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Unique “Cradled Barbell” Complex between a Secondary Diammonium Ion and Bis(*m*-phenylene)-32-crown-10

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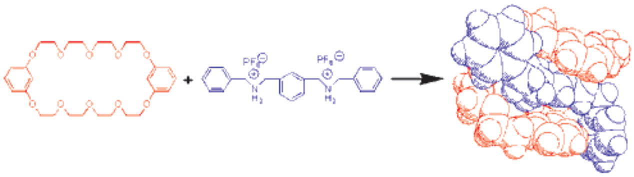
ABSTRACT



The complexation between *N*,*N*′-dibenzyl(*m*-xylylene)diammonium bis(hexafluorophosphate) (2) and bis(*m*-phenylene)-32-crown-10 (5) was shown to occur in solution by nuclear magnetic resonance with 1:1 stoichiometry and a K_a value of 189 ± 19 M^{-1}. A crystal structure of 2:5 revealed a unique 1:1 “exo” or “cradled barbell” complex, instead of the expected pseudorotaxane. This unexpected result illustrates that caution be used in interpreting the results from these types of complexes in the solution and “gas” phases on the basis of crystal structures.

Our current research is focused on the formation of rotaxanes and pseudorotaxanes[1] from bis(phenylene)-based crown ethers and secondary ammonium salts.[2] The term “rotaxane” derives its meaning from the Latin terms for “wheel” and “axle” in which a linear unit is threaded through the cavity of a cyclic unit (Figure 1). Pseudorotaxanes differ from rotaxanes because they lack bulky end groups on the linear unit that prevent dethreading of the cyclic unit. These self-assembly complexes are of special interest to our research because of their unique structural aspects and their association constants are relatively high, making them likely candidates for the formation of polyrotaxanes and polypseudorotaxanes.[1]

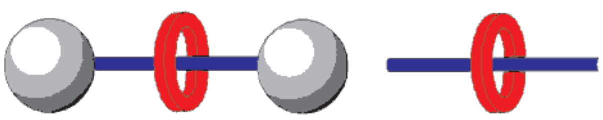


Figure 1. Cyclic unit in red, linear unit in blue, and blocking group in gray.

Stoddart et al.[3] reported that unsubstituted bis(*o*-phenylene) and bis(*p*-phenylene) crown ethers form complexes with secondary ammonium salts that exist as pseudorotaxanes in the solid state. Because of their utility in polymer chemistry[4] we decided to investigate bis(*m*-phenylene) crown ethers.

Stoddart et al. have studied and isolated a [4]pseudorotaxane (2:2 complex) in which two *N*,*N*′-dibenzyl(*p*-xylylene)diammonium bis(hexafluorophosphate) (**1**) molecules are threaded through the cavities of two bis(*p*-phenylene)-34-crown-10 (**3**) molecules (Figure 2).[3b] The crystal structure

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(1) For reviews of rotaxanes and polyrotaxanes see: (a) Schill, G. *Catenanes, Rotaxanes, and Knots*; Academic Press: New York, 1971. (b) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843. (c) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725. (d) Gibson, H. W. In *Large Ring Molecules*; Semlyen, J. A., Ed.; Wiley: New York, 1996; p 191.

(2) Bryant, W. S.; Guzei, I. A.; Rheingold, A. L.; Merola, J. S.; Gibson, H. W. *J. Org. Chem.* **1998**, *63*, 7634.

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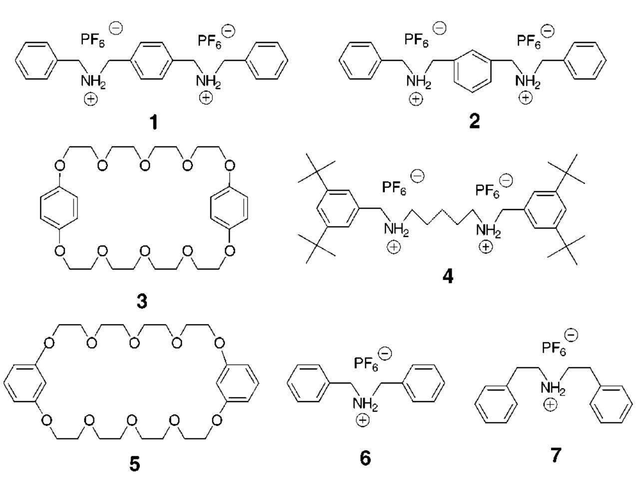

