Altering the Inclusion Properties of CTV through Crystal Engineering: CTV, Carborane, and DMF Supramolecular Assemblies

Michaele J. Hardie,* Colin L. Raston, and Bradley Wells[a]

Abstract: The complexes $[Na(CTV)_2(OH)(H_2O)](H_2O)(DMF)_2$(*o*-carborane) (**3**; CTV = cyclotriveratrylene), $[K(OH)(CTV)(DMF)]_2$(*o*-carborane) (**4**), $[(DMF)(CTV)]_2(H_2O)_4$(*o*-carborane) (**5**), and (*o*-carborane)(CTV)(DMF)$_2$ (**6**) all form as crystalline inclusion complexes from *N,N'*-dimethylformamide (DMF) solution. Complexes **3** and **4** are the first reported examples of CTV acting as a chelating ligand, with two CTV molecules coordinating *cis* to the six-coordinate M^+ centers (M = Na, K). The extended structures of complexes **3**–**5** are similar, forming extended coordinate and/or hydrogen-bonding interactions and all feature intracavity complexation of DMF by CTV, while the complex **6** forms an assembly of (*o*-carborane) $\cap$ (CTV) ball-and-socket supermolecules with DMF as a channel-type included guest.

Keywords: alkali metals · carboranes · crystal engineering · cyclotriveratrylene · inclusion compounds

Introduction

Cyclotriveratrylene (CTV) is a rigid cyclic molecule with a curved aspect similar to the cone conformation of many calixarenes, albeit with a somewhat shallower cavity.[1] Like the calixarenes, CTV displays a rich inclusion chemistry with small guest molecules; however, in contrast to calixarene inclusion chemistry,[2] such inclusion complexes are usually only formed in the solid state and do not feature intracavity complexation of the guest molecules.[1, 3] Instead CTV usually forms channel-type structures in one of two phases, α or β, depending on the nature of the guest molecule, which can form hydrogen-bonding interactions to the dimethoxy groups of the CTV.[3] The related host molecule cyclotricatechylene (CTC) with six hydroxy groups in place of the methoxy groups of CTV also forms inclusion complexes with a number of small organic molecules, but unlike CTV, the guest molecules can be bound within the CTC cavity.[3, 4] Notably the solid-state structures of such inclusion complexes show infinite hydrogen-bonded chains of CTC molecules, interacting through their hydroxy groups.[3] Catechol-like coordination to square-planar platinum centers through these hydroxy groups can extend the size of the CTC cavity, and such complexes also bind guest solvent molecules within the cavity.[5]

Intracavity complexation of guest molecules by CTV is known to occur for a small number of large spherical main group cage molecules such as fullerenes[6, 7] and 1,2-dicarbadodecaborane(12) (*o*-carborane),[7, 8] as well as cationic organometallic complexes $[FeCp(C_6H_5R)]^+$ where Cp = cyclopentadiene.[9] *o*-Carborane can act as either an intracavity guest for CTV or as a hydrogen-bond donor to CTV dimethoxy groups.[7, 8] The C–H groups of carboranes are acidic[10] and a limited number of other supramolecular complexes have been established, notably complexes with hexamethylphosphoramide,[11] cyclodextrins,[12] aza-crown ethers,[13] and calix[5]arene.[14] Fullerene C_{60} forms two inclusion complexes in the solid state and, unusually for CTV inclusion chemistry, also forms a complex in solution.[6] The higher fullerene C_{70} is not normally complexed by CTV; however, addition of *o*-carborane to a C_{70}/CTV mixture in toluene or 1,2-dichlorobenzene leads to the isolation of the crystalline complex (C_{70})(*o*-carborane)(CTV)(solvent) which has an infinite hydrogen-bonded helical chain of CTV and *o*-carborane molecules and C_{70} complexed within the CTV cavity.[7] Thus binding the CTV molecule through hydrogen bonding changes its properties as a host molecule.

CTV is ideal for a more general exploration of the concept that the inclusion properties of a known host molecule can be altered by extended hydrogen bonding or coordinate interactions, such as those found in crystal-engineered systems. CTV has a trigonal arrangement of hydrogen bond acceptor functional groups and, as such, can be used a tecton for crystal engineering strategies.[15] We report herein a number of crystalline supramolecular assemblies of CTV, *o*-carborane, and dimethylformamide (DMF) that further illustrate this

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concept. Under the usual conditions for the formation of inclusion compounds CTV does not form a complex with DMF;[3] however, the complexes $[Na(CTV)_2(OH)(H_2O)](H_2O)(DMF)_2$(*o*-carborane), $[K(OH)(CTV)(DMF)]_2$(*o*-carborane), and $[(DMF)(CTV)]_2(H_2O)_4$(*o*-carborane) all feature intracavity complexation of DMF by CTV, while the complex (*o*-carborane)(CTV)$(DMF)_2$ has DMF as a channel type included guest. The solid-state structures of the complexes were determined from X-ray diffraction data collected at low temperatures.

