ELSEVIER

Coordination Chemistry Reviews
189 (1999) 169–198

COORDINATION
CHEMISTRY
REVIEWS

www.elsevier.com/locate/ccr

Supramolecular assemblies of globular main group cage species

Philip C. Andrews, Michaele J. Hardie, Colin L. Raston*

Department of Chemistry, Monash University, Clayton, Melbourne, Victoria 3168, Australia

Received 23 November 1998; accepted 1 April 1999

Contents

Abstract

A comprehensive survey of the supramolecular chemistry of main group cage species covers their host–guest chemistry, molecular recognition, and inclusion/intercalation compounds. A major part of the review deals with carboranes, *o*-, *m*-, *p*-$B_2C_{10}H_{12}$, which show a remarkable ability to self assemble via hydrogen bonds involving the C–H groups, bifurcated hydrogen bonds ($C–H\cdots(O)_2$) and $C–H\cdots\pi$ interactions. Group 15/16 cage molecules form host–guest supermolecules and extended structures with rigid saddle shape metal macrocycles. Insight into future prospects in this field is presented. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Supramolecules; Host–guest chemistry; Inclusion compounds; Intercalation compounds; Hydrogen bonds; Metal macrocycles

---

* Corresponding author.

E-mail address: c.raston@sci.monash.edu.au (C.L. Raston)

PII: S0010-8515(99)00134-4

1. Overview

This review article covers the recent developments in the supramolecular chemistry of globular species covalently constructed from main group elements, those constructed of carbon, i.e. fullerenes, excepted which are dealt with elsewhere [1] and are beyond the scope of a review in Coordination Chemistry Reviews. The criteria for inclusion in the review are based on consideration of the principles of supramolecular chemistry [2], notably the association of two or more components in an organised array using weak intermolecular forces, van der Waals, hydrogen bonding, electrostatic and labile coordination interactions. Such interactions are inherently weak and some can be comparable to crystal packing forces, as well as competing interactions with solvent, and between the main group cages, and between the other constituents. Gaining control over these interactions is a major challenge and underpins much of the basic aims and ideals of supramolecular chemistry [2]. The range of possible interactions is often extensive even for simple systems, illustrated by the quite distinct nano-structures formed, for example, for *o*-, *m*-, *p*-$C_2B_{10}H_{12}$ [1,2-, 1,7-, 1,12-dicarbadodecaborane(12)] (hereafter *o*-, *m*-, and *p*-carborane).

The definition of a globular or cage like species is a molecule or ion which has three dimensional structure approaching a spherical or isotropic shape without regard to charge distribution or dipole moments. Thus icosahedral, isomeric carboranes *o*-, *m*-, and *p*-carborane, all with different dipole moments, and the mixed Group 15/16 cage molecules such as P_4(S or Se)$_3$ are included and indeed are the main focus of the review. Clearly there are many other main group species which are potential candidates for supramolecular chemistry, including molecular As_3S_3, and ionic species such as $Sb_4Te_4^{4-}$, As_{10}(S, Se or Te)$_3^{2-}$ and M_9^{3-} (M = Sn, Pb, Ge).

The main group supramolecular chemistry encompasses (i) host–guest species in supermolecules and beyond (synonymous with receptor–substrate interactions) where the guest is the main group species; (ii) molecular recognition; and (iii) inclusion and intercalation complexes. The significance of the area relates to the potential of supramolecular chemistry in building up new materials with novel function, and in separation science, for example in the separation of the isomeric mixtures of o-, *m*-, and *p*-carborane which currently relies on conventional chromatographic techniques [3].

2. Carboranes and related cages

Carbon containing polyhedral boranes, the carboranes, are extremely stable cage molecules known for over 30 years. Carboranes and their derivatives have applications in a number of diverse fields such as boron neutron capture therapy, boron carbide-type ceramics, complexing agents for extraction of metal ions, nonlinear optics, conducting polymers and more [4]. The *o*-, *m*-, *p*-carboranes are 12-vertex icosahedral cages whose potential as components or building blocks in supramolecular systems is beginning to be explored [5–16]. Rigid rod-like and trigonal carborane-based molecular building units have been synthesised [5], as well as metallodendrimers [6]. A number of carborane derived macrocycles are known, with the cages linked through their carbon centres by both organic groups [7] and mercury centres [8,9]. The use of covalent chemistry to link up carboranes through organic groups [5–7] is beyond the scope of this review.

Carboranes have high C–H acidity [3] and consequently show potential for hydrogen bonding [10]. Indeed, intermolecular C–H···O hydrogen bonding, including bifurcated interactions, features in much of the supramolecular chemistry of carboranes (Fig. 1a, b) [11–16]. Weak C–H to aromatic ring interactions 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 are also known [13]. The energy of interaction between benzene with *o*-carborane, as a model system and shown schematically in Fig. 1c, has been calculated at the 6–31G* level to be energetically favoured by 2.74 kcal mol^{-1} [13]. The protons on carbon of the carborane have residual charge of + 0.299 cf. 0.068–0.091 for the hydrogen atoms on boron. The calculated CH···benzene ring centroid distance 2.694 Å is comparable with calculations for interactions between hydrogen atoms attached to carbon of chloroform and benzene, which are energetically favoured by 3.94 kcal mol^{-1} [17]. Such non-classical hydrogen bonding has precedence in methylene chloride [18] and water [19] inclusion complexes of calix[4]arenes. This

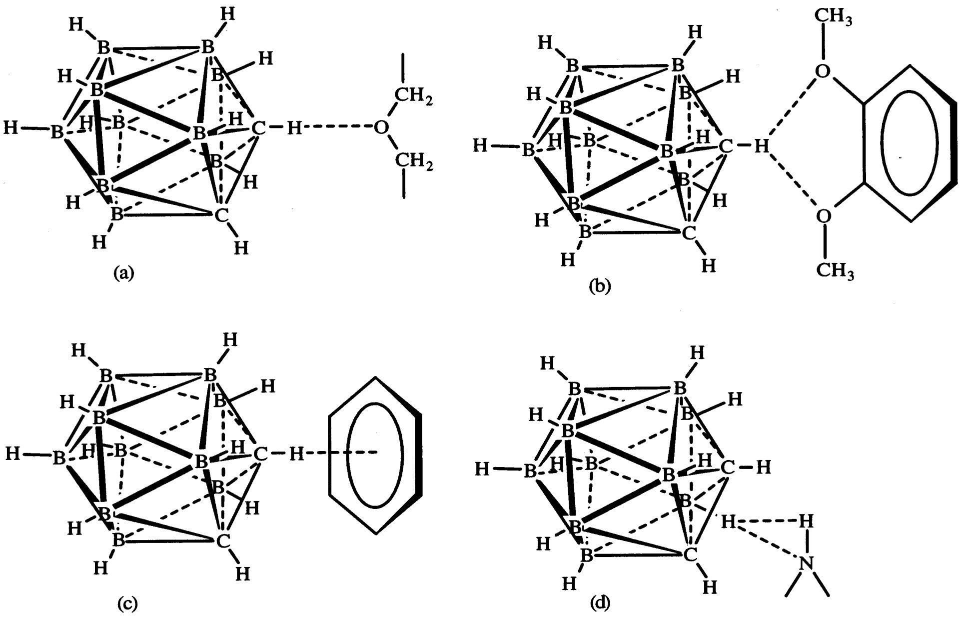


Fig. 1. Established types of interactions of carboranes (shown for the *o*-isomer): (a) Classical C–H···O hydrogen bond; (b) bifurcated hydrogen bond; (c) non-classical C–H···π hydrogen bond; and (d) B–H···H–N interplay.

type of interaction is usually described as a weak non-classical C–H···π hydrogen bond. Another type of interaction in complexes of carboranes involves the less common B–H···H–N interplay with amines [20].

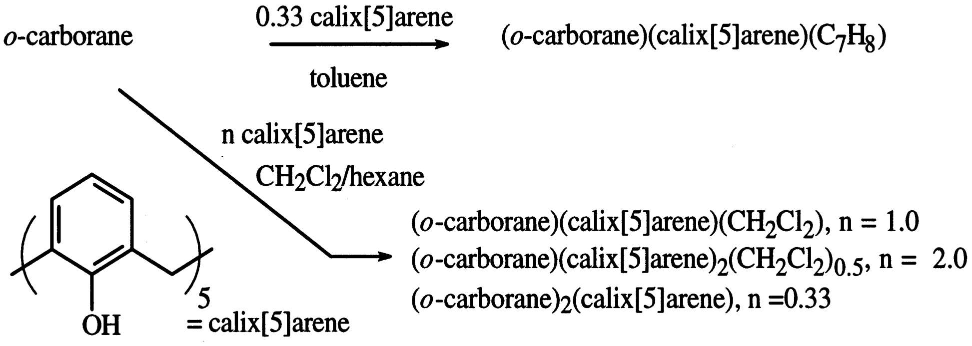
Theoretical calculations on a model system of *o*-carborane and 1,2-dimethoxybenzene give a bifurcated $\mathrm{C{-}H_{carborane}\cdots(O)_2}$ interaction energetically favoured by 5.48 kcal $\mathrm{mol^{-1}}$ (Fig. 1b) [15]. This energy is close to double the calculated energy 2.74 kcal $\mathrm{mol^{-1}}$ found for a single $\mathrm{C{-}H_{carborane}\cdots\pi}$ non-classical hydrogen bond [13]. Calculations on the same model system for the corresponding bifurcated $\mathrm{B{-}H_{carborane}\cdots(O)_2}$ interaction gave it less favoured energetically at 1.13 kcal $\mathrm{mol^{-1}}$, as would be expected by the lower charge on H-atoms attached to boron [13]. However, this energy corresponds to a saddle point on the hyper-energy surface, and stabilisation of a $\mathrm{B{-}H_{carborane}\cdots(O)_2}$ interaction presumably requires co-operative forces such as the adjacent C–H groups also being involved in bifurcated hydrogen bonding as was found in the complex (*o*-carborane)$_2$(CTV), (CTV = cyclotriveratrylene) [15].

2.1. Host–guest chemistry

The first examples of host–guest complexes to be reported were the series of complexes with cyclodextrin host molecules and *o*-carborane as the guest [21]. Thermally stable 1:1 cyclodextrin:carborane complexes were formed with α-, β- and γ-cyclodextrin, and a 2:1 complex was also found for α-cyclodextrin. Presumably in the 2:1 complex the carborane is shrouded by two host molecules, [(*o*-carborane) ⊂ (α-cyclodextrin)$_2$], since the 1:1 species would have a perched structure, the cavity of the cyclodextrin being too small to accommodate the carborane. This is related to icosahedral C_{60} forming a 2:1 complex for the larger γ-cyclodextrin, noting the smaller cyclodextrins do not form complexes with the fullerene, and the larger cyclodextrin is required for a larger cage molecule relative to the *o*-carboranes [22]. However, the nature of interaction of the guest within the supermolecules, either [(*o*-carborane) ⊂ (α-cyclodextrin)$_2$], [(*o*-carborane) ∩ (α-cyclodextrin)], [(*o*-carborane) ⊂ (β-cyclodextrin)] or [(*o*-carborane) ⊂ (γ-cyclodextrin)$_2$], is unclear.

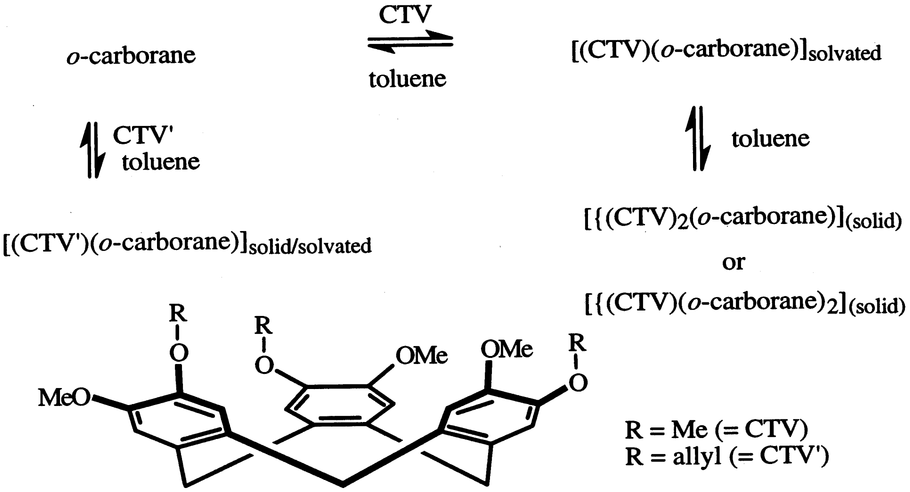
Other systems studied deal with hydrophobic host container molecules such as calix[5]arene [14,16] and related CTV [13,15]. These have shallow cavities and the resulting 1:1 supermolecules are at best described as perched structures. CH_2Cl_2 solutions of 1:1 and 1:2 mixtures of *o*-carborane and calix[5]arene afford crystalline complexes on diffusion of hexane vapours of overall composition (*o*-carborane)(calix[5]arene)(CH_2Cl_2) and (*o*-carborane)(calix[5]arene)$_2$(CH_2Cl_2)$_{0.5}$ (Scheme 1) [14]. In addition, a 2:1 complex (*o*-carborane)$_2$(calix[5]arene) has been isolated from a 3:1 mixture of *o*-carborane and calixarene [16], and a 3:1 mixture in toluene gave a toluene solvated 1:1 complex (*o*-carborane)(calix[5]arene)(C_7H_8). All complexes have been structurally authenticated [14,16].