Figure 2. *N,N′*-Dibenzyl(*p*-xylylene)diammonium bis(hexafluorophosphate) (**1**), *N,N′*-dibenzyl(*m*-xylylene)diammonium bis(hexafluorophosphate) (**2**), bis(*p*-phenylene)-34-crown-10 (**3**), 1,5-bis((3,5-di-*tert*-butylbenzyl)ammonium)pentane bis(hexaflurorophosphate) (**4**), bis(*m*-phenylene)-32-crown-10 (**5**), dibenzylammonium hexafluorophosphate (**6**), and diphenethylammonium hexafluorophosphate (**7**).

reveals that the [4]pseudorotaxane is stabilized by both hydrogen bonding and $\pi-\pi$ intermolecular interactions. They have also shown that *both* a pseudorotaxane and an "exo" "hot dog" complex can form independently under different crystallization conditions for 1,5-bis((3,5-di-*tert*-butylbenzyl)-ammoniumyl)pentane bis(hexaflurorophosphate) (**4**) and **3**.[5] The isolation of two different complexes suggests that both complexes can exist, and probably do, in solution. It is further suggested that the "hot dog" complex may be an intermediate to the formation of the pseudorotaxane. Neither the stoichiometry nor the association constants were determined in solution for the complexes.

Whereas para-substituted dibenzylammonium ions, such as **1**, and their azomethine precursors, because of their linearity, can lead to insoluble polymers, the meta-substituted analogues are expected to be soluble, making possible simplified synthesis and characterization of polyrotaxanes. Determination of the stoichiometries and association constants for the monomeric complexes will allow us to determine if the complexation is structure dependent. Thus, we investigated the complexation between *N,N′*-dibenzyl-(*m*-xylylene)diammonium bis(hexafluorophosphate) (**2**)[6] and bis(*m*-phenylene)-32-crown-10 (**5**)[7] (Figure 2). An equimolar solution of the two components was made in acetone-d_6 and analyzed by ^{1}H NMR (Figure 3). The chemical shifts of the protons on both the salt and the crown ether change significantly from their "native" positions. For instance, the α-protons of **5** and the benzylic methylene protons of **2** shift downfield, whereas the γ-protons of **5** shift upfield. This result suggests that complexation of some type occurs in solution.

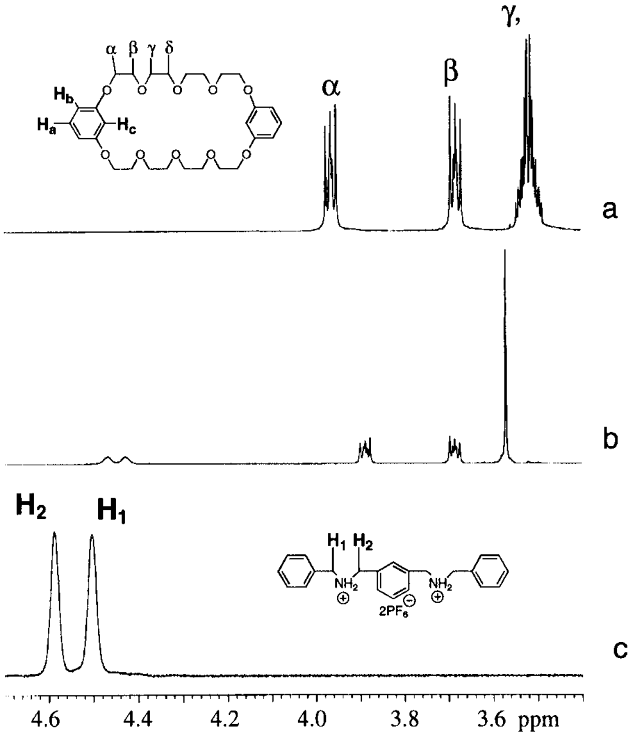

Figure 3. Stacked ^{1}H NMR (400 MHz, acetone-d_6) spectra of (a) **5** (0.01 M), (b) 1:1 solution of **2** and **5** (0.01 M), and (c) **2** (0.01 M).