Results and Discussion

Synthesis of compounds **3**–**6** are summarized in Scheme 1. Slow evaporation of a mixture of CTV (**1**) and *o*-carborane (**2**) in 1:1 or 1:2 proportions in DMF with an excess of aqueous NaOH gave colorless crystals of composition $[Na(CTV)_2(OH)(H_2O)](H_2O)(DMF)_2$(*o*-carborane) (**3**). The complex crystallizes in a monoclinic cell ($a = 23.5316(3)$, $b = 14.5838(2)$, $c = 19.6828(8)$ Å, $\beta = 109.254(7)°$) and the structure was solved in space group *C*2/*c* (Figure 1). The structure is complicated, with many levels of supramolecular interaction such as coordinate bonding, hydrogen bonding, π stacking, and intracavity and channel-type host–guest interactions. Most strikingly, the CTV molecules act as chelating ligands, with two symmetry-equivalent CTV molecules coordinating to each sodium center (Na–O distances 2.412(2) and 2.532(1) Å). This is the first reported example of CTV coordinating to any metal center, although the coordination of its catechol analogue CTC to Pt is known.[5] The sodium ion has a six-coordinate extremely distorted octahedral geometry with *cis* hydroxy and water ligands completing the coordination sphere (Na–O distance 2.313(2) Å). The water and hydroxy ligands are disordered having half water and half hydroxy character as both positions are crystallographically equivalent. All ligands around the Na center are terminally bound; however, all form additional interactions through hydrogen bonds to either a water molecule or the water/hydroxy ligand of another Na complex. Each CTV molecule chelates to a Na center through one dimethoxy moiety, hydrogen bonds to a water molecule in a bifurcated interaction through a second dimethoxy unit, and hydrogen bonds to a coordinated water/hydroxy ligand through one methoxy oxygen atom of the third dimethoxy moiety (O···HO distance 2.21 Å;). The water molecule acts as both a hydrogen-bond donor to the CTV molecule (OH···O distances 2.25 and 2.42 Å) and as a hydrogen-bond acceptor from the coordinated water/hydroxy ligands (O···HO distance 1.98 Å).

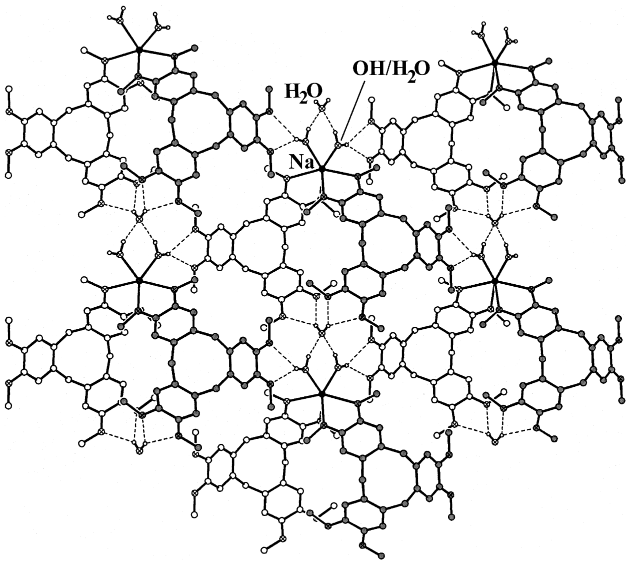
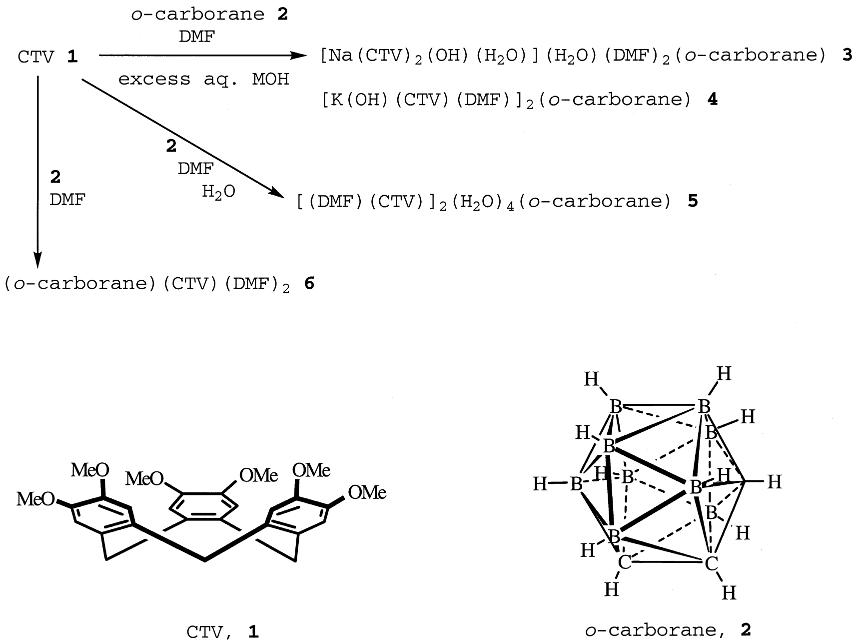


Figure 1. Section of the two-tiered, infinite two-dimensional sheet structure formed by a combination of coordinate and hydrogen-bonding interactions in **3**. Na atoms are shaded black. All CTV molecules with their cavities oriented in the same direction have the same shading. Only hydrogen atoms involved in hydrogen-bonding interactions are shown for clarity.



