a part of it showing the concave cavity provided by the two hosts. (a and b) The hosts are red and yellow and **2** is blue. Four PF_6^- ions and hydrogens except the ones on **2** or involved in hydrogen bonding or the CH/π

interaction have been omitted for clarity. CH/π interaction parameters: distance between the hydrogen and the closest carbon on the aromatic ring (**A**) 2.85 Å; hydrogen-centroid distance 2.72 Å; carbon-centroid distance 3.62 Å; C-H···centroid angle: 150.8°. Hydrogen-bonding parameters: H···O distances (Å), C-H···O angles (deg), and C-O distances (Å) **B** = 2.55, 131, 3.26; **C** = 2.40, 127, 3.07; **D** = 2.43, 154, 3.31; **E** = 2.41, 145, 3.27; **F** = 2.38, 144, 3.23; **G** = 2.51, 154, 3.43; **H** = 2.34, 141, 3.13; **I** = 2.46, 143, 3.27; **J** = 2.48, 133, 3.23; **K** = 2.51, 124, 3.17; **L** = 2.40, 160, 3.31. Face-to-face π-stacking parameters: centroid-centroid distances (Å) and dihedral angles (deg) 3.63 and 10.2, 3.69 and 8.90. The dihedral angle and the centroid-centroid distance between two pyridinium rings (deg and Å): 14.9 and 4.23.

12.3. CONCLUSIONS

In a summary, we report an inclusion complex of diquat in the concave cavity provided by two dibenzo-24-crown-8 hosts.

12.4. ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

† ^{1}H NMR characterizations were done on solutions with constant $[\mathbf{1}]_0$ and varied $[\mathbf{2}]_0$. Based on these NMR data, Δ_0, the difference in δ values for H_1 of **1** in the uncomplexed and fully complexed species, was determined using the Benesi-Hildebrand method.[10] Then K_a was calculated from $K_a = (\Delta/\Delta_0)/\{\{1-(\Delta/\Delta_0)\}\{[\mathbf{2}]_0-(\Delta/\Delta_0)[\mathbf{1}]_0\}\}$.

Crystal data of **2**: plate, colorless, 0.065 × 0.172 × 0.176 mm^3, $C_{12}H_{12}F_{12}N_2P_2$, *FW* 474.18, monoclinic, space group $P2_1$, a = 6.3160(12), b = 14.707(3), c = 9.0800(16) Å, β

= 104.176(16)º, V = 817.8(3) Å^3, Z = 2, D_c = 1.926 g cm^{-3}, T = 100 K, μ = 3.710 mm^{-1}, 3224 measured reflections, 2698 independent reflections, 254 parameters, F(000) = 472, R_1 = 0.0436, wR_2 = 0.1151 (all data), R_1 = 0.0433, wR_2 = 0.1147 [$I > 2\sigma(I)$], and goodness-of-fit (F^2) = 1.139. Crystal data of **1**$_2$•**2**: plate, orange, 0.11 × 0.27 × 0.32 mm^3, $C_{60}H_{76}F_{12}N_2O_{16}P_2$, *FW* 1371.17, triclinic, space group *P*-1, a = 10.9850(9)**,** b = 12.7106(10), c = 23.5191(19) Å, α = 86.653(7)º, β = 85.675(7)º, γ = 80.459(7)º, V = 3225.7(4) Å^3, Z = 2, D_c = 1.412 g cm^{-3}, T = 100 K, μ = 0.170 mm^{-1}, 20240 measured reflections, 14899 independent reflections, 852 parameters, F(000) = 1432, R_1 = 0.1095, wR_2 = 0.2614 (all data), R_1 = 0.0834, wR_2 = 0.2284 [$I > 2\sigma(I)$], and goodness-of-fit (F^2) = 1.116. For both structures, nonhydrogen atoms were treated anisotropically and hydrogen atoms were placed in calculated positions. They were solved by direct methods using SHELXS-97[11] and refined by full-matrix least squares using SHELXL-97.[12] CCDC 244377 and CCDC 244378.

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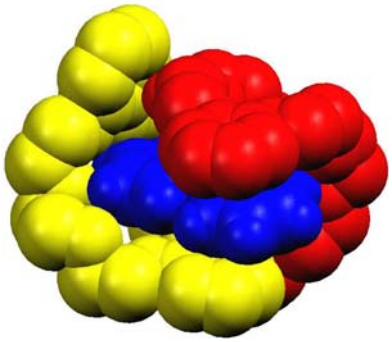

Abstract: An inclusion complex of diquat in the concave cavity provided by two dibenzo-24-crown-8 hosts was formed in the solid state as shown by X-ray analysis.