Calix[5]arenes usually adopt a cone conformation. The smaller calix[4]arenes also adopt a cone conformation but the cavity is too small to accommodate carboranes. The readily available higher calix[6,8]arenes have thus far failed to give crystalline host–guest complexes with *o*- and *m*-carboranes. These calixarenes can adopt



Scheme 1.

double cone conformation, and in this context we note that calix[6]arene gives a complex with C_{60}, and also C_{70}, with a fullerene in each of the cavities of each double cone shaped calixarene [23], as does C_{60} with *p*-Bu^t-calix[8]arene [24]. Bowl shaped cyclotriveratrylene (= CTV) and a symmetrically tris-allyl substituted analogue, CTV′, with a deeper cavity form complexes with *o*-carborane (Scheme 2) [13]. CTV′ gave a 1:1 complex which has not been fully characterised whereas CTV affords two complexes in the solid, either a 2:1 complex rich in CTV despite using equimolar amounts of the two compounds, or a 1:2 ratio using an excess of the *o*-carborane. While the 2:1 ratio can be indicative of two host molecules encapsulating the cage, the X-ray structure revealed only one of the CTV molecules to be associated with the cage, the other seemingly acting as a space filler (see below).



Scheme 2.

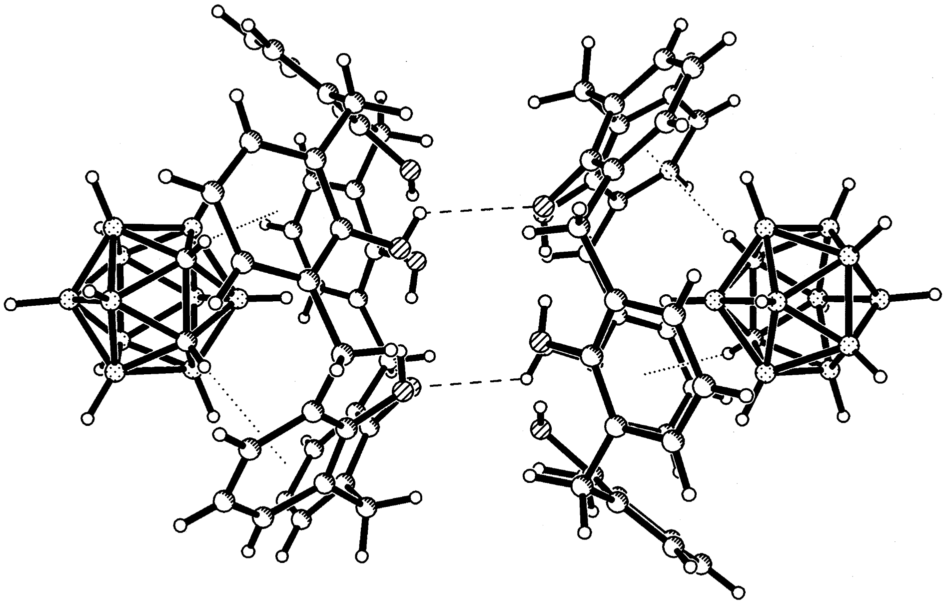


Fig. 2. The dimeric [(*o*-carborane)$\cap$(calix[5]arene)]$_2$ nano-structures of (calix[5]arene)(*o*-carborane)(CH_2Cl_2). The hydrogen-bonded (calix[5]arene)$_2$ unit can be considered to be acting as a divergent receptor. Potential non-classical C–H π hydrogen bonds are indicated as dashed lines [14].

All the complexes of calix[5]arene with *o*-carborane have a common structural motif in the solid state with a 1:1 ball and socket nano-structure comprised of the carborane in a cone shaped calixarene [14,16]. It is most likely that the carborane interacts with the calixarene via non-classical C–H···π hydrogen bonding (Fig. 1c). IR of the complexes is consistent with such bonding with shifts of the carborane ν_{C-H} to lower energy and ν_{B-H} to higher energy compared with those of free carborane. 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) [14] both C–H vectors of the carborane are directed towards aromatic rings of the host molecule with $C_{carborane}$···aromatic centroid separations of 3.55 and 3.44 Å. The ball-and-socket units organise into larger dimeric supermolecules with calixarene hydroxy groups facing each other, forming a hydrophilic core shown in Fig. 2. The O···O contacts between the calixarenes are quite close at 2.96, 3.01, 3.09, 3.14 and 3.22 Å.

Supermolecules in (*o*-carborane)(calix[5]arene)(C_7H_8) [14] have the *o*-carborane slightly closer to the host molecule. The C–H vectors of the carborane point towards the edges of aromatic rings of the calix[5]arene host at $C_{carborane}$···aromatic centroid separations of 3.40 and 3.49 Å. Here the (*o*-carborane)$\cap$(calix[5]arene) supermolecules stack with the same orientation (Fig. 3), to form columns of the supermolecule. The *endo*-cavity *o*-carborane of one supermolecule has contacts to the hydroxy groups of the next (*o*-carborane)$\cap$(calix[5]arene) at a closest B···O distance of 3.55 Å.

Crystals of (*o*-carborane)(calix[5]arene)$_2$(CH$_2$Cl$_2$)$_{0.5}$ [14] undergo a phase change from primitive monoclinic (room temperature, $P2_1/m$: $a = 11.679(1)$, $b = 18.128(2)$, $c = 16.394(1)$ Å, $\beta = 97.12(1)°$) to triclinic ($-100°$C: $a = 11.6151(13)$, $b = 16.3617(17)$, $c = 18.014(2)$ Å, $\alpha = 90.699(9)$, $\beta = 91.612(9)$, $\gamma = 96.739(9)$) on cool-

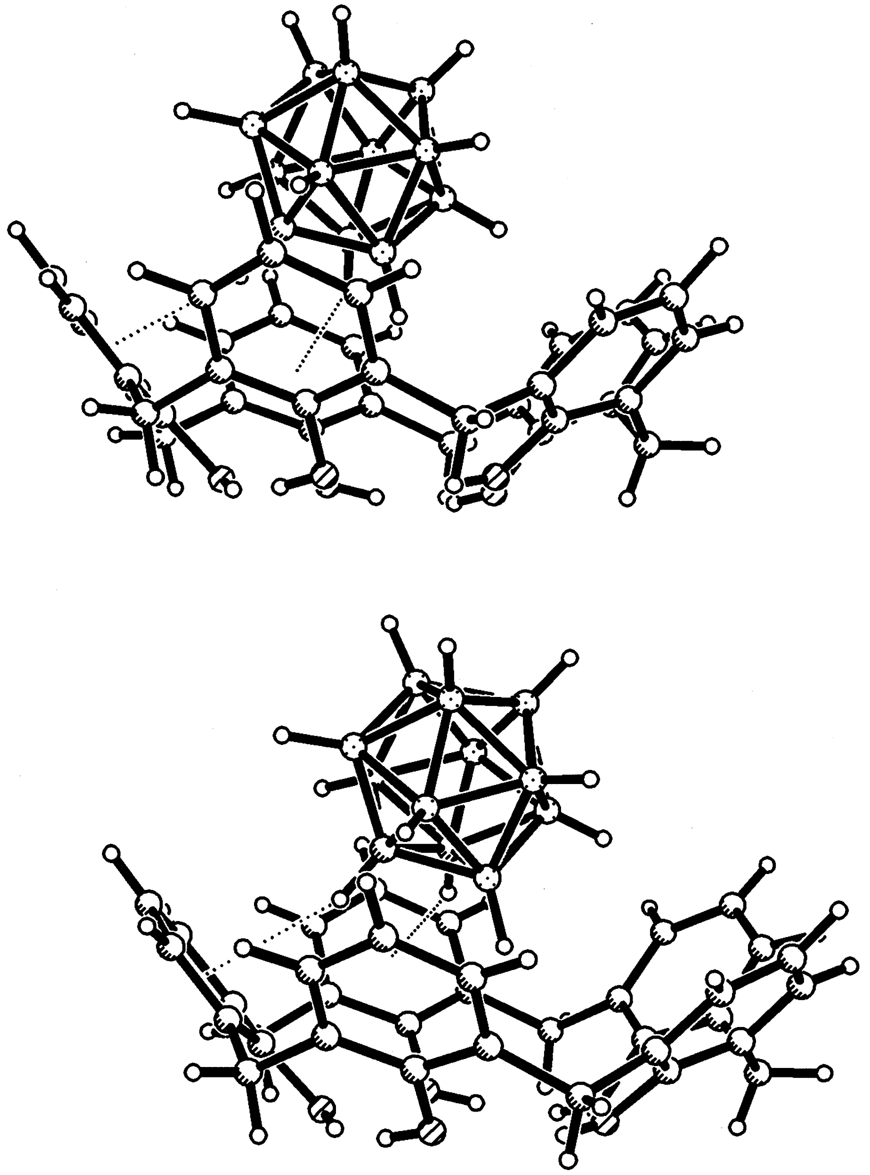


Fig. 3. Side view of two ball-and-socket (*o*-carborane)∩(calix[5]arene) supermolecules. Potential non-classical C–H π hydrogen bonds are indicated as dashed lines [14].

ing. The room temperature and low temperature structures are essentially the same, although the carborane displays some positional disorder in the room temperature structure. The overall structure is remarkable. Both calix[5]arene molecules adopt a bowl conformation, and their ability to act as host molecules manifests itself in two distinct manners. The curvature of the two calixarenes is quite different; one calixarene acts as a host molecule for the *o*-carborane, forming the familiar ball-and-socket arrangement while the other acts as a secondary host for the (*o*-carborane)$\cap$(calix[5]arene) assembly via $\pi\cdots\pi$ interactions forming the [(*o*-carborane)$\cap$(calix[5]arene)]$\cap$(calix[5]arene) nano-structure illustrated in Fig. 4. The (*o*-carborane)$\cap$(calix[5]arene) unit is similar to those discussed previously with both C–H vectors of the *o*-carborane directed towards aromatic rings of the host calix[5]arene at C$\cdots$aromatic centroid separations of 3.51 and 3.57 Å. The carborane is offset from the centre of the calixarene bowl. The complexation of a host–guest species by a secondary host is relatively uncommon; other examples include the complexation of alkali metal-crown ethers by cyclodextrins [25].

In the solid state structure of (*o*-carborane)$_2$(calix[5]arene) [16] the carborane forms both *endo* and *exo* associations with the host calixarene (Fig. 5). The included carborane sits close to the centre of the calixarene bowl. This carborane has the symmetry equivalent C–H vectors pointing towards the corners of adjacent aromatic rings of the host calixarene at $C_{carborane}\cdots$aromatic centroid distance of 3.53 Å. The second, disordered, *o*–carborane forms a weak association with the hydroxy groups of the calixarene through one triangular face of the carborane icosahedron (C/B$\cdots$O separations 3.86–4.12 Å), resulting in the *endo* and *exo* associated *o*-carboranes shown in Fig. 5. The *endo* and *exo* carboranes form pairs within the crystal lattice with a closest B$\cdots$B separation of 4.38 Å. The association of carboranes is more prevalent in the 1:1 complex of aza-18-crown-6 with *o*-carborane which forms an intercalation compound (see Section 2.3) [12].

In all the structures of the supermolecules [(*o*-carborane)$\cap$(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 [1] 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} [26,27] and the ability of CTV to accommodate spherical like molecules with different diameters (8 Å carborane cf. 10 Å C_{60}) relates to the shallower cavity of the rigid CTV relative to the diameter of the host molecule which is even less penetrating than in the perched structures involving calix[5]arene.