The stoichiometry of the complex was determined by ^{1}H NMR using the mole ratio (titration) method.[8] A plot of [**2**]/[**5**] versus the chemical shift of the H_a proton of **5** (Figure 4) shows a break point in the curve at a mole ratio of 1:1 to

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(3) (a) Ashton, P. R.; Campell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. T.; Williams, D. J. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1865. (b) Ashton, P. R.; Campell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. T.; Williams, D. J. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1869. (c) Ashton, P. R.; Glink, P. T.; Martínez-Díaz, M.-V.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 1930. (d) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. T.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709. (e) Ashton, P. R.; Glink, P. T.; Stoddart, J. F.; Tasker, P. T.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 729. (f) Feiters, M. C.; Fyfe, M. C. T.; Martínez-Díaz, M.-V.; Menzer, S.; Nolte, R. J. M.; Stoddart, J. F.; van Kan, P. J. M.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 8119. (g) Ashton, P. R.; Collins, P. R.; Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 59. (h) Ashton, P. R.; Collins, P. R.; Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 735. (i) Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2068.

(4) (a) Delaviz, Y.; Gibson, H. W. *Macromolecules* **1992**, *25*, 18. (b) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 8585. (c) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 5862. (d) Gibson, H. W.; Nagvekar, D. S.; Powell, J.; Gong, C.; Bryant, W. S. *Tetrahedron* **1997**, *53*, 15197. (e) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 310. (f) Gong, C.; Balanda, P. B.; Gibson, H. W. *Macromolecules* **1998**, *31*, 5278.

(5) Ashton, P. R.; Fyfe, M. C. T.: Martínez-Díaz, M.-V.; Menzer, S.; Schiavo, C.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, *4*, 1523.

(6) **2** was synthesized by a method reported for the bis(perchlorate) salt: Ruggli, P.; Leupin, E.; Dahn, H. *Helv. Chim. Acta* **1947**, *30*, 1845.

(7) **5** was prepared by a literature method: Delaviz, Y.; Gibson, H. W. *Polym. Commun.* **1991**, *32*, 103.

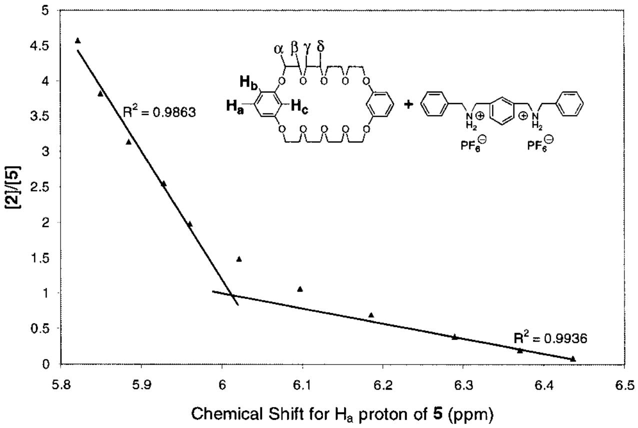

Figure 4. Mole ratio plot for **2** and **5**. The solvent is acetone-d_6.

give **2**:**5**. This method does not, however, reveal if the complex is either a 1:1 or a 2:2 complex but does eliminate the possibility of an uneven complex stoichiometry (i.e. 1:2, 2:3, etc.). The association constant was calculated for a 1:1 complex using two graphical methods, the modified, iterative Creswell−Allred and Rose−Drago methods,[9] and were 185 ± 12 and 193 ± 26 M^{-1}, respectively. ^1H NMR has been used extensively to determine the association constants and free energy values for these types of molecular complexes.[3a,b,f,e,10]

Crystals suitable for X-ray analysis were grown by vapor diffusion of *n*-pentane into an equimolar solution of **2** and **5** in acetone.[11] The resulting X-ray structure was not the expected pseudorotaxane structure but, rather, the 1:1 "*exo*" complex **2**:**5** (Figure 5). The complex resembles a "cradled barbell" where the secondary ammonium salt **2**, the "barbell", is surrounded by the "cradle" of the crown ether **5**. The conformation of the crown ether is reminiscent of the "seam of a tennis ball" previously observed for dibenzo-30-crown-10 in its complex with one potassium ion from the early work of Truter et al.[12]

