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Confinement and recognition of icosahedral main group cage molecules: fullerene C_{60} and *o*-, *m*-, *p*-dicarbadodecaborane(12)

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Supramolecular chemistry of icosahedral main group cage molecules, fullerene C_{60} and the carboranes *o*-, *m*- , *p*-$B_2C_{10}H_{12}$, is of interest in the purification of these molecules and in building up novel materials. The non-polarised, spherical like nature of C_{60} requires specific shape and electronic complementarity between the interacting supramolecular synthons which leads to polarisation of the fullerene, whereas for the carboranes, hydrogen bonding involving the C–H groups, including the formation of bifurcated hydrogen bonds [C–H$\cdots$(N,O)$_2$], and C–H$\cdots\pi$ interactions, along with shape complementarity, facilitate the self assembly process. Insight into future prospects in this field is presented.

Background

Highly symmetrical icosahedral molecules have captured the imagination of the chemical sciences community and beyond. This is particularly the case since 1985 with the discovery of a new allotropic form of carbon now known as the family of electron deficient fullerenes for which C_{60} is the most abundant and widely studied, having a truncated icosahedral structure.[1] A plethora of organic chemistry of C_{60} resulted in the 1990s which pertains to addition reactions across the 6,6′ position ring junction of two six membered rings, in accordance with the double bonds avoiding the five membered rings of the polyhedron.[2] Exohedral metal complexes of C_{60}, the metal to fullerene binding usually associated with the same 6,6′ positions of the fullerene, are also known,[3] as are endohedral species,[4] and the electrochemical behaviour of C_{60} is remarkable showing reversible reduction to $C_{60}{}^{6-}$.[5] Then there is the supramolecular chemistry of C_{60},[6] which is a focus of this article, with advances coming mainly from our research group, and those of Atwood, Fuji, Fukazawa, Matsubara, Shinkai, Verhoeven, and Wennerstrom.

Another focus of this article is the supramolecular chemistry of the related icosahedral main group cage molecules, the carboranes, 1,2-, 1,7-, 1,12-dicarbadodecaborane(12), *viz o*-, *m*-, *p*-$C_2B_{10}H_{12}$ (hereafter abbreviated *o*-, *m*-, and *p*-carborane). These carboranes have a rich organometallic chemistry (direct metal–carbon bonds),[7] and a rich organic chemistry associated with replacing one or more hydrogen atoms of the C–H groups as well as the boron atoms.[8] The supramolecular chemistry of the carboranes is even less developed than that of C_{60}. This is surprising given the nexus between these cages, and that unlike C_{60}, the carboranes have been known for several decades.[9] Fullerene C_{60} and the carboranes are all remarkably thermally stable, icosahedral cages with not too dissimilar diameters of 10.0 and ≈ 8 Å respectively.

In embracing the principles of supramolecular chemistry for C_{60} and the carboranes, the goal is to encourage the association of two or more components (a molecular cage and a second or more supramolecular synthon) in an organised array using weak intermolecular forces, namely van der Waals, hydrogen bonding, electrostatic and labile coordination interactions.[10] Such interactions are inherently weak and some can be comparable to crystal packing and other competing forces. Gaining control over these interactions is a major challenge and underpins much of the basic aims and ideals of supramolecular chemistry.[10] Complementarity of shape of the interacting synthons is important, as is taking advantage of the electron deficient nature of C_{60} and the acidic nature of the C–H groups of the carboranes[9] in optimising interactions between the two different synthons, in effectively negating competing solvent–cage, cage–cage, and host–host interactions.

The overall chemistry of the higher fullerenes is less developed than that of C_{60} with the supramolecular chemistry limited to a few reports, and for completeness, and that given one of the host–guest complexes of C_{70} is isomorphous with that of the C_{60} analogue,[11] the supramolecular chemistry of C_{70} is also included herein.

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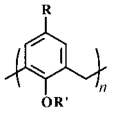
Fullerene C_{60} (and C_{70})

Fullerene C_{60} (and C_{70}) form supramolecular complexes with a variety of hydrophobic host systems including calixarenes, **1**,[5,11–28] oxacalix[3]arenes, **2**,[20,21,29] and related resorcina[4]-arenes, **3**,[30] and cyclotriveratrylene, **4,** R = Me (=

CTV),[5,28,31,32] and related molecules,[33] Ni(II) macrocycles, **5**,[34] as well as complexes with γ-cyclodextrin (included a silica supported system),[35] azacrown ethers,[36] and a porphyrazine.[37] There is also complexation of C_{60} or C_{70} by hydrogen bonded hydroquinones in a super-cube,[38] and with thiafulvalenes.[6,39] We have focused on hydrophobic systems, **1**–**4**, and related saddle shaped Ni(II) macrocycles, **5**,[34] and the work encompasses the incorporation of C_{60} into mesoporous silica.[28]



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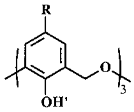

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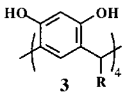

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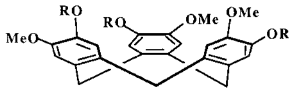

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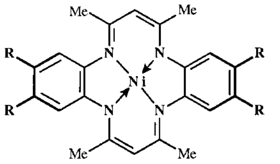

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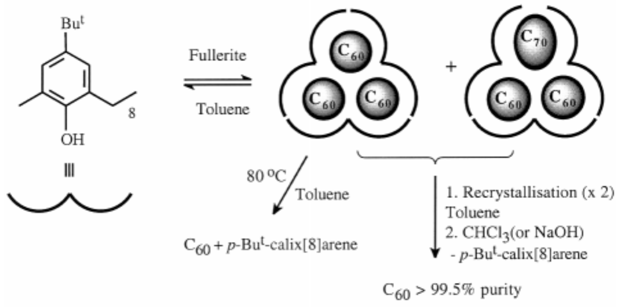
Calix[6,8]arenes

In 1994 we[12] and Shinkai and coworkers[13] reported the use of *p*-*tert*-calix[8]arene for the retrieval of high purity C_{60} from toluene solutions of fullerite derived from carbon soot, involving the recrystallisation of the precipitate from toluene followed by decomposition of the 1 : 1 complex when added to chlorinated hydrocarbons in which the fullerene is only sparingly soluble, Scheme 1. The resulting C_{60} is $>99.5\%$ pure whereas the initially formed precipitate contains up to 11% C_{70}. An independent study on the solid state ^{13}C NMR spectrum of the 1 : 1 complex between C_{60} and this calixarene has been reported.[18] Since the original foregoing reports, significant advances have been made in understanding the nature of the host–guest complex,[4,5,14] albeit with some conflicting reports, and in building up complex arrays based on other calixarenes, notably calix[5,6]arenes[11,21] and substituted calix[4,5,6,8]arenes,[15,16,19–28] and a resorcinarene.[30] This includes electrochemical studies, both solid state and solution, for C_{60} with calix[4,5,8]arenes and CTV.[5]



Scheme 1

The 1 : 1 complex of C_{60} with *p*-*tert*-butylcalix[8]arene crystallises essentially quantitatively from toluene in the presence of *ca*. 10% excess of the calixarene. Decomposition of the complex by chloroform or dichloromethane possibly relates to the formation of a C–H$\cdots\pi$ interaction between the chlorinated solvent and aromatic rings of the calixarene taking precedence over the host–fullerene interactions. This type of interaction is found in dichloromethane inclusion complexes of calix[4]arenes.[40] Pure C_{70} does not form a complex with the same calixarene in toluene, but does so in benzene, crystallising as the 2 : 1 complex, $(C_{70})_2$(*p*-calix[8]arene).[15] Interestingly C_{70} also forms a 2 : 1 complex with *p*-*tert*-butylcalix[6]arene and its precipitation from toluene solutions can be used to retrieve 87% purity C_{70} from C_{60} depleted fullerite.[12]