The structure of the 2:1 complex of CTV and *o*-carborane is comprised of 1:1 supermolecules of CTV and *o*-carborane, (*o*-carborane)$\cap$(CTV) [13], the other CTV forming a zig–zag π-stacked column with the inter-CTV contacts at the van

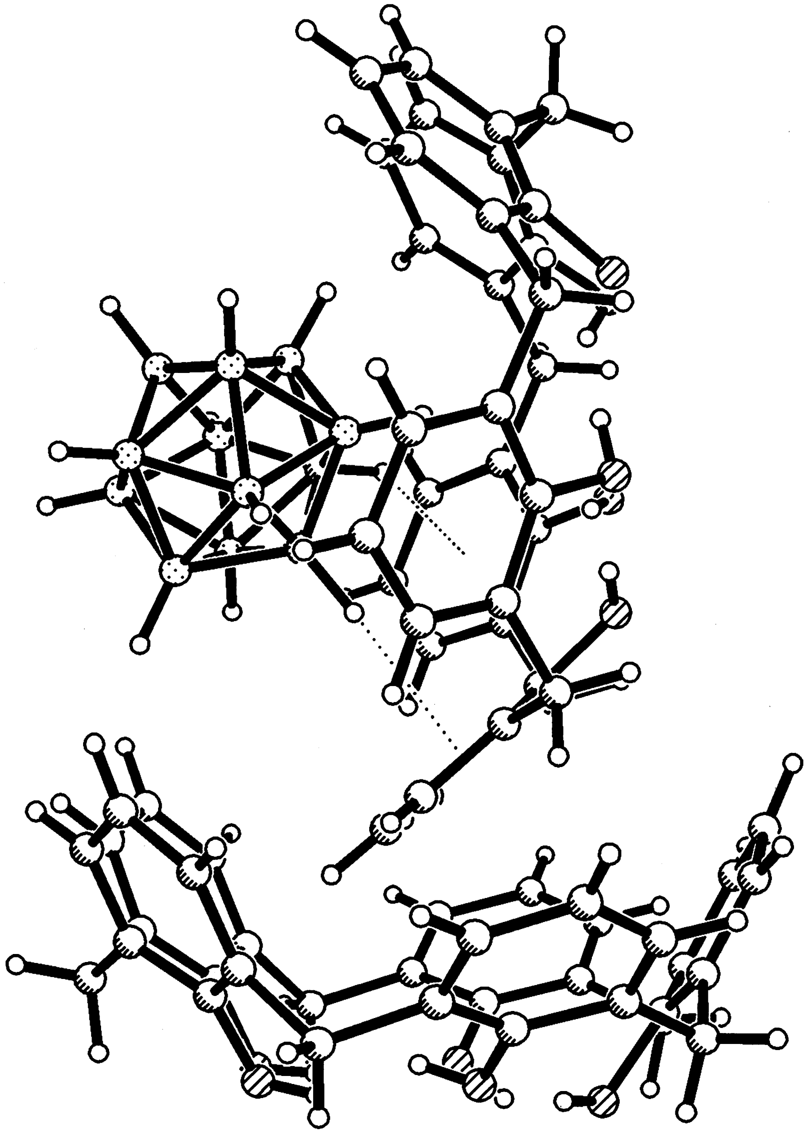


Fig. 4. The (o-carborane)∩[(calix[5]arene)]∩(calix[5]arene) nano-structure of (calix[5]arene)$_2$(o-carborane)(CH$_2$Cl$_2$)$_{0.5}$; potential non-classical C–H π hydrogen bonds are indicated as dashed lines [14].

der Waals limit (Fig. 6). This type of association of CTV molecules is common 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 [28]. 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)$\cap$(CTV) show that three hydrogens of a triangular face of the icosahedron are directed towards the aromatic rings of the CTV albeit unsymmetrically (Fig. 7). This most likely arises from the energetically favoured $C-H_{carborane}\cdots\pi$ hydrogen bonds between each of the two acidic hydrogens attached to carbon cage atoms and two aromatic rings of the CTV versus repulsion between the hydrogen attached to a boron atom of the cage and the third aromatic ring of the CTV. Thus alignment of the carborane in the CTV cavity is consistent with the acidic nature of the protons attached to the carbon centres of the carborane and theoretical considerations [13].

In crystals of (*o*-carborane)$_2$(CTV) [15] one of the carborane molecules forms three symmetry equivalent bifurcated hydrogen bonds to the methoxy groups of three equivalent CTV molecules (Fig. 1b); the C/B···O distance is 3.33 Å with the corresponding C/B–H···O distance at 2.53 Å [15]. 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 (Fig. 8). The formation of infinite 2D hexagonal sheets through hydrogen

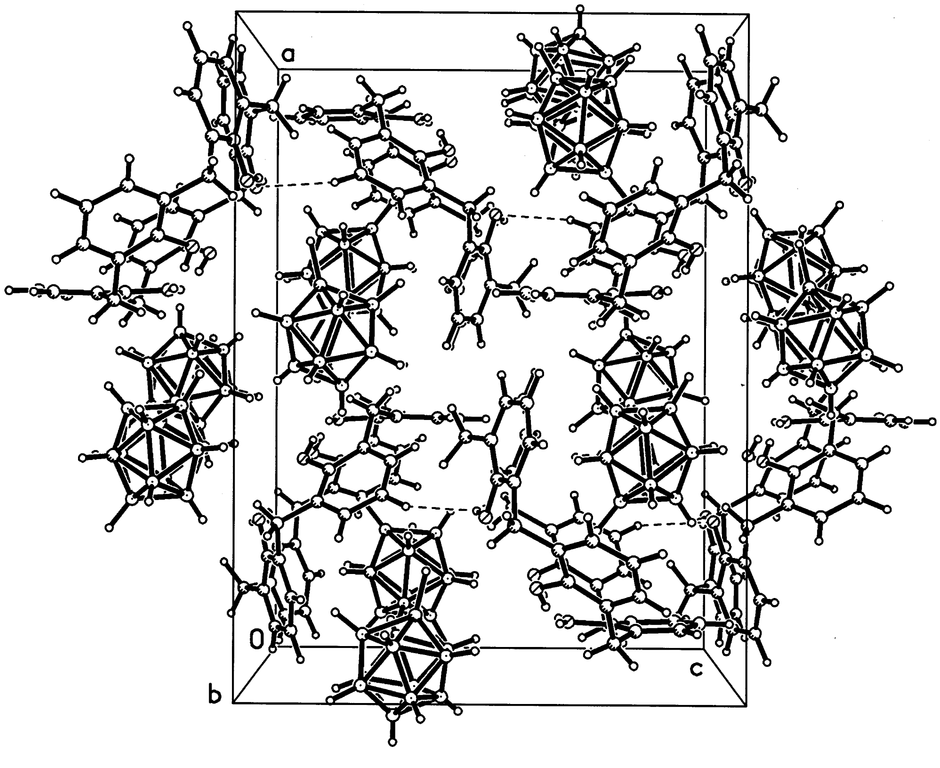


Fig. 5. Packing diagram of (calix[5]arene)(*o*-carborane)$_2$; close contacts between C–H and O of neighbouring calix[5]arene molecules are shown as dashed lines [16].

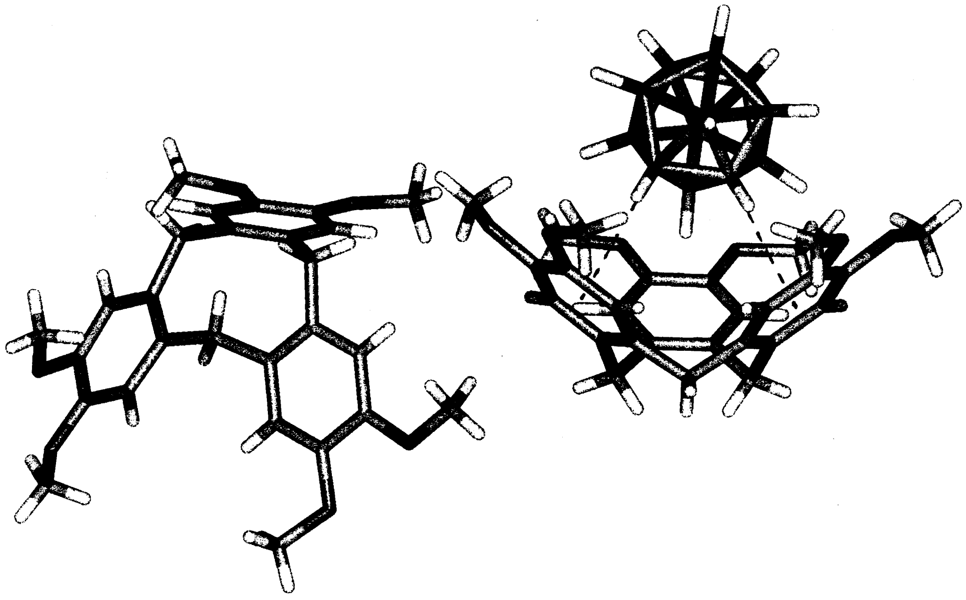


Fig. 6. Projection of the host–guest structure in [(CTV)$_2$(*o*-carborane)] with the nearest contact shown as broken line; distances from the centroid of the aromatic rings to the H atoms attached to C(1), C(2), and B(4) are 2.184, 2.556, and 2.765 Å, respectively (corresponding distances from C(1), C(2), and B(4) to the centroids, 3.299, 3.503, 3.701 Å).

bonding interactions has been seen for a number of other systems, the best known being various clathrates of urea [29]. What makes this example more intriguing is the presence of receptor sites within the 2D grid. 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)$\cap$(CTV) nano-structure throughout the hydrogen bonded grid (Fig. 8; see Section 2.2).

The host–guest interplay within the supermolecule (*o*-carborane)$\cap$(CTV) 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 [15]. However the difference is consistent with the inherently weak interactions holding the supermolecule together. In an elegant example of symmetry matching, the vertices of one of the triangular faces of the carborane icosahedron lies parallel to the triangle formed by the methylene bridges of the CTV. The three symmetry equivalent icosahedron faces adjacent to this face are arranged nearly parallel to the three aromatic rings of the CTV. The centroid separation between the aromatic ring and triangular face represents the closest contact between the molecules at 3.77 Å and the faces are slightly inclined from each other with a torsion angle of 6.4°. It is notable that this is a considerably longer interaction (by up to ~0.45 Å) than was seen for (*o*-carborane)(CTV)$_2$ [13]. Interestingly, the atomic displacement parameters for the carborane included in the CTV cavity are considerably larger than those for the hydrogen bonded carborane (average U_{iso} 0.098 and 0.050 Å^2, respectively), indicating greater librational motion for the included carborane, and implying that the hydrogen bonded carborane is more tightly bound within the crystal lattice than is the guest carborane.

^{1}H-NMR spectra recorded in toluene for the 2:1 complex [(CTV)$_2$(*o*-carborane)] show rapid exchange processes occurring between complex and uncomplexed carborane as single peaks were observed for the *o*-carborane C–H groups and they were significantly shifted upfield. 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 would indicate that *o*-carborane can bind both *endo*- and *exo*- to the cavity of the CTV.

The complexation of *o*-carborane by calixarenes and CTV is reminiscent of much of the host–guest chemistry of the fullerenes C_{60} (and C_{70}) [1,23,24,26,27,30,31]. Both the carboranes and fullerenes are thermally stable, icosahedral cage molecules

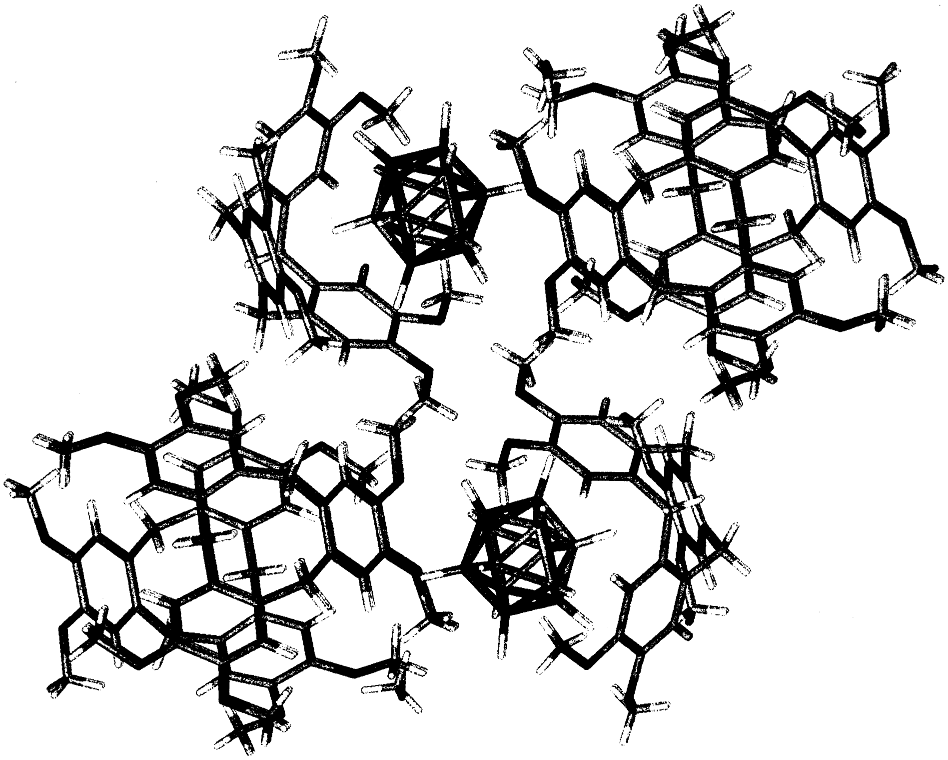


Fig. 7. Crystal packing diagram for [(CTV)$_2$(*o*-carborane)] projected down the *b* axis [13].

