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Taco grande: a dumbbell bis(crown ether)/paraquat [3](taco complex)

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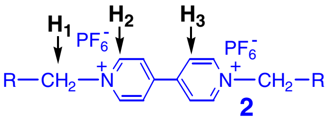
Abstract—The first paraquat-based [3](taco complex) was successfully prepared from a linear bis(crown ether) host and paraquat as shown by proton NMR characterization and X-ray analysis. It has a dumbbell shape in the solid state. The two crown ether binding sites are independent of each other during their complexation in solution.

Paraquat derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium salts) are one of the most widely used families of guests in preparation of host–guest complexes.[1] We reported the first solid state paraquat-based taco complex, in which the guest is sandwiched within the folded host, from a bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivative (diol **1a**) and paraquat (**2a**).[2] Based on this finding, we designed and prepared a series of crown ether-based cryptands which can complex paraquat derivatives much more strongly than the corresponding simple crown ethers.[3] Furthermore, we reported the preparation of the first solid state supramolecular poly(taco complex).[4] Recently it was found that host folding is an addressable step for the formation of taco complexes and can be promoted by proper introduction of substituents that provide additional attractive host–guest interactions.[5]

The synthesis of high order assemblies with more than two components remains a considerable challenge for supramolecular chemists.[6] Therefore, we are interested in making high order paraquat-based taco complexes.



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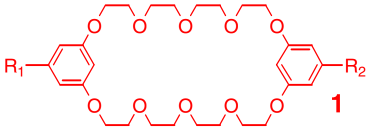
a. R = H; b. R = $CH_2OOCNHC_6H_5$



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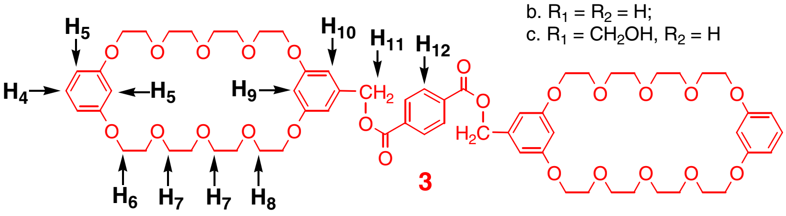
a. $R_1 = R_2 = CH_2OH$;
b. $R_1 = R_2 = H$;
c. $R_1 = CH_2OH$, $R_2 = H$



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Keywords: Host–guest system; Self-assembly; Taco complex; Crown ether; Paraquat.

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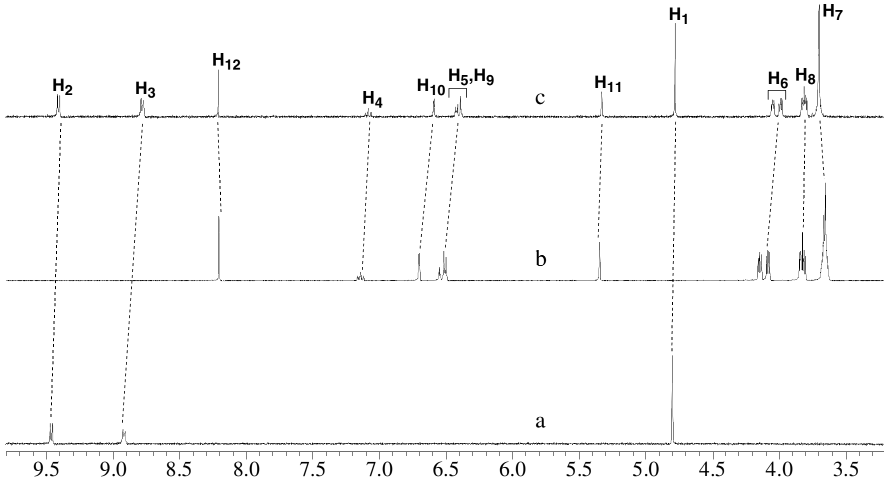

Figure 1. Partial proton NMR spectra (400 MHz, acetone-d_6, 22 °C) of paraquat **2a** (a, bottom), bis(crown ether) **3** (b, middle), and 1.33 mM **2a** and 0.67 mM **3** (c, top).

