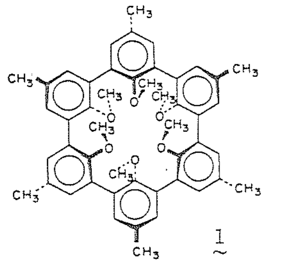
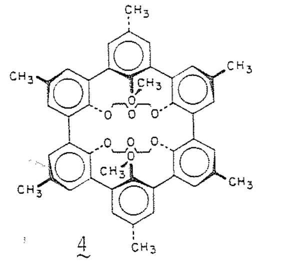
04.5-02 STRUCTURAL STUDIES OF HOST-GUEST COMPLEXES: SPHERANDS AND HEMISPHERANDS. By R. C. Helgeson, I. Dicker, G. M. Lein, D. J. Cram, E. F. Maverick, C. B. Knobler and K. N. Trueblood, Department of Chemistry, University of California, Los Angeles, CA 90024, USA

Many hosts undergo considerable conformational reorganization upon complexation. Spherands such as 1, however, are designed so that they cannot significantly reorganize (Cram, Kaneda, Helgeson & Lein (1979) J. Amer. Chem. Soc. 101, 6752). 1 is one of the strongest and most selective complexers of Li^+ and Na^+ known; it does not form complexes with any other ions. We will describe the crystal and molecular structures of 1 and of its complexes with Li^+, 2, and Na^+, 3.



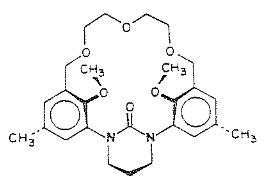
1



4

We will describe as well the structures of Li^+ complexes of two bridged spherands. One of the hosts is depicted in 4, in which four of the $-OCH_3$ groups of 1 have been replaced by two $-O(CH_2CH_2O)_2-$ bridges, which are on the same face of the molecule. The Li^+ lies within the host, coordinated (in a distorted octahedron) to six of the oxygen atoms. The other bridged spherand, 5, differs from 4 in that the central $-CH_2OCH_2-$ unit of each bridge has been replaced by $-CH_2-$. These molecules are severely distorted, with unusually short O---O contacts.

Hemispherands have some conformational rigidity and some flexibility; a representative host is shown in 6. We will discuss the structures of t-butylammonium complexes of 6 and of a closely related hemispherand (7) with a 4-methylanisole moiety (like the other two rings) in place of the central urea-containing ring.



6

For each compound, we give data in this order: formula, space group, Z,T,a,(b),(c)Å,(α),β,(γ)°, radiation, limit of sinθ/λ, current R.

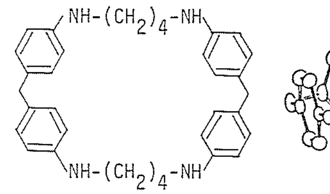
1: $C_{48}H_{48}O_6$,R$\bar{3}$,1,22°C,11.697(3),114.25(2),CuKα, 0.63,0.053. 2: $C_{48}H_{48}O_6\cdot LiCl$,R$\bar{3}$,1,22°C, 11.152(1), 110.60(1),CuKα, 0.63, 0.047

3: $C_{48}H_{48}O_6\cdot NaOSO_3CH_3$,P2/c,2,22°C,11.572(5), 10.467(5),22.072(7),108.97(3),MoKα,0.595 0.15. 4: $C_{52}H_{52}O_8\cdot LiCl$,P$\bar{1}$,2,115K,12.773(3), 14.125(3),15.147(4),79.99(2),67.50(2), 67.72(2),MoKα,0.65,0,12. 5: $C_{50}H_{48}O_6\cdot LiFeCl_4$, $P2_1/c$,4,115K,12.251(3),22.582(7), 17.236(4),101.33(3),MoKα,0.70,0.08.

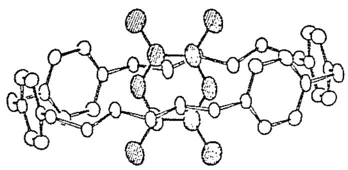
6: $C_{26}H_{34}N_2O_6\cdot C_4H_{12}NClO_4$,Cc,8,115K,10.898(3), 25.932(5),23.654(5),103.28(2),MoKα,0.62, 0.09. 7: See A.C.A. Honolulu, 1979,57

04.5-03 THE STRUCTURES AND STABILITIES OF GUEST MOLECULES IN HOST-GUEST INCLUSION COMPLEXES. By A. Itai, Y. Ikeda, A. Watanabe, K. Odashima, K. Koga and Y. Iitaka, Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan.

The water soluble paracyclophane (to be abbreviated as CP44 hereafter) forms inclusion complexes with various aromatic compounds in the solid as well as in solution. We carried out X-ray structure analyses of free CP44 and three complexes with durene (J. Am. Chem. Soc. 102, 2504 (1980)), naphthalene and 1,3-naphthalenediol as guests. In the presence of guest molecules, CP44 forms a rectangular, intramolecular cavity (3.5Åx7.9Å (x6.5Å depth)) in which the guest molecules are trapped. The CP44 molecules are bonded to each other mainly by hydrophilic forces such as hydrogen, whereas the inside of the cavity is decorated by hydrophobic groups. To determine the locations of the guest molecules within the complex in solution and in the crystal, we applied energy calculation and energy minimization. In case of 2,8-naphthalene-diol, the calculation was in good accord with the structure of the complex expected from the observed chemical shift differences in nmr spectra of non-included and included guest molecules. The method of energy calculations is now applied to various other host-guest inclusion complexes.



CP44 $\cdot 4HX$ (X=Cl,Br)


CP44•durene complex