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Bis(*m*-phenylene)-32-crown-10/monopyridinium [2]pseudorotaxanes

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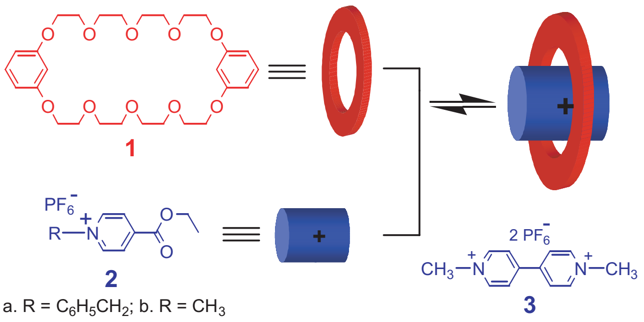
Abstract—The first crown ether/monopyridinium threaded structures, which are [2]pseudorotaxanes based on a new bis(*m*-phenylene)-32-crown-10/monopyridinium recognition motif, were successfully prepared as confirmed by proton NMR spectroscopy, electrospray ionization mass spectrometry, and X-ray analysis.

Threaded structures, including pseudorotaxanes, rotaxanes, catenanes, polypseudorotaxanes, polyrotaxanes, and polycatenanes, are attractive to scientists all over the world not only because of their topological importance but also due to their potential applications in preparation of nanoscale devices.[1] Crown ethers have been widely used in preparing threaded structures as hosts of organic salts, such as paraquat derivatives[2] and secondary ammonium compounds.[3] Monopyridinium salts have also been widely studied in chemistry due to their easy availability.[4] Though Beer and co-workers used monopyridinium salts in fabrication of some threaded structures based on ion-pair recognition by ditopic hosts[5] and we recently reported some cryptand/monopyridinium [2]pseudorotaxanes,[6] threaded structures based on crown ether/monopyridinium recognition motifs, which have not been reported up to now. Herein, we report the first crown ether/monopyridinium threaded structures, which are [2]pseudorotaxanes based on a new bis(*m*-phenylene)-32-crown-10/monopyridinium recognition motif.



1

2

a. R = $C_6H_5CH_2$; b. R = CH_3

3

The yellow colors of solutions of crown ether **1**[7] and monopyridinium salts **2**[6] are much weaker than solutions of **1** and paraquat **3**, indicating that the charge transfer between **1** and **2** is weaker. Partial proton NMR spectra of **1**, **2a**, and an equimolar solution of **1** and **2a** are shown in Figure 1. Only one set of peaks was found in the proton NMR spectrum of the solution of **1** and **2**, indicating fast-exchange complexation. After complexation, peaks corresponding to pyridinium protons (H_8 and H_9) on **2a** and aromatic protons H_2 and H_3 and α-ethyleneoxy protons H_4 of **1** moved upfield. Furthermore, phenyl protons (H_{11} and H_{12}) on **2a** and γ- and δ-ethyleneoxy protons H_5 of **1** moved downfield, while aromatic proton H_1 and β-ethyleneoxy protons H_6 of **1** and benzyl protons H_{10} and ethyl ester methylene protons H_7 of **2a** moved upfield. The stoichiometries of the complexes between **1** and **2** were determined to be 1:1 in solution by Job plots[8] using proton NMR data (e.g., Fig. 2). The association constants for the complexation between **1** and **2a** and between **1** and **2b** are 95 (±11) and 78 (±14) M^{-1} in 1:1 $CDCl_3/CD_3COCD_3$, respectively,[9] showing that the *N*-benzyl group is perhaps slightly better for complexation than the *N*-methyl group as we observed in the study of cryptand/monopyridinium [2]pseudorotaxanes.[6]

Electrospray ionization mass spectra of solutions of **1** and **2** in 4:1 acetonitrile/chloroform confirmed the 1:1