Scheme 1.

The sum of these interactions is a two-tiered, infinite two-dimensional sheet structure formed by a combination of coordinate and hydrogen-bonding interactions. While most crystal engineering studies aim to produce infinite networks through coordinate[16] or hydrogen bonds,[17] the combination of the two is by no means unknown.[18] The network of complex (**3**) is shown in projection in Figure 1. There are two tiers of coplanar CTV molecules, each with their CTV cavities pointing inwards but in inverted orientations. Each

CTV molecule within the network acts as a host for one molecule of guest DMF. The DMF is positioned directly above one phenyl group of the CTV; the nitrogen atom of DMF lies roughly above the center of the aromatic ring (N $\cdots$ centroid separation 3.54 Å). The plane of the DMF is tilted slightly away from that of the phenyl group (torsion angle 14.4°).

The combined coordinate and hydrogen-bonded networks stack together within the crystal lattice through $\pi-\pi$ interactions. Each CTV forms three such interactions through each of its phenyl rings to another CTV molecule of an adjacent network. The CTV phenyl rings π stack in a coplanar but slightly slipped fashion (aromatic centroid $\cdots$ centroid separations 3.63, 3.62, and 3.91 Å, Figure 2). The packing of the networks is such that channels are formed, lined by methyl groups from CTV molecules. The carborane guest molecules are located within these hydrophobic channels (closest carborane C/B to CTV methyl distance 3.85 Å).

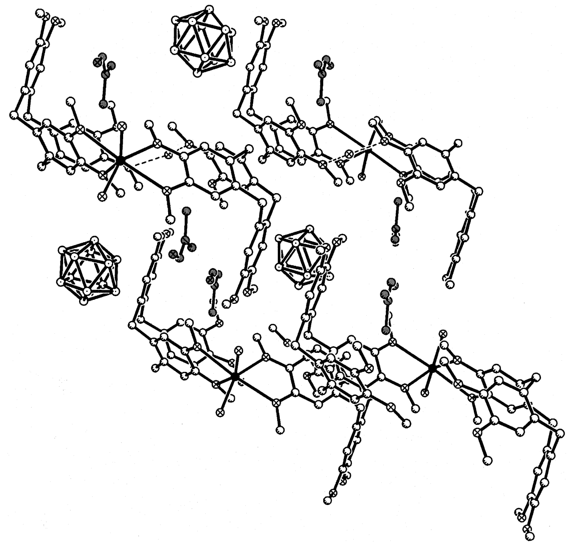


Figure 2. Packing diagram of complex **3**. DMF molecules are shaded gray and hydrogen atoms have been omitted for clarity.

The use of other alkali metal hydroxides was also investigated. The addition of the hydroxide salt of the smaller alkali metal Li to a mixture of CTV (**1**) and *o*-carborane (**2**) in DMF did not result in the isolation of any crystalline complexes; however, the slow evaporation of a 1:1 mixture of **1** and **2** in DMF with aqueous KOH gave colorless crystals of composition $[K(OH)(CTV)(DMF)]_2$(*o*-carborane) (**4**). The complex crystallizes in a monoclinic cell ($a = 19.3270(3)$, $b = 14.8709(2)$, $c = 12.5698(1)$ Å, $\beta = 116.021(1)°$) that is related to that of **3** but with the *a* axis approximately halved and swapped with the *c* axis. The structure was solved in the space group *C2/m*, and, in terms of the arrangement of the major structural components, is essentially the same as that of **3**.

