

Supramolecular assemblies based on calixarenes

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Abstract

Supramolecular assemblies have been constructed from calixarenes and organic molecules or ions, from calixarenes and transition metal coordination complexes, and from calixarenes themselves. Two-component systems, or host-guest complexes, are now common, but we report here the assembly of four-component super-molecules and aggregates as large as two transition metal complexes and six calix[4]arenes have been characterized crystallographically.

Supramolecular chemistry deals with the construction of large structures from small building blocks. These building blocks are generally held together by weak (non-covalent) interactions. This discussion will deal with calix[4]arenes and with transition metal coordination complexes as the units upon which larger structures are based. The organizational principle is the assembly of second-sphere coordination complexes.

Calixarenes (1,2), as shown schematically in Fig. 1, are macrocycles which can be functionalized at either the rim (R) or the base (R'). For this discussion the focus will be on rim-derivatized calix[4]arenes. At pH > 3.5 p-sulfonatocalix[4]arene exists as the 5- anion (3,4) and X-ray diffraction studies have shown that neutral organic molecules (3) and organic anions (5) may be complexed into the hydrophobic cavity. Shinkai has further demonstrated that the trimethylanilinium cation is bound both in solution and in the solid state by the [calix[4]arene sulfonate]⁴⁻ anion (6). Work in our laboratories has been primarily concerned with the water soluble p-sulfonatocalix[4]arene (as either the 4- or 5- anion), and the discussion will treat (a) the hydrophobic pocket, (b) second-sphere coordination, and (c) the use of second-sphere coordination to assemble large aggregates.

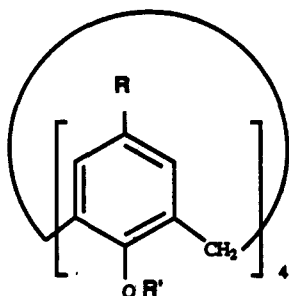


Fig. 1. Schematic view of a calix[4]arene.

In the cone conformation, the hydrophobic pocket of *p*-sulfonatocalix[4]arene is of appropriate size to accommodate small molecular or ionic guests, as is seen in Fig. 2 (7). In the absence of an appropriate guest, the water-soluble calix[4]arene must take one or more water molecules into the cavity. For $\text{Na}_4[\textit{p}\text{-sulfonatocalix[4]arene}] \cdot 13.5 \text{ H}_2\text{O}$, one water molecule is deeply imbedded in the cavity (8). The (water)...centroid(aromatic) distances are 3.16, 4.19, 3.19, and 4.08 Å and the hydrogen atoms are directed toward the two closest aromatic centroids. The H...centroid distances are 2.38 and 2.50 Å, and the O-H...centroid angles are 127 and 133°. The H-O-H bond angle is 125°.

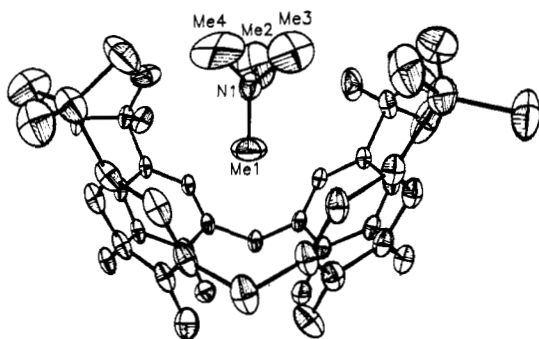


Fig. 2. NMe_4^+ as a guest in the cavity of $[\textit{p}\text{-sulfonatocalix[4]arene}]^{5-}$.

Second-sphere coordination has been defined by Stoddart (9) as the 'non-covalent bonding of chemical entities to the first coordination sphere of a transition metal complex'. Crown ethers (10,11) and cyclodextrins (9, 12-21) have been employed as second-sphere ligands, but the first report of the use of calixarenes only appeared in 1991 (22-25).