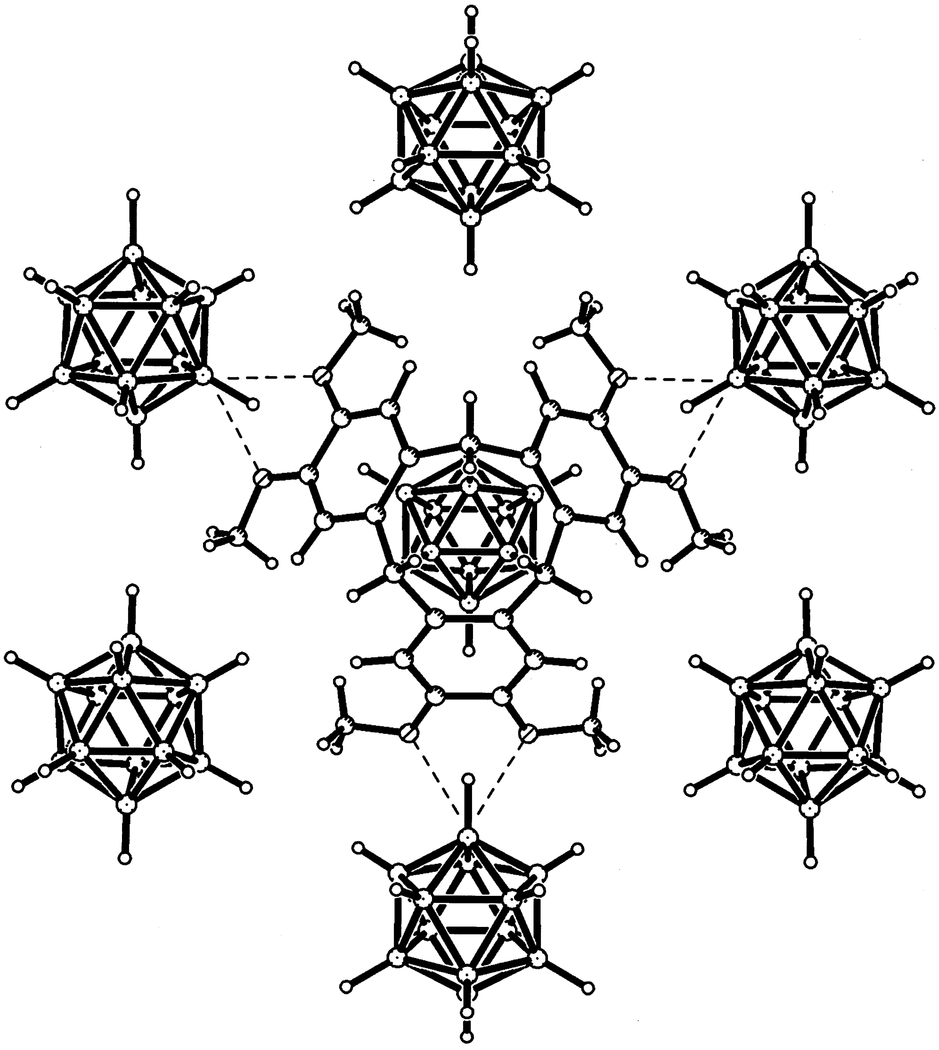


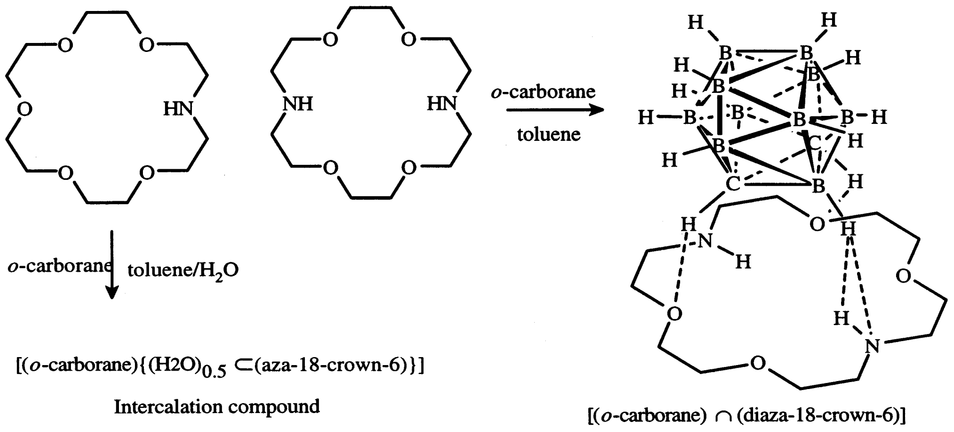
Fig. 8. Section of the crystal structure of (o-carborane)$_2$(CTV) highlighting the formation of three bifurcated B/C–H···O hydrogen bonds around the CTV, the centred hexagonal pattern of o-carboranes about the CTV and the inclusion of a guest o-carborane in the CTV bowl [15].

with diameters of about 8 and 10 Å, respectively. Fullerene C_{60} forms inclusion complexes with CTV [15,26,27,30] and a number of calixarenes [31], and indeed the selective complexation of C_{60} by p-Bu^t-calix[8]arene is a simple and efficient means of C_{60} extraction from a mixture of fullerenes [24]. The supramolecular chemistry of carboranes with bowl-shaped potential host molecules is, by comparison, in its infancy and may also lead to simplified separation procedures, currently reliant on chromatographic techniques [3].

Host–guest of *o*-carborane has also been developed with diaza-18-crown-6, [= 1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane], where a 1:1 complex is formed [12] (Scheme 3). On the basis of the product, [(*o*-carborane) ∩ (diaza-18-crown-6)], it was thought that the aza-18-crown-6, [1,4,10,13-tetraoxa-7-aza-cyclooctadecane] would form a similar host–guest complex, but while it gave a 1:1 complex it is an intercalation compound with alternating layers of *o*-carboranes and crown ethers (see Section 2.3). In principle a second *o*-carborane could bind to the other face of the diaza-crown ether in the same way, albeit rotated by 180°. Nevertheless, even in the presence of excess carborane only the 1:1 complex was formed in the solid state. The difference in structure between the two complexes is striking and reflects the 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 (Fig. 9). The two components are linked through $\mathrm{C{-}H_{carborane}\cdots O}$ hydrogen bonding interactions (Fig. 1a), with O(4)···H(7A) at 2.36 Å and O(2A)···H(1A) at 2.49 Å, coupled with B–H···H–N (Fig. 1b), interplay with H(8)···H(21) at 2.15Å and H(8)···N(2) at 2.34 Å. The H···H distance is close to the upper limit for unconventional dihydrogen bonds established for B–H···H–N contacts in aminoboranes which lie in the range 1.7–2.2 Å [20]. The $\mathrm{O\cdots H_{carborane}}$ distances are similar to those found in the *o*-, *m*-, and *p*-carborane adducts with HMPA [11]. The IR spectra of the complex shows a shift of 33 $\mathrm{cm^{-1}}$ to lower energy for the carborane $\nu_{\mathrm{C-H}}$ and a shift of 25 $\mathrm{cm^{-1}}$ to higher energy for $\nu_{\mathrm{B-H}}$.

Theoretical studies give the docking of the carborane with diaza-18-crown-6 to be favoured by 9.32 kcal $\mathrm{mol^{-1}}$. The optimised C–H···O distances at 2.471 Å compare well with experimental values at 2.49 Å. The B–H···N and B–H···H–N optimised at 2.924 and 2.721 Å, respectively [12]. These are much longer than experimental values at 2.34 and 2.15 Å, and analogous distances in aminoboranes [20]. The



Scheme 3.

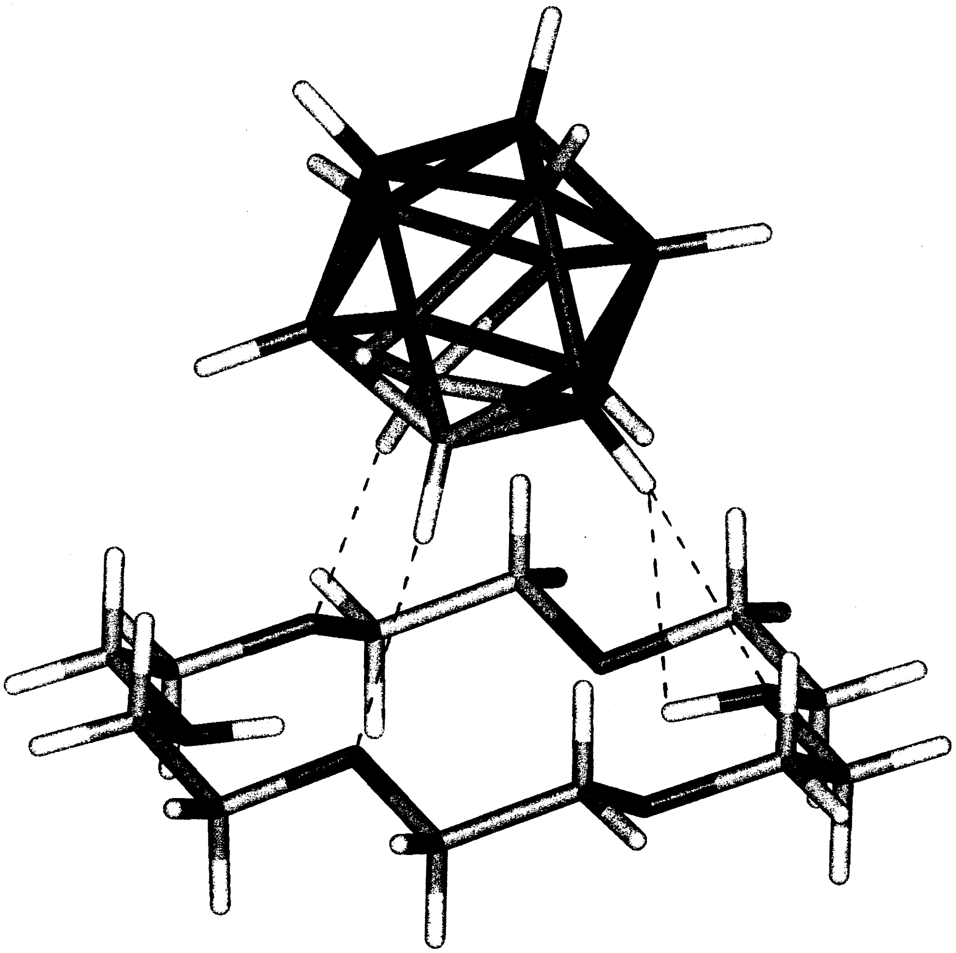


Fig. 9. Host–guest structure of [(o-$C_2B_{10}H_{12}$)∩(diaza-18-crown-6)]; the nearest contacts are shown as broken line with O(4)...H(7A), 2.36 Å, O(2A)...H(1A) 2.49 Å, and N(2)...H(8) 2.34 Å (corresponding N–H...H distance 2.15 Å) [12].

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 that the short B–H···H–N contacts for aminoboranes [20] arise from residual negative charge on the H-atoms attached to boron, cf. positive charge in [(o-carborane)∩(diaza-18-crown-6)].

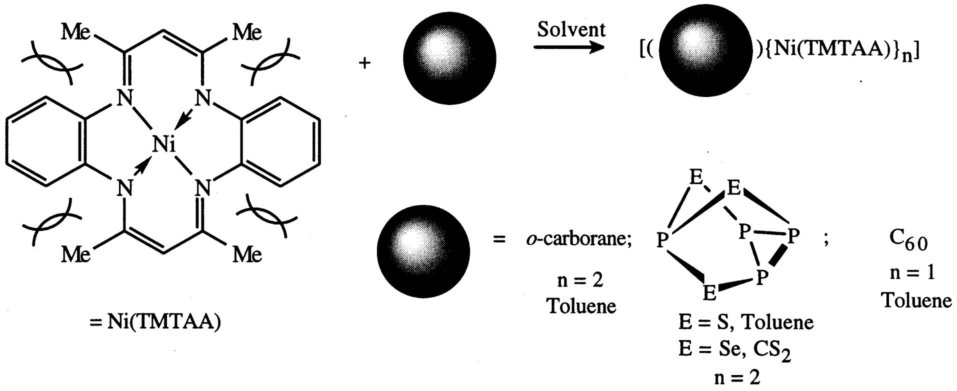
^{1}H-NMR in d^6-benzene at 25°C for a range of concentration of diaza-18-crown-6 (0.0–0.14 M) for a fixed o-carborane concentration (0.07 M) resulted in shifts in the o-carborane C–H resonance from 2.05 to 2.20 ppm and N–H resonance for diaza-18-crown-6 from 2.26 to 2.85 ppm. A near linear relationship indicate a low equilibrium constant (< 5 M^{-1}) (Eq. (1)).

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

For *m*-carborane small differences in the chemical shift for C–H (25°C, δ 1.94; -75°C, δ 1.43) relative to a 1:1 mixture of the carborane and diaza-18-crown-6 (0.07 M; 25°C, δ 1.98; -75°C, δ 1.51) in d^6-benzene indicate little or no complexation. In support of this there was no evidence of 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 with **2** suggests that separation of isomeric carboranes via selective binding is possible rather than using conventional chromatography [3]. 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 [12].

The nickel(II) macrocycle Ni(TMTAA)[= 5,7,12,14-tetramethyldibenzo[b,i]-[1,4,8,11]-tetraazacyclo-tetradecinenickel(II)] (Scheme 4), which has two divergent concave surfaces is a versatile receptor molecule [32]. 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. This occurs with *o*-carborane [32], and also with the phosphorus chalcogenides P_4(S or Se)$_3$ (see Section 3.). This is a new approach to the confinement of globular species in general, and relates to the use of molecules with rigid curved surfaces to regulate and stabilise nano-particles of binary compounds which can exhibit size dependent functionality [33].

