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Water assisted formation of a pseudorotaxane and its dimer based on a supramolecular cryptand†

Feihe Huang,[a] Lev N. Zakharov‡,[b] Arnold L. Rheingold‡,[b] Jason W. Jones[a] and Harry W. Gibson*[a]
[a] *Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212, USA. E-mail: hwgibson@vt.edu; Fax: 01 540 231 8517; Tel: 01 540 231 5902*
[b] *Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA*

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Water acts as a "molecular clip" to form a supramolecular cryptand structure that improves complexation of a diammonium salt by pseudorotaxane formation, and leads to a novel dimer in the solid state.

Water is very important in supramolecular chemistry; it can stabilize complexes by acting as a hydrogen bonding bridge between components as demonstrated in many publications.[1] We now report that water can act as a "molecular clip" to connect the two OH moieties of bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10[2] (**1**) to form a supramolecular cryptand[3] and thence a pseudorotaxane[4] analogous to our previously reported system with trifluoroacetate anion.[5] A novel pseudorotaxane dimer forms in the solid state as shown by X-ray analysis.

Previously we demonstrated that bis(*m*-phenylene)-32-crown-10 (**2**) and *N*,*N*′-dibenzyl-*m*-xylylenediammonium bis(hexafluorophosphate) (**3**) formed a non-threaded, cradled barbell or taco complex (Fig. 1).[6] We now find that **1** is a better host than **2** for **3**. For undried **3**, the upfield chemical shifts of time-averaged signals corresponding to H_1 and H_2 were larger with **1** than with **2** (Fig. 2c *vs.* 2b). The Benesi–Hildebrand method[7] was used to determine Δ_0 values, the shifts for the fully complexed species, in both cases. The apparent association constants (K_a) of **2**·**3** and **1**·**3** were 2.1 (± 0.1) × 10^2 and 9.5 (± 0.6) × 10^2 M^{-1}, respectively, at 0.20 mM initial concentrations.§

Why is **1** a better host than **2** for **3**? CH_2OH has a Hammett σ value of zero[9] and thus is not expected to influence the complexation of **1** with **3** electronically. Because salts are often hygroscopic, we dried **3** in vacuum for 48 hours, resulting in a ~75% decrease of water content. Chemical shifts of H_1 and H_2 on undried and dried **3** were the same within experimental error. We then examined the complexation between **1** and dried **3** in freshly opened solvents (dried with molecular sieves) and found that H_1 and H_2 shifted much less than with undried **3** (Fig. 2d *vs.* 2c); the apparent K_a value was reduced to 2.9 (± 0.3) × 10^2 M^{-1}.§ With **2** and dried **3** the chemical shifts of H_1 and H_2 did not change within experimental error (Fig. 2b *vs.* 2f) and hence neither did the apparent K_a. Therefore, adventitious water from the hygroscopic salt enhanced the complexation between **1** and **3** in solution, but did not affect **2**·**3**, in spite of the fact that in bulk water no complexation would occur because of competitive H-bonding of the ammonium sites. To explain our observations we hypothesized that a supramolecular cryptand complex was formed by linking the OH moieties of **1** *via* hydrogen bonding with the limited quantity of water present.

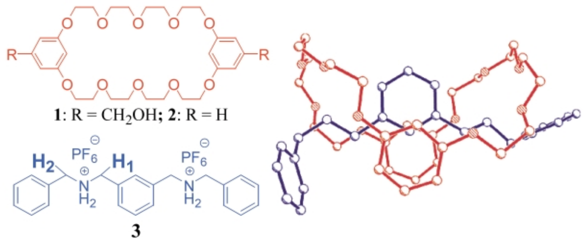

Fig. 1 Compounds used in this study and an orthogonal view[6] of the cradled barbell complex **2**·**3**.

X-Ray analysis of crystals of **1**·**3** grown from solution c of Fig. 2 confirmed this hypothesis. As shown in Figs 3a,b,¶ a pseudorotaxane is formed from a supramolecular cryptand that results from interaction of the OH moieties with water. Eight N–H···O hydrogen bonds exist, compared to only 5 N–H···O hydrogen bonds in the complex **2**·**3**.[6] Each NH is involved in bifurcated hydrogen bonds to two ether oxygens of **1**. There are no C–H···O hydrogen bonds. Just like **2**·**3**, **1**·**3** is stabilized by two types of π–π interactions: edge-to-face interaction between one of the terminal phenylene rings of **3** and one phenylene ring of **1**, and offset face-to-face π-stacking interactions between the central phenylene ring of **3** and the two phenylene rings of **1** (Fig. 3c). The centroid–centroid distances change from 3.98 and 4.22 Å for **2**·**3**[6] to 3.875 and 4.357 Å for **1**·**3**.