An example of a two-component or host-guest complex utilizing second-sphere coordination is found in Fig. 3 for the structure of $[(\text{H}_2\text{O})_4\text{Cu}(\text{NC}_5\text{H}_5)_2](\text{H}_3\text{O})_3[\textit{calix[4]arene sulfonate}] \cdot 10 \text{ H}_2\text{O}$ (22). Fig. 4 illustrates the calix[4]arene bilayer for this structure. One pyridine ring is imbedded in the calixarene cavity, while the other is intercalated into the

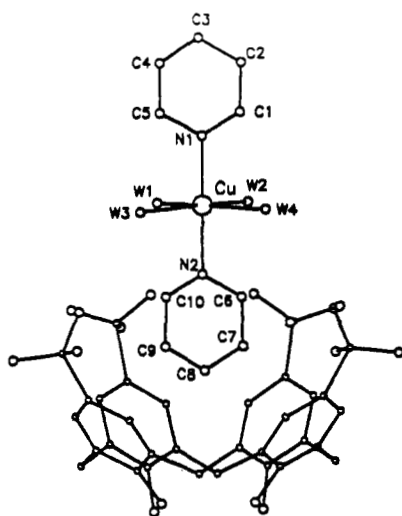


Fig. 3. $[\text{Cu}(\text{NC}_5\text{H}_5)_2(\text{H}_2\text{O})_4]^{2+}$ as a guest in $[\textit{p}\text{-sulfonatocalix[4]arene}]^{5-}$.

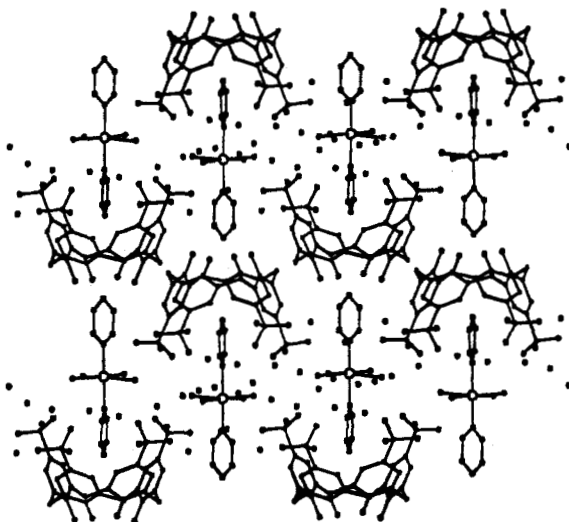


Fig. 4. Crystal packing for $[(\text{H}_2\text{O})_4\text{Cu}(\text{NC}_5\text{H}_5)_2](\text{H}_3\text{O})_3[\textit{calix[4]arene sulfonate}] \cdot 10 \text{ H}_2\text{O}$.

bilayer. The copper complex thus spans the hydrophilic layer. The primary coordination sphere of the Cu^{2+} is composed of two pyridine and four aqua ligands; the calix[4]arene is coordinated to the metal ion in a second-sphere fashion. Hydrophobic effects or van der Waals forces bind the calixarene to the coordination complex.

We have recently discovered that host-guest supramolecular compounds based on calix[4]arenes can be further organized into larger dimeric assemblies by a combination of weak forces such as those based on ion-dipole, dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole interactions (23). In biological assemblies, combinations of many if not all of these may be expected to be important in determining structure and function. Recently, a combination of hydrogen bonding and aromatic stacking has been used by Hamilton to prepare two-component supermolecules (24). Hydrogen bonding and hydrophobic effects have also been used by Stoddart (9) in the formation of second-sphere coordination complexes of cyclodextrins and transition metal compounds noted above. However, the formation of higher aggregates such as dimers has not been observed.

Fig. 5 shows that a similar host-guest relationship exists between the [calix[4]arene sulfonate] $^{5-}$ anion and the pyridinium cation (23), but closer scrutiny reveals that N-H...O hydrogen bonding between pyridinium ions and sulfonate oxygen atoms across the hydrophilic layer produces a dimeric arrangement. The dimer is held together by a combination of two hydrogen bonds and two hydrophobic interactions.