The *p*-*tert*-butylcalix[8]arene–C_{60} complex has a resonant inter-fullerene molecular transition at 470 nm,[14] similar to that observed in thin films of C_{60}.[36] Formation of the complex possibly involves a monomeric 1 : 1 transient intermediate, Fig. 1, which distorts the electron cloud of the fullerene[14] resulting in micelle-like formation featuring fullerene–fullerene interactions in the interior core with the fullerenes encapsulated by the host calixarene molecules, Scheme 1. Additional ^{13}C CP MAS NMR data[41] suggest that no well ordered structure of the complex exists and a variety of modifications are possible in the solid state. Nevertheless there is a common underlying ratio of *ca*. 2 : 6[18] for two different types of *tert*-butylphenyl groups. A structure which is consistent with this ratio has each calixarene in the double cone conformation spanning two fullerenes. This double cone conformation of the calixarene would require minimal perturbation of the H-bonded phenol network relative to uncomplexed *p*-*tert*-butylcalix[8]arene. Determination of the number of fullerenes in the cluster comes from molecular mechanics[14] with the minimised structure for $[(C_{60})_3$(*p*-*tert*-butylcalix[8]arene)$_3]$ shown in Fig. 1. C_{70} is complexed by *p*-*tert*-butylcalix[8]arene only in the presence of C_{60}, which is consistent with an aggregate of fullerenes with at least one of the C_{60} molecules replaced by C_{70}, the maximum molar incorporation of C_{70} in the complex being $15 \pm 1.0\%$.[14] Comparison of the X-ray powder diffraction pattern of the C_{60} complex with that containing some C_{70}[41] is consistent with some isomorphous replacement of C_{60} by C_{70}. Incorporating more than one molecule of C_{70} per trimer of fullerenes, Scheme 1, may be too disruptive to the tight fullerene/calixarene meshing as suggested by molecular mechanics. Reports on the electrochemistry of the *p*-*tert*-butylcalix[8]arene complex have the complex breaking apart on reduction (at 400 mV more negative potential).[5] The vibrational spectrum of the complex has also been probed, using

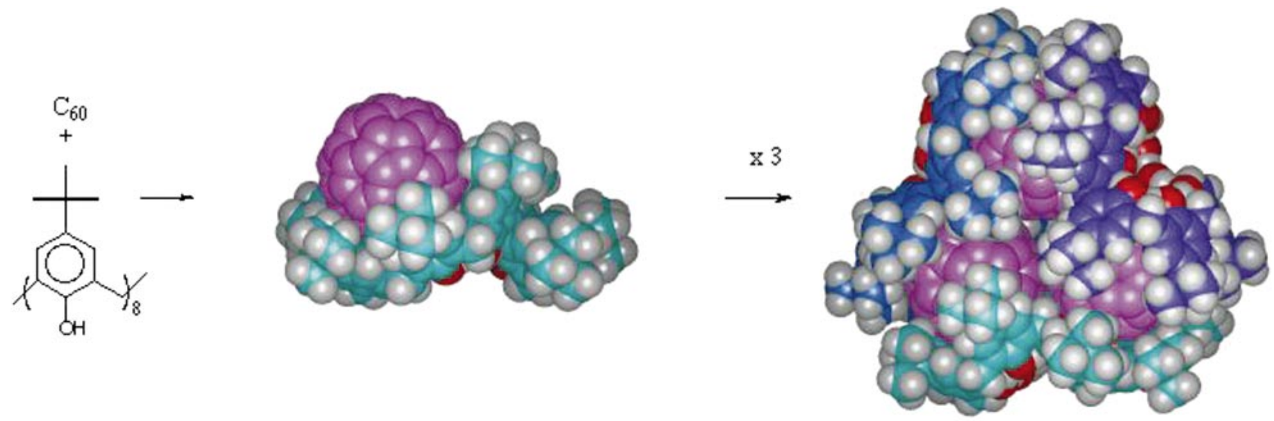


Fig. 1 Formation of the micelle like species $[(C_{60})_3$(*p*-*tert*-butylcalix[8]arene)$_3]$ *via* a monomeric transient 1 : 1 intermediate (C_{60})(*p*-*tert*-butylcalix[8]arene).[14]

Raman, IR and neutron scattering,[16] with the results consistent with the C_{60} molecules being almost isolated, suggesting any fullerene–fullerene interactions are weak. Other calix[8]arene complexes have been reported, **1** (n = 8, R = Pr^i or Et).[15]

The fullerene rich calix[6]arene complex, $(C_{60})_2$(calix[6]arene), has been structurally authenticated[11] and as expected[6] the calixarene is in double cone conformation and associated with two fullerenes, one in each cavity as a perched structure. This arrangement resembles the jaws of a pincer acting on two adjacent spheres, and can be regarded as a building component for the three dimensional structure which has fullerene–fullerene contacts close to 10.0 Å, as well as fullerenes interacting with the aromatic rings *exo*- to the two shallow cavities, Fig. 2. Fullerene C_{70} forms the analogous 2 : 1 complex and is surprisingly isostructural with the C_{60} complex, both crystallising in space group $P4_12_12$. The principle axis of the fullerene is aligned such that the end of the fullerene close to this axis, where the curvature of the cage is similar to that of C_{60}, resides in the cavity. The double cone conformations provide further credence for the proposed structure of *p*-(C_{60})(*p-tert*-butylcalix[8]arene), and suggest the other 2 : 1 complexes, *p*-$(C_{70})_2$(*p-tert*-butylcalix[6,8]arene),[15] are also likely to have the calixarenes in the double cone conformation with a fullerene in each cavity. A calix[6]arene bearing *N*,*N*-dialkylaniline or *m*-phenylenediamine units forms complexes of C_{60} in toluene solution, with association constants of 7.9–1.1 × 10^2 $dm^3\ mol^{-1}$.[19]

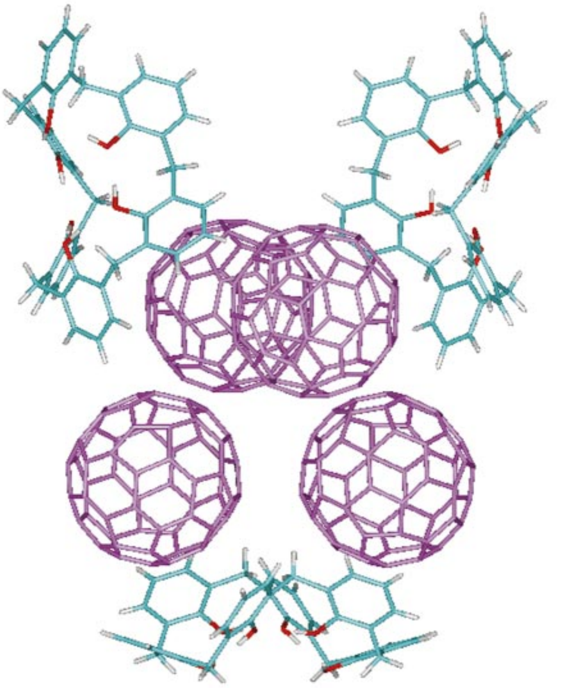


Fig. 2 Extended structure of $(C_{60})_2$(calix[6]arene) showing the double cone conformation of the calix[6]arene and interfullerene interactions.[11]

Calix[5]arenes and oxacalix[3]arenes

For the calix[6,8]arenes pre-organisation of the calixarenes *via* torsion along the C–CH_2–C moieties within the macrocycle is required for complexation with C_{60}. While both the calix[4,5]arenes prefer the cone conformation, and are thus organised for host–guest formation, only the cavity of the calix[5]arene is large enough for binding C_{60} (but *exo*-cavity complexation is also possible—see below). The oxacalix[3]arenes require minimal torsion for complementarity of curvature with C_{60}.[29]

Calix[5]arene itself forms a 1 : 1 complex with C_{60},[11,21] and other calix[5]arenes give either 1 : 1 or 2 : 1 complexes.[22] Molecular mechanics gives maximum overlap of the π-cloud of the calixarenes with the C_{60} where there is alignment of a C_5 axis of the fullerene with the C_5 axis of the calixarene.

p-Benzylcalix[5]arene and *p*-benzylhexahomooxacalix[3]arene form 2 : 1 complexes with C_{60} from toluene solutions, as the octa-toluene solvate in the case of the calix[5]arene. In both structures the fullerene is shrouded by two staggered, *trans*-host molecules in cone conformations either with dangling benzyl groups, calix[5]arene, or edge on to the fullerene benzyl groups, oxacalix[3]arene, Fig. 3.[29] Either the benzyl groups are now directed away from the fullerene, θ = 180°, or are such that there are C–H···fullerene interactions, θ = 90°, Scheme 2. In both C_{60} structures, the alignment of the symmetry axis of the calixarene with the same symmetry element of C_{60}, C_5 and C_3, respectively, highlights the importance of symmetry matching in designing host molecules for fullerenes. This maximises the points of contact and efficiency of π–π interactions between the two interacting moieties. The only other authenticated structure with C_{60} encapsulated by two container molecules, hence precluding interfullerene contacts, is a calix[5]arene complex with three methyl and two iodo groups (1,3 disposition) in the *p*-positions of the upper rim.[22] The synthesis of covalently linked biscalix[5]arenes capable of encapsulating C_{60} or C_{70} has also been reported with binding constants indicating that C_{70} is bound preferentially.[23]

