

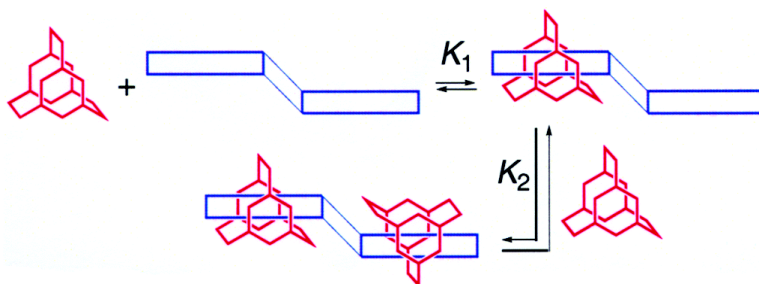
Communication

**A Cryptand/Bisparaquat [3]Pseudorotaxane by Cooperative Complexation**

Feihe Huang, Frank R. Fronczek, and Harry W. Gibson

*J. Am. Chem. Soc.*, **2003**, 125 (31), 9272-9273 • DOI: 10.1021/ja0355877 • Publication Date (Web): 12 July 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



**More About This Article**

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 9 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



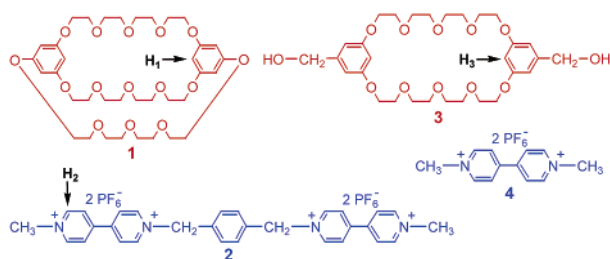
## A Cryptand/Bisparaquat [3]Pseudorotaxane by Cooperative Complexation

Feihe Huang,<sup>†</sup> Frank R. Fronczek,<sup>‡</sup> and Harry W. Gibson\*<sup>†</sup>

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, and  
Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Received April 11, 2003; E-mail: hwgibson@vt.edu

Paraquat (*N,N'*-dialkyl-4,4'-bipyridinium) derivatives are common guests in supramolecular chemistry.<sup>1</sup> Bisparaquat derivatives have been widely used in the construction of pseudorotaxanes, catenanes, and rotaxanes<sup>1</sup> with potential applications in electronics.<sup>2</sup> We have demonstrated that cryptands are much better hosts than corresponding simple crown ethers for paraquat derivatives.<sup>3</sup> Here we report the self-assembly of the first cryptand/bisparaquat [3]pseudorotaxane by cooperative complexation and compare it with an analogous crown ether-based system. Cooperative complexation is the basis of enzyme control and many other vital biological processes.<sup>4</sup>



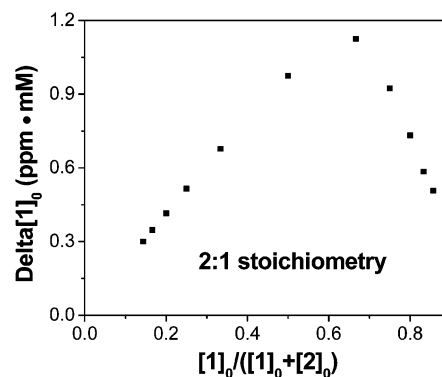
Host-guest complexation is manifest in the observations that equimolar solutions of cryptand **1**<sup>3a</sup> with ditopic bisparaquat guest **2**,<sup>5</sup> and crown ether **3**<sup>6</sup> with **2**, are orange and yellow, respectively, due to charge-transfer interactions. A Job plot<sup>7</sup> (Figure 1) demonstrated that in solution the complex of cryptand **1** with **2** has 2:1 stoichiometry. This is consistent with our observation that **1** and **4** form a 1:1 complex in solution, even though crystals of both **1**·**4** and **1**·**4** have been characterized.<sup>3a,c</sup>

The 1:1 stoichiometry of the complex between crown ether **3** and **2** was established by the mole ratio method<sup>8</sup> (Figure 2) and a Job plot using NMR data of H<sub>3</sub> on **3**. Thus, despite the formation of the 1:1 complex **3**·**4** both in solution and solid state,<sup>3a,b</sup> **3**·**2** is not observed in solution, perhaps due to the ability of both the host and guest to fold such that the host interacts with both paraquat units simply by folding back and forth. Due to its rigidity cryptand **1** cannot interact in this way and therefore forms the 2:1 complex.

