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Inclusion chemistry of cyclotriveratrylene and cyclotricatechylene

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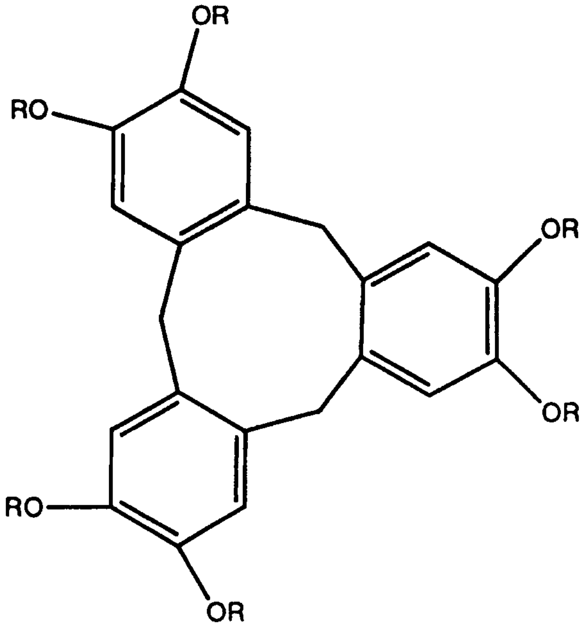
The structures of six crystalline inclusion complexes of cyclotriveratrylene (1) (CTV) containing water, toluene, bromobenzene, chloroform, acetone and dimethoxyethane have been determined by X-ray crystallography. Four are of the α phase whilst the other two are the first reported structures of the β phase. Based upon this information the previously unexplained differences between these two types of inclusion compound have been elucidated and the relationship of the crystal packing to the characteristic infrared spectra of each phase rationalised. The crystal structure of the cyclotricatechylene (3) (CTC) inclusion complex (3.2dmf.2H_2O) has also been examined and exhibits a novel alternating hydrophobic/hydrophilic bilayer structure reminiscent of that found for hydrated calix[4]arenesulfonate complexes.

INTRODUCTION

Depending upon the reaction conditions, the condensation of *o*-dimethoxybenzene (veratrole) with formaldehyde has been shown to yield both a cyclic trimer, cyclotriveratrylene (1) (CTV) and the analogous tetrameric species, cyclotetraveratrylene (2) (CTTV).[1] Apart from the utility of compounds derived from (1) in the synthesis of cryptophanes and other effective small molecule complexing agents,[2] CTV and, to a lesser extent, CTTV also exhibit an extensive host-guest chemistry in their own right.[3,4] Recently, we have reported the crystal structure of guest-free CTV.[5] Prior to that time, however, CTV had been shown to form an unexpectedly wide range of solid state inclusion complexes with both small, polar molecules such as water,[6] as well as larger, hydrophobic guests such as benzene, butyric acid and even decalin.[3a] In general these clathrate-type complexes exhibit channel structures in which CTV molecules stack along the crystallographic *b* axis whilst the enclathrated guests occupy linked "cages" formed by the methoxy substituents, resulting in variations in the *a* and *c* unit cell dimensions. The resulting structures are sufficiently self consistent to enable their classification into so-called α and β phases, apparently depending upon the size and shape of the guest molecules.[3a]

Clearly the crown conformation of the CTV unit is such as to preclude close packing in the crystalline lattice and is in part responsible for the wide range of inclusion complexes formed by CTV. Also the presence of weak hydrogen bonds to the methoxy oxygen atoms has been noted[6,7] and may well contribute to the stability of these inclusion complexes. In view of the paucity of full structural investigations upon CTV solvates, however, the factors behind the formation of these inclusion



(1) R = Me

(3) R = H

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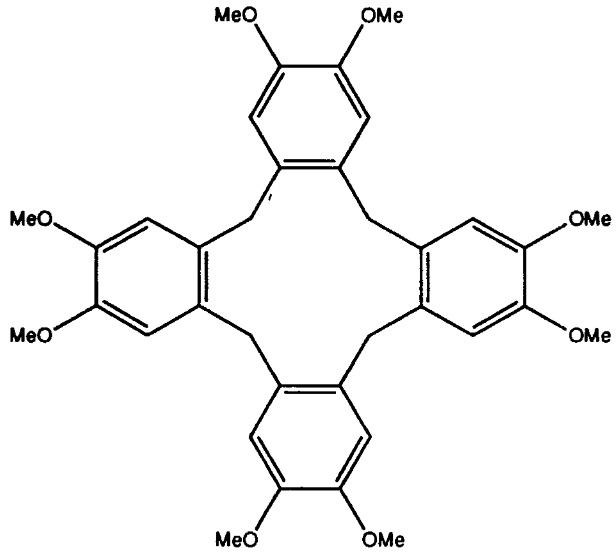