The two divergent concave surfaces of Ni(TMTAA) arise from otherwise unfavourable non-bonding interactions between the methyl groups and the hydrogen atoms on the aromatic rings *ortho* to the N-centres. Binding globular cage molecules which have curvature complementarity with these shallow saddle-shaped voids will be favoured entropically over the binding of solvent molecules, and importantly there is no pre-organisational energy requirement of the rigid macrocy-



Scheme 4.

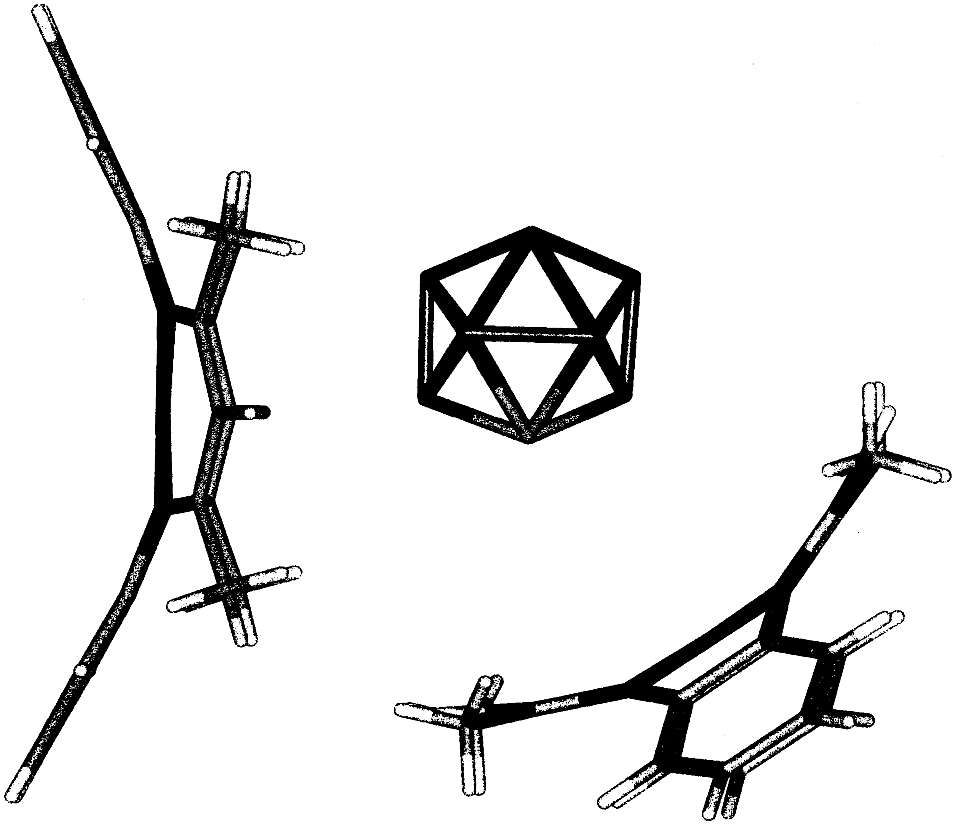


Fig. 10. Projection of the supramolecular arrays found in [(*o*-carborane){Ni(TMTAA)}$_2$] [32].

cle prior to complexation with such species. *o*-Carborane, C_{60}, and P_4(S or Se)$_3$ have comparable surface complementarity with Ni(TMTAA). The 2:1 complexes of *o*-$C_2B_{10}H_{12}$ was favoured even for an excess of the cage, and indeed these conditions were best for driving the precipitation of the complexes from solution, the complex being more soluble in toluene than Ni(TMTAA) itself [32].

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. 10). The sandwich supermolecules form extended structures by locking together the pendant phenyl rings of one Ni(TMTAA) of one supermolecule with that of another with the methyl groups all directed towards the cage. The carborane has van der Waals contacts with hydrogen atoms of four Ni(TMTAA) moieties with no contacts to other carboranes. Alternatively the structures can be viewed as two associated Ni(TMTAA) molecules acting as a divergent receptor for two *o*-carboranes. The self assembly of two Ni(TMTAA) moieties at 90° to each other is driven by the complementarity of curvature of the interlocking components, as well as by Ni···π-arene interactions.

B–H···N distances within the structure are at ~2.7 Å (equidistant to two N atoms) for a single triangular face of the carborane to one macrocycle N_4 plane, and B–H···N distances at ~2.9 and 3.4 Å (each equidistant to two N atoms) for an edge of the cage to the N_4 plane of the other macrocycle. These distances are significantly longer than those for H-atoms of *o*-carborane interacting with N and O donors of diaza-18-crown-6, as hydrogen bonds, $B–H_{carborane}···N$ 2.34 Å, $C–H_{carborane}···O$ 2.36, 2.49 Å [12].

Crystal structures of the 1:1 complexes of hexamethylphosphoramide (HMPA) with *o*-, *m*- and *p*-carboranes derived from toluene solutions have been reported [11]. 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, $C–H_{carborane}···O$ 1.54(4)–1.60(4) Å (Fig. 11), whereas the other isomers give polymeric structures with the HMPA O-centre bridging to two C–H groups from different carborane molecules (Section 2.2).

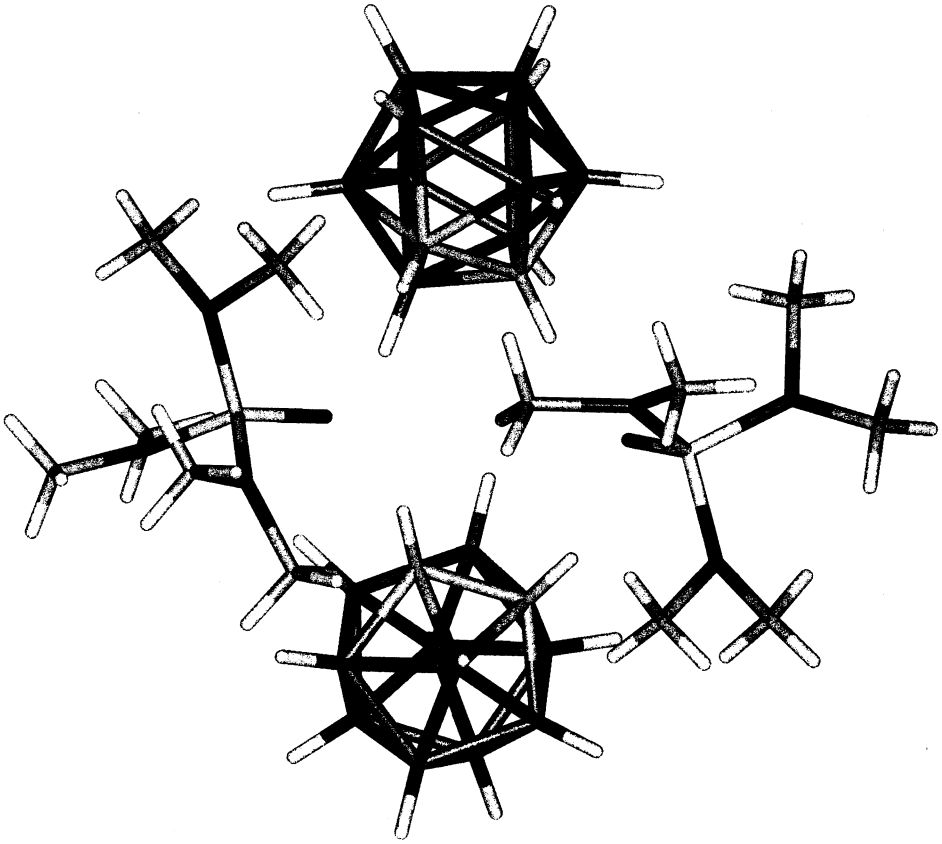


Fig. 11. Projection of the hydrogen bonded dimers in [(*o*-carborane)(HMPA)] [11]

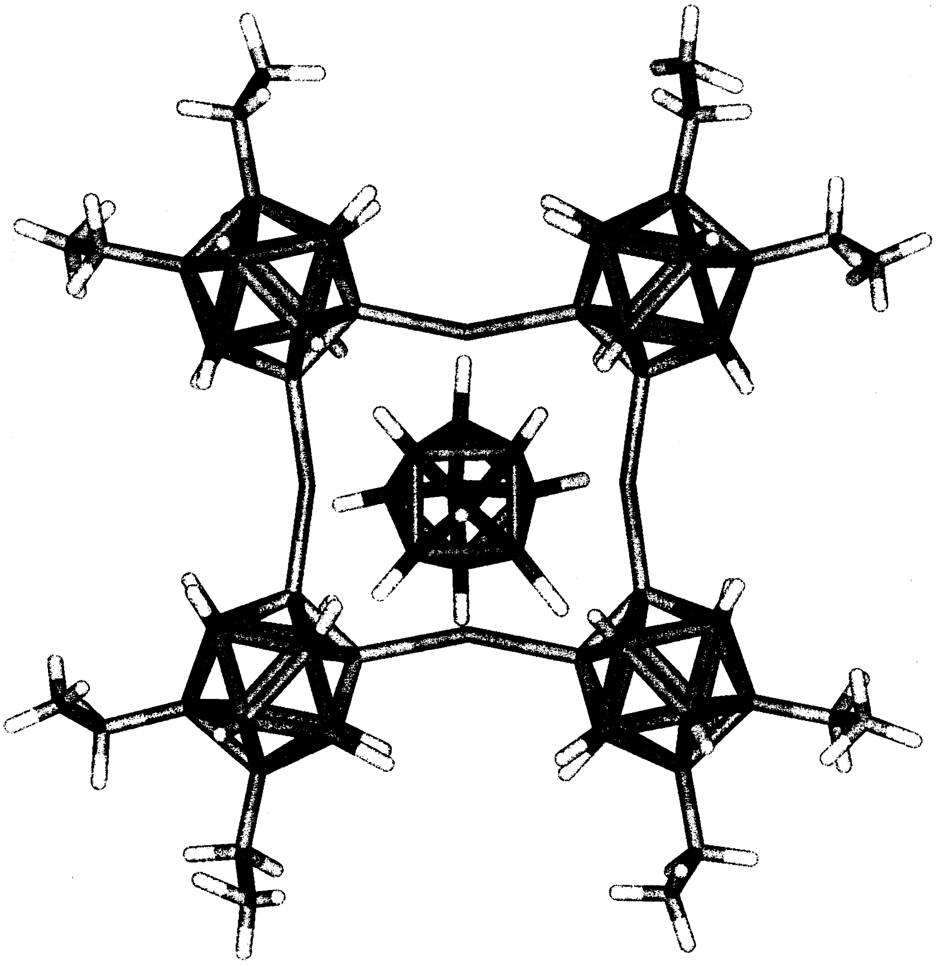


Fig. 12. Projection of the *bis* $B_{10}H_{10}^{2-}$ adduct, (octaethylmercuraborand-4)(*closo*-$B_{10}H_{10}^{2-}$)$_2$. The B–H vertices form a set of four three-centre two-electron Hg–H–B bonds to the mercury atoms [9].

Macrocycles formed by linking carborane cages via mercury bridges show host–guest complexation of halide ions. The tetrameric macrocycles mercuracarborand-4 and octaethylmercuracarborand-4 can also act as hosts for the globular borane anions *closo*-$B_{10}H_{10}^{2-}$, *closo*-$B_{10}I_{10}^{2-}$ and *closo*-$B_{12}H_{12}^{2-}$ [8,9]. ^{199}Hg-NMR studies have demonstrated that 1:1 complexes are formed in acetone solution even with an excess of anion present, however in the solid state 2:1 anion to host complexes are isolated [9]. The crystal structure of (octaethylmercuraborand-4)(*closo*-$B_{10}H_{10}^{2-}$)$_2$ is shown in Fig. 12. Each of the two *closo*-$B_{10}H_{10}^{2-}$ ions uses four equatorial B–H vertices to form a set of four three-centre two-electron Hg–H–B bonds to the mercury atoms of the macrocycle.

2.2. Extended arrays

The polymeric structures of [*m*-, *p*-carborane(HMPA)] [11] have the O-centre of HMPA bridging to two C–H groups from different carborane molecules, C–$H_{carborane}\cdots O$ 1.75(4) and 1.644 (*m*-isomer) or 1.52(3) (*p*-isomer) Å. The bridging is similar to that in the dimeric structure found in the *o*-isomeric complex [11]. Polymeric structures are also found in (*o*-carborane)$_2$(CTV) and (C_{70})(*o*-carborane)(CTV)(1,2-dichlorobenzene) [15]. Here hydrogen bonding is also prevalent, but involving bifurcated units (Fig. 1b), rather than the classical hydrogen bond (Fig. 1a). In (*o*-carborane)$_2$(CTV) a carborane molecule resides in the cavity of the CTV, the other involved in the hydrogen bonding in a two dimension grid, and this structure, along with the synthesis of the complex, is discussed in Section 2.1.

The complex (C_{70})(*o*-carborane)(CTV) crystallises from 1,2-dichlorobenzene containing the three supramolecular synthons as a mono-solvate [15]. In the solid state each C–H proton is involved in a bifurcated hydrogen bond to adjacent methoxy oxygens of the CTV (Fig. 1b). 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. 13). The CTV cavities are directed outwards from the helices, hence an infinite hydrogen-bonded array with in-built curved receptor sites is formed, with each CTV complexing a molecule of C_{70}. 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) [26,27], and that C_{60} and CTV in the presence of *o*-carborane also affords $(C_{60})_{1.5}$(CTV).