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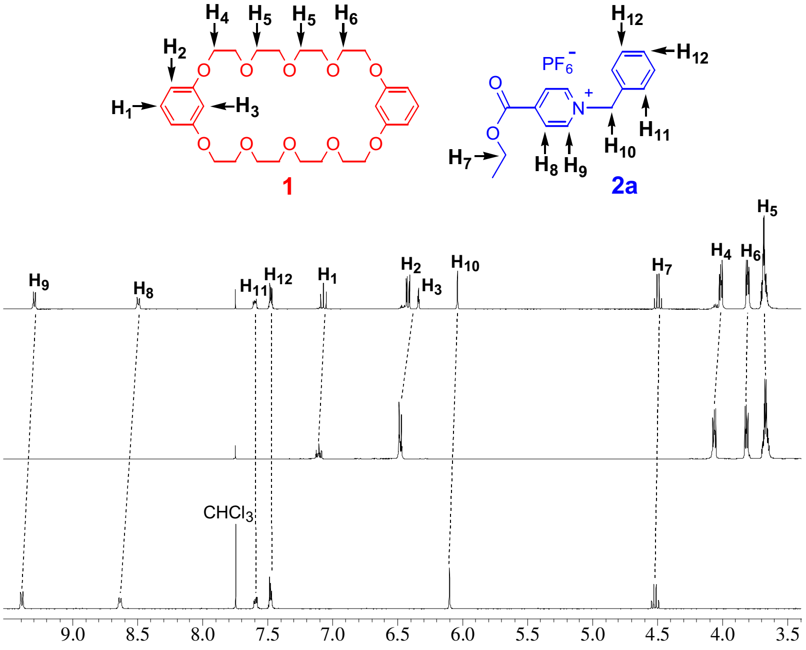

Figure 1. Partial proton NMR spectra (400 MHz, 1:1 $CDCl_3/CD_3COCD_3$, 22 °C) of monopyridinium salt **2a** (a, bottom), crown ether **1** (b, middle), and 30.0 mM **1** and **2a** (c, top).

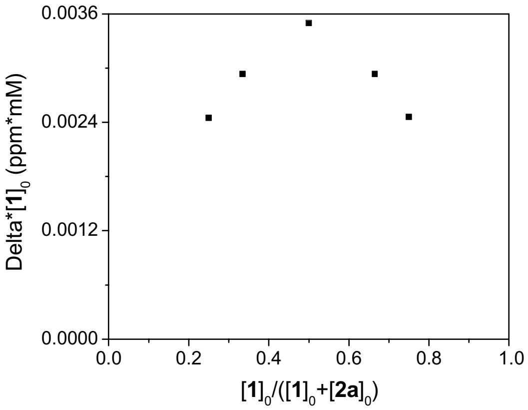

Figure 2. Job plot showing the 1:1 stoichiometry of the complex between crown ether **1** and monopyridinium **2a** in 1:1 $CDCl_3/CD_3COCD_3$. $[\mathbf{1}]_0+[\mathbf{2a}]_0 = 2.00$ mM. Delta = the chemical shift change of H_1.

stoichiometry of the complexes. For the mass spectrum of a solution of **1** and **2a** with molar ratio 3:1, the base peak was at *m/z* 559.4, corresponding to $[\mathbf{1}+Na]^+$; three peaks were found for **1**·**2a**: *m/z* 946.4 (4%) $[\mathbf{1}\cdot\mathbf{2a}+Na]^+$, 778.2 (9%) $[\mathbf{1}\cdot\mathbf{2a}-PF_6]^+$, and 750.3 (8%) $[\mathbf{1}\cdot\mathbf{2a}-PF_6-C_2H_4]^+$. For the mass spectrum of a solution of **1** and **2a** with molar ratio 1:5, the base peak was at *m/z* 629.2, corresponding to 'triple ion'[10] $[\mathbf{2a}_2-PF_6]^+$; two peaks were found for **1**·**2a**: *m/z* 912.4 (4%) $[\mathbf{1}\cdot\mathbf{2a}-C_2H_5+H_2O]^+$ and 778.3 (82%) $[\mathbf{1}\cdot\mathbf{2a}-PF_6]^+$. For the mass spectrum of a solution of **1** and **2b** with molar ratio 3:1, the base peak was at *m/z* 559.4, corresponding to $[\mathbf{1}+Na]^+$; four peaks were found for **1**·**2b**: *m/z* 870.4 (7%) $[\mathbf{1}\cdot\mathbf{2b}+Na]^+$, 702.5 (31%) $[\mathbf{1}\cdot\mathbf{2b}-PF_6]^+$, 674.3 (37%) $[\mathbf{1}\cdot\mathbf{2b}-PF_6-C_2H_4]^+$, and 658.3 (25%) $[\mathbf{1}\cdot\mathbf{2b}-PF_6-OC_2H_4]^+$.

