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COMMUNICATION

Supramolecular assemblies of calix[4]arenes organized by feeble forces

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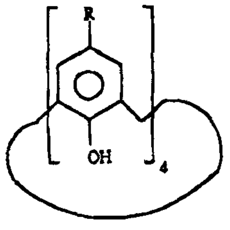
X-ray crystallographic investigations have shown that dimeric supramolecular assemblies of water-soluble calix[4]arenes are formed by a combination of hydrophobic effects and either hydrogen bonding or secondary bonding. For Na_4(pyridinium)[calix[4]arene sulfonate]·$8H_2O$, a dimeric arrangement based on hydrogen bonding and hydrophobic effects is found. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 11.873(3), b = 24.345(6), c = 14.846(3) Å, β 96.78(2)°, and $D_c = 1.66\,g\,cm^{-3}$ for Z = 4. Refinement based on 3492 observed reflections led to a final R value of 0.051. For $[Cu(NC_5H_5)_2(H_2O)_3](Na)_3$[calix[4]arene sulfonate]·13 H_2O, the dimeric association is based on a secondary bonding interaction between the copper(II) ion and a sulfonate oxygen atom combined with hydrophobic interactions. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 14.672(3), b = 25.577(5), c = 15.457(3) Å, β = 101.94(4)°, and $D_c = 1.55\,g\,cm^{-3}$ for Z = 4. Refinement based on 3602 observed reflections afforded a final R value of 0.064.

Self-assembly in nature is based largely on hydrogen bonding,[1] with added stabilization from other weak forces. For example, aromatic stacking forces are of importance in protein structure.[2] In order to gain insight into the action of feeble forces[3] on a molecular level, several model systems have been studied.[4-9] In this contribution we show that large host-guest supramolecular compounds based on calix[4]-arenes,[10-13] **1**, can be organized into larger dimeric assemblies by a combination of weak forces.



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The catalogue of feeble binding forces includes those based on ion-dipole, dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole interactions. In supramolecular chemistry these are more commonly referred to under such headings as hydrogen bonding, secondary bonding forces, and van der Waals interactions (aromatic stacking, hydrophobic forces). 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.[6] Hydrogen bonding and hydrophobic effects have also been used by

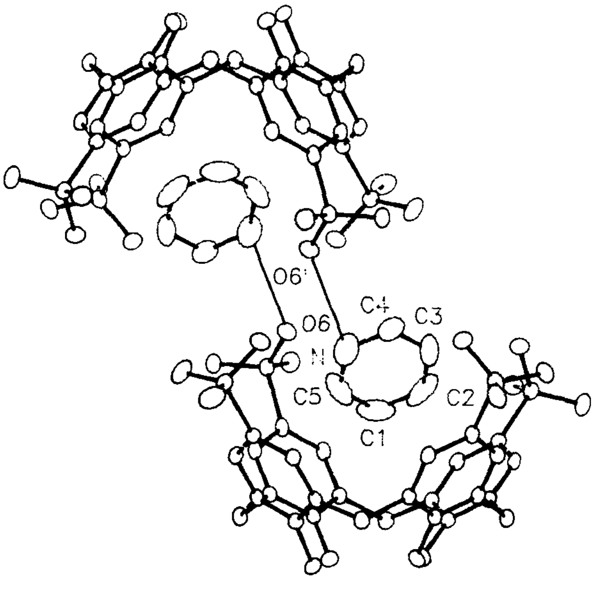

Figure 1 Structure of the pyridinium inclusion complex. Two such units exist as a dimer linked via inter-complex N-H...O hydrogen bonds. The hydrogen atom involved was not located, but the presence of the hydrogen bond is clearly evidenced by the N...O separation of 2.89(1) Å. The Na^+ ions and the interlayer H_2O molecules are not shown. All Na^+ ions are either 5- or 6-coordinate with Na-O distances ranging from 2.246(6) to 2.528(6) Å.

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Stoddart in the formation of second-sphere coordination complexes of cyclodextrins and transition metal compounds.[14] However, the formation of higher aggregates such as dimers has not been noted.