Fig. 6 presents the dimeric association involving the coordination complex $[\text{Cu}(\text{NC}_5\text{H}_5)_2(\text{H}_2\text{O})_3\text{-p-sulfonatocalix[4]arene}]$. The copper(II) ion is strongly coordinated to a square planar array of two pyridine nitrogen atoms (at 1.98(1) and 2.00(1) Å) and two water oxygen atoms (at 2.00(1) and 2.01(1) Å). The remaining two axial sites of a strongly Jahn-Teller distorted octahedral arrangement are filled by the oxygen atoms of a water molecule (at 2.50(1) Å) and a sulfonate oxygen atom (at 2.55(1) Å). The latter weak interaction is seen to bind the copper complex to the exterior of one calixarene, while one of the pyridine ligands is inserted into a calixarene cavity across the hydrophilic layer. Thus, the dimer is held together by two

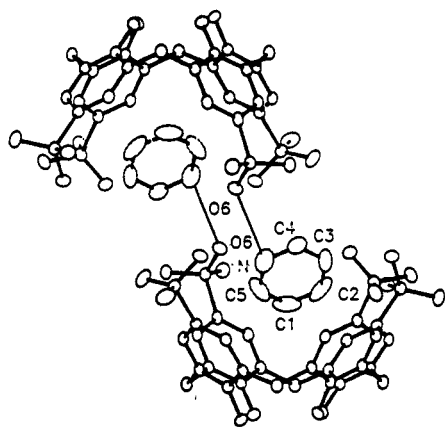


Fig. 5. [p-sulfonatocalix[4]arene] $^{5-}$ with a pyridinium cation as a guest. The assembly exists as a dimer.

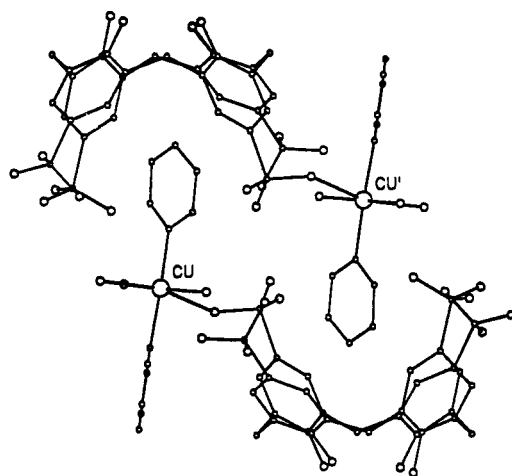


Fig. 6. Dimer formation with $[\text{Cu}(\text{NC}_5\text{H}_5)_2(\text{H}_2\text{O})_3\text{-p-sulfonatocalix[4]arene}]$.

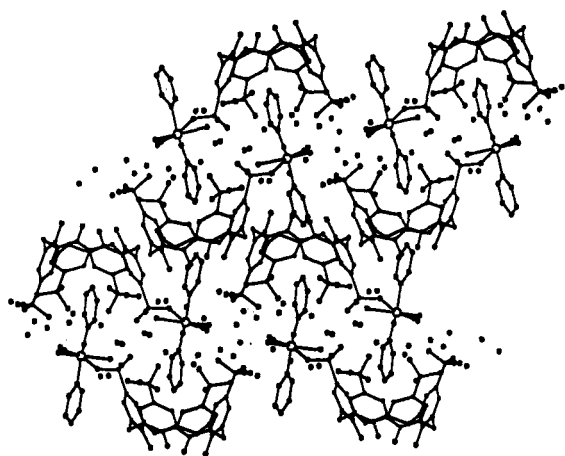


Fig. 7. Crystal packing for $[\text{Cu}(\text{NC}_5\text{H}_5)_2(\text{H}_2\text{O})_3 \cdot \text{p-sulfonatocalix[4]arene}]$.