2.3. Inclusion/intercalation chemistry

Section 2.1 detailed the synthesis of the 1:1 complex of *o*-carborane and diaza-18-crown-6 which is a host–guest system, [(*o*-carborane)$\cap$(diaza-18-crown-6)]. Mono-aza-18-crown-6 also gave a 1:1 complex (Scheme 3), but this is an intercalation complex (Fig. 14) [12]. 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*-carborane){$(H_2O)_{0.5}\subset$(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 dominate over host–guest interactions in the solid state. A similar effect was observed in the absence of moisture but in this case no host–guest or intercalation complex could be isolated.

Although the structure of [(o-carborane){$(H_2O)_{0.5}\subset$(aza-18-crown-6)}] is highly disordered, it clearly shows the absence of any close intermolecular contacts like those observed in [(*o*-carborane)$\cap$(diaza-18-crown-6)]. The polarised cages form a two dimensional sheet, the nearest inter-carborane contacts, C/B–H···H–B/C at 2.41 Å and the packing of the crown ether involves C–H···H–C interactions, the nearest contacts at 2.72 Å.

3. Group 15/16 cages

The nickel(II) macrocycle Ni(TMTAA) [= 5,7,12,14-tetramethyldibenzo-[b,i][1,4,8,11]-tetraazacyclo-tetradecinenickel(II)] (Scheme 4; Section 2.1), forms 1:2 complexes with the phosphorus chalcogenides P_4(S or Se$)_3$, [{P_4(S or

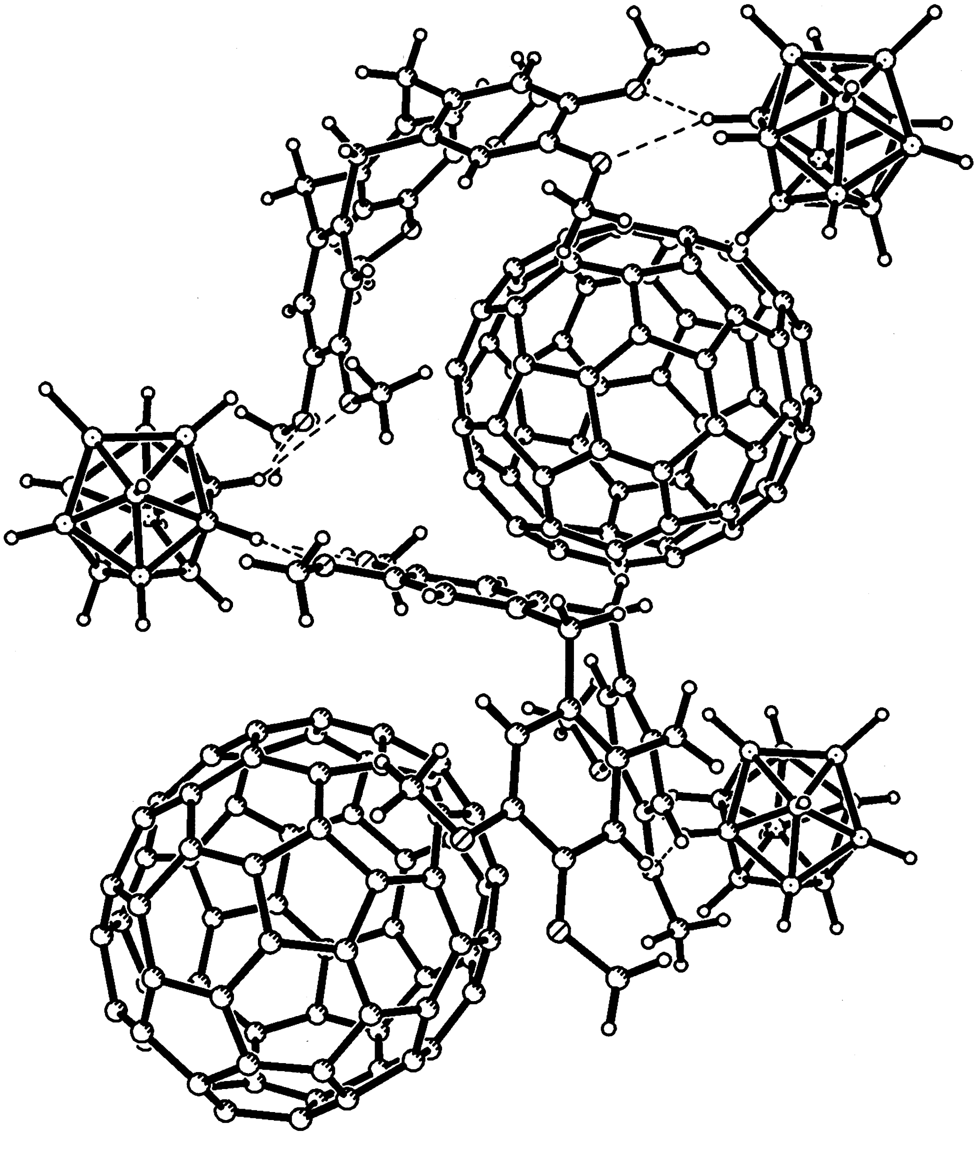


Fig. 13. Side view of a helix in (C_{70})(*o*-carborane)(CTV)(1,2-dichlorobenzene) showing the binding of C_{70} molecules within the CTV bowls [15].

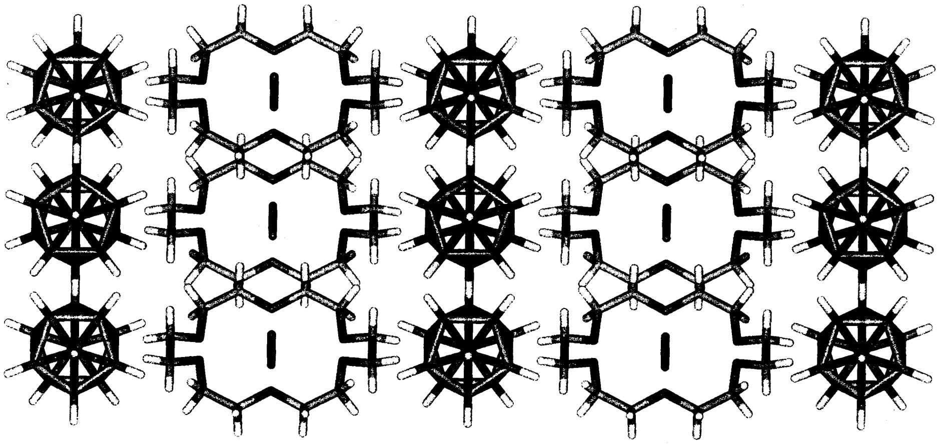


Fig. 14. Projection of [(*o*-carborane){$(H_2O)_{0.5}$ ⊂ (aza-18-crown-6)}] [12].

Se$)_3$}{Ni(TMTAA)}$_2$], Scheme 4, as for *o*-caborane which has a similar diameter to that of the phosphorus chalcogenides [32,34]. The 1:2 complexes of P_4(S or Se$)_3$ are favoured even for an excess of the cage, in toluene and CS_2, respectively, Scheme 4. These conditions are best for driving the precipitation of the complex from solution, the complex being more soluble than Ni(TMTAA).

All three structures containing *o*-carborane and P_4(S or Se$)_3$ are isostructural, which is consistent the complementarity of curvature of the components as an important controlling factor in their formation. Despite the well established chemistry of chalcogenide cage molecules over several decades, [(P_4(S or Se$)_3$}{Ni(TMTAA)}$_2$] are the only reported host–guest complexes of Group 15 chalcogenide cage species.

In the solid state two Ni(TMTAA) molecules lock together forming a homotopic divergent receptor with a cage in each of the methyl lined shallow cavities (Fig. 15). Disorder was evident for the cage in both cases [32,34] which was resolved into two components. The closest approach of the cages molecules to the metal centres is 3.22 and 3.24 Å, respectively. The same cage molecule in [Ni{P_4(S or Se$)_3$}{tris(2-(diphenylphosphino)ethyl)amine)}] is in fact bound to the metal centre through the unique phosphorus of the cage molecule with Ni–P at 2.072(5) Å [35], 2.075 Å [36]. Any metal to cage interaction in the present structure is weak and the P_4(S or Se$)_3$ cage to Ni(TMTAA) contacts are close to the van der Waals limit. Other attempts to complex these cages have resulted in cage fragmentation [37].

The Ni(TMTAA) macrocycle also forms a 1:2 complex with toluene [34]. Here the interplay of the macrocycles is opposite to that of the foregoing complexes, now with the methyl lined faces locked together. This finding further highlights the versatility of the rigid macrocycle to accommodate a range of host species, globular *o*-carborane and P_4(S or Se$)_3$, larger C_{60}, and the planar molecule, toluene.

The homoatomic molecular P_4 cage forms a 2:1 inclusion complex with C_{60} [38]. Addition of a CS_2 solution of white phosphorus to a toluene solution of C_{60} results in a 90% yield of the analytically pure blue–black crystals of $[(P_4)_2C_{60}]$. ^{31}P-NMR revealed that no electron transfer had occurred between the C_{60} and the P_4 units, though an upfield chemical shift change when compared with crystalline P_4 did indicate that the neighbouring C_{60} molecules had some electronic influence. X-ray powder diffraction analysis revealed the structure to have the same hexagonal AAA stacking with close packed C_{60} layers as found in $[(I_2)_2C_{60}]$ with P_4 tetrahedra located in the tetragonal prismatic sites between the C_{60} units.

4. Others

In the 1930s Zintl and co-workers identified the presence of many homopolyatomic main group ionic cage molecules from the dissolution of the appropriate sodium alloy in liquid ammonia [39]. Unfortunately removal of ammonia led only to the reformation of the amorphous sodium alloys. However in the 1970s, Corbett discovered a general method by which the anions could be stabilised irreversibly by dissolution of the alloy in ethylenediamine (= en) with encapsulation and coordinative saturation of the alkali metal cation by 2,2,2-crypt (2,2,2-crypt = 4, 7, 13, 16,

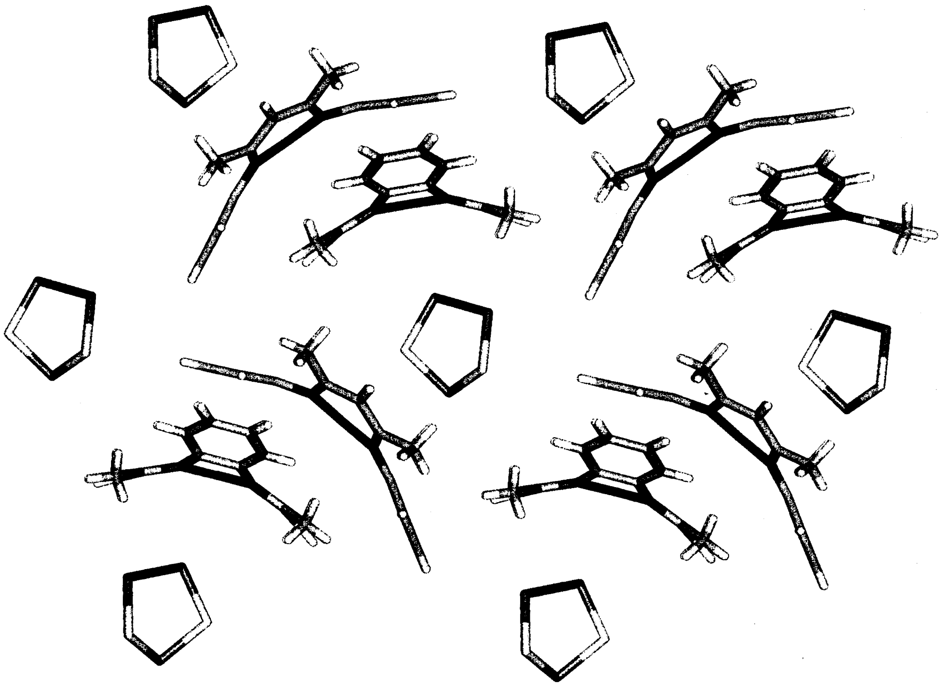


Fig. 15. Supramolecular interplay found in $[(P_4Se_3)\{Ni(TMTAA)\}_2]$ [34]; the same structure is also found in the P_4S_3 analogue [32].

21, 24-hexaoxa-1, 10-diazobicyclo[8.8.8]hexacosane) [40]. Two other types of stabilised complexes are also known where the alkali metal cation is stabilised by en only or is subsequently reacted with a quaternary phosphine or amine, $R_4P^+X^-$ ($X = Cl$, Br, $R = Ph$, Bz), $R_4N^+X^-$ ($X = Br$, Br_3, $R = Me$, Et, Bz) resulting in the phosphonium, R_4P^+, or ammonium, R_4N^+, cation being the counterion to the main group cage. Thus many homo- and hetero-atomic globular main group anions have now been investigated by single crystal diffraction methods, and supramolecular chemistry of such species is an exciting new direction for consideration.

