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Crystalline Supramolecular Complexes of C_{60} with Calix[5]arenes

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Abstract: The structure of the crystalline supramolecular complexes of calix[5]arenes (**1** - **3**) with C_{60} is described. The composite ratios of these complexes are 2 : 1 for **1** and C_{60} and 1 : 1 for **2** and **3** with the guest. Van der Waals attractive interaction between the heavy halogen atoms on the upper rim of the host (**1**) is responsible for the formation of the 2 : 1 complex.
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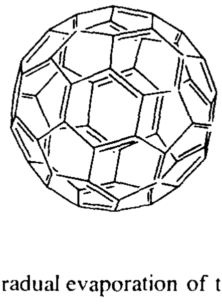
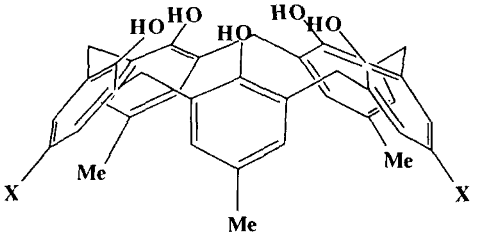
The structure and property of Buckminsterfullerene, C_{60} have attracted much attention in recent years. It is well-known that the C_{60} molecule has a highly symmetric spherical structure.1) This molecule is hydrophobic and has no polar functional group. Recent studies have focused on a bowl-shaped receptor molecule which can bind C_{60} within the cavity in solution2) and in voids in the crystalline lattice3). In our previous paper we reported that calix[5]arenes (**1** - **3**) can strongly bind C_{60} in various organic solvents.4) The stoichiometry of the host and guest is always 1 : 1 in solution; however, that of the crystalline complex between **1** and C_{60} is 2 : 1. In order to understand the apparent contradictory host-guest ratios, the structure of the crystalline host-guest complexes between the other calix[5]arenes (**2** and **3**) and C_{60} was analyzed and in this paper, we now report that the ratio of the host and guest of these complexes is 1 : 1 in the crystal.