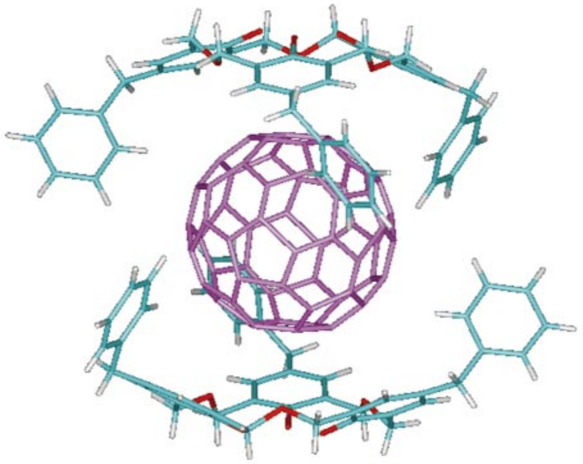
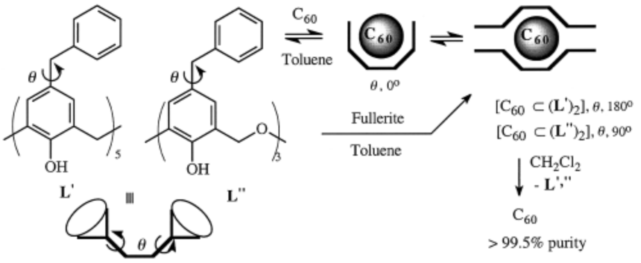


Fig. 3 The supermolecule $[(C_{60})(p\text{-benzylhexahomooxacalix[3]arene})_2]$.[29] The encapsulation of the fullerene by two oxacalix[3]arenes precludes the formation of extended supramolecular arrays *via* interfullerene interactions as were seen in Fig. 2.



Scheme 2

Even a 1 : 1 mixture of calixarenes, L′ or L″, with C_{60} in toluene, Scheme 2, still gives the 2 : 1 complexes in the solid, and in both cases it is also the exclusive complex formed when treating a fullerite mixture in toluene, from which C_{60} [> 99.5% purity (HPLC)] can be readily isolated on the addition of methylene chloride and represents an effective one step purification of C_{60}.

Solution studies on complexation of L′ with C_{60} in toluene give an association constant, K_1 = 2800 ± 200 $dm^3\ mol^{-1}$ at low concentrations of the calixarene, and K_2 = 230 ± 50 $dm^3\ mol^{-1}$ at higher concentrations. This is consistent with the initial formation of the 1 : 1 complex $[C_{60} \subset (L')]$, followed by the formation of a 2 : 1 supermolecule, [$C_{60} \subset (L')_2$], and is in agreement with densitometry studies which support the displacement of two toluene molecules from L′ in toluene and formation of 1 : 1 complex in solution, $q = 0°$, Scheme 2.[24] The K_1 values for related 1 : 1 [$C_{60} \subset$ (substituted-calix[5]arene)] complexes studied by Fukazawa and coworkers are 2120 and 76 ± 5 $\times 10^3$ dm^3 mol^{-1} in toluene.[22] In these studies there was no report of a second equilibrium. Similar UV–VIS studies involving L″ suggest the presence of more than one species in solution, the overall 2 : 1 association constant is estimated to be *ca.* 100 dm^3 mol^{-1}. In contrast, Fuji and coworkers[20] obtained a 1 : 1 association constant of 35.6 dm^3 mol^{-1} for a related oxacalixarene (R = Bu^t, **2**; or 64 ± 5 dm^3 mol^{-1} in an independent study[21]) and C_{60} in toluene, and obtained 1 : 1 complexes rather than a 2 : 1 complex in the solid state, showing interfullerene interactions.[20] Other solution studies on oxacalix[3]arenes and calix[5]arenes have also been reported[21,25] including the electrochemical behaviour.[5]

Calix[4]arenes and resorcina[4]arene

Shinkai and coworkers screened a wide range of calixarenes for complexation of C_{60} in toluene and found little change in the electronic spectrum for the calix[4]arenes, and thus no evidence for complexation.[21] Nevertheless, some calix[4]arenes have been shown to form stable crystalline complexes with C_{60}, including (i) *p*-phenylcalix[4]arene which has a toluene molecule in the cavity, the overall structure dominated by fullerene–fullerene and *exo*-calixarene–fullerene interactions,[42] (ii) *p*-bromocalix[4]arene propyl ether, the structure showing very close interfullerene contacts in a columnar structure, which most likely results in opposing induced dipoles from the unidirectionally aligned calixarenes,[26] and (iii) *p*-iodocalix[4]arene benzyl ether where the fullerenes are ordered without appreciable interfullerene interactions.[27] There is also a resorcin[4]arene, R = CH_2CH_2Ph, **2**, which has a molecular capsule derived from head to head hydrogen bonding of two resorcinarenes and propan-2-ol molecules, with the fullerene arranged in columns.[30] The fourfold symmetry of calixarenes and resorcinarenes relates to complexation of octaphenylcyclotetrasiloxane, [$\{SiPh_2(\mu\text{-}O)\}_4$], with C_{60} in toluene. The 1:1 supramolecular complex is a hemi-toluene solvate where the fullerenes are arranged in double columnar arrays shrouded by edge on siloxanes, the siloxanes interlocking by one of the phenyl groups of one molecule residing in the cavity of another.[43]

Cyclotriveratrylene

Complexation of C_{60} in toluene solutions of CTV results in polymeric structures in the solid, either a fullerene rich phase $(C_{60})_{1.5}$(CTV), or a 1 : 1 phase (C_{60})(CTV).[31,32] The structures are dominated by fullerene–fullerene interactions, and each CTV has a C_{60} associated within the cavity of the CTV as a 'ball and socket' nanostructure. For $(C_{60})_{1.5}$(CTV) the fullerenes collectively comprise a two dimensional close packed array with half of the fullerenes devoid of CTV, Fig. 4.[31] Solvated host–guest species, [(CTV)(C_{60})], are formed first in solution. This results in polarisation of the fullerene promoting aggregation which is evident by a resonant interfullerene transition band as 475 nm. The substituted analogue **4**, R = allyl, with C_{60} shows only solvated host–guest species.

The incorporation of aromatic pendant arms on CTV leads to strong binding of C_{60}, that of *N*-methylpyrrole showing the highest association constant, 48 × 103 dm^3 mol^{-1} in benzene. With six benzoyl arms a 1:1 complex forms in the solid state with two host molecules surrounding one fullerene, with a second 'bare' C_{60} in the lattice.[33] The host molecule, R = benzoyl, **4**, can be used to retrieve C_{60} from fullerite.[33] A planar analogue of CTV with a central six membered ring (without the bridging methylene units of CTV) forms a 1 : 2 complex in the solid state with isolated fullerenes surrounded by four planar molecules.[44]

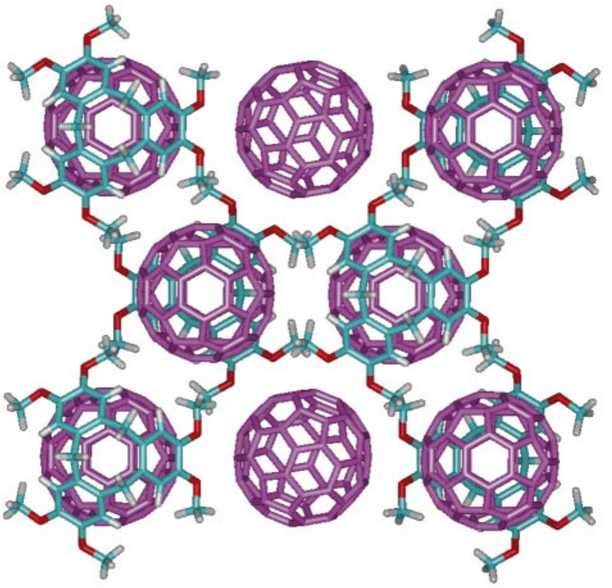
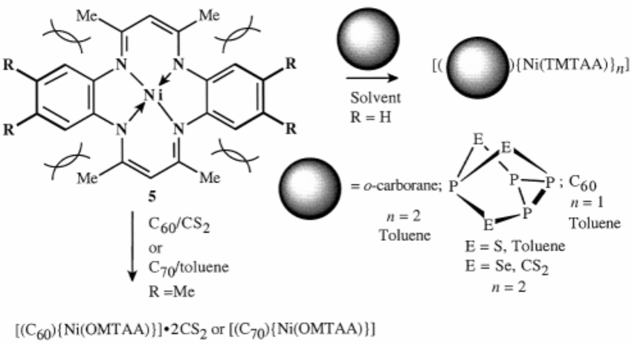


Fig. 4 Crystal packing of $(C_{60})_{1.5}(CTV)\cdot C_7H_6$.[31]