The K cation in **4** is six-coordinate in a very distorted octahedral geometry similar to that of the Na^+ ion in **3**. The coordination sphere consists of two symmetry-equivalent chelating CTV molecules with cavities in opposite orientations (K–O distances 2.722(2) and 2.935(2) Å) and two symmetry-related *cis* hydroxy ligands (K–O distance 2.729(3) Å). Unlike in complex **3** in which the hydroxy/water ligands are terminal, the hydroxy ligands bridge to another K center to form an unusual planar K-μ-$(OH)_2$-K core with a K $\cdots$ K distance of 4.034(3) Å (Figure 3). The observed coordination number of six is low for potassium, and appears to be as a result of the steric crowding of the metal center by the methyl groups of the CTV ligands; the closest contact between CTV methyl carbon atoms and K is 3.51 Å. To the best of our knowledge, this is the first structurally authenticated example of a di-μ-OH bridge between two K centers in a metal-organic species.[19] Hydroxy bridges are known for cluster complexes of the smaller alkali metals,[20] and are common for transition metal complexes.[21] A single bridge between potassium centers by a ligand of either hydroxide or water or of mixed character has been reported for a dipotassium cyclodextrin complex.[22] Both chelating CTV ligands bridge to a second K-μ-$(OH)_2$-K unit and a linear coordinate -K-μ-$(OH)_2$-K-μ-$(CTV)_2$-K-μ-$(OH)_2$-K- chain is formed in the *b* direction. In **3** this structural motif is found in the $\cdots (OH)(H_2O)Na(CTV)_2 \cdots (H_2O) \cdots (OH)(H_2O)Na(CTV)_2 \cdots$ coordinate and hydrogen-bonded chain also along the *b* direction. Each K coordinate chain hydrogen bonds to two adjacent and identical chains through the K-μ-$(OH)_2$-K hydroxy hydrogens forming a bifurcated interaction to the non-coordinating dimethoxy units of CTV ligands on adjacent chains (OH $\cdots$ $(OMe)_2$ distance 2.37 Å; corresponding to O $\cdots$ O 2.98 Å; Figure 4). This combination of coordinate and hydrogen-bonding interactions forms a two-tiered, infinite two-dimensional sheet structure that is topologically identical to that of **3**, and these networks stack together through $\pi-\pi$ interactions (aromatic centroid $\cdots$ centroid distances 3.64, 3.59, and 3.59 Å).

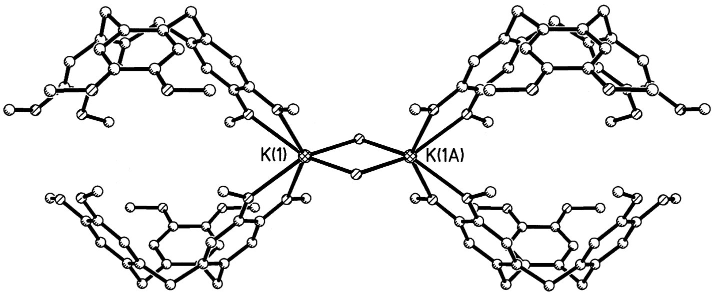


Figure 3. Potassium coordination sphere with μ-OH bridging ligands in complex **4**. Hydrogen atoms have been omitted for clarity.

The host–guest or inclusion behavior of complex **4** is also analogous to that of **3**. The carborane acts as a guest in channel-type inclusion behavior. The DMF guest molecules show a static disorder of the CO and one CH_3 group. Each DMF molecule sits above a phenyl ring of a CTV host at a $N_{DMF} \cdots$ aromatic centroid distance of 3.55 Å and a torsion angle of 18.1° with a methyl group directed towards the center of the CTV.

The absence of MOH (M = Na, K) but presence of water in a DMF solution of *o*-carborane and CTV also results in the formation of a crystalline complex containing infinite networks, in this case hydrogen-bonded water–CTV networks.

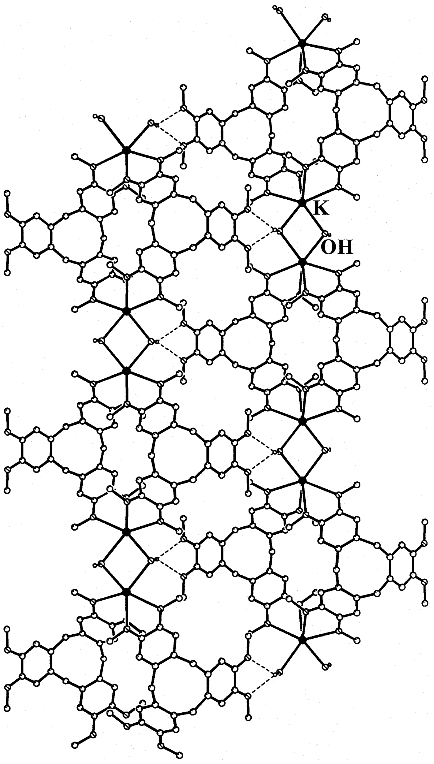


Figure 4. Section of the extended two-dimensional network in complex **4**. Potassium centers are shaded black. Only hydroxide hydrogen atoms involved in hydrogen bonding interactions are shown for clarity.

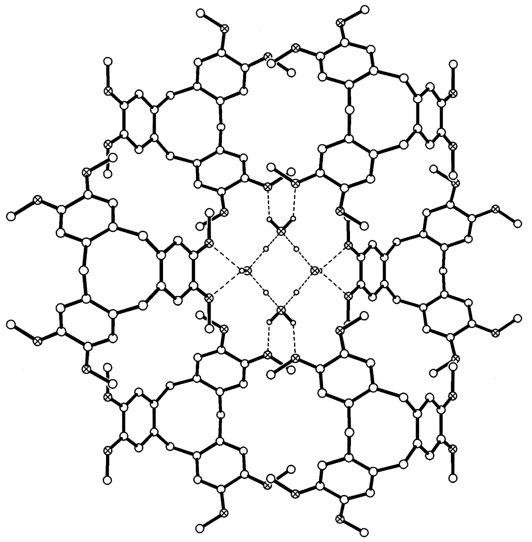


Figure 5. Hydrogen-bonding interactions between the water tetramer and CTV molecules in **5**. Only hydrogen atoms on the water tetramer are shown and have a symmetry-imposed disorder, each hydrogen along an O−H ⋯ O edge of the tetramer is in a position central to the two O atoms, indicating the hydrogen atom is at an averaged O−H ⋯ O/O ⋯ H−O site.