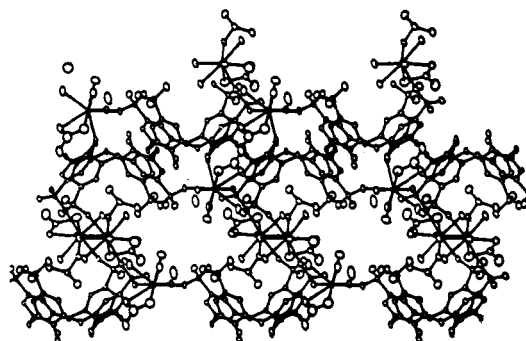


Fig. 8. Crystal packing diagram for $[\text{La}(\text{DMSO})(\text{NO}_3)(\text{H}_2\text{O})_4][\text{p-sulfonatocalix[4]arene}] \cdot 2 \text{H}_2\text{O}$.

weak $\text{Cu} \cdots \text{O}(\text{sulfonate})$ bonds and two hydrophobic interactions. As is shown in Fig. 7, the remaining pyridine rings are intercalated into the calixarene bilayers.

Second-sphere coordination as discussed above is useful for the formation of supramolecular assemblies. However, this mode of interaction is not restricted to the insertion of aromatic moieties into the calix[4]arene cavity. Virtually all ligands with a hydrophobic surface of appropriate size and shape may be used. The dimethylsulfoxide ligand has been studied, for example in the structure of $[\text{La}(\text{DMSO})(\text{NO}_3)(\text{H}_2\text{O})_4][\text{p-sulfonatocalix[4]arene}] \cdot 2 \text{H}_2\text{O}$. This complex arrangement, shown in the crystal packing diagram as Fig. 8, can be best understood by viewing the assembly in parts. Fig. 9 illustrates the second-sphere coordination of the $[\text{p-sulfonatocalix[4]arene}]^{4-}$ anion to a methyl group of the DMSO. Fig. 10 shows the coordination of the DMSO to the La^{3+} , labelled as La2. La1 is bound to the calixarene via coordination to one of the phenolic oxygen atoms, as is shown in Fig. 11.

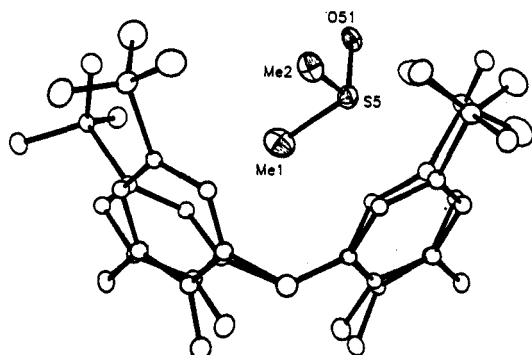


Fig. 9. Second-sphere coordination of $[\text{p-sulfonatocalix[4]arene}]^{4-}$ to DMSO.

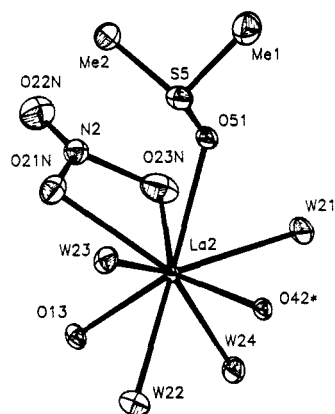


Fig. 10. Coordination environment of La2.

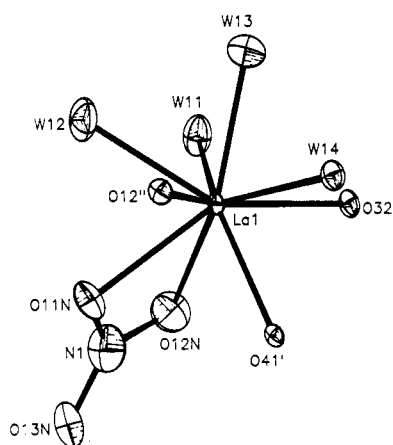


Fig. 11. Coordination environment of La1.