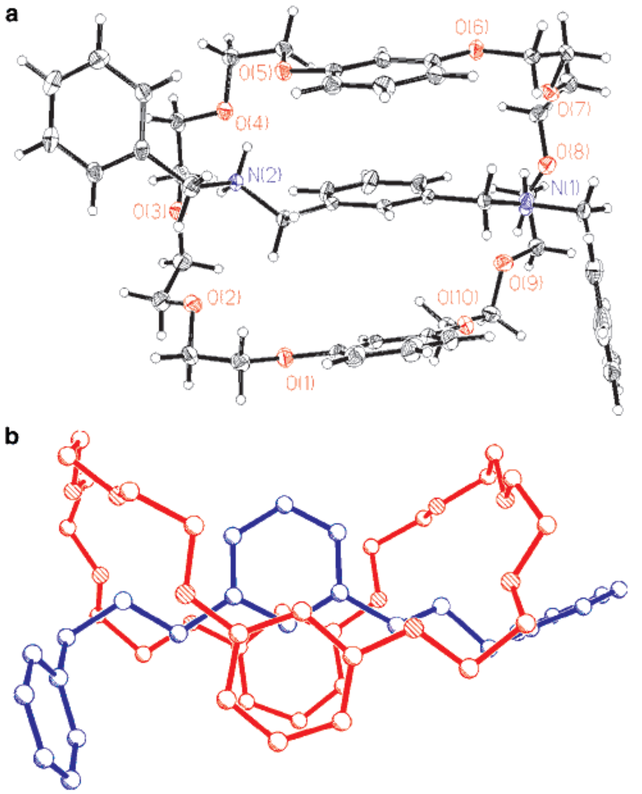

Figure 5. Crystal structure of "cradled barbell" complex between **2** and **5**. (A) Ortep representation. Oxygens are red, nitrogens are blue. Hydrogen-bond parameters are as follows: H- - -O distances (Å) 2.18, 2.24, 2.01, 2.02, 2.07; N- - -O distances (Å) 2.95, 2.89, 2.87, 2.92, 2.98; N−H- - -O angles (deg) 142.3, 126.9, 155.8, 168.7, 170.9. $\pi-\pi$ Edge-to-face parameters: centroid−centroid distance, 4.91 Å; H−centroid distance, 2.78 Å; C−centroid distance, 3.70 Å; C−H−centroid angle, 164.2°. $\pi-\pi$ face-to-face parameters for the "sandwich": centroid−centroid distances (Å), 4.22 and 3.98; ring plane/ring plane inclinations (deg), 13.1 (top/middle), 4.9 (middle/bottom), 16.7 (top/bottom). (B) Orthogonal view. **2** is blue and **5** is red. Counterions and solvent molecules have been omitted for clarity.

The primary stabilizing interaction between the components is hydrogen bonding. All four ammonium hydrogens are bonded to ether oxygens (one is hydrogen-bonded to two ether oxygens, giving a total of five N−H- - -O hydrogen bonds). One of the four ammonium hydrogens is bonded to a phenolic oxygen. There is no carbon−hydrogen−oxygen hydrogen bonding. Further stabilization occurs via two types of $\pi-\pi$ stacking interactions. One of the terminal phenyl rings of **2** is aligned perpendicularly to one of the resorcinol rings of **5**; this results in a favorable edge-to-face π-stacking interaction. The concave shape of **5** allows the central phenylene ring of **2** to be "cradled" between the two resorcinol rings of **5**, resulting in face-to-face π-stacking. This alignment is repeated in the packing diagram (Figure 6) as an extended π-stacking column.

Low-resolution fast-atom bombardment mass spectroscopy (LRFAB-MS, matrix: 3-NBA/Gly) was done on the crystals. Two peaks were observed that gave direct evidence for the

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(8) 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.

(9) These graphical methods have been successfully applied to pseudorotaxane and polypseudorotaxane systems in our lab.[4f]

(10) For examples see: (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradský, M.; Gandolfi, M. T.; Philp, D.; Prodi, L.; Raymo, F. M.; Reddington, M. V.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 4931. (b) Asakawa, M.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradský, M.; Gandolfi, M. T.; Kocian, O.; Prodi, L.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *J. Am. Chem. Soc.* **1997**, *119*, 302.