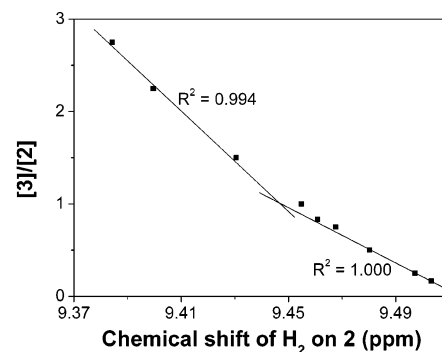
Electrospray ionization mass spectra (ESIMS) confirmed the stoichiometries of the complexes: for **1**·**2** *m/z* 1095 [**1**·**2** - 2PF<sub>6</sub>]<sup>2+</sup> and 681 [**1**·**2** - 3PF<sub>6</sub>]<sup>3+</sup>; for **2**·**3** *m/z* 675 [**3**·**2** - 2PF<sub>6</sub> + H<sub>2</sub>O]<sup>2+</sup> and 396 [**3**·**2** - 3PF<sub>6</sub>]<sup>3+</sup>, only 1:1 stoichiometry.

Ultimate proof of the formation of the cryptand-based [3]pseudorotaxane **1**·**2** is its X-ray structure (Figure 3).<sup>9</sup> As in the 1:1 and 2:1 complexes between cryptand **1** and **4**,<sup>3a,c</sup> **1**·**2** is stabilized by hydrogen bonding and face-to-face  $\pi$ -stacking interactions. As in **1**·**4**<sup>3a</sup> two  $\beta$ -protons of each paraquat unit are connected to a cryptand host by a water bridge. One  $\alpha$ -proton of each paraquat unit is directly hydrogen bonded to an ether oxygen.

However, in the complex between **1** and **4**, methyl hydrogens are not involved in hydrogen bonding, but in **1**·**2**, four hydrogen



**Figure 1.** Job plot showing the 2:1 stoichiometry of the complex between cryptand **1** and ditopic guest **2** in acetone-*d*<sub>6</sub> using data for H<sub>1</sub>. Delta is the chemical shift change corresponding to H<sub>1</sub>. [**1**]<sub>0</sub> + [**2**]<sub>0</sub> = 3.00 mM.



**Figure 2.** Mole ratio plot for **2** and **3**, indicating 1:1 stoichiometry. The solvent is acetone-*d*<sub>6</sub>.

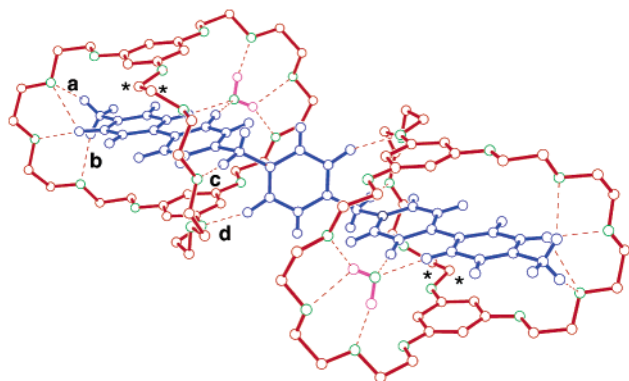
bonds involve methyl protons. Furthermore, two hydrogen bonds involve xylyl methylene protons, and two hydrogen bonds involve xylyl aromatic hydrogens.<sup>10</sup>

For solutions of **2** and crown ether **3** the extent of complexation, *p*, of the paraquat units was determined based on data for H<sub>2</sub> on **2**.<sup>11</sup> From the slope and the intercept of a Scatchard plot<sup>13</sup> (Figure 4a) the average apparent association constant<sup>14</sup> is  $(6.3 \pm 0.4) \times 10^2 \text{ M}^{-1}$ . For the complexation between **2** and cryptand **1** the Scatchard plot (Figure 4b) is nonlinear and has a maximum, which indicates that the two paraquat units of **2** act cooperatively.<sup>13</sup> Further analysis of the Scatchard plot<sup>4</sup> enables the estimates  $K_1 = (1.2 \pm 0.3) \times 10^3 \text{ M}^{-1}$  and  $K_2 = (2.0 \pm 0.5) \times 10^4 \text{ M}^{-1}$ .<sup>15</sup> Indeed, the ratio  $K_2/K_1 = 17$  is significantly higher than the value of 0.5 expected for statistical complexation.<sup>13</sup>