Slow evaporation of a 1:1 mixture of CTV (**1**) and *o*-carborane (**2**) in DMF with about 10 % water gave colorless crystals of composition $[(DMF)(CTV)]_2(H_2O)_4$(*o*-carborane) **5**. The complex crystallizes in a monoclinic cell very close to that of **4** ($a = 19.0438(6)$, $b = 14.8451(3)$, $c = 12.5575(4)$ Å, $\beta = 113.565(1)°$). The structure was solved in space group *C*2/*m*. Despite the absence of alkali metal ions, the extended structure of **5** is virtually identical to that of **3** and **4**.

The interactions that create the two-tiered, infinite two-dimensional sheet structure in **5** are hydrogen-bonding interactions between CTV and water molecules. There are two crystallographically distinct water molecules which form a hydrogen-bonded water tetramer (O ⋯ O separations 2.75 Å). The water tetramer also acts as a hydrogen-bond donor to six CTV molecules. Two water molecules of opposite corners of the tetramer each form a bifurcated hydrogen bond to the dimethoxy moieties of two different CTV molecules (OH ⋯ O distance 2.38 Å; corresponding O ⋯ O 2.93 Å). The remaining water molecules each form hydrogen-bonding interactions to the methoxy groups of two CTV molecules (OH ⋯ O distance 1.94 Å; corresponding O ⋯ O 2.83 Å; Figure 5). Each CTV molecule hydrogen bonds to three water tetramers to create a two-dimensional network directly analogous to that of **3** and **4**. Packing of the networks within the crystal lattice is identical to that of **3** and **4** with coplanar π stacking between aromatic rings of the CTV molecules (centroid ⋯ centroid separations 3.53, 3.53, and 3.55 Å). The host – guest behavior of **5** is similar to that of **3**, with DMF perched within the CTV cavity and positioned above one phenyl ring, although the DMF plane is tilted further from the phenyl plane at a $N_{DMF} \cdots$ aromatic centroid separation of 3.60 Å and a torsion angle of 25.4°. The DMF shows a static disorder of the CO and CH_3 groups. The carborane acts as a guest in channel-type inclusion behavior, with hydrophobic channels formed in the *c* direction (Figure 6).

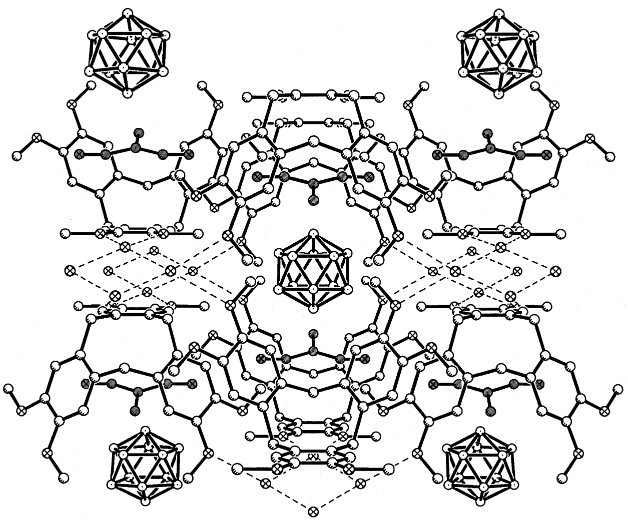


Figure 6. Packing diagram of **5** along the *c* direction. Note the carborane molecules positioned within a methyl-lined channel. DMF molecules are shaded. Hydrogen atoms have been omitted for clarity.

In circumstances where infinite hetero-molecular hydrogen-bonded networks involving CTV are not formed, the host – guest behavior is radically altered. Slow evaporation of a 1:1 mixture of CTV (**1**) and *o*-carborane (**2**) in DMF gave colorless crystals of composition (*o*-carborane)(CTV)$(DMF)_2$ (**6**). Complex **6** crystallizes in an orthorhombic cell ($a = 22.4054(8)$, $b = 17.8735(6)$, $c = 10.3919(2)$ Å) and the structure was solved in noncentrosymmetric space group *Cmc*2$_1$. The complex features intracavity complexation of *o*-carborane by CTV to give a (*o*-carborane) ∩ (CTV) ball-and-socket type supramolecular assembly.