Since interest has centered almost exclusively on the structure of the anionic cages there is almost no discussion presented on the extended lattice, orientation or interactions of the constituent molecules and/or ions. This makes it particularly difficult to assess and describe the structural cohesion of these complexes. This review therefore begins the process of identifying those complexes with structures which would now be of interest in terms of supramolecular chemistry and highlights any structural and/or bonding features which may now be of interest to the supramolecular chemist.

The bonding in these complexes is best described in terms of electrostatics: when the alkali metal cation is present the crystal lattice is composed of pseudo solvent separated ion-pairs and when R_4P^+ or R_4N^+ is the cation, then a salt-like structure is adopted with the main group cage occupying cavities formed by aryl groups and between the E^+ centers.

Complexes in which there is a clear, direct bond between the cation and the anionic cage, as in those en–M^+ stabilised complexes such as $[Na_4{\cdot}7en][Sn_9]$ [41], fall outside the definition of supramolecular chemistry and therefore this review, as do non-globular anions and those globular anions which contain transition metals.

The known solid state structures are reviewed here in relation to which cation is present.

4.1. $[R_4P^+]_n$, $[R_4N^+]_n$

The addition of Ph_4PBr to an en solution containing K_3P_7 results in the formation, via oxidative coupling, of the dumb-bell shaped P_{16}^{2-} molecule [42]. This molecule, which is essentially two coupled P_7^{3-} globular units, occupies the interstices created by the packing of Ph_4P^+ ions. The same interstitial arrangement is found for $[Ph_4P]^+[H_2P_7]^-$, which adopts a CsCl type lattice [43]. Two different positions are found for the $H_2P_7^-$ anion (75:25 occupation) as a result of a large degree of rotation allowed by the large cavity left by the Ph_4P^+ cations. It would appear that there is no significant interaction between the anion cage and the phenyl rings. This protonated P_7 complex arose from the reaction of Na_3P_7 with Ph_4PCl in liquid NH_3. In a similar vein the more controlled soft protonation reaction of Cs_3P_{11} with the quaternary ammonium and phosphonium salts $[Me_3BzN]Br_3$ and $[Ph_3BzP]Br$ in liquid NH_3 produced the discrete globular HP_{11}^{2-} anion in the complexes $[Me_3BzN]_2HP_{11}$ and $[Ph_3BzP]_2HP_{11}$, while $[Me_3EtN]_3P_{11}$ was formed by the straight forward metathesis reaction [44]. Such complete metathesis reactions can prove difficult due to the retention of one or more of the alkali metal cations in the structure.

The irradiation of $W(CO)_6$ and $Ph_4P[As_2SCl_5]$ in THF with UV light produced yellow crystals of $[Ph_4P]Cl{\cdot}4As_4S_3$ as one of three products [45]. The tetragonal structure is composed of separate Ph_4P^+ and Cl^- ions with the four neutral As_4S_3 molecules located at all points in the interstices.

The reaction of As_4Se_3 with K in en produced, after removal of KSe_2 and subsequent reaction with Ph_4PBr, crystals of $[Ph_4P]_2[As_{10}Se_3]$ [46]. The anion is related to the As_{11}^{3-} cage and, as is often found with globular anions, it is disordered over two symmetry sites in the ratio 85.4:14.6. While there are no direct interactions between the anions and cations there is a weak interaction between the apical Se and a C in the Ph ring (Se···K 3.38(4) Å, Se···H(calc) 2.94 Å). These distances are short with respect to their van der Waals radii and can be considered as non-classical interactions. Unfortunately there is no discussion as to whether similar interactions are present in the analogous Te complex, $[Ph_4P]_2[As_{10}Te_3]$ [47], as is the case with $[Ph_4P][As_7Se_4]$ [48]. The anionic cage in the complex $[Ph_4P]_2[As_6Br_8]$ [49] contains a cubic core with the six As atoms adopting a chair configuration with two bridging Br. The six other Br are bound to each As, however due to the large size of the cation there are no intermolecular As···Br contacts. The cubane-like anionic As_6I_2 core is also present in the unusual complex $[NiI(CH_3C(CH_2PPh_2))]_2[As_6I_8]$ [50].

The cathodic dissolution of a Sb_2Te_3 electrode in a solution of $[(n\text{-}C_3H_7)_4N]_4Br$ and en results in the formation of the two ammonium complexes $[(n\text{-}C_3H_7)_4N]_4[Sb_4Te_4]$ and $[(n\text{-}C_3H_7)_4N]_3[Sb_9Te_6]$. The $Sb_4Te_4^{4-}$ anion has non-crystallographically imposed 2 mm point group symmetry [51].

4.2. [2,2,2, Crypt–M^+]$_n$

Addition of 0.5 As_4S_4 to an equimolar solution of K and 2,2,2-crypt in liquid NH_3 results in the crystallisation of $[2,2,2\text{-cryptK}]_2[As_{10}S_3]$ as red needles [52]. The anionic cage is isostructural with $As_{10}Se_3^{2-}$ and $As_{10}Te_3^{2-}$ which have been isolated with Ph_4P^+ as the counterion as described above. Reaction of $K_{1.6}As_{1.6}Te$ alloy with 2,2,2-crypt in en produces the closely related complex $\{[2,2,2\text{-cryptK}]_3[As_{10}Te]{\cdot}en\}$ [53]. The anionic cage here, while having no symmetry, is closely related to the 17 vertice polyhedron D_3 symmetry of the As_{11}^{3-} anion which is found in $[2,2,2\text{-cryptK}]_3As_{11}^{3-}$ [54]. The unit cell contains three crypt-K units and one anionic cage.

$[2,2,2\text{-cryptK}]_4[SnAs_{14}]$, formed from $K_{1.5}Sn_1As_{3.5}$, and $\{[2,2,2\text{-cryptRb}]_4\text{-}[As_{22}]{\cdot}4DMF\}$ (DMF = dimethyformamide), formed from $Fe_2(CO)_9$ with Rb_3As_7 in en/crypt and recrystallised in DMF, both contain dumb-bell shaped anions with the former consisting of two As_7^{3-} units asymmetrically linked by the single three coordinate Sn(II) and the latter formed by the oxidative coupling of two As_{11}^{3-} cages [55]. The two sub-units of both anions retain the same structure as found in discrete As_7^{3-} and As_{11}^{3-} anions, respectively.

The reaction of $KE_{2.25}$ (E = Ge, Sn, Pb) with 2,2,2-crypt in en all give paramagnetic [2,2,2-cryptK]$_3$[E$_9$] salts: Ge_9^{3-} as red needles, Sn_9^{3-} as dark brown crystals and Pb_9^{3-} as black crystals [56]. The anionic polyatomic cages are best described as distorted tricapped prisms and are well separated in the lattice from the cationic moiety. While Sn_9^{3-} shows little distortion from D_{3h} symmetry, a strong distortion towards C_{2v} symmetry is found for the Ge_9^{3-} anion in {[2,2,2-cryptK]$_3$[Ge$_9$]·Ph$_3$P} [57]. The centrosymmetric unit cell here contains six [2,2,2-cryptK] cations, six anionic cages and two Ph_3P ligands. These crystals were obtained from the reaction of Ni(Ph$_4$P), Ph_3P and $KGe_{1.8}$ with en/crypt, a reaction mixture which also produced crystals of [2,2,2-cryptK]$_2$[Ge$_{10}$]. The absence of Ph_3P and an excess of crypt in the reaction with the $KGe_{1.8}$ phase led to the isolation of crystals containing two differently charged anion cages; {[2,2,2-cryptK]$_6$[$Ge_9^{4-}Ge_9^{2-}$].2.5en} [58]. The Ge_9^{4-} adopts a monocapped square anti-prism structure with symmetry close to C_{4v} and closely analogous to Sn_9^{4-} in [2,2,2-cryptNa]$_4$[Sn$_9$] [59], while the structure of the Ge_9^{2-} unit is that of a tricapped triangular prism moving from D_{3h} towards C_{2v} symmetry.

Similar complexes containing mixtures of the anionic polyatomic cage have been prepared in the reactions of $KE_{2.25}$ with 2,2,2-crypt in en and toluene. The resulting dianionic species, {[2,2,2-cryptK]$_6$[$E_9^{3-}E_9^{3-}$]·1.5en·0.5toluene} differ from the Ge complex above in that both anionic cages retain their formal 3 − charge [60].

Trigonal bipyramidal cages with D_{3h} symmetry of E_5^{2-} have been characterised in [2,2,2-cryptM]$_2$[Sn$_5$] [61], {[2,2,2-cryptK]$_2$[Ge$_5$]·THF} [62] and in [2,2,2-cryptM]$_2$[Pb$_5$] [61] (M = Na, K) and are isovalent with Tl_5^{7-} and Bi_5^{3+}. The crystal packing in the Ge complex differs from the high symmetry and centrosymmetric packing of the Sn and Pb complexes in that the well ordered anionic cages form layers between the cationic moieties and THF molecules.

The importance of stoichiometry in the assembly of the supramolecular lattices is highlighted especially well both by the formation of the Ge dianion complex above and in the formation of the Pb_9^{4-} and Pb_9^{3-} anions. In the reaction of $KPb_{2.05}$ with 2,2,2-crypt in en an exact stoichiometric 1:1 mixture of $KPb_{2.05}$ and crypt results in the Pb_9^{4-} anion while a slight stoichiometric excess of crypt leads to the formation of the paramagnetic Pb_9^{3-} anion. Unlike for the Pb_9^{3-} complex which is made of discrete ions, in K^+[2,2,2-cryptK]$_3$[Pb$_9$] uncomplexed K cations bridge the waist edges of the anion leading to an infinite ···K···(Pb)$_9$···K···(Pb)$_9$···K··· chain, as can be seen in Fig. 16 [63].

5. Future prospects

Carboranes have recently gained prominence in supramolecular chemistry, the cohesion of the supermolecules and solid state structures coming from different interactions associated primarily with the acidic C–H groups. Solvent molecules can also play a vital role in determining the crystal packing and overall topology of the systems. Interactions involving the carboranes with themselves, and with solvent and other molecules has potential in assembling complex structures. Complexation

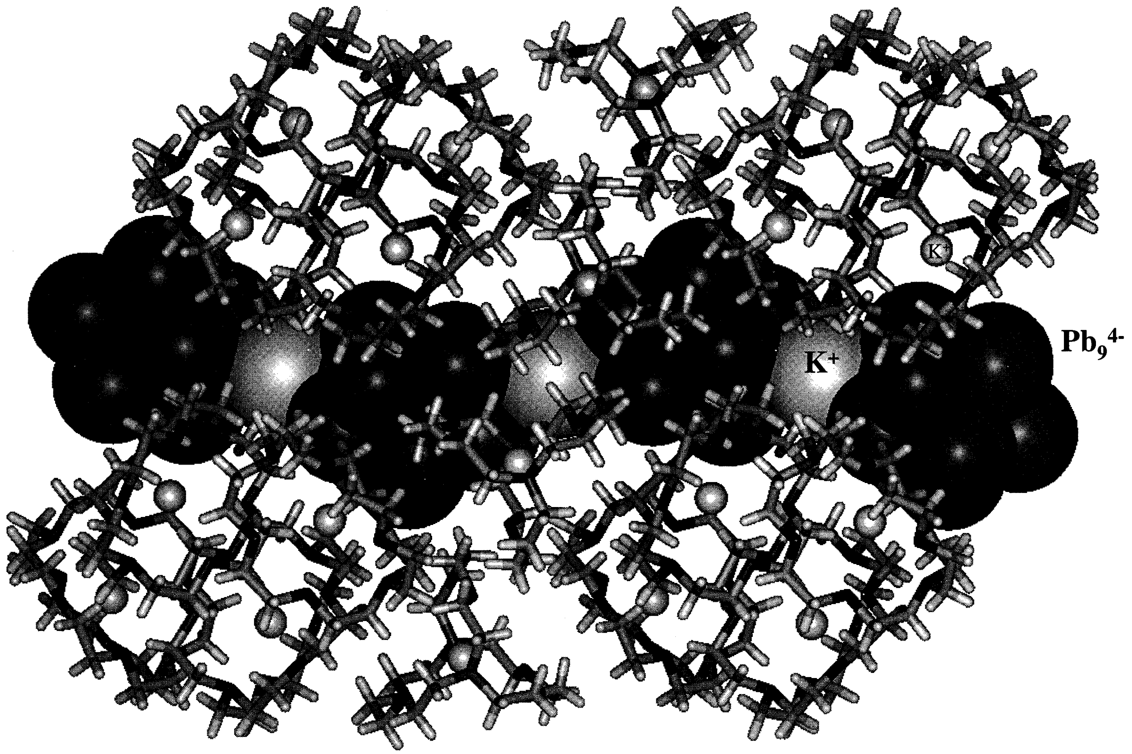


Fig. 16. Space filling representation of the ...K...Pb_9...K...Pb_9... chain in $K^+[2,2,2\text{-cryptK}]_3[Pb]_9$ with the accompanying crypt and encapsulated K cations represented in stick form [63].

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 carborane) where the host–guest components otherwise fail to assemble.

The receptor macrocyle Ni(TMTAA) is versatile in accommodating a range of cage like molecules, either in each saddle or in either saddle of the associated dimers of the macrocycle. In establishing ground rules in the area, the use of more easily oxidised metal(II) derivatives of $TMTAA^{2-}$ offers a direct electron transfer route to supramolecular arrays of reduced cages with the oxidised macrocycle as the counter ion, $M^{2+}(TMTAA) \rightarrow [M^{2+n}(TMTAA)]^{n+}$, and the prospect of generating materials with novel function.