X-ray analysis[11] was done on a yellow crystal of **1**·**2a** grown by vapor diffusion of pentane into an equimolar acetone solution of crown ether **1** and monopyridinium salt **2a**. The crystal structure (Fig. 3) demonstrated that the crown/monopyridinium complex **1**·**2a** is a pseudorotaxane; the linear molecule **2a** is threaded through the cavity of the cyclic host. For this pseudorotaxane the main stabilization interactions in the solid state are hydrogen bonding, face-to-face π-stacking, and charge transfer interactions. One α-pyridinium hydrogen of **2a** is hydrogen bonded (**A**) to an oxygen atom on an ethyleneoxy chain of the crown ether host, while the other α-pyridinium hydrogen is connected indirectly to the other ethyleneoxy chain by a water bridge (**B**, **C**, and **D**). The other hydrogens of **2a** are not involved in interactions with the crown ether host. The centroid–centroid distances, 4.02 and 4.19 Å, between the electron-poor pyridinium ring of **2a** and the electron-rich phenylene rings of the crown ether host are about equal to each other, presumably in order to maximize face-to-face π-stacking. The dihedral angle and centroid–centroid distance between the phenylene rings of the crown ether host in **1**·**2a** are 4.3° and 7.03 Å, while the corresponding values are 3.2° and 6.90 Å in a complex between **1** and a paraquat derivative.[2b] These results indicate that charge transfer interactions between the crown ether host **1** and monopyridinium guest **2a** in **1**·**2a** are weaker than those in **1**·paraquat complexes, consistent with the weaker yellow color of crystals of **1**·**2a** versus the yellow-orange of crystals of **1**·paraquat complexes.

In summary, though bis(*m*-phenylene)-32-crown-10 derivatives form 1:1 taco complexes with paraquat derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium) in the solid state,[2a,b] [2]pseudorotaxanes can be made based on the new bis(*m*-phenylene)-32-crown-10/monopyridinium