Herein, we report the preparation of the first paraquat-based [3](taco complex) from a linear bis(crown ether) host **3**[7] and paraquat guest **2a**. Furthermore, to understand the formation mechanism of this [3](taco complex) could be helpful for future higher order paraquat-based taco complexes, so we studied how the two crown ether binding sites of host **3** interact with each other during its complexation with guest **2a** by using the Scatchard plot method.[8]

Solutions of **3** and **2a** have a yellow color due to charge transfer between the electron-poor pyridinium rings of guest **2a** and the electron-rich aromatic rings of host **3**. Partial proton NMR spectra of **2a**, **3**, and a mixture of **2a** and **3** are shown in Figure 1. Only one set of peaks was found in the proton NMR spectrum of the mixed solution of **2a** and **3**, indicating fast-exchange complexation. After complexation, peaks corresponding to β-pyridinium protons H_3 on **2a** and aromatic protons H_4, H_5, H_9, and H_{10} and α-ethyleneoxy protons H_6 of **3** moved upfield significantly. Furthermore, *N*-methyl protons H_1 and α-pyridinium protons H_2 on **2a** and β-ethyleneoxy H_8 and ester methylene protons H_{11} on **3** also moved upfield, while γ-ethyleneoxy protons H_7 and phenylene protons H_{12} of **3** moved downfield. The stoichiometry of the complex between paraquat guest **2a** and linear bis(crown ether) host **3** was determined to be 2:1 in solution by a mole ratio plot[9] using proton NMR data (Fig. 2).

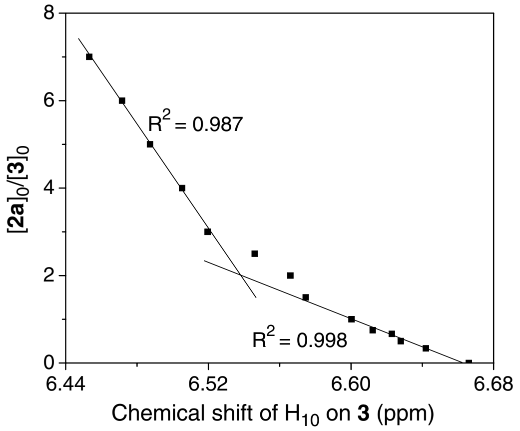

Figure 2. Mole ratio plot for **2a** and **3**, indicating 2:1 stoichiometry. The solvent is acetone-d_6. $[\mathbf{3}]_0 = 0.500$ mM.

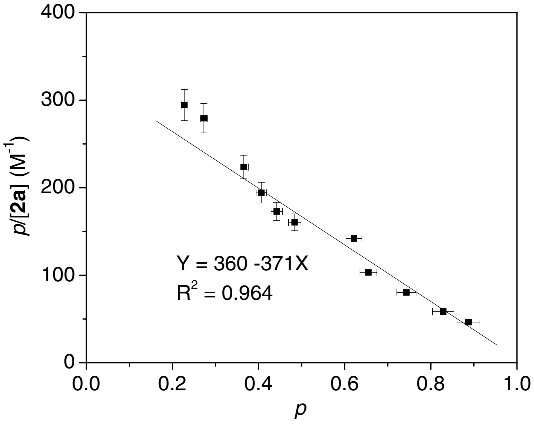

Figure 3. Scatchard plot for the complexation of paraquat guest **2a** with bis(crown ether) host **3** in acetone-d_6 at 22 °C. p = fraction of crown ether units bound. Error bars in p: ±0.03 absolute; error bars in $p/[\mathbf{2a}]$: ±0.06 relative. $[\mathbf{3}]_0 = 0.500$ mM.

In order to study the relationship between the two crown ether binding sites of **3** during its complexation with **2a**, proton NMR characterizations were done on a series of acetone solutions for which the initial concentration of host **3** was kept constant at 0.500 mM while the initial concentration of guest **2a** was varied systematically. Based on these proton NMR data, the extent of complexation, p, of the crown ether units was determined[10] and a Scatchard plot was made (Fig. 3). The linear nature of this plot demonstrated that the two crown ether binding sites are independent of each other during the complexation;[8] that is, the complexation between **2** and **3** is statistical.[11] From the intercept and the slope of the plot the average association constant[12] (K_{av}) is