A major advance in supramolecular chemistry is the ability to construct large encapsulating supermolecules assembled by hydrogen bonding [64,65] or metal coordination chemistry [66]. These systems have very large internal voids and in principle could accommodate, and incarcerate, several carboranes and even larger main group cages species. Finally the supramolecular chemistry of zintl ions has exciting possibilities in stabilising new species, in their separation from complex mixtures, and in generating novel structures and materials.

References

[1] see for example (a) R.M. Williams, J.M. Zwier, J.W. Verhoeven, J. Am. Chem. Soc. 116 (1994) 6965. (b) T. Suzuki, K. Nakashima, S. Shinkai, Chem. Lett. (1994) 699. (c) T. Suzuki, K. Nakashima, S. Shinkai, Tetrahedron Lett. 36 (1995) 249. (d) C.L. Raston, J.L. Atwood, P.J. Nichols, I.B.N. Sudria, H. J. Chem. Soc. Chem. Commun. (1996), 2615. (e) K. Araki, K. Akao, T. Suzuki, S. Shinkai, Tetrahedron Lett. 37 (1996) 73. (f) A. Ikeda, S. Shinkai, Chem. Rev. 97 (1997) 1713. (g) T. Haino, M. Yanase, Y. Fukazawa, Angew. Chem. Int. Ed. Engl. 36 (1997) 259. (h) T. Haino, M. Yanase, Y. Fukazawa, Tetrahedron Lett. 38 (1997) 3739. (i) K. Tsubaki, K. Tanaka, T. Kinoshita, K. Fuji, J. Chem. Soc. Chem. Commun. (1998) 8955. (j) T. Haino, M. Yanase, Y. Fukazawa, Angew. Chem. Int. Ed. Engl. 37 (1998) 997.

[2] J.-M. Lehn, Supramolecular Chemistry, Concepts and Perspectives, VCH, Weinham, 1995.

[3] R.N. Grimes, Carboranes, Academic, New York, 1970.

[4] J. Plesek, Chem. Rev. 92 (1992) 269.

[5] (a) H.M. Colquhoun, J.A. Daniels, I.R. Stephenson, K. Wade, Polym. Commun. 32 (1991) 272. (b) X. Yang, W. Jiang, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 114 (1992) 9717. (c) J. Müller, K. Base, T.F. Magnera, J. Michel, J. Am. Chem. Soc. 114 (1992) 9721. (d) W. Jiang, C.B. Knobler, M.D. Mortimer, M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 34 (1995) 1332. (e) W. Jiang, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 35 (1996) 3056. (f) W. Jiang, D.E. Harwell, M.D. Mortimer, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 35 (1996) 4355.

[6] D. Armspach, M. Cattalini, E.C. Constable, C.E. Housecroft, D. Philips, J. Chem. Soc. Chem. Commun. (1996) 1823.

[7] (a) R.N. Grimes, Angew. Chem. Int. Ed. Engl. 32 (1993) 1289. (b) W. Clegg, J. Plesek, Chem. Rev., 92 (1992) 269. (c) W.R. Gill, J.A.H. MacBride, K. Wade, Angew. Chem. Int. Ed. Engl. 32 (1993) 1328. (d) I.T. Chizhevsky, S.E. Johnson, C.B. Knobler, F.A. Gomez, M.F. Hawthorne, J. Am. Chem. Soc. 115 (1993) 6981. (e) W. Jiang, I.T. Chizhevsky, M.D. Mortimer, W. Chen, C.B. Knobler, S.E. Johnson, F.A. Gomez, M.F. Hawthorne, Inorg. Chem. 35 (1996) 5417. (f) W.R. Gill, P.L. Herbertson, J.A.H. MacBride, K. Wade, J. Organomet. Chem. 507 (1996) 249.

[8] (a) A.A. Zinn, Z. Zheng, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 118 (1996) 70. (b) Z. Zheng, C.B. Knobler, M.D. Mortimer, G. Kong, M.F. Hawthorne, Inorg. Chem. 35 (1996) 1235l. (c) M.F. Hawthorne, Z. Zheng, Acc. Chem. Res. 30 (1997) 267 and references therein.

[9] X. Yang, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 115 (1993) 4904.

[10] (a) L.A. Leites, Chem. Rev. 92 (1992) 279. (b) G. Harakas, T. Vu, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 120 (1998) 6405, and references therein.

[11] M.G. Davidson, T.G. Hibbert, J.A.K. Howard, A. Mackinnon, K. Wade, J. Chem. Soc. Chem. Commun. (1996) 2285.

[12] P.D. Godfrey, W.J. Grigsby, P.J. Nichols, C.L. Raston, J. Am. Chem. Soc. 119 (1997) 9283.

[13] R.J. Blanch, M. Williams, G.D. Fallon, M.G. Gardiner, R. Kaddour, C.L. Raston, Angew. Chem. Int. Ed. Engl. 36 (1997) 504.

[14] M.J. Hardie, C.L. Raston, Eur. J. Inorg. Chem. (1999) 195.

[15] M.J. Hardie, P.D. Godfrey, C.L. Raston, Chem. Eur. J. (1999) in press.

[16] M.J. Hardie, C.L. Raston, unpublished results.

[17] W. Jorgenson, D. Steverance, J. Am. Chem. Soc. 112 (1990) 4768.

[18] J L. Atwood, S.G. Bott, C. Jones, C.L. Raston, J. Chem. Soc. Chem. Commun. (1992) 1349.

[19] J.L. Atwood, F. Hamada, K.D. Robinson, G.W. Orr, R.L. Vincent, Nature 349 (1991) 683.

[20] T.B. Richardson, S. deGala, R.H. Crabtree, P.E.M. Seigbahan, J. Am. Chem. Soc. 117 (1995) 12875.

[21] A. Harada, S. Takahashi, J. Chem. Soc. Chem. Commun., (1988) 1352.

[22] (a) T. Anderson, K. Nillson, M. Sundahl, G. Westman, O. Wennerstrom, J. Chem. Soc. Chem. Commun. (1992) 604. (b) P. Kutner, P. Boules, K.M. Kadish, J. Electrochem. Soc. 139C (1992) 243. (c) R.M. Williams, J.W. Verhoeven, Recl. Trav. chim. Pays-Bas Beig. 111 (1992) 531.

[23] J.L. Atwood, L.J. Barbour, C.L. Raston, I.B.N. Sudria, Angew. Chem. Int. Ed. Engl. 37 (1998) 981.

[24] J.L. Atwood, G.A. Koutsantonis, C.L. Raston, Nature 368 (1994) 229.

[25] (a) S. Kamitori, K. Hirotsu, T. Higuchi, J. Am. Chem. Soc. 109 (1987) 2409. (b) S. Kamitori, K. Hirotsu, T. Higuchi, Bull. Chem. Soc. Jpn. 61 (1988) 3825.

[26] J.L. Atwood, M. Barnes, M.G. Gardiner, C.L. Raston, J. Chem. Soc. Chem. Commun. (1996) 1449.

[27] J.L. Atwood, M.J. Barnes, R.S. Burkhalter, P.C. Junk, J.W. Steed, C.L. Raston, J. Am. Chem. Soc. 116 (1994) 10346.

[28] A. Collet, in: J.L. Atwood, J.E.D. Davies, D.D. Macnicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, vol. 6, Permangon, UK, 1996 and references therein.

[29] M.D. Hollingsworth, K.D.M. Harris, in: J.L. Atwood, J.E.D. Davies, D.D. Macnicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, vol. 6, Permangon, UK, 1996 and references therein.

[30] V.S. Mastryukov, O.V. Dorofeeva, L.V. Vilkov, Russ. Chem. Rev. (Engl. Trans.) 49 (1980) 1181.

[31] F. Vogtle, E. Weber, Host Guest Complex Chemistry, Macrocycles, Synthesis, Structure, Applications, Springer-Verlag, Berlin, 1985.

[32] P.C. Andrews, J.L. Atwood, L.J. Barbour, P.J. Nichols, C.L. Raston, Chem. Eur. J. 4 (1998) 1384.

[33] H. Weller, Angew. Chem. Int. Ed. Engl. 35 (1996) 1079 and references therein.

[34] P.C. Andrews, P.J. Nichols, C.L. Raston, unpublished results.

[35] M.D. Vaira, M. Peruzzini, P. Stoppioni, Inorg. Chem. 22 (1983) 2196.

[36] M.D. Vaira, M. Peruzzini, P. Stoppioni, J. Organomet. Chem. 258 (1983) 373.

[37] (a) F.A. Cotton, J. Czuchajowsha-Wiesinger, Acta Cryst. C48 (1992) 1434. (b) G. Ricciardi, A. Bavoso, A. Rosa, F. Lelj, Y. Cizov, J. Chem. Soc. Dalton Trans. (1995) 2385.

[38] R.E. Douthwaite, M.L.H. Green, S.J. Heyes, M.J. Rosseinsky, J.F.C. Turner, J. Chem. Soc. Chem. Commun. (1994) 1367.
[39] (a) E. Zintl, J. Goudeau, W. Dullenkopf, Z. Phys. Chem. Abt. A 154 (1931) 1. (b) E. Zintl, A. Harder, Z. Phys. Chem. Abt. A 154 (1931) 47. (c) E. Zintl, W. Dullenkopf, Z. Phys. Chem. Abt, B 16 (1932) 183.
[40] (a) J.D Corbett, D.G. Adolphson, D.J. Merryman, P.A. Edwards, F.J. Armatis, J. Am. Chem. Soc. 97 (1975) 6267. (b) J.D. Corbett, P.A. Edwards, J. Chem. Soc. Chem. Commun. (1975) 984. (c) D.G. Adolphson, J.D. Corbett, D.J. Merryman, J. Am. Chem. Soc. 98 (1976) 7234. (d) A. Cisar, J.D. Corbett, Inorg. Chem. 16 (1977) 632.
[41] L. Diehl, K. Kodadadeh, D. Kummer, J. Strähle, Chem. Ber. 109 (1976) 3404.
[42] H.-G. von Schnering, V. Manriquez, W. Hönle, Angew. Chem. Int. Ed. Engl. 20 (1981) 594.
[43] N. Korber, H-G. von Schnering, J. Chem. Soc. Chem. Commun. (1995) 1713.
[44] N. Korber, J. Daniels, H.-G. Schnering, Angew. Chem. Int. Ed. Engl. 35 (1996) 1107.
[45] B. Siewart, U. Müller, Z. Anorg. Allg. Chem. 609 (1992) 77.
[46] C. Belin, V. Angilella, H. Mercier, Acta Cryst. C 47 (1991) 61.
[47] R.C. Haushalter, J. Chem. Soc. Chem. Commun. (1987) 196.
[48] V. Angilella, H. Mercier, C. Belin, J. Chem. Soc. Chem. Commun. (1989) 1654.
[49] U. Müller, H. Sinning, Angew. Chem. Int. Ed. Engl. 28 (1989) 185.
[50] P. Zanello, A. Cinquantini, C.A. Ghilardi, S. Midollini, S. Moneti, A, Orlandini, A. Bencini, J. Chem. Soc. Dalton Trans. (1990) 3761.
[51] C.J. Warren, D.M. Ho, R.C. Haushalter, A.B. Bocarsly, Angew. Chem. Int. Ed. Engl. 32 (1993) 1646.
[52] D.M. Smith, C.-W. Park, J.A. Ibers, Inorg. Chem. 35 (1996) 6682.
[53] C. Belin, H. Mercier, J. Chem. Soc. Chem. Commun. (1987) 190.
[54] C. Belin, J. Am. Chem. Soc. 102 (1980) 6036.
[55] R.C. Haushalter, B.W. Eichhorn, A.L. Rheingold, S.J. Geib, J. Chem. Soc. Chem. Commun. (1988) 1027.
[56] T.F. Fässler, M. Hunziker, Inorg. Chem. 33 (1994) 5380.
[57] V. Angilella, C. Belin, J. Chem. Soc. Faraday Trans. 87 (1991) 203.
[58] C. Belin, J.D. Corbett, A. Cisar, J. Am. Chem. Soc. 99 (1977) 7163.
[59] J.D. Corbett, P.A. Edwards, J. Am. Chem. Soc. 99 (1977) 3313.
[60] T.F. Fässler, M. Hunziker, Z. Anorg. Allg. Chem. 622 (1996) 837.
[61] S. Ulvenlund, K. Stähl, L. Bengsson-Kloo, Inorg. Chem. 35 (1996) 223.
[62] J. Campbell, G.J. Schrobilgen, Inorg. Chem. 36 (1997) 4078.
[63] J. Campbell, D.A. Dixon, H. Mercier, G.J. Schrobilgen, Inorg. Chem. 34 (1995) 5798.
[64] L.R. MacGillivray, J.L. Atwood, Nature 389 (1997) 469 and references therein.
[65] T. Heinz, D.M. Rudkevich, J. Rebek, Nature 394 (1998) 764 and references therein.
[66] T.N. Parac, D.L. Clauder, K.N. Raymond, J. Am. Chem. Soc. 120 (1998) 8003.