(2)

compounds and the occurrence of α and β phases are still poorly understood. We have consequently undertaken a structural survey of six CTV solvates as well as one of the related cyclotricatechylene (3) (CTC) in an attempt to clarify the existing wealth of spectroscopic and chemical data. Related work on the inclusion chemistry of CTTV has been reported.[8]

RESULTS AND DISCUSSION

Preparation of inclusion complexes of CTV and CTC

Single crystals of inclusion complexes of CTV and its demethylated analogue CTC were obtained either by slow evaporation of CTV solutions in acetone, toluene, bromobenzene, chloroform, dimethoxyethane (DME) or dimethylformamide (DMF), or by slow cooling. The complexes prepared, along with host: guest stoichiometry and other relevant data are summarised in Table 1. Details of free CTV[5] as well as previously reported CTV[6,7] and CTC[9] structures are also included for comparison.

Structure determinations of CTV complexes

i) Structure of the CTV molecule. A representative view of the crystallographically determined structure of the CTV molecule is given in Figure 1 along with the atom numbering scheme adopted for all six CTV structures. Unsurprisingly, the present series of structure determinations serves merely to confirm the observations made by ourselves upon uncomplexed CTV[5] and by others upon the two previous CTV inclusion complexes.[6,7] In each case the asymmetric unit contains one unique molecule of CTV (space group *C2/c* except in the case of $1.2CHCl_3$; $P2_1/n$) in which the molecule adopts an umbrella shaped cavity with the nine-membered ring in the crown conformation. The structures exhibit the usual pseudo mirror symmetry rather than the full C_{3v} observed on the ^1H NMR timescale. This asymmetry, which results from the repulsion of one benzenoid ring away from the other two, causes a distortion of the crown conformation of the molecule relative to that observed for free cyclononatriene (CNT),[10] *e.g.* the angles subtended at the methylenic carbon atoms C(7), C(14), and C(21) are expanded from the ideal 109.5° to an average value of 114.4(6)° in two of three cases in all the structure examined. The third angle, between the two rings lying either side of the pseudo mirror plane, exhibits an average value of 110.1(6)°, close to free CNT 108°.[10] Interestingly, however, the departure from threefold symmetry in the case of the clathrate complexes studied here is slightly less than in free CTV which exhibits angles at C(7), C(14) and C(21) of 108.5(4), 114.8(4), 116.4(5)°, respectively.[5] Strain within the nine-membered ring is evinced in all the internal angles at the sp^2 carbon atoms which are expanded to *ca.* 123° in each case.

The distortion of CTV away from C_{3v} symmetry is thought to be caused by the lack of homoaromaticity in the molecule resulting in repulsive π-π interactions.[6,7] This observation is highlighted by the recent synthesis in this group of the hexacationic transition metal complex $[\{Ru(\eta^6\text{-}MeC_6H_4CHMe_2)\}_3(\eta^6{:}\eta^6{:}\eta^6\text{-}CTV)][BF_4]_6$[11] which, because of the π-electron withdrawing effect of the transition metal centres, exhibits precise threefold molecular symmetry both in solution and in the solid state.

Also, as with many *o*-dimethoxybenzene derivatives, some bond length alternation is observed within the aromatic rings with long bonds C(1)-C(2), C(3)-C(4), C(5)-C(6) *etc.* 1.401 Å av. and shorter bonds C(2)-C(3), C(4)-C(5), C(1)-C(6) *etc.* 1.378 Å av.

iii) Intermolecular interactions and crystal packing. As early as 1958[3a] it was recognised that CTV (then thought to possess a hexameric structure) formed clathrates belonging to one of two distinct crystalline phases: α or β. The α phase is characterised by a slightly longer *b* crystallographic axis (9.61–9.78 Å, *cf.* 8.07–8.39 Å for the β phase). Also, in the infrared spectrum of the β phase a number of bands in the 1040–840 cm^{-1} region are split into doublets, whilst they occur as singlets in the α phase.[3a] Furthermore, the infrared spectrum of the β phase exhibits a band at *ca.*