Further stabilization of **1**·**3** in the solid state results from the formation of a dimeric structure in which two pseudorotaxanes are connected by a hydrogen-bonded 6-membered (oxygen) chair and a face-to-edge π-stacked 4-membered (phenylene) ring (Fig. 4). The terminal OH moieties of the two host molecules are connected by hydrogen bonds. The chair arrangement of the oxygen atoms (Figs. 4a, b) is very similar to that of one form of hexameric H_2O, a topic of great current interest relevant to the structures of liquid water and ice.[11] The average O···O distance in this 6-membered chair is 2.676 Å, which is different from that of liquid water hexamers,[11e] 2.776 Å, and that in ice I_h at −90 °C, 2.759 Å.[12] The average O···O···O angle is 115.5°, a value close to the average O···O···O angle of liquid water hexamers (116.5°), but different from the average O···O···O angle in hexagonal ice

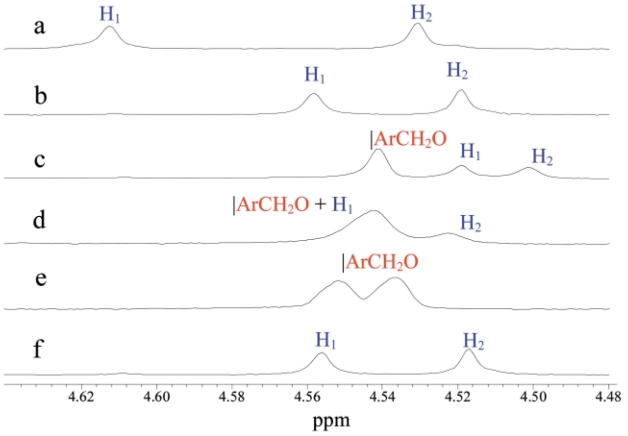

Fig. 2 Partial ^1H NMR spectra (400 MHz, 2.5 : 1 acetone-d_6 : chloroform-d, 22 °C) of (a) 1.11 mM undried **3** (5.00 mM water), (b) 1.11 mM undried **3** and 2.29 mM **2** (5.50 mM water), (c) 1.11 mM undried **3** and 2.29 mM **1** (5.50 mM water), (d) 1.11 mM dried **3** and 2.29 mM **1** (1.38 mM water), (e) 2.29 mM **1** (0.50 mM water) and (f) 1.11 mM dried **3** and **2** (1.50 mM water).

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† Electronic supplementary information (ESI) available: Experimental details. See http://www.rsc.org/suppdata/cc/b3/b304995g/

‡ *Present address:* Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, USA 92093.

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(109.3°).[11e] Four terminal phenylene rings on the guest molecules form a four-membered (phenylene) ring by edge-to-face π-stacking interactions (Fig. 4c).

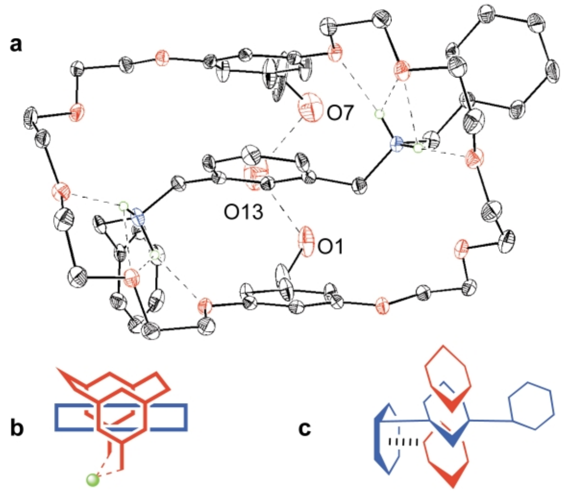

Fig. 3 (a) ORTEP diagram of **1**·**3**, (b) its cartoon representation, and (c) the cartoon representation of the offset face-to-face and edge-to-face π-stacking interactions. (a) O = red, N = blue, C = black and H = green. PF_6^- ions and hydrogens except NHs have been omitted for clarity. Hydrogen-bond parameters are as follows: N–H distances (Å) 0.93(3), 1.00(4), 0.88(4), 1.16(7); H···O distances (Å) 2.03(4), 1.95(5), 2.51(3), 2.06(4), 2.50(4), 1.94(7); N–H···O angles (°) 174(3), 168(4), 108(2), 155(4), 107(3), 158(5); O13···O1 distance (Å) 2.634(7); O13···O7 distance (Å) 2.596(8); O1···O13···O7 angle (°) 102.5(3). Edge-to-face π-stacking parameters: C-centroid distance (Å) 3.82(2); H-centroid distance (Å) 2.95(3). Face-to-face π-stacking parameters: centroid-centroid distances (Å) and dihedral angles (°) 3.874(5) and 20(2) (top/middle), 4.356(5) and 9(1) (middle/bottom); (b) and (c) **3** is blue, **1** is red, and water is green. The dashed line represents the edge-to-face π-stacking interaction.