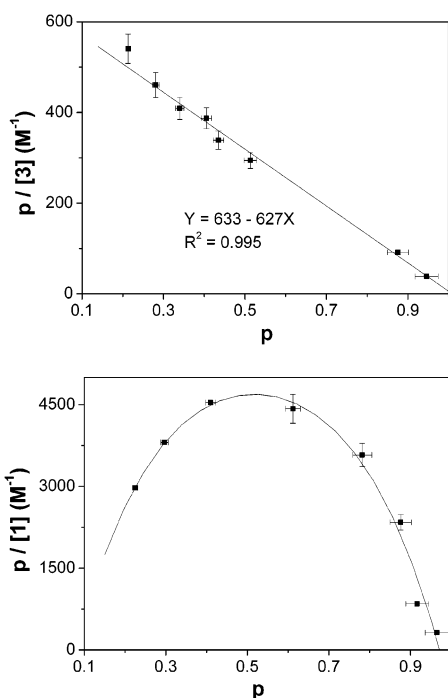
One explanation of the apparent cooperativity is that formation of the 1:1 complex effectively restricts rotation about the N-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> bonds because of the hydrogen bonding of both the CH<sub>2</sub> and ortho protons to the cryptand (see Figure 3) and this conformational restriction facilitates complexation of the second paraquat site. This argument is supported by the fact that  $K_1$  is significantly lower

<sup>†</sup> Virginia Polytechnic Institute and State University.

<sup>‡</sup> Louisiana State University.



**Figure 3.** X-ray structure of  $1_2 \cdot 2$ . Oxygens are green, **2** is blue, **1** molecules are red, and water molecules are magenta. Disordered solvent molecules, four  $\text{PF}_6^-$  ions, and hydrogens except the ones on **2** and water molecules have been omitted for clarity. Selected hydrogen-bond parameters: C–O distances (Å) **a** = 3.34, **b** = 3.35, **c** = 3.22, **d** = 3.36; H···O distances (Å) **a** = 2.54, **b** = 2.57, **c** = 2.24, **d** = 2.35; C–H···O angles (deg) **a** = 137, **b** = 135, **c** = 158, **d** = 150. \* These four carbons are disordered.



**Figure 4.** Scatchard plots for complexation of bisparaquat guest **2** ( $[\mathbf{2}]_0 = 0.500$  mM) with (a) (top) crown ether **3** and (b) (bottom) cryptand **1** in acetone- $d_6$  at 22 °C.  $p$  = fraction of paraquat units bound.<sup>11</sup> Error bars in  $p$ :  $\pm 0.03$  absolute; error bars in  $p/[\text{host}]$ :  $\pm 0.06$  relative. The fourth order polynomial fit line in b is simply to guide the eye.

than the apparent association constant ( $6.1 \times 10^4 \text{ M}^{-1}$ ) for formation of  $1 \cdot 4$ ,<sup>3a</sup> indicating that there is indeed an additional barrier to formation of the 1:1 complex  $1 \cdot 2$ . Another possible factor is host–host interaction in  $1_2 \cdot 2$  in solution; hydrogen bonding of an aromatic proton of each host to an ether oxygen atom of the other was observed in the crystal structure of a 2:1 complex based on another cryptand and **4**;<sup>3c</sup> and finally it must be noted that the effects of the first complexation event on ion pairing<sup>16</sup> and the local environment<sup>17</sup> may also play key roles in facilitating the second binding step.

In summary, for the first time, a cryptand was used in the preparation of a [3]pseudorotaxane with a ditopic guest and the complexation appears to be cooperative. Our current efforts are focusing on preparation of rotaxanes and catenanes based on cryptands and bisparaquat derivatives.