One of the C–H vectors of the carborane is directed towards an aromatic ring of the CTV forming a nonclassical C–H ··· π-hydrogen bond ($C_{carborane}$ ··· aromatic centroid separation 3.29 Å, $C-H_{carborane}$ ··· centroid angle 19.4°). This type of nonclassical hydrogen bonding, a Coulombic interaction between an acidic C–H and basic π cloud, has also been reported for (*o*-carborane)$(CTV)_2$[8] and (*o*-carborane)$_n$(calix[5]arene)$_m$ assemblies,[15] in which, however, both C–H vertices of the carborane are involved. The ball-and-socket substructures form chains in the *c* direction, interacting through a bifurcated nonclassical $C-H_{methylene}$ ··· $(OMe)_2$ hydrogen bond between adjacent CTV molecules (C–H ··· O distance 2.50 Å; Figure 7). This type of inter-CTV interaction is quite distinct from other known modes of CTV packing.[3, 7, 8] Two such chains with opposite orientations pack such that a zigzag arrangement of guest *o*-carborane molecules is formed (closest B ··· B distance 4.23 Å). The packing of these double chains of ball-and-socket assemblies within the crystal lattice is such that channels, which are occupied by DMF molecules, are formed along the *c* direction. Each DMF molecule forms close interactions to two CTV molecules; the DMF carbonyl group to CTV aromatic C–H groups at O ··· H–C distances of 2.38 and 2.55 Å, and the C(O)H to a methoxy oxygen atom of the CTV molecule at 2.55 Å.

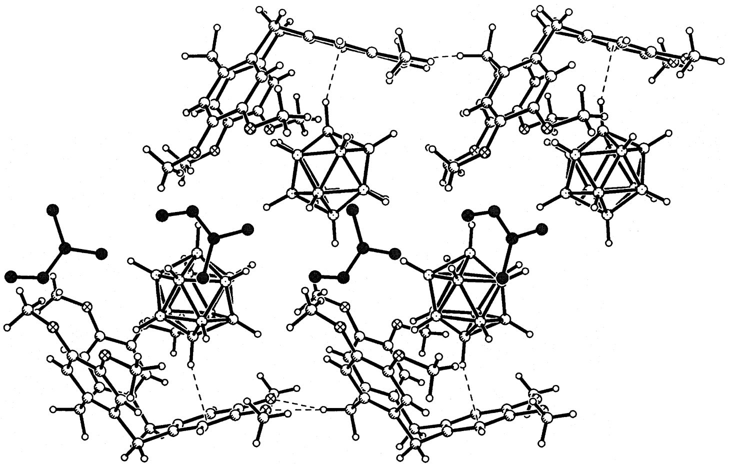


Figure 7. Extended structure of **6**, showing the formation of ball-and-socket assemblies with $C-H_{carborane}$ ··· π hydrogen bonding and bifurcated C–H ··· $(OMe)_2$ hydrogen bonding between CTV molecules. DMF molecules are shaded and shown without hydrogen atoms for clarity.

Under the same conditions as for the formation of **6**, a 1:2 mixture of **1** and **2** gives crystalline (*o*-carborane)$_2$(CTV), which also forms from toluene or 1,2-dichlorobenzene solutions and has an infinite hexagonal grid structure with one carborane hydrogen bonding to the dimethoxy groups of the CTV molecule and the other carborane acting as an intracavity guest.[7] A 1:1 complex has never been isolated from solvents such as toluene from which (*o*-carborane)$_2$(CTV) or (*o*-carborane)$(CTV)_2$[8] crystallize depending on reactant ratios.

Conclusion

The incorporation of CTV into an infinite supramolecular network has a dramatic effect on its properties as a host molecule in crystalline complexes. While previous studies have shown that CTV does not form any type of inclusion complex with DMF,[3] the complexes $[Na(CTV)_2(OH)(H_2O)](H_2O)(DMF)_2$(*o*-carborane), $[K(OH)(CTV)(DMF)]_2$(*o*-carborane), and $[(DMF)(CTV)]_2(H_2O)_4$(*o*-carborane) all show intracavity inclusion of DMF by CTV. All three complexes show extensive hydrogen bonding or a combination of hydrogen-bonding and coordinate interactions and, significantly, all three have an extremely similar arrangement of CTV molecules within their respective crystal lattices. The use of CTV as a chelating ligand is novel and is another crystal engineering parameter in the expansion of CTV inclusion chemistry.

Experimental Section

Synthesis

$[Na(CTV)_2(OH)(H_2O)](H_2O)(DMF)_2$(*o*-carborane) (3): CTV (4.7 mg, 0.010 mmol) and *o*-carborane (2.6 mg, 0.018 mmol) were dissolved separately in DMF, mixed, and 0.1M NaOH (0.10 mL) was added, and the solution allowed to stand. Colorless prismatic crystals of $[(DMF)(CTV)]_2[Na(OH)(H_2O)](H_2O)$(*o*-carborane) (4.3 mg, 65%) appeared after a week.

$[K(OH)(CTV)(DMF)]_2$(*o*-carborane) (4): CTV (4.3 mg, 0.01 mmol) and *o*-carborane (1.5 mg, 0.01 mmol) were dissolved separately in DMF, mixed, and 0.1M KOH (0.10 mL) added, and the solution allowed to stand. Colorless prismatic crystals of $[K(OH)(CTV)(DMF)]_2$(*o*-carborane) (4.9 mg, 79%) appeared after three weeks.