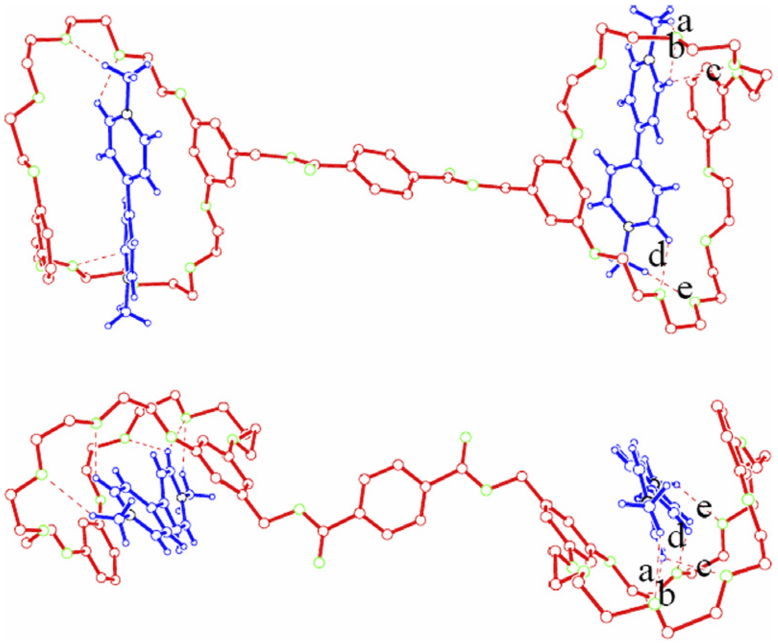

Figure 4. Two views of the X-ray structure of **3**·**2a**$_2$. Compound **3** is red, **2a** is blue, oxygens are green, and nitrogens are black. Four PF_6 counterions, solvent molecules, and hydrogens except the ones on **2a** were omitted for clarity. Hydrogen-bond parameters: C···O distances (Å), H···O distances (Å), C–H···O angles (deg) a, 3.31, 2.43, 149; b, 3.35, 2.51, 147; c, 3.10, 2.45, 126; d, 3.27, 2.57, 130; e, 3.30, 2.43, 147. Face-to-face π-stacking parameters: centroid–centroid distances (Å) 3.59, 3.66; ring plane/ring plane inclinations (deg): 5.1, 7.9. The centroid–centroid distance (Å) and dihedral angle (deg) between two phenylene rings of **3**: 7.47 and 20.5.

$3.7\,(\pm 0.4) \times 10^2\ M^{-1}$ for the complexation between **2a** and **3**. This average association constant is lower than the association constants $5.5\,(\pm 0.5) \times 10^2\ M^{-1}$ for **1b**·**2a**[3b] and $8.2\,(\pm 0.8) \times 10^2\ M^{-1}$ for **1c**·**2a**[5] in acetone. This is understandable considering the steric and conformational effects caused by the introduction of a large group on the crown ether moieties, similar to our previous results on the host–guest systems based on polymeric host[13] or guest.[7]

Ultimate proof of the formation of the first paraquat-based [3](taco complex) **3**·**2a**$_2$ is from X-ray analysis (Fig. 4).[14] X-ray quality yellow single crystals of **3**·**2a**$_2$ were grown by vapor diffusion of pentane into an acetone solution of **3** with excess **2a**. This [3](taco complex) has a dumbbell shape in the solid state as shown in Figure 4. As in the 1:1 complexes **1a**·**2a**,[2] **1b**·**2b**,[4] and **1c**·**2a**[5] between BMP32C10 and paraquat derivatives, the 1:2 complex **3**·**2a**$_2$ is stabilized by hydrogen bonding and face-to-face π-stacking interactions (Fig. 4). However, there are still some notable differences. Firstly, at each end of **3**, two α-pyridinium hydrogens (H_2) of **2a** are involved in hydrogen bonding to ethyleneoxy oxygen atoms of the crown ether unit (**b**–**d** in Fig. 4) and none of the β-pyridinium hydrogens (H_3) are involved in hydrogen bonding between the crown ether host unit and the paraquat guest. This is the same as we observed in 1:1 paraquat-based complexes **1a**·**2a**[2] and **1b**·**2b**,[4] but different from what we saw in **1c**·**2a**, where only one α-pyridinium hydrogen (H_2) is involved in hydrogen bonding between the host and the guest and two β-pyridinium hydrogens (H_3) are hydrogen bonded to the oxygen atom of the end OH moiety of the host **1c**.[5] Secondly, at each end of **3**, two *N*-methyl hydrogens (H_1) of **2a** are hydrogen bonded (**a** and **e** of Fig. 4) to ethyleneoxy oxygens of the crown ether unit in the 1:2 complex **3**·**2a**$_2$. None of the *N*-methyl hydrogens (H_1) of **2a** are involved in hydrogen bonding between the host and guest in 1:1 complex **1a**·**2a**,[2] while two of them are hydrogen bonded to the host in 1:1 complex **1c**·**2a**.[5]