Calix[4]arenes may be derivatized at the rim position, R, with groups such a R = $-SO_3Na$ that provide water solubility.[15,16] At pH > 7 the calix[4]-arene sulfonate exists at the 5- anion, **2**,[17,18] and X-ray diffraction studies have shown that neutral organic molecules[17] and organic anions[19] 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.[20] Figure 1 shows that a similar host-guest relationship exists between the [calix[4]arene sulfonate]$^{5-}$ anion and the pyridinium cation,[21] 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, $[C_5H_5NH\cdot\mathbf{2}]_2$.

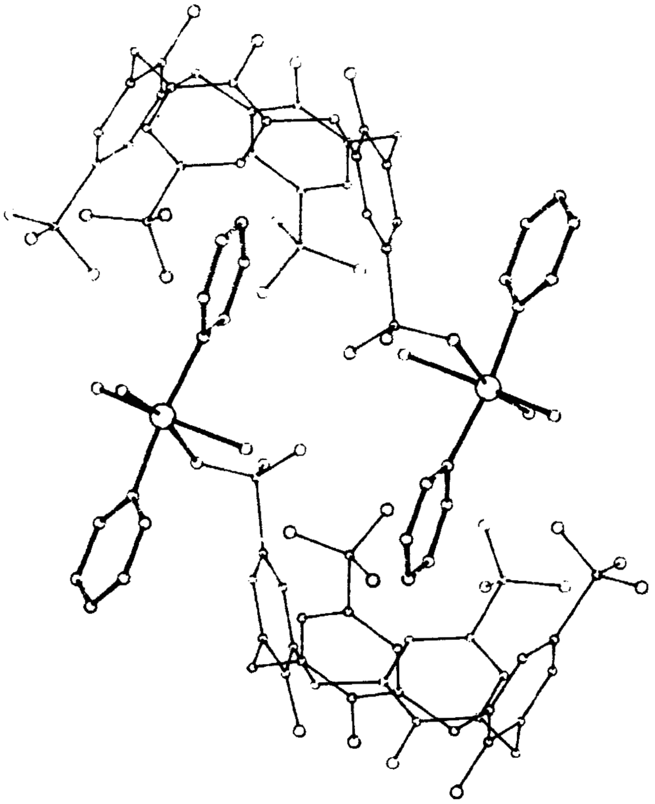

Figure 2 Structure of the $[Cu(NC_5H_5)_2(H_2O)_3](Na)_3$[calix[4]-arene sulfonate]·13 H_2O inclusion complex. Two such units form the super-dimer via secondary Cu...O(sulfonate) bonds and hydrophobic interactions between the cavity and one of the two pyridine rings.