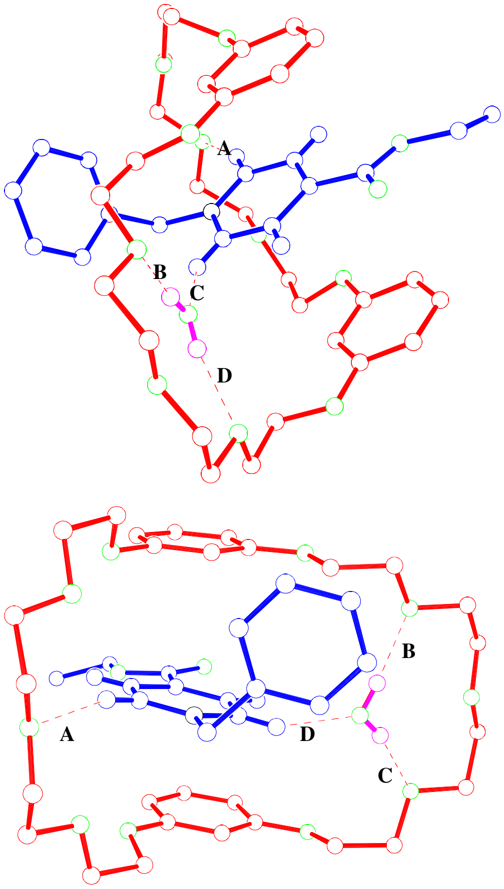

Figure 3. Two views of the X-ray structure of **1**·**2a**. Solvent molecules, a PF$_6$ counterion, and hydrogens except pyridinium hydrogens on **2a** and two hydrogens on the water molecule have been omitted for clarity. Oxygens are green, **1** is red, **2a** is blue, the water molecule is magenta, and nitrogen is black. Hydrogen-bond parameters: C(O)$\cdots$O distances (Å), H$\cdots$O distances (Å), C(O)–H$\cdots$O angles (deg) A: 3.45, 2.53, 162; B: 2.85, 1.99, 174; C: 2.90, 2.08, 166; D: 3.00, 2.29, 131. Face-to-face π-stacking parameters: centroid–centroid distances (Å) 4.02, 4.19; ring plane/ring plane inclinations (deg): 7.6, 3.9.

recognition motif. These pseudorotaxanes are the first crown ether/monopyridinium threaded structures. Considering the ready availabilities of bis(*m*-phenylene)-32-crown-10 and pyridinium derivatives, this new recognition motif should be easily extended to preparation of other supramolecular threaded structures. Once interlocked structures (rotaxanes or catenanes) based on monopyridinium salts are made, they have the potential to be reduced in order to prepare neutral interlocked structures.[12] The study presented here may stimulate further studies on complexation of other crown ethers with monopyridinium salts. We are focusing on such projects now.

Acknowledgments

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Supplementary data

The Job plot for **1**·**2b**, and the details on the determination of Δ_0 of H_1 on **1** for the complexation between **1** and **2**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.07.011.

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9. ^{1}H NMR characterizations were done on solutions with constant $[\mathbf{1}]_0$ and varied $[\mathbf{2}]_0$. Based on these NMR data, $\Delta_{0,1}$ (0.0437 ppm for **1·2a** and 0.0291 ppm for **1·2b**), the difference in δ values for H_1 of **1** in the uncomplexed and fully complexed species, was determined as the y-intercept of a plot of $\Delta = \delta - \delta_u$ versus $1/[\mathbf{2}]_0$ in the high initial concentration range of **2**. Then $K_{a,\mathbf{1\cdot2}}$ values at different $[\mathbf{1}]_0$ and $[\mathbf{2}]_0$ were calculated from $K_{a,\mathbf{1\cdot2}} = (\Delta_1/\Delta_{0,1})/\{1 - (\Delta_\mathbf{1}/\Delta_{0,\mathbf{1}})\}\{[\mathbf{2}]_0 - (\Delta_\mathbf{1}/\Delta_{0,\mathbf{1}})[\mathbf{1}]_0\}$. The values and errors of $K_{a,\mathbf{1\cdot2}}$ are the means and standard derivations from seven or nine data points with different $[\mathbf{1}]_0$ and $[\mathbf{2}]_0$ and $0.1 < \Delta_\mathbf{1}/\Delta_{0,\mathbf{1}} < 0.9$.
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11. Crystal data of **1·2a**: prism, yellow, $C_{43}H_{58}F_6NO_{13}P$, FW 941.87, monoclinic, space group ($P2_1/n$, $a = 13.5444(10)$, $b = 19.5351(13)$, $c = 17.0637(14)$ Å; $\beta = 92.206(6)°$; $V = 4511.6(6)$ Å^3, $Z = 4$, $T = 100$ K, $\mu = 1.50$ cm^{-1}, 21,258 measured reflections, 7986 independent reflections [R(int) = 0.0462], 586 parameters, $F(000) = 1984$, $R_1 = 0.0947$, $wR_2 = 0.0773$ (all data), $R_1 = 0.0438$, $wR_2 = 0.0647$ [$I > 2\sigma(I)$], and GooF (F^2) = 0.939. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 257731. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
12. Monopyridinium nuclei can be easily reduced by sodium borohydride to the neutral tetrahydro derivatives. See: *Pyridine and its Derivatives*; Shaw, E. N., Klingsberg, E., Eds.; Interscience: New York, 1960; Part 2, pp 47–55; Paquette, L. A.. *Modern Heterocyclic Chemistry*; W.A. Benjamin: New York, 1968; pp 240–241.