(11) Crystal data for $[C_{50}H_{66}N_2O_{10}][P_2F_6]_2\cdot 2CH_3C(O)CH_3$: MW = 1261.14, monoclinic, $P2_1/c$, $a = 10.2919(2)$ Å, $b = 22.9186(5)$ Å, $c = 26.2672(4)$ Å, $\beta = 94.8390(10)°$, $V = 6173.7(2)$ Å^3, $Z = 4$, $T = 173(2)$ K, μ(Mo Kα) = 1.66 cm^{-1}, $D_{calcd} = 1.357$ mg/m^3, $R(F) = 10.24\%$ for 8503 observed independent reflections ($4° \leq 2\theta \leq 56°$). There are two solvate molecules of acetone in the asymmetric unit. All non-hydrogen nondisordered atoms were refined anisotropically. Disordered atoms F(2), F(3), and F(7) of two counterions and atoms C(51) and C(53) of an acetone molecule were refined isotropically. Hydrogen atoms were treated as idealized contributions.

(12) Truter, M. R.; Bush, M. A. *J. Chem. Soc., Perkin Trans. 2* **1972**, 345.

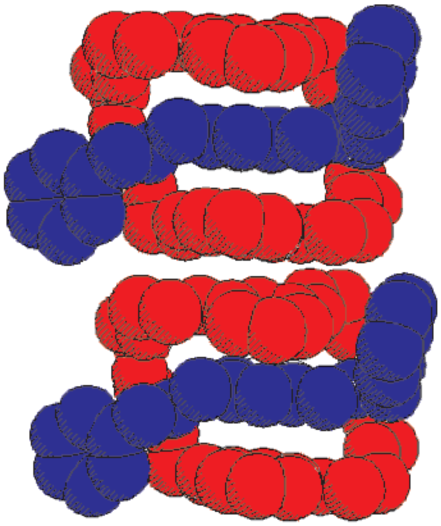

Figure 6. Packing diagram illustrating the π-stacking between the aromatic rings of **2** (blue) and **5** (red). Counterions, solvent molecules, and hydrogens have been omitted for clarity.

1:1 complex **2**:**5**: *m*/*z* 853.5 ($\mathbf{2} + \mathbf{5} - PF_6^- - HPF_6$) and 999.5 ($\mathbf{2} + \mathbf{5} - PF_6^-$)[13]. The highest mass peak was *m*/*z* 1607.9, which corresponds to the 2:1 complex $\mathbf{2_2}$:**5** minus one PF_6 counterion. The observance of these peaks does not, however, prove that 1:1 or 2:1 pseudorotaxane structures exist, but it does suggest that they might exist. It is unlikely that any structures other than a [2]- or [3]pseudorotaxane would be stable enough to be detected under the conditions of the LRFAB-MS experiment. That is, we believe, but cannot prove, that nonthreaded complexes would rapidly decomplex upon vaporization.

In our previous work[2] we have shown that **5** forms complexes with dibenzylammonium hexafluorophosphate (**6**) and its diphenethyl analogue **7**. The stoichiometry (in CD_3CN) for the complex between **5** and **6** was determined to be 1:1, and the association constants were 12.9 ± 0.4 and 12.8 ± 1.4 M^{-1} by the Creswell−Allred and Rose−Drago methods, respectively.[14] Again, however, the LRFAB-MS (peaks for **5**:**6** and **5**:$\mathbf{6}_2$ were observed) and X-ray crystallographic (revealing a [3]pseudorotaxane) analyses did not agree with the solution stoichiometry. As for **5** and **7**, ^1H NMR indicated only very weak interaction in solution (CD_3CN), disallowing stoichiometry and association constant(s) determination. LRFAB-MS gave evidence for only **5**:**7**. However, crystals by X-ray diffraction again proved to be exclusively the [3]pseudorotaxane **5**:$\mathbf{7}_2$!

The above experimental observations demonstrate that it is generally difficult, if not impossible, to determine precisely what type of complexation is occurring in the solution and "gas" phases. The possibility of both "*endo*" and "*exo*" complexation complicates the interpretation of the experimental results. Although in the present case a 1:1 "*exo*" complex was observed in the solid state, one cannot assume that the same complex exists exclusively in solution. Taken together, our results dictate that great caution be used in interpreting solution and "gas" phase data for such complexes on the basis of X-ray crystal structures.

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Supporting Information Available: Crystal data, structure refinement details, and SHELXTL file (.res) for **2**:**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] High-resolution fast-atom bombardment mass spectroscopy gave *m*/*z* 999.4364 (deviation 0.6 ppm).

[14] In ref 2 the overall association constant (in CD_3CN) was calculated to be 5 M^{-2} for the complex **5**:$\mathbf{6}_2$.