Thirdly, the face-to-face π-stacking distances between the pyridinium rings of **2a** and the phenylene rings of the crown ether host unit are about equal (3.59 and 3.66 Å) to each other, presumably in order to maximize this donor–acceptor orbital interaction, while these two distances are not so close to each other in 1:1 complexes **1a**·**2a** (3.55 and 3.71 Å),[2] **1b**·**2b** (3.94 and 4.20 Å)[4] and **1c**·**2a** (3.98 and 4.39 Å).[5] Strong charge transfer between the electron-rich crown ether host units and the electron-poor paraquat guests in the 1:2 complex **3**·**2a**$_2$ gave rise to the bright yellow color of its crystals.

The ^{1}H NMR chemical shift changes (Fig. 1) of host **3** and guest **2a** upon complexation are consistent with a structure in solution similar to that of **3**·**2a**$_2$ in the solid state (Fig. 4). Protons H_4, H_5, H_6, H_8, H_9, H_{10}, and H_{11} are in shielding regions of the pyridinium rings, while H_7 resides in the deshielding environment of these rings. Aromatic protons H_{12} are far away from these pyridinium rings so their chemical shift does not change appreciably. The upfield shift of *N*-methyl (H_1) and pyridinium protons (H_2 and H_3) of the guest **2a** is consistent with their positions in the shielding region of the aromatic moieties of the crown ether host unit.

In summary, we successfully prepared the first paraquat-based [3](taco complex) from a linear bis(crown ether) host **3** and paraquat guest **2a** as proved by proton NMR characterization and X-ray analysis. It has a dumbbell shape in the solid state. The two crown ether binding sites are independent of each other during their complexation in solution. This work should be helpful for the future preparation of high order complexes.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.09.022.

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10. Δ_0, the difference in δ values for H_{10} of **3** in the uncomplexed and fully complexed species, was determined as the y-intercept of a plot of $\Delta = \delta - \delta_u$ versus $1/[\mathbf{2a}]_0$ in the high initial concentration range of **2a**; $\Delta_0 = 0.434$ ppm. Then $p = \Delta/\Delta_0$; $\Delta =$ observed chemical shift change relative to uncomplexed species.
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12. $K_1 = [\mathbf{3{\cdot}2a}]/\{[\mathbf{3}][\mathbf{2a}]\}$ and $K_2 = [\mathbf{3{\cdot}2a_2}]/\{[\mathbf{3{\cdot}2a}][\mathbf{2a}]\}$. $K_{av} = (K_1 + K_2)/2$. The value of K_{av} is equal to the y-intercept and the absolute slope of the best fit line in Figure 3. Since $K_1{:}K_2 = 4{:}1$ for statistical systems,[8] K_1 and K_2 were calculated to be $5.8\,(\pm 0.8) \times 10^2$ and $1.5\,(\pm 0.2) \times 10^2\ M^{-1}$, respectively.
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14. Crystal data of $\mathbf{3{\cdot}2a_2}$: rod, yellow, $0.60 \times 0.20 \times 0.10\ mm^3$, $C_{51}H_{69}O_{14}N_2P_2F_{12}$, *FW* 1224.02, monoclinic, space group $C2/c$, $a = 44.547(6)$, $b = 15.905(2)$, $c = 17.224(2)$ Å; $\beta = 110.575(2)°$; $V = 11425(3)$ Å^3, $Z = 8$, $D_c = 1.423\ g\ cm^{-3}$, $T = 100(2)$ K, $\mu = 1.79\ cm^{-1}$, 16,218 independent reflections, 690 parameters, $F(000) = 5112$, $R_1 = 0.1207$, $wR_2 = 0.3314$ $[I > 2\sigma(I)]$, maximum residual density $0.955\ e\ Å^{-3}$, and $GooF(F^2) = 1.113$. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Numbers 294214. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].