Nickel(II) macrocycles

Compound **5**, R = H, has two divergent concave surfaces in a saddle shape arrangement which arises from the otherwise unfavourable interactions between the methyl groups and the adjacent H-atoms on the aromatic rings.[34] It can act as a divergent heterotopic receptor towards C_{60}, or it can self-associate into dimeric species which in turn can act as a divergent homotopic receptor, for smaller clusters such as *o*-carborane (see below),[34] and also with the phosphorus chalcogenides P_4(S or Se)$_3$, Scheme 3.[34,45]



Scheme 3

In the structure of (C_{60})Ni(TMTAA) (TMTAA = tetramethyltetraazaannulene), Scheme 3, two host molecules shroud the fullerene such that a fullerene is in the saddle of one Ni(TMTAA) molecule with the methyl groups directed towards it and in the opposite saddle of another Ni(TMTAA) molecule, the overall host–guest contacts form a continuous zigzag array, Fig. 5, with the fullerenes forming a corrugated two dimensional sheet.[34] Cu(II) and Zn(II) TMTAA molecules similarly bind C_{60} and are isostructural with the Ni(II) analogue.[46] For R = Me, **5**, (= OMTAA) a 1 : 1 complex is formed with C_{60}, isolated as [Ni(OMTAA)C_{60}](CS_2)$_2$. The extended supramolecular array is based on linear chains of close contact C_{60} molecules, and linear chains of π-stacked alternating molecules of C_{60} and Ni(OMTAA) with adjacent chains running in opposite directions and thus cancelling out dipole moments, Fig. 6. Surprisingly the same macrocycle forms a 1:1 complex with C_{70} which is isostructural with the C_{60} complex of Ni(TMTAA), *viz.* zigzag alternating C_{70}–Ni(OMTAA) chains with corrugated sheets of close contact C_{70} molecules.[47] In all of

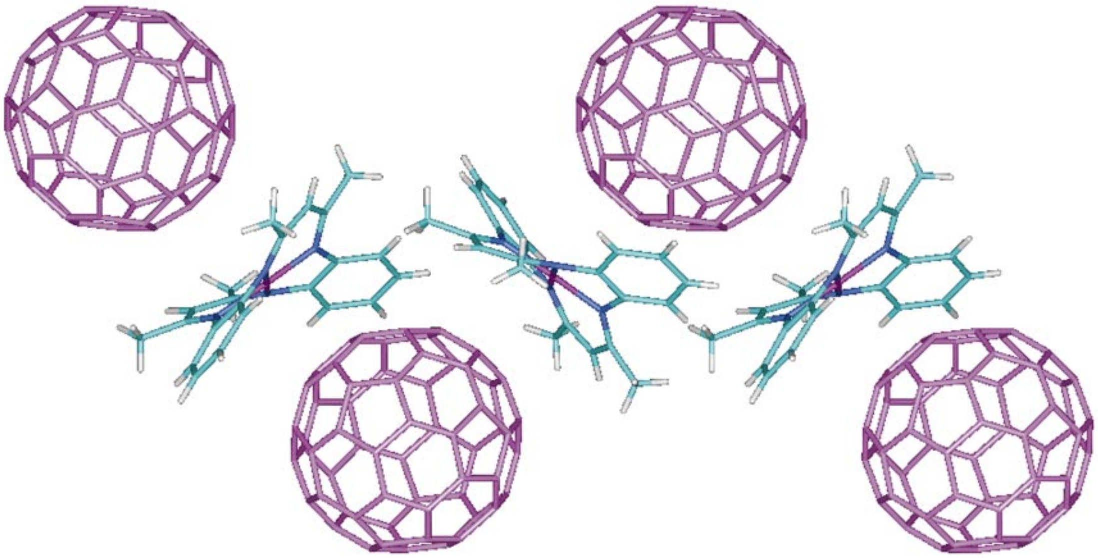


Fig. 5 The continuous zigzag array of [(C_{60}){Ni(TMTAA)}], highlighting the host–guest interactions between the C_{60} and both types of Ni(TMTAA) saddle.[34]

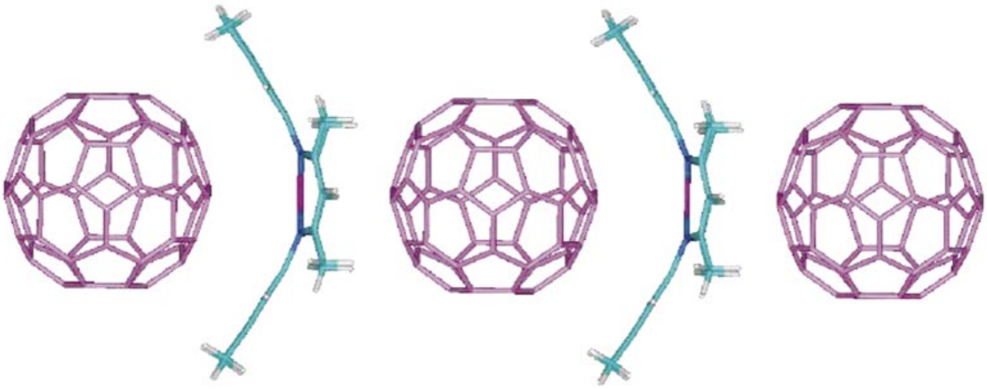


Fig. 6 The linear chains of π stacked C_{60} and Ni(OMTAA) molecules in [{Ni(OMTAA)}(C_{60})]·$2CS_2$.[47]

these Ni(II) macrocycle structure there are no significant contacts between the metal centres and the fullerenes. As in other systems there is evidence for the formation of 1:1 solvated supermolecules in solution which then go on to form micelle like species.[28,32,45] A planar Co(II) octaethylporphyrin also forms a 2:1 complex with C_{60} (and C_{70} and $C_{60}O$) in a 'bent metallocene' arrangement, with contacts of the metal to the fullerene in between van der Waals type interactions and a direct metal–fullerene interaction.[3] Here only one face of the macrocycle interacts with a fullerene, unlike in the C_{60} and C_{70} structures of Ni(TMTAA) and Ni(OMTAA). A silica supported zinc(II) tetraphenylporphyrin used in a HPLC column can separate metallofullerenes from C_{60} and higher fullerenes.[48]

Mesoporous silica studies

In addressing the difficulties in identifying and encouraging host–guest interactions of C_{60}, a new amorphous mesoporous silica (= $MPSiO_2$) with sufficient pore size to allow mobilisation of C_{60} was developed.[28] The material has a narrow range of pores, *ca*. 5.4 nm, which are large enough to accommodate small aggregates of fullerenes and associated host molecules, at least for small aggregates where conventional particle size analysis would be difficult. When this material is loaded with C_{60} it offers a qualitative test for supramolecular complexation of the fullerene, and the silica devoid of C_{60} is a material for uptake of preformed micelle like species $\leqslant$5.4 nm in diameter.

Contact of magenta coloured toluene solutions of C_{60} with $MPSiO_2$ results in magenta colouration of the silica. Subsequent addition of toluene solutions of a variety of calixarenes and CTV yields brown–yellow material which shows a new broad resonant interfullerene transition band at *ca*. 450 nm. This is consistent with the formation of aggregates of C_{60}, most likely as part of micelle-like structures with the fullerene cores surrounded by host molecules in the pores of $MPSiO_2$, represented in Fig. 7. As an example, the addition of CTV solutions to the mesoporous silica with premobilised C_{60} gives a spontaneous change in colour (magenta to brown) whereas addition of preformed solutions of C_{60} and CTV which are

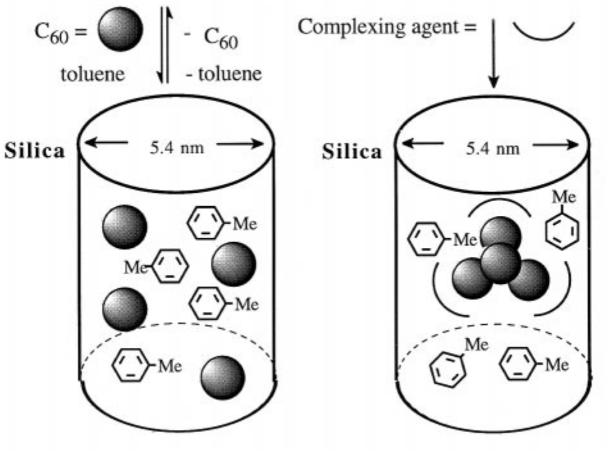


Fig. 7 Schematic representation of the formation of C_{60}–host aggregates inside the pores of mesoporous silica.

brown show little mobilisation of fullerenes into the channels, and thus the micelle like species present in the solution have diameters $\geqslant$ 5.4 nm.[28] Fullerene C_{60} has also been incorporated into molecular sieves (gas phase diffusion).[49]