We also wish to disclose in a preliminary fashion the assembly of two transition metal complexes and six *p*-nitrocalix[4]arenes to form a supermolecule of remarkable complexity. The arrangement consists of the dimer $\{[La(DMSO)_8]^{3+}[p\text{-nitrocalix[4]arene}][p\text{-nitrocalix[4]arene}^-]_2(NO_3^-)_2\}$. That is to say, for each coordination complex there are two *p*-nitrocalix[4]arenes with 1- charge and one which is neutral. The two halves of the dimer are related by a crystallographic center of inversion. The remarkable feature of the assembly is that the six calixarenes are wrapped around the lanthanum complexes much as insulation is wrapped around a wire. The calixarenes interact with the methyl groups of the DMSO ligands and exhibit second-sphere coordination of the La^{3+} . Two calixarenes belong to each metal and two bridge the two complexes together.

Acknowledgement

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REFERENCES

1. C. D. Gutsche, Calixarenes, Royal Society of Chemistry, Cambridge (1989).
2. Calixarenes, a Versatile Class of Macrocyclic Compounds, V. Bohmer and J. Vicens, Eds., Kluwer, Dordrecht (1990).
3. A. W. Coleman, S. G. Bott, S. D. Morley, C. M. Means, K. D. Robinson, H. Zhang, and J. L. Atwood, Angew. Chem. Int. Ed. Engl. **27**, 1361-1362 (1988).
4. J. L. Atwood, A. W. Coleman, H. Zhang, and S. G. Bott, J. Incl. Phenom. **7**, 203-211 (1989).
5. S. G. Bott, A. W. Coleman, and J. L. Atwood, J. Am. Chem. Soc. **110**, 610-611 (1988).
6. S. Shinkai, K. Araki, T. Matsuda, N. Nishiyama, H. Ikeda, I. Takasu, and M. Iwamoto, J. Am. Chem. Soc. **112**, 9053-9058 (1990).

7. J. L. Atwood, G. W. Orr, and K. D. Robinson, unpublished results.
8. J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr, and R. L. Vincent, Nature **349**, 683-684 (1991).
9. D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, Angew. Chem. Int. Ed. Engl. **24**, 786-787 (1985).
10. D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, J. Chem. Soc. Chem. Commun. 1602-1604 (1985).
11. H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, Angew. Chem. Int. Ed. Engl. **27**, 1986-1987 (1988).
12. D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, and R. Arazycki, Angew. Chem. Int. Ed. Engl. **27**, 1184-1185 (1988).
13. P. R. Ashton, J. F. Stoddart, and R. Zarzycki, Tetrahedron Lett. **29**, 2103-2106 (1988).
14. D. R. Alston, P. R. Ashton, T. H. Lilley, J. F. Stoddart, R. Zarzycki, A. M. Z. Slawin, and D. J. Williams, Carbohydrate Research **192**, 259-281 (1989).
15. A. Harada, Y. Hu, S. Yamamoto, and S. Takahashi, J. Chem. Soc. Dalton Trans. 729-732 (1988),
16. T. Hoh, A. Harada, and S. Takahashi, Mem. Inst. Sci. Ind. Res. **46**, 37-50 (1989).
17. A. Harada, M. Shimada, and S. Takahashi, Chem. Lett. 275-276 (1989).
18. A. Harada, K. Saeki, and S. Takahashi, Organometallics **8**, 730-733 (1989).
19. A. Harada, S. Yamamoto, and S. Takahashi, Organometallics **8**, 2560-2563 (1989).
20. N. Kobayshi and M. Opallo, J. Chem. Soc. Chem. Commun. 477-478 (1990).
21. B. Klingert and G. Rihs, Organometallics **9**, 1135-1141 (1990).
22. J. L. Atwood, G. W. Orr, F. Hamada, R. L. Vincent, S. G. Bott, and K. D. Robinson, J. Am. Chem. Soc. **113**, 2760-2761 (1991).
23. J. L. Atwood, G. W. Orr, K. D. Robinson, and F. Hamada, Supramol. Chem. **1**, 15-17 (1992).
24. J. L. Atwood, G. W. Orr, F. Hamada, R. L. Vincent, S. G. Bott, and K. D. Robinson, J. Incl. Phenom., in press.
25. J. L. Atwood and G. W. Orr, unpublished results.