**Acknowledgment.** This work was supported by the National Science Foundation (DMR0097126, H.W.G.).

**Supporting Information Available:** An X-ray crystallographic file (CIF) for  $1_2 \cdot 2$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Reviews: Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, *99*, 1643–1664. *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C. O., Eds.; Wiley-VCH: Weinheim, 1999. Mahan E.; Gibson H. W. In *Cyclic Polymers*, 2nd ed.; Semlyen, A. J., Ed.; Kluwer Publishers: Dordrecht, 2000; pp 415–560. A recent paper on paraquat complexes: Jones, J. W.; Bryant, W. S.; Bosman, A. W.; Janssen, R. A. J.; Meijer, E. W.; Gibson, H. W. *J. Org. Chem.* **2003**, *68*, 2385–2389.
- Recent publications: Duerr, H.; Bossmann, S. *Acc. Chem. Res.* **2001**, *34*, 905–917. Luo, Y.; Collier, C. P.; Jeppesen, J. O.; Nielsen, K. A.; Delonno, E.; Ho, G.; Perkins, J.; Tseng, H.-R.; Yamamoto, T.; Stoddart, J. F.; Heath, J. R. *Chem. Phys. Chem.* **2002**, *3*, 519–525.
- (a) Bryant, W. S.; Jones, J. W.; Mason, P. E.; Guzei, I. A.; Rheingold, A. L.; Nagvekar, D. S.; Gibson, H. W. *Org. Lett.* **1999**, *1*, 1001–1004. (b) Jones, J. W.; Zakharov, L. N.; Rheingold, A. L.; Gibson, H. W. *J. Am. Chem. Soc.* **2002**, *124*, 13378–13379. (c) Huang, F.; Gibson, H. W.; Bryant, W. S.; Nagvekar, D. S.; Fronczek, F. R. *J. Am. Chem. Soc.* **2003**, *125*, in press.
- Perlmutter-Hayman, B. *Acc. Chem. Res.* **1986**, *19*, 90–96.
- Cooke, G.; de Cremiers, A. A.; Duclairioir, F. M. A.; Gray, M.; Vaquero, P.; Powell, A. V.; Rosair, G.; Rotello, V. M. *Tetrahedron Lett.* **2001**, *42*, 5089–5091.
- Gibson, H. W.; Nagvekar, D. S. *Can. J. Chem.* **1997**, *75*, 1375–1384.
- Job, P. *Ann. Chim.* **1928**, *9*, 113–203.
- Tsukube, H.; Furuta, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Inoue, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Elsevier: New York, 1996; Vol. 8, p 425.
- Single crystals were prepared by vapor diffusion of isopropyl ether into an acetonitrile solution of **1** and **2** (molar ratio 3:1). Crystal data: prism, orange,  $0.08 \times 0.10 \times 0.35$  mm<sup>3</sup>,  $\text{C}_{114}\text{H}_{140}\text{O}_{38}\text{N}_4\text{P}_4\text{F}_{24} \cdot \text{H}_2\text{O}$ , FW 2754.22, Triclinic, space group  $P-1$ ,  $a = 10.974(3)$  Å,  $b = 17.451(4)$  Å,  $c = 19.735(6)$  Å;  $\alpha = 80.08(1)^\circ$ ,  $\beta = 75.44(1)^\circ$ ,  $\gamma = 73.94(2)^\circ$ ;  $V = 3493.8(17)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.309$  g cm<sup>-3</sup>,  $T = 100$  K,  $\mu = 1.60$  cm<sup>-1</sup>, 24134 measured reflections, 12707 independent reflections, 875 parameters,  $F(000) = 1432$ ,  $R1 = 0.0760$ ,  $wR2 = 0.0779$  [ $I > 3\sigma(I)$ ], maximum residual density  $0.92 \text{ e} \cdot \text{Å}^{-3}$ , and  $\text{Goof} = 1.0585$ .
- For other examples of this type of hydrogen bonding see: Pierce, A. C.; Sandretto, K. L.; Bemis, G. W. *Proteins: Struct., Funct. Genet.* **2002**, *49*, 567–576. Scheiner, S.; Kar, T.; Pattanayak, J. J. *Am. Chem. Soc.* **2002**, *124*, 13257–13264.
- <sup>1</sup>H NMR characterizations were done on solutions with constant  $[\mathbf{2}]$  and varied  $[\mathbf{1}]$  or  $[\mathbf{3}]$ . On the basis of these NMR data,  $\Delta_0$ , the difference in  $\delta$  values for  $\text{H}_2$  of **2** in the uncomplexed and fully complexed species was determined by the Benesi–Hildebrand method.<sup>12</sup> Then  $p = \Delta/\Delta_0$ ;  $\Delta$  = observed chemical shift change relative to uncomplexed species.
- Gong, C.; Balanda, P. B.; Gibson, H. W. *Macromolecules* **1998**, *31*, 5278–5289.
- Marshall, A. G. *Biophysical Chemistry*; J. Wiley and Sons: New York, **1978**; pp 70–77. Freifelder, D. M. *Physical Biochemistry*; W. H. Freeman and Co.: New York, 1982; pp 659–660. Connors, K. A. *Binding Constants*; J. Wiley and Sons: New York, 1987; pp 78–86.
- The apparent association constant,  $K_a$ , is defined as  $K_a = p[\mathbf{2}]_0 / \{(1 - p)[\mathbf{2}]_0\} \{[\mathbf{3}]_0 - p[\mathbf{2}]_0\}$ . Errors are based on a 6% variation in  $K_a$  values.
- $K_1 = [\mathbf{1} \cdot \mathbf{2}] / \{[\mathbf{1}][\mathbf{2}]\}$  and  $K_2 = [\mathbf{1}_2 \cdot \mathbf{2}] / \{[\mathbf{1}]^2[\mathbf{2}]\}$ . The slope of the first three data points for low  $p$  (Figure 4b) gave the value of  $2K_2 - K_1$ , while the slope of the last four data points for high  $p$  (Figure 4b) gave the value of  $-2K_2$ .<sup>4</sup> Errors of the two apparent association constants were calculated on the basis of errors of the slopes.
- Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 7001–7004.
- Haj-Zaroubi, M.; Mittel, N. W.; Schmidtchen, F. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 104–107.

JA0355877