Aggregation of fullerenes has been suggested in the incorporation of C_{60} into membranes,[50] and fullerene aggregates (mean diameter 10 nm) have been established in the solubilisation of C_{60} in aqueous media, with a band at 440 nm assigned to aggregate formation (*cf.* 450 nm for the above systems).[51] Aggregation of C_{60} is also prevalent in dissolution of the fullerene in a wide range of solvents, with significant reduction in its solubility.[52]

Carboranes

The C–H groups of carboranes are acidic[9] and intermolecular C–H···O,N hydrogen bonding is important in the supramolecular chemistry of carboranes, Fig. 8.[53–57] This includes bifurcated hydrogen bonding for 1,2-di(methoxy)benzenes and *o*-phenanthroline,[56,57] Fig. 8(b). Also important are the C–H···π-aromatic ring interactions, Fig. 8(c), where the $C–H_{carborane}$ is directed towards the centroid of an aromatic ring as a Coulombic interaction between a polarised C–H bond and the basic π-electrons of an aromatic ring, and can be regarded as a non-classical hydrogen bond.[53] This is calculated to be energetically favoured by 2.74 kcal mol^{-1},[53] at the 6-31G* level, for the model system of benzene interacting with *o*-carborane. The protons on carbon of the carborane have a residual charge of +0.299 *cf.* 0.068–0.091 for the hydrogen atoms on boron. Such non-classical hydrogen bonding has precedence in dichloromethane[40] inclusion complexes of calix[4]arenes. A less common type of interaction in complexes of carboranes involves B–H···H–N interplay with amines, Fig. 8(d).[58]

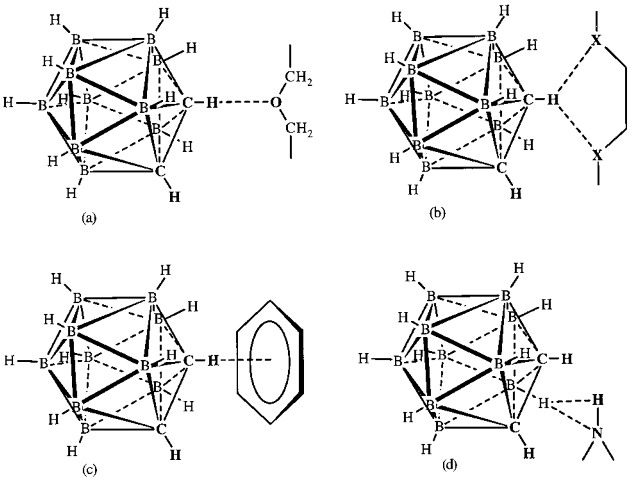
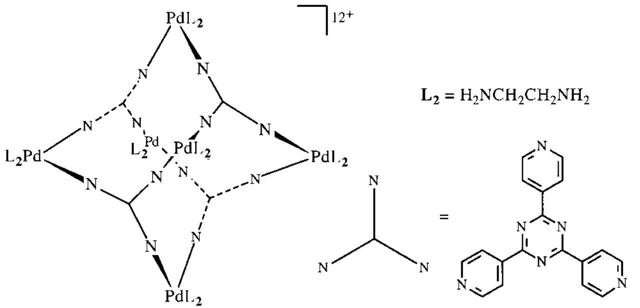


Fig. 8 Established types of interactions of carboranes (shown for the *o*-isomer): (a) classical C–H···O hydrogen bond, (b) bifurcated hydrogen bond, X = O (1,2-dimethoxylbenzene systems), N (in *o*-phenanthroline), (c) non-classical C–H···π hydrogen bond, and (d) B–H···H–N interplay.

Theoretical calculations on a model system of *o*-carborane and 1,2-dimethoxybenzene give the $C–H_{carborane}\cdots(O)_2$ interaction energetically favoured by 5.48 kcal mol^{-1}.[57] This is close to double the calculated energy of 2.74 kcal mol^{-1} for a single $C–H_{carborane}\cdots\pi$ interaction.[53] This highlights a delicate balance between the carborane being involved in bifurcated hydrogen *versus* C–H···π bonding in the cavity of the CTV.

Host–guest chemistry

The first host–guest complexes of carboranes were the 1:1 complexes with α-, β- and γ-cyclodextrin, and a 2:1 complex for α-cyclodextrin.[59] Presumably in the 2:1 complex the carborane is shrouded by two host molecules, [(*o*-carborane)⊂(α-cyclodextrin)$_2$], which is related to C_{60} forming a 2:1 complex for the larger γ-cyclodextrin, noting the smaller cyclodextrins here do not form complexes with the fullerene.[35] The self-assembled ionic capsule, **6**, arising from interplay between (ethylenediamine)palladium(II)$^{2+}$ ions and four triply bridging pyridyl ligands, with the metal centres at the corners of an octahedron and the pyridyl ligands centred at the corners of a tetrahedron, has a large internal volume capable of binding four *o*-carborane molecules, presumably as a tetrahedral aggregate.[60] This encapsulation renders the carboranes water soluble, as do the cyclodextrin complexes.[59]



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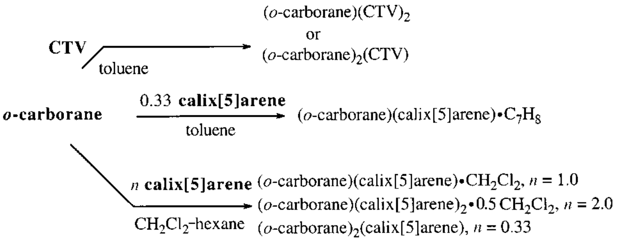
Other systems deal with hydrophobic host container molecules and the natures of the species formed are more substantiated with several X-ray structure determinations. These have shallow cavities and the resulting 1:1 supermolecules are at best described as perched structures. These involve calix[5]arene[56] and cyclotriveratrylene (= CTV).[53,57] Compounds prepared thus far and structurally authenticated are summarised in Scheme 4. A symmetrically tris-allyl substituted analogue of CTV with a deeper cavity forms a 1:1 complex with *o*-carborane,[53] but has yet to be fully characterised. These complexes have IR shifts for $\nu_{C–H}$ of the carborane to lower energy, and a shift to higher energy for $\nu_{B–H}$,[53–57] consistent with the presence of non-classical hydrogen bonding for the C–H bonds with dispersal of the extra charge on the carbons resulting in strengthening of the B–H bonds.



Scheme 4

The calix[5]arene–*o*-carborane complexes have a common structural motif in the solid state with a 1:1 ball and socket nanostructure comprised of the carborane in a cone shaped calixarene.[56] The carboranes interact with the calixarene most likely *via* the non-classical C–H···π hydrogen bonding, Fig. 8(c), and in all cases the C–H vectors of the carborane are directed towards aromatic rings of the host molecule. The interplay of the supermolecules with the other components, solvent, additional calixarene or carborane builds up the supramolecular arrays. In (*o*-carborane)(calix[5]arene)·CH_2Cl_2[56] the ball-and-socket units organise into larger dimeric supermolecules with calixarene hydroxy groups facing each other, forming a hydrophilic core shown in Fig. 9.

In (*o*-carborane)(calix[5]arene)·C_7H_8[56] the (*o*-carborane)∩(calix[5]arene) supermolecules stack along the same direction. The *endo*-cavity *o*-carborane of one supermolecule has contacts to the hydroxy groups of the next (*o*-carborane)∩(calix[5]arene). The calixarene rich complex (*o*-carborane)(calix[5]arene)$_2$·0.5CH_2Cl_2[56] has a remarkable structure with both calix-

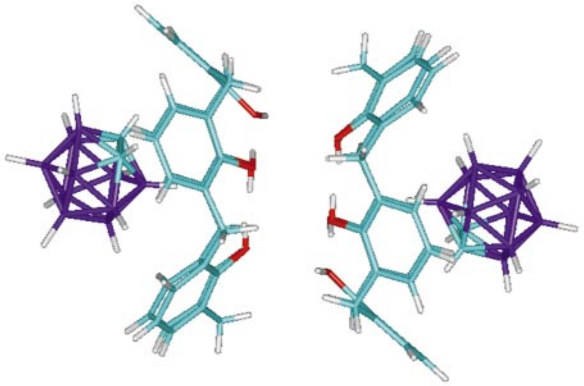


Fig. 9 The dimeric [(*o*-carborane)∩(calix[5]arene)]$_2$ nano-structure of [(calix[5]arene)(*o*-carborane)]·CH_2Cl_2. The dimer acts as a divergent receptor.[56]

[5]arene molecules acting as host molecules in quite distinct manners. One calixarene acts as a host molecule for the *o*-carborane, forming the ball-and-socket arrangement while the other acts as a secondary host for the (*o*-carborane)∩(calix[5]arene) assembly *via* $\pi\cdots\pi$ interactions forming the [(*o*-carborane)∩(calix[5]arene)]∩(calix[5]arene) nano-structure illustrated in Fig. 10. The complexation of a host–guest species by a secondary host is relatively uncommon.