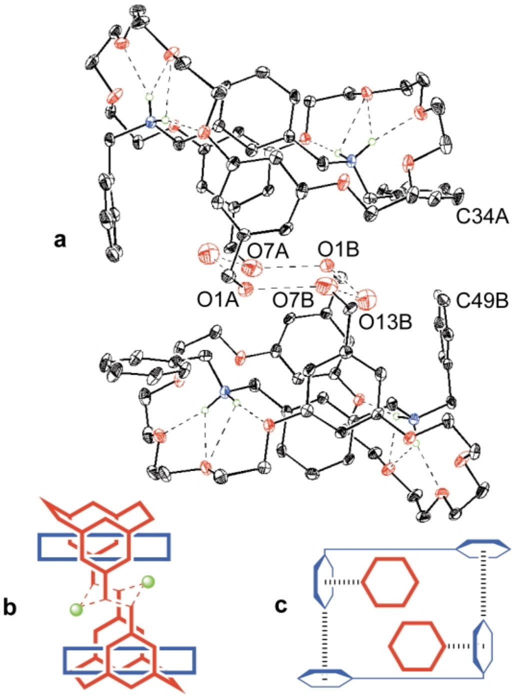

Fig. 4 (a) ORTEP diagram of the dimer of **1**·**3**, (b) its cartoon representation, and (c) the cartoon representation of edge-to-face π-stacking interactions. (a) O = red, N = blue, C = black and H = green. PF_6^- ions and H except the NHs have been omitted for clarity. Selected interatomic distances (Å) and angles (°): O1A···O7B 2.796(6), O7B···O13B 2.596(8), O13B···O1B 2.634(7), O1A···O7B···O13B 136.2(3), O7B···O13B···O1B 102.5(3), O13B···O1B···O7A 107.9(3); C49B···C34A 3.929(5); (b) **3** is blue, **1** is red, and water is green; (c) **3** is blue and **1** is red. Dashed lines represent edge-to-face π-stacking interactions.

In summary, for the first time we showed that water can act as a "molecular clip" to enhance a complexation process by formation of a supramolecular cryptand structure.

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Notes and references

§ Errors correspond to experimentally established 5% reproducibililty of Δ/Δ_0 values over the range 0.2 to 0.8. Apparent association constants K_a {= $(\Delta/\Delta_0)/[[\mathrm{Host}]_0 - [\mathbf{3}]_0(\Delta/\Delta_0)][1 - (\Delta/\Delta_0)]$} for some pseudorotaxane systems are concentration dependent,[8] so it is necessary to specify concentrations. Water concentrations were estimated by the integration of the NMR spectra.

¶ Crystal data: block, colorless, 0.15 × 0.10 × 0.05 mm³, $C_{54}H_{71}Cl_6F_{12}N_2O_{13}P_2$, FW 1458.77, Monoclinic, space group $P2(1)/c$, a = 10.2441(7), b = 17.1962(11), c = 36.879(3) Å, β = 95.1190(10)°, V = 6470.6(7) Å³, Z = 4, D_c = 1.497 g cm^{-3}, T = 150(2) K, μ = 4.10 cm^{-1}, 40140 measured reflections, 14887 independent reflections, 748 parameters, $F(000)$ = 3012, $R1$ = 0.1839, $wR2$ = 0.2003 (all data), $R1$ = 0.0778, $wR2$ = 0.1675 [$I > 2\sigma(I)$], max. residual density 0.586 e·Å^{-3}, max./min. transmission 1.000/0.885, and goodness-of-fit (F^2) = 0.849. Nonhydrogen atoms were treated anisotropically and hydrogen atoms were placed in calculated positions. 14887 Reflections were used in refinements by full-matrix least-squares on F^2. CCDC 203145. Two disordered $CHCl_3$ molecules not involved in the H-bonding were treated by the SQUEEZE program;[10] the corrected data, 413 electrons per cell, is close to the required value, 464 electron per cell. CCDC 203145. See http://www.rsc.org/suppdata/cc/b3/b304995g/ for crystallographic data in .cif or other electronic format.

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