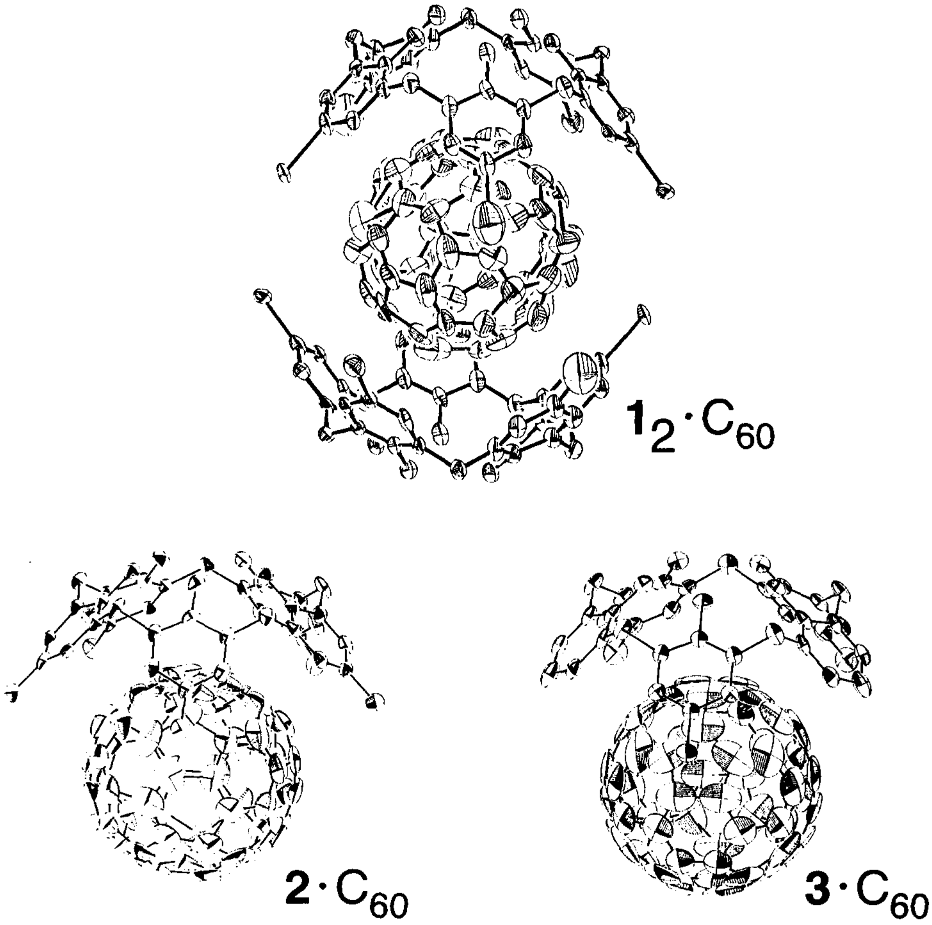




1: X=I
2: X=Me
3: X=H

Gradual evaporation of the solvent from CS_2 solutions of **1**, **2**, and **3** with an equimolar amount of C_{60} on standing at room temperature for a few days yielded purple prisms of supramolecular complexes of C_{60} with calix[5]arenes. The presence of a trace amount of water and/or methanol is essential for the specimens suitable for analysis. X-ray crystallographic studies disclosed the precise structures of these supramolecular complexes.5) ORTEP drawings of which are shown in Figure 1.

In the solid state, the 2 : 1 complex, $\mathbf{1}_2\cdot C_{60}$ has a highly symmetric pseudo D_{5d} structure because of the positional disorder of the two iodine atoms over each para position of the five phenols. The $\mathbf{2}\cdot C_{60}$ complex has a roughly C_{5d} symmetric structure in the solid state; thus, the five-fold rotation axis of the host coincides with one of the five-fold rotation axes of the guest, and a five-membered ring of the guest is parallel to the mean plane composed of the five phenol oxygens of the host. The structure of the $\mathbf{3}\cdot C_{60}$ complex is almost the same as that of $\mathbf{2}\cdot C_{60}$: the north hemisphere of C_{60} is covered with the bowl-shaped interior of the host composed of the five phenol rings. The free rotation of C_{60}6) is considerably suppressed in all these crystalline complexes since all the atoms of the guest can be identified clearly, although the magnitude of the thermal ellipsoids of the individual atoms in these guests is significantly larger than those of the hosts.

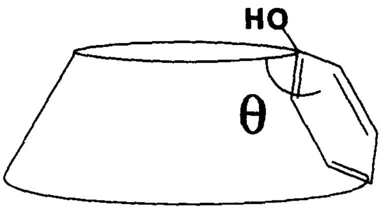


$\mathbf{1}_2\cdot C_{60}$

$\mathbf{2}\cdot C_{60}$

$\mathbf{3}\cdot C_{60}$

Fig. 1 Structures of the supramolecular complexes.



Cambridge X-ray data base search[7)] disclosed that an empty cavity of the calix[5]arene is not circular but oval as can be seen in the inclination angles (θ) of the five phenol rings from the mean plane composed of the five carbon atoms of the bridging five methylenes. These are 147.2, 135.5, 120.5, 120.5, and 122.9° in the structure of n-hexane clathrate of *p-t*-butyl-calix[5]arene.[8)] A similar oval shape is found in the empty cavity of ethyl acetate clathrate[9)] and the flat guest included cavities (acetone guest[10)] and tetraline guest[11)]. On the other hand, the cavities of the hosts which included C60 are circular as can be seen with almost the same five inclination angles of the phenols (average of the five angles, **1**: 133.7 (2)°, **2**: 134.8 (7)°, **3**: 135.7 (7)°). The small change in the host cavity shape suggested an induced-fit type adjustment of the host to the globular guest. As a result of the structure modification of these hosts, the intramolecular hydrogen bonds are shorter (average of the five O -- O distances **1**: 2.75 (1), **2**: 2.75 (2), **3**: 2.77 (2) Å) than those of the flat guest included hosts (acetone guest: 2.84 (1), tetraline guest: 2.90 (1) Å). There are altogether 72 short interatomic distances (< 4.0 Å) between the sp^2 carbons in the guest and one of the hosts for $\mathbf{1}_2 \cdot C_{60}$: the average of these distances is 3.61 (2)Å. The number of short contacts increased to 78 and 77 for **2** and **3** with the guest: the average values are 3.60 (2) and 3.63 (2)Å , respectively. From these analyses, it is clear that the structure of the calix[5]arene hosts has ideal cyclic hydrogen bonds and a symmetrical cone shape. Thus, the spherical outer surface of C_{60} matches the interior substructure of the hosts both in size and shape.