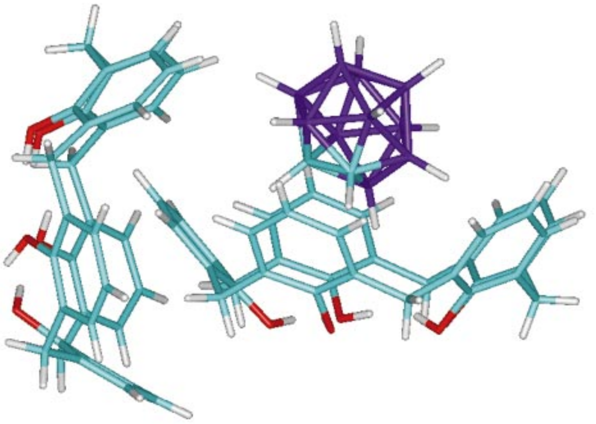


Fig. 10 The [(*o*-carborane)∩(calix[5]arene)]∩(calix[5]arene) nanostructure of [(calix[5]arene)$_2$(*o*-carborane)·0.5CH_2Cl_2].[56]

In the structure of (*o*-carborane)$_2$(calix[5]arene)[56] the carborane forms both *endo* and *exo* associations with the host calixarene, Fig. 11, with the second *o*-carborane forming a weak association with the hydroxy groups of the calixarene through one triangular face of the icosahedron. The *endo* and *exo* carboranes form pairs of cage molecules. The association of carboranes is also prevalent in the 1 : 1 complex of aza-18-crown-6 with *o*-carborane which forms an intercalation compound (see below),[55] and in the interplay between the four carboranes in the ionic capsule, **1**.[60]

In all the structures of the supermolecules [(*o*-carborane)∩(calix[5]arene)] the cage molecule is not a snug fit in the calixarene and thus while the formation of these complexes in solution is entropically driven there is some degree of torsional flexibility in the cone conformation of the calixarene to adapt to both the interactions with the cavity guest and the surroundings. Fullerene C_{60} in contrast has an excellent complementarity of curvature with calix[5]arenes in general (see above) and the calixarenes are in symmetrical conformations with little or no torsion mobility. In contrast, host–guest complexes of CTV and *o*-carborane clearly show a more snug fit of the cage species in the cavity of the host molecule, *i.e.* there is greater complementarity of curvature of the two supramolecular synthons. Surprisingly CTV also has complementarity with C_{60}[31,32] and the ability of CTV to accommodate spherical like molecules with different diameters (8 Å carborane *cf.* 10 Å C_{60}) relates to a shallower cavity of the rigid CTV relative to the diameter of the host molecule.

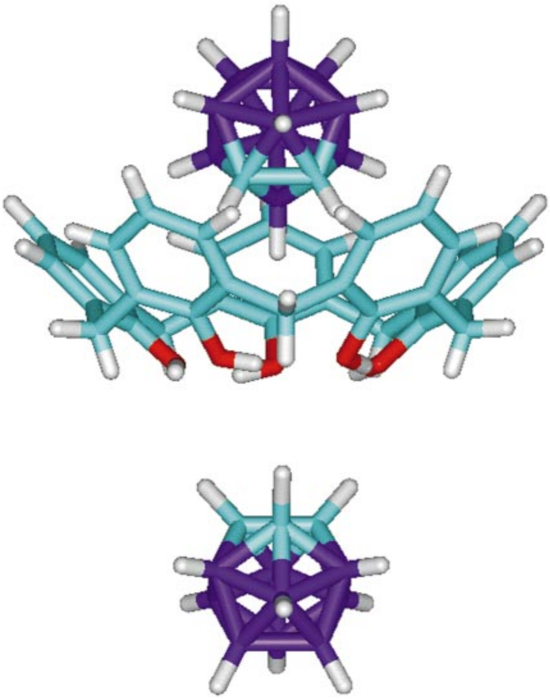


Fig. 11 The *exo* and *endo* associated *o*-carboranes of [(*o*-carborane)$_2$(calix[5]arene)].[56]

The structure of the 2 : 1 complex of CTV and *o*-carborane, Scheme 4, is comprised of 1 : 1 supermolecules of CTV and *o*-carborane, (*o*-carborane)∩(CTV),[53] the other CTV forming a zigzag π-stacked column with the inter-CTV contacts at the van der Waals limit. This type of association of CTV molecules is common even in inclusion complexes of CTV where the guest species are not in the cavities of the CTV molecules, the so called α-phase for CTV.[61] Thus the formation of complexes of *o*-carborane, and also C_{60}, with the guest species in the cavity of the CTV represents a major development in CTV chemistry. Non-bonded contact distances of the supermolecule (*o*-carborane)∩(CTV) show that three hydrogens of a triangular face of the icosahedron are directed towards the aromatic rings of the CTV albeit unsymmetrically, Fig. 12. This most likely arises from the energetically favoured $C–H_{carborane}\cdots\pi$ hydrogen bonds to two aromatic rings of the CTV *versus* repulsion between the B–H and the third aromatic ring of the CTV.

In (*o*-carborane)$_2$(CTV)[57] one of the carborane molecules forms three symmetry equivalent bifurcated hydrogen bonds to the methoxy groups of three equivalent CTV molecules, Fig. 8(b).[57] All three interactions originate from the same triangular face of the carborane icosahedron and, due to symmetry imposed disorder, each of the three carborane centres involved has 2/3 carbon and 1/3 boron character. A puckered hexagonal 2D hydrogen bonded network is formed, shown in Fig. 13. All CTV molecules within the grid, and indeed throughout the crystal lattice, have their bowl vertices pointing in the same direction. The second *o*-carborane molecule resides in the receptor sites forming a ball-and-socket (*o*-carborane)∩(CTV) nanostructure throughout the hydrogen bonded grid. The host–guest interplay within the supermolecule (*o*-carborane)∩(CTV) in the 2 : 1 complex is remarkably different to that found in (*o*-carborane)(CTV)$_2$. Here the alignment of the carborane within the CTV cavity is symmetrical with all carborane C–H vectors directed away from the CTV aromatic rings, Fig. 13.[57] However, the difference is consistent with the inherently weak interactions holding the supermolecule together.

^{1}H NMR spectra recorded in toluene for the 2 : 1 complex [(*o*-carborane)(CTV)$_2$] show rapid exchange processes occurring

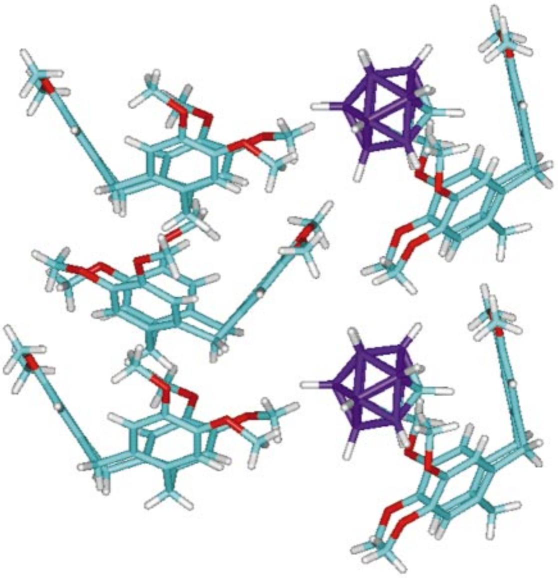


Fig. 12 Section of the crystal structure of [(*o*-carborane)(CTV)$_2$] showing the host–guest species and π stacked CTV molecules.[53]

between complexed and uncomplexed carborane. No significant changes to the ^{1}H NMR of CTV in the complexed and uncomplexed systems were evident. Variation in mole fraction of the carborane relative to CTV showed a non-linear relation with the chemical shift of the carborane C–H protons which implies that complexation is not a simple 1:1 supermolecule formation. The inability to fit the NMR data to this simple model indicates that *o*-carborane binds both *endo* and *exo* to the cavity of the CTV.