$[(DMF)(CTV)]_2(H_2O)_4$(*o*-carborane) (5): A 1:1 mixture of CTV and *o*-carborane in DMF:H_2O in 10:1 proportions yielded fine needles of CTV and a small amount of $[(DMF)(CTV)]_2(H_2O)_4$(*o*-carborane) upon standing for several weeks. Accurate yields could not be determined due to contamination with CTV.

(*o*-carborane)(CTV)$(DMF)_2$ (6): CTV (8 mg, 0.018 mmol) and *o*-carborane (2.6 mg, 0.02 mmol) were dissolved separately in DMF, mixed, and allowed to stand. After several weeks colorless, blocklike crystals of (*o*-carborane)(CTV)$(DMF)_2$ appeared (5.4 mg, 41%).

Complexes **3**–**6** lost solvent molecules to a varying degree on prolonged exposure to the atmosphere and reliable microanalyses could not be obtained.

Crystal structure determinations: Details of data collections and structure refinements for **3** to **6** are given in Table 1. All crystals were mounted on a glass capillary under oil and data were collected at 123(1) or 100(1) K on an Enraf-Nonius KappaCCD diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Data were corrected for Lorentzian and polarization effects but not absorption. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on $|F^2|$ using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Where possible, assignment of carbon positions within the carborane cages was made by an analysis of anisotropic displacement parameters; however, as the X-ray scattering factors for C and B are similar, assigments should be regarded as tentative. Treatment of hydrogens and disorder are outlined below.

$[Na(CTV)_2(OH)(H_2O)](H_2O)(DMF)_2$(*o*-carborane) (3): Hydrogen atoms on the guest DMF molecule were included at geometrically estimated positions with a riding refinement, all other hydrogen atoms were located in the difference map and fully refined. The coordinated water and hydroxy ligadns could not be distinguished due to a symmetry-imposed disorder and hydrogen atoms on these ligands were refined with an occupancy of 0.75. The carborane also showed a symmetry-imposed disorder and four

Table 1. Crystal structure data and details of structure refinement for **3**–**6**.

	3	**4**	**5**	**6**
formula	$C_{62}H_{91}B_{10}N_2NaO_{17}$	$C_{62}H_{88}B_{10}K_2N_2O_{16}$	$C_{62}H_{94}B_{10}N_2O_{18}$	$C_{35}H_{56}B_{10}N_2O_8$
M_r [g mol^{-1}]	1267.46	1303.64	1263.49	740.92
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$C2/c$	$C2/m$	$C2/m$	$Cmc2_1$
a [Å]	23.5316(3)	19.3270(3)	19.0438(6)	22.4054(8)
b [Å]	14.5838(2)	14.8709(2)	14.8451(3)	17.8735(6)
c [Å]	19.6828(8)	12.5698(1)	12.5575(4)	10.3919(2)
β [°]	109.254(7)	116.021(1)	113.565(1)	90
V [Å^3]	6376.9(1)	3246.48(7)	3254.0(2)	4161.6(2)
Z	4	2	2	4
ρ_{calcd} [g cm^{-1}]	1.320	1.334	1.290	1.183
crystal size [mm]	0.42 × 0.30 × 0.20	0.28 × 0.23 × 0.13	0.28 × 0.25 × 0.13	0.48 × 0.28 × 0.23
μ [mm^{-1}]	0.097	0.215	0.090	0.077
T [K]	100(1)	123(1)	123(1)	123(1)
θ range [°]	2.19–27.50	2.35–27.50	3.27–27.50	3.51–27.49
reflns collected	63803	36378	33377	15549
unique reflns	7258	3823	3873	4619
R_{int}	0.071	0.051	0.068	0.053
obs. refln $I > 2\sigma(I)$	5585	3110	3060	3662
data/restraints/parameters	7258/0/574	3823/1/226	3873/0/249	4619/1/319
R_1 (obs data)	0.0586	0.0855	0.0843	0.0595
wR_2 (all data)	0.1734	0.2786	0.2184	0.1454
S	1.060	1.059	1.234	1.064

positions within the icosohedral cage were refined with some carbon character.

[K(OH)(CTV)(DMF)]$_2$(*o*-carborane) (4): All hydrogen atoms were included at geometrically estimated positions aside from the hydroxide hydrogen which was fully refined with the O–H bond length restrained to a chemically reasonable length. The DMF shows a symmetry-imposed disorder over two positions for the carbonyl oxygen atom, the carborane was refined with a similar symmetry imposed disorder to that of **3**.

[(DMF)(CTV)]$_2$(H$_2$O)$_4$(*o*-carborane) (5): Hydrogen atoms on the CTV and DMF were included at geometrically estimated positions with a riding refinement, all other hydrogen atoms were located in the difference map and fully refined. The DMF and carborane were treated as for **4**. The eight hydrogen atoms on the water molecules (four of which are crystallographically distinct) were also disordered by symmetry over ten positions and hence each was given an occupancy of 0.8. The water molecules form a hydrogen-bonded tetramer, each hydrogen along an O–H ··· O edge of the tetramer is in a position central to the two O, indicating the hydrogen atom is at an averaged O–H ··· O/O ··· H–O site.