The X-ray analyses indicated that the structural features of these complexes are very similar to each other and no provable reasoning for 2 : 1 complex formation of $\mathbf{1}_2 \cdot C_{60}$ was provided. Hence, van der Waals interaction between the two upper rims of the hosts was evaluated using molecular mechanics calculation. The host **1** has three methyl groups and two iodines on its upper rim and the attractive interaction energy between these substituents of the two facing hosts was calculated with MM3 van der Waals parameters using the geometry obtained above. The attractive energy between the two hosts of **1** is 0.391 kcal/mol. On the other hand, the attractive energies between the two hosts are 0.086 and 0.043 kcal/mol for **2** and **3**, respectively, when using the same geometry as that of the 2 : 1 complex of $\mathbf{1}_2 \cdot C_{60}$. Due to the presence of the heavy halogen atoms, the attractive interaction between the two upper rims of the host **1** is 4~8 fold larger than that of the others. The calculated results indicate that the integration of intermolecular host-host interactions of **1** provided appreciable stabilization of the crystalline 2 : 1 supramolecular complex of **1** and C_{60}. The intermolecular interactions between the two upper rims of the other hosts are not large enough to stabilize the dimer formation similar to the 2 : 1 complex. The same calculation predicted that the attractive interaction between the two upper rims bearing five iodine atoms on each of them is 1.14 kcal/mol, provably sufficient for dimer formation even in an organic solvent.

In summary, we succeeded in disclosing the structure of the supramolecular complex of C_{60} and calix[5]arene derivatives. The interior cavity of calix[5]arene fits the spherical outer surface of C_{60} to yield the stable inclusion complex.

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5) Crystal data for $C_{60}\cdot\mathbf{1}_2\cdot 8H_2O$ 4)

Crystal data for $C_{60}\cdot\mathbf{2}\cdot MeOH\cdot 3H_2O$: $C_{101}H_{50}O_9$, triclinic space group $P\ \bar{1}$, a=13.292(2), b=13.522(1), c=19.913(2) Å, α=76.92(1)°, β=74.47(1)°, γ=70.44(1)°, V=3212(1) Å^3, ρcalc=1.454 gcm^{-3},μ(CuKa)=9.53 cm^{-1}, Z=2. MXC-3 diffractometer with graphite-monochlomated CuKa radiation, λ=1.54178 Å, T=293K, $\omega/2\Theta$ scan, 8461 reflection measured ($3.0<2\Theta<110.0°$). Structure solution by direct method (SIR92) 12), refinement on F_o^2(SHELXL93) 13), hydrogen atoms isotropic and in a rigid model, 997 parameters, wR^2=0.276 (observed reflections), corresponds to conventional R=0.097 using reflection with $|F_o|>4.0\sigma|F_o|$.

Crystal data for $C_{60}\cdot\mathbf{3}\cdot 4H_2O$: $C_{98}H_{44}O_9$, monoclinic space group $C\,2/m$, a=22.178(3), b=15.151(3), c=19.731(3) Å, β=108.21(1)°, V=6297(2) Å^3, ρcalc=1.439 gcm^{-3}, μ(CuKa)=9.53 cm^{-1}, Z=4. MXC-3 diffractometer with graphite-monochlomated CuKa radiation, λ=1.54178 Å, T=293(2)K, $\omega/2\Theta$ scan, 5785 reflection measured ($3.0<2\Theta<110.0°$). Structure solution by direct method (SIR92) 12), refinement on F_o^2(SHELXL93) 13), hydrogen atoms isotropic and in a rigid model, 511 parameters, wR^2=0.253 (observed reflections), corresponds to conventional R=0.085 using reflection with $|F_o|>4.0\sigma|F_o|$.

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