The nickel(II) macrocycle Ni(TMTAA), Scheme 3, can act as a divergent heterotopic receptor towards C_{60},[34] or it can self-associate into dimeric species which in turn can act as a divergent homotopic receptor, and this is found in the complex of *o*-carborane, and also for the phosphorus chalcogenides P_4(S or Se)$_3$.[34,46] In the solid state structure the *o*-carborane resides in the saddle of two Ni(TMTAA) molecules as bent sandwich like supermolecules with the two host molecules adjacent to each other, Fig. 14. The sandwich supermolecules form extended structures by locking together the pendant phenyl rings of one Ni(TMTAA) of one supermolecule with that of Ni(TMTAA) of another with the methyl groups all directed towards the cage. Alternatively the structures can be viewed as two associated Ni(TMTAA) molecules acting as a divergent receptor for two *o*-carboranes. The two Ni(TMTAA) moieties are at 90° to each other, and this is driven by the complementarity of curvature of the interlocking components, as well as by Ni···π-arene interactions.

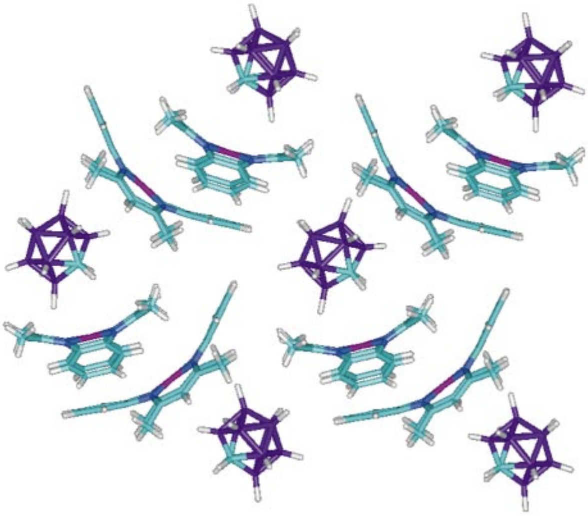


Fig. 14 Crystal stucture of [(*o*-carborane){Ni(TMTAA)}$_2$].[34]

Diaza-18-crown-6, [1,4,10,13-tetraoxa-7,16-diazacyclooctadecane] forms a 1 : 1 host–guest complex with *o*-carborane,[55] Scheme 5. While aza-18-crown-6, [1,4,10,13-tetraoxa-7-azacyclooctadecane] gives a 1 : 1 complex it is an intercalation compound with alternating layers of *o*-carboranes and crown ethers (see below). The striking difference in structure

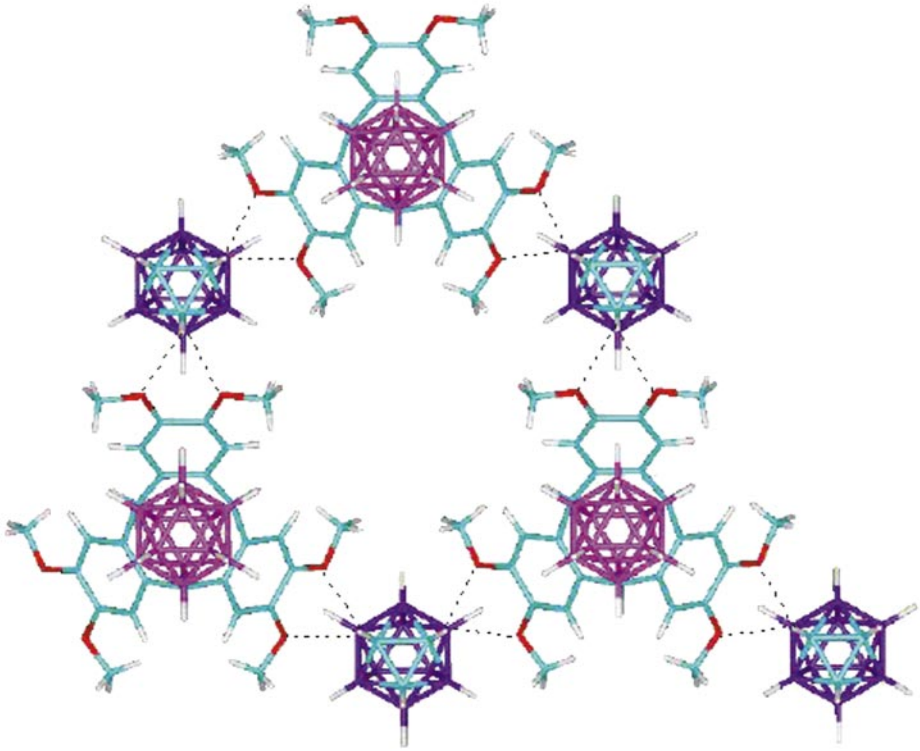
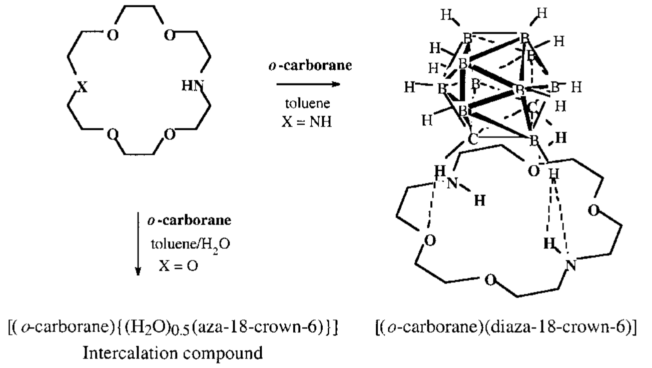


Fig. 13 Section of the crystal structure of [(*o*-carborane)$_2$(CTV)], showing the 2D hexagonal network formed through bifurcated B/C–H···O hydrogen bonds around the CTV, and guest carboranes (in pink).[57]



Scheme 5

between the two complexes reflects the delicate balance between weak intermolecular interactions, host–host, host–guest and guest–guest, which are within the realms of crystal packing forces.

In the supermolecules of [(*o*-carborane)∩(diaza-18-crown-6)], three H-atoms of a triangular face of the *o*-carborane polyhedron bearing the two carbon atoms reside above the diaza-18-crown-6. The two components are linked through $C–H_{carborane}\cdots O$ hydrogen bonding interactions, Fig. 8(a) coupled with B–H···H–N, Fig. 8(d), interplay. The H···H distance is close to the upper limit for unconventional dihydrogen bonds established for B–H···H–N contacts in aminoboranes.[58] The $O\cdots H_{carborane}$ distances are similar to those found in the *o*-, *m*-, and *p*-carborane adducts with HMPA.[54] A $\nu_{C–H}$ shift of the carborane of 33 cm^{-1} to lower energy and $\nu_{B–H}$ shift to higher energy of 25 cm^{-1} is observed.

Theoretical studies give the docking of the carborane with diaza-18-crown-6 to be favoured by 9.32 kcal mol^{-1}.[55] The optimised C–H···O distances at 2.471 Å compare well with experimental values at 2.49 Å, whereas optimised B–H···N and B–H···H–N at 2.924 and 2.721 Å, respectively are much longer than experimental values at 2.34 and 2.15 Å, and analogous distances in aminoboranes.[58] The reason for this is unclear. The high error in the position of the H-atom attached to nitrogen in [(*o*-carborane)∩(diaza-18-crown-6)] may be a problem, and the short B–H···H–N contacts for aminoboranes[58] arise from residual negative charge on the H-atoms attached to boron, *cf.* positive charge in [(*o*-carborane)∩(diaza-18-crown-6)].

^{1}H NMR in benzene at 25 °C for a range of concentrations of diaza-18-crown-6 (0.0–0.14 M) for a fixed *o*-carborane concentration (0.07 M) resulted in shifts in the *o*-carborane C–H resonance from δ 2.05–2.20 and the N–H resonance for diaza-18-crown-6 from δ 2.26–2.85. A near linear relationship indicate a low equilibrium constant (< 5 $dm^3\ mol^{-1}$), eqn. (1).

$$o\text{-carborane} + \text{diaza-18-crown-6} \xrightleftharpoons{\text{benzene}} [(o\text{-carborane}) \cap (\text{diaza-18-crown-6})] \quad (1)$$

For *m*-carborane small differences in the chemical shift for C–H relative to a 1 : 1 mixture of the carborane and diaza-18-crown-6 indicate little or no complexation. Furthermore there is no complex formation in the solid state. Presumably the ability for *m*-carborane to form two C–H···O interactions within the same supermolecule while maintaining the crown conformation of the host is lost. The different binding prowess of *o*- and *m*-carborane suggests that separation of isomeric carboranes *via* selective binding is possible rather than using conventional chromatography.[9] Interestingly, ^{1}H NMR data show the corresponding *N*,*N*′-dibenzyldiaza-18-crown-6 forms a complex with *o*-carborane in benzene but attempts to isolate this complex were unsuccessful.[55]

Crystal structures of the 1 : 1 complexes of hexamethylphosphoramide (HMPA) with *o*-, *m*- and *p*-carboranes derived from toluene solutions have been reported.[54] The three complexes show extensive C–H···O hydrogen bonding and all adopt quite different supramolecular structures, commensurate with their differing arrangement of C–H sites. The *o*-isomer gives a dimeric structure, $C–H_{carborane}\cdots O$ 1.54(4)–1.60(4) Å, whereas the other isomers give polymeric structures with the HMPA O-centre bridging to two C–H groups from different carborane molecules (see below).