(*o*-carborane)(CTV)(DMF)$_2$ (6): CTV hydrogen atoms were fully refined, all other hydrogen positions were included at geometrically estimated positions with a riding refinement.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-139400, CCDC-139401, CCDC-139403, and CCDC-139402. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] A. Collet in *Comprehensive Supramolecular Chemistry, vol. 6* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNichol, F. Vögtle), Pergamon, Oxford, **1996**.

[2] C. D. Gutsche, *Calixarenes*, Royal Society Chemistry, Cambridge, **1989**.

[3] J. W. Steed, H. Zhang, J. L. Atwood, *Supramol. Chem.* **1996**, *7*, 37.

[4] J. A. Hyatt, E. N. Duesler, D. Y. Curtin, I. C. Paul, *J. Org. Chem.* **1980**, *45*, 5074.

[5] D. S. Bohle, D. Stasko, *Chem. Commun.* **1998**, 567.

[6] a) J. L. Atwood, M. J. Barnes, M. G. Gardiner, C. L. Raston, *Chem. Commun.* **1996**, 1449; b) J. L. Atwood, M. J. Barnes, R. S. Burkhalter, P. C. Junk. J. W. Steed, C. L. Raston, *J. Am. Chem. Soc.* **1994**, *116*, 10346; c) A. M. Bond, W. Miao, C. L. Raston, T. J. Ness, M. J. Barnes, J. L. Atwood, *Chem. Eur. J.* submitted.

[7] M. J. Hardie, P. D. Godfrey, C. L. Raston, *Chem. Eur. J.* **1999**, *5*, 1828.

[8] R. J. Blanch, M. Williams, G. D. Fallon, M. G. Gardiner, R. Kaddour, C. L. Raston, *Angew. Chem.* **1997**, *109*, 520; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 504.

[9] K. T. Holman, J. W. Steed, J. L. Atwood, *Angew. Chem.* **1997**, *109*, 1840; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1736.

[10] a) R. N. Grimes, *Carboranes*, Academic Press, New York, **1970**; b) L. A. Leites, *Chem. Rev.* **1992**, *92*, 279.

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

[12] A. Harada, S. Takahashi, *J. Chem. Soc. Chem. Commun.* **1988**, 1352.

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

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

[15] G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311.

[16] For example a) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460; b) O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703; c) K. A. Hirsch, S. R. Wilson, J. S. Moore, *Inorg. Chem.* **1997**, *36*, 2960;d) M. Fujita, Y. J. Kwon, S. Wahizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151; e) S. Subramanian, M. Zaworotko, *Angew. Chem.* **1995**, *107*, 2295; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2127.

[17] For example:a) C. B. Aakeröy, *Acta Crystallogr. Sect. B* **1997**, *53*, 1475; b) G. R. Desiraju, *Chem. Commun.* **1997**, 569, and references therein.

[18] a) A. D. Burrows, D. M. P. Mingos, A. J. P. White, D. J. Williams, *Chem. Commun.* **1996**, 97; b) M. M. Chowdhry, D. M. P. Mingos, A. J. P. White, D. J. Williams, *Chem. Commun.* **1996**, 899; c) C. B. Aakeröy, A. M. Beatty, D. S. Leinen, *J. Am. Chem. Soc.* **1998**, *120*, 7383; d) C. B. Aakeröy, A. M. Beatty, B. A. Helfrich, *Dalton Trans.* **1998**, 1943; d) C. B. Aakeröy, A. M. Beatty, *Chem. Commun.* **1998**, 1067.

[19] A search of the Cambridge Structural Database, October 1999 release revealed no structures with di-μ-(OH) bridged potassium ions.

[20] For example:a) C. Lambert, F. Hampel, P. von R Schleyer, M. G. Davidson, R. Snaith, *J. Organomet. Chem.* **1995**, *487*, 139; b) M. Baier, P. Bissinger, H. Schmidbaur, *Organometallics* **1993**, *12*, 2208.

[21] For example: a) L. Spiccia, H. Stoeckli-Evans, W. Marty, R. Giovanoli, *Inorg. Chem.* **1987**, *26*, 474; b) F. J. Lahoz, D. Carmona, L. A. Oro, M. P. Lamata, M. P. Puebla, C. Foces-Foces, F. H. Cano, *J. Organomet. Chem.* **1986**, *316*, 221; c) P. Chaudhuri, D. Ventur, K. Wieghardt, E.-M. Peters, K. Peters, A. Simon, *Angew. Chem.* **1985**, *97*, 55; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 57.

[22] P. R. Ashton, G. Gattuso, R. Königer, J. F. Stoddart, D. J. Williams, *J. Org. Chem.* **1996**, *61*, 9553.

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