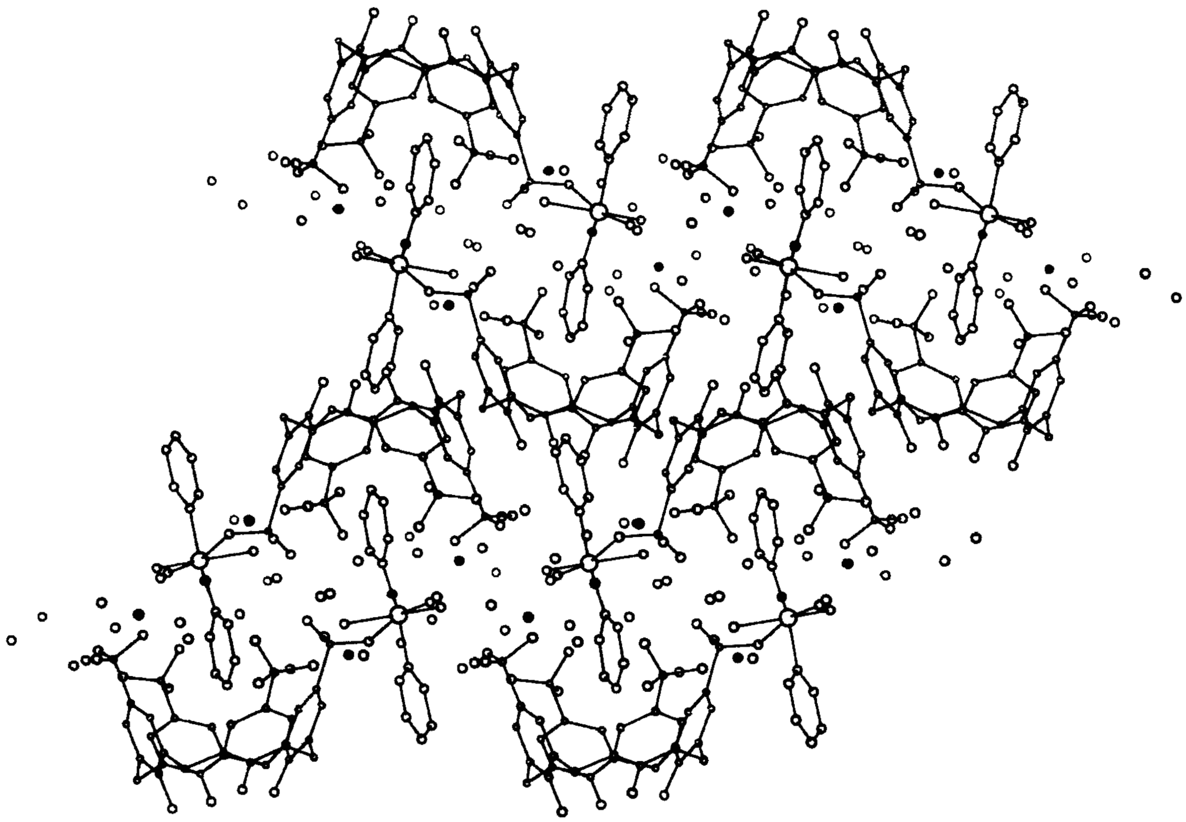

Figure 3 Unit cell packing illustration of $[Cu(NC_5H_5)_2(H_2O)_3](Na)_3$[calix[4]arene sulfonate]·13 H_2O displaying four super-dimers. The Na^+ ions are shaded and the water molecules in the interlayer space are open circles.

The dimer is held together by a combination of two hydrogen bonds and two hydrophobic interactions.

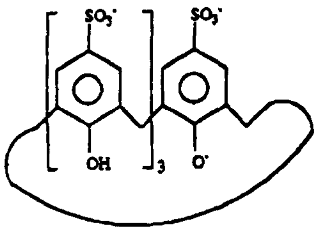

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Figure 2 presents the dimeric association [Cu$(NC_5H_5)_2(H_2O)_3 \cdot \mathbf{2}]_2$.[22] The copper(II) ion is strongly coordinated to a square planar array of two pyridine nitrogen atoms (at 1.98(1) and 2.00(1) Å) and two water oxygen atoms (at 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 hydrophobic layer. Thus, the dimer is held together by two weak Cu...O(sulfonate) bonds and two hydrophobic interactions. As is shown in Figure 3, the remaining pyridine rings are intercalated into the calixarene bilayers.[17,18]

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21. Na_4(pyridinium)[calix[4]arene sulfonate]$\cdot 8\ H_2O$, **1**, belongs to the monoclinic space group $P2_1/n$ with $a = 11.873(3)$, $b = 24.345(6)$, $c = 14.846(3)$ Å, $\beta = 96.78(2)°$, and $D_c = 1.66\ g\ cm^{-3}$ for $Z = 4$. Refinement based on 3492 observed reflections led to a final R value of 0.051. The complex may be prepared from the parent compound and pyridinium chloride or by addition of pyridine (gas or liquid) to the parent at acidic pH.
22. $[Cu(NC_5H_5)_2(H_2O)_3](Na)_3$[calix[4]arene sulfonate]$\cdot 13\ H_2O$, **2**, belongs to the monoclinic space group $P2_1/n$ with $a = 14.672(3)$, $b = 25.557(5)$, $c = 15.457(3)$ Å, $\beta = 101.94(4)°$, and $D_c = 1.55\ g\,cm^{-3}$ for $Z = 4$. Refinement based on 3602 observed reflections led to a final R value of 0.064. The compound may be prepared by the addition of an aqueous solution of $[Cu(NC_5H_5)_2(H_2O)_2](NO_3)_2$ to the parent calixarene.