Tetrameric macrocycles mercuracarborand-4 and octaethylmercuracarborand-4 can also act as hosts for *closo*-$B_{12}H_{12}^{2-}$, as well as related globular borane anions *closo*-$B_{10}H_{10}^{2-}$ and *closo*-$B_{10}I_{10}^{2-}$.[7]

Extended arrays

The polymeric structures of [(*m*-, *p*-carborane)(HMPA)][54] have the O-centre of HMPA bridging to two C–H groups from different carborane molecules. Polymeric structures are also found in (*o*-carborane)$_2$(CTV) and (C_{70})(*o*-carborane)(CTV)·1,2-dichlorobenzene.[57] Here hydrogen bonding is also prevalent, but involving bifurcated units, Fig. 8(b), rather than the classical hydrogen bond, Fig. 8(a). In the ternary system C_{70}–*o*-carborane–CTV–1,2-dichlorobenzene, each *o*-carborane interacts with two CTV molecules and in turn, each CTV is hydrogen bonded to two carboranes forming an infinite helical chain, Fig. 15. The CTV cavities are directed outwards from the helices, and each CTV complexes one C_{70} molecule. It is noteworthy that in the absence of carborane, C_{70} fails to form a complex with CTV, in contrast to C_{60} which forms two complexes, (C_{60})(CTV) and $(C_{60})_{1.5}$(CTV),[31,32] and that C_{60}

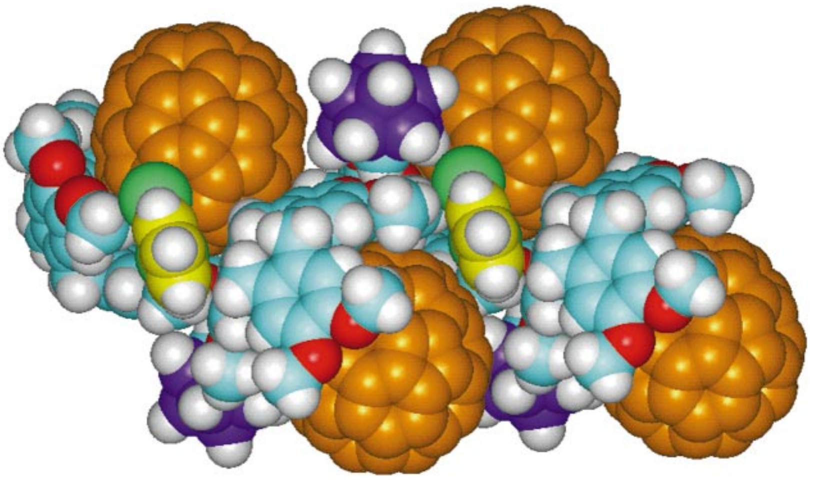


Fig. 15 Side view of a helix in [(C_{70})(*o*-carborane)(CTV)·1,2-dichlorobenzene] showing the binding of C_{70} molecules within the CTV bowls.[57]

and CTV in the presence of *o*-carborane also affords $(C_{60})_{1.5}(\text{CTV})$.

Inclusion/intercalation chemistry

Monoaza-18-crown-6 also gives a 1 : 1 complex, Scheme 5, with *o*-carborane but this is an intercalation complex, Fig. 16.[55]

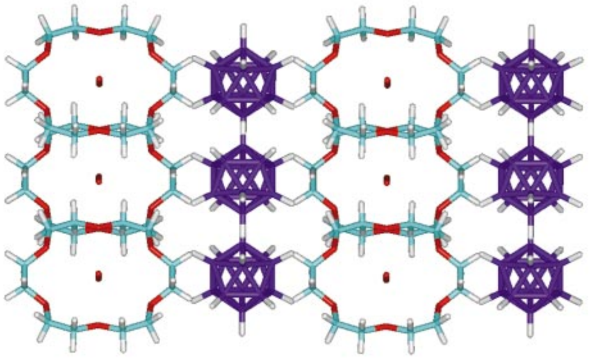


Fig. 16 Projection of $[(o\text{-carborane})\{(H_2O)_{0.5}\subset(\text{aza-18-crown-6})\}]$.[55]

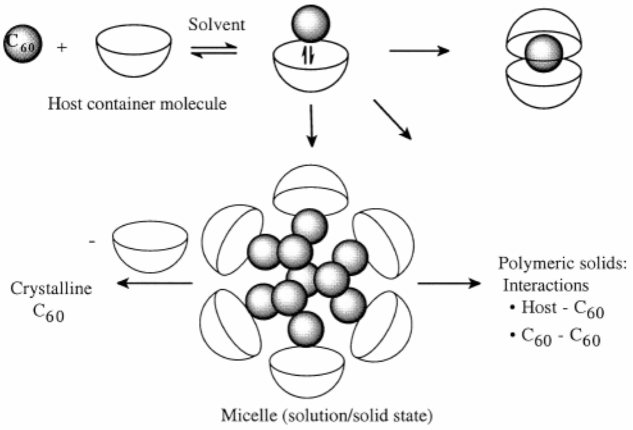
Moreover, the crown ether requires a water molecule in its cavity for the complex to form, and the isolated material has a 50% occupancy of water in the cavity, $[(o\text{-carborane})\{(H_2O)_{0.5}\subset(\text{aza-18-crown-6})\}]$. ^{1}H NMR of a mixture of the *o*-carborane and crown ether suggests intimate contact of the two components in solution, but in this case host–host and guest–guest interactions are predominant in the solid state. A similar effect was observed in the absence of moisture but in this case no host–guest or intercalation complex was isolated.

Although the structure of $[(o\text{-carborane})\{(H_2O)_{0.5}\subset(\text{aza-18-crown-6})\}]$ is highly disordered, it clearly shows the absence of any close intermolecular contacts like those observed in $[(o\text{-carborane})\cap(\text{diaza-18-crown-6})]$. The polarised clusters form a two dimensional sheet, the nearest intercarborane contacts C/B–H···H–B/C at 2.41 Å.

Future prospects

Both icosahedral C_{60} and carboranes have recently gained prominence in supramolecular chemistry, the cohesion of the supermolecules and solid state structures coming from different interactions. Solvent molecules can also play a vital role in determining the crystal packing and overall topology of the systems. Interactions involving C_{60} or carboranes with themselves, including the formation of micelle like species for C_{60}, and with solvent and other molecules has potential in assembling complex structures. Complexation of other cage molecules is even less established and the ground rules for their confinement are beginning to emerge. Foremost is the use of rigid concave host molecules with complementarity of curvature with the cage molecule; any pre-organisational energy requirements of flexible host molecules may be at the expense of host–guest complexation. Moreover, combining carboranes with container molecules capable of the bifurcated hydrogen bonding with the carborane (such as CTV) offers scope for swaying the competing energies of interaction in favour of host–guest complexes (for cage molecules other than for carborane—demonstrated for C_{70}) where the host–guest components otherwise fail to assemble.

The ability to purify C_{60} by supramolecular complexation is noteworthy. The primary process in the binding of C_{60} is the formation of a host–guest species with polarisation of the fullerene resulting in aggregation of the fullerenes. The fate of this is complete encapsulation of a single fullerene, the formation of a stable micelle-like structure (in mesoporous silica as well as in bulk solution), or the breakdown of the latter resulting in crystallisation of pure C_{60}, Scheme 6. Complexation of higher fullerenes is a synthetic goal as is the complexation of reduced fullerenes, for which the associated complexes are likely to possess unusual properties. This may be possible using the receptor macrocycle M(TMTAA) where the metal centre is easily oxidised, $M^{2+}(\text{TMTAA}) \rightarrow [M^{2+n}(\text{TMTAA})]^{n+}$, *via* electron transfer to the cage molecule. The binding of carboranes is largely through C–H···.O,N hydrogen bonds, and C–H···π-cloud interaction, with some evidence for the association of the carboranes.



Scheme 6

A major advance in supramolecular chemistry is the ability to construct large encapsulating supermolecules assembled by hydrogen bonding[62] or metal coordination chemistry.[60] These systems have very large internal voids and in principle could accommodate, and incarcerate, several fullerenes, as has been achieved for four carboranes,[60] and even larger main group cages species. Finally the supramolecular chemistry has exciting possibilities in stabilising new species, in their separation from complex mixtures, and in generating novel structures and materials.

Acknowledgments

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