Table 1 Scope and properties of cyclotriveratrylene inclusion compounds

Solvent and technique[a]	*Guest(s)*	*Host : guest ratio*	*Unit cell dimensions a, b, c, β (Å, °)*	*Type*	*Physical properties & spacegroup*	*Refs.*
CTV						
Dry toluene SE (1)	none	-	12.582(3) 9.575(5) 19.738(5) 95.15(2)	α	colorless plates $P2_1/n$	5 5
Undried toluene SE ($1.0.5H_2O$)	water	1 : 0.5	24.375(5) 9.690(5) 24.267(6) 123.49(2)	α	colorless plates $C2/c$	this work
Undried toluene SE CTVW	water	1 : 0.16	24.216(21) 9.6362(2) 23.117(4) 118.08(5)	α	pale yellow prisms $C2/c$	6
Undried toluene SC ($1.0.5tol.0.5H_2O$)	toluene water	1 : 0.5 : 0.5	32.736(10) 9.657(6) 24.386(7) 135.70(3)	α	colorless plates $C2/c$	this work
Undried bromobenzene SE ($1.0.5bbz.0.5H_2O$)	bromobenzene water	1 : 0.5 : 0.5	32.7009(9) 9.559(4) 24.437(7) 135.21(2)	α	pale yellow plates $C2/c$	this work
Undried benzene SE CTVBW	benzene water	1 : 0.5 : 1	33.908(9) 9.629(3) 22.748(5) 134.02(1)	α	colorless prisms $C2/c$	7
Chloroform SE ($1.2CHCl_3$)	chloroform	1 : 2	16.702(5) 9.766(4) 20.468(4) 92.64(2)	α	colorless prisms $P2_1/n$	this work
Acetone SE (1.0.5acet)	acetone	1 : 0.5	32.948(8) 8.351(3) 30.090(8) 141.76(2)	β	colorless prisms readily de-solvate $C2/c$	this work
Dimethoxyethane SE (1.0.5dme)	dimethoxyethane	1 : 0.5	33.315(10) 8.259(4) 31.064(9) 142.35(2)	β	colorless needles $C2/c$	this work
CTC						
Dimethylformamide SE ($3.2dmf.2H_2O$)	DMF water	1 : 2 : 2	10.614(1) 11.289(1) 12.108(1)	-	pale yellow prisms $P\bar{1}$	this work
2-Propanol SE (3.2prop)	2-propanol	1 : 2		-	pinkish needles $P\bar{1}$	9

a) SE = slow evaporation, SC = slow cooling.

905 cm^{-1} which is absent in complexes of the α type. It has been suggested that the difference results from the presence of either "bulky" (α) or "threadlike" (β) guest molecules within the lattice.[7] However, given previous results this means that water must be thought of as "bulky" whilst acetone is "threadlike"!

On closer examination, the experimental evidence suggests that on going from the α to the β phase there is both a structural or conformational change within the CTV molecule itself along with a correlated change in crystal packing. Consideration of the geometry of the CTV molecule suggests that there are only two significant types of conformational freedom: (a) inversion of the umbrella as a whole and (b) rotation about the C_{ring}-OMe bonds. Umbrella inversion in CTV has been shown to be an extremely high energy process[1a] by the rate of racemisation of deuterated CTV analogues ($t_{1/2}$ for racemisation at 20°C = *ca.* 1 month) and hence the difference between the two CTV phases ***must be connected with rotation of the methoxy substituents***. It is no surprise therefore, that the differences in the infrared spectra of the α and β phases occur in the region of the spectrum expected to contain vibrations arising from the C-O single bonds.

Previous X-ray crystal structure determinations, including that of CTV itself, have all exhibited materials belonging to the α phase and have clearly demonstrated that the 9.6 Å crystallographic *b* axis is a consequence of the stacking of two CTV molecules, one in the cavity of the other, along the *b* direction.[5–7] In the present

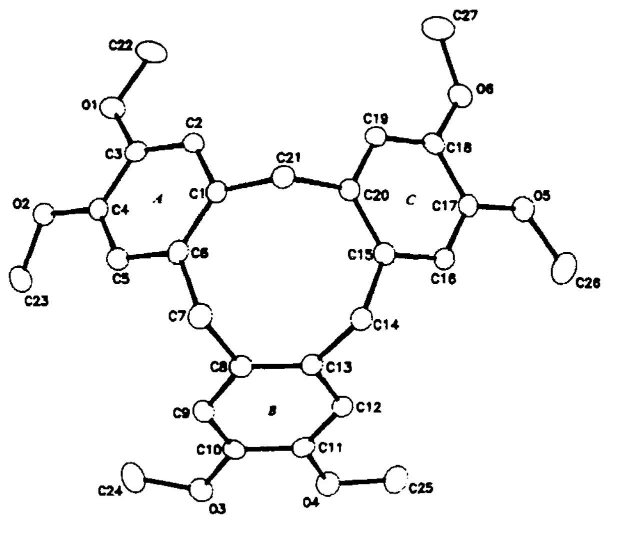

Figure 1 Representative view of the X-ray crystal structure of the CTV molecule (1) showing the atom numbering scheme adopted.

study four further structures of the α type are described (**1**.0.5H_2O, **1**.0.5toluene.0.5H_2O, **1**.0.5bromobenzene.0.5H_2O and **1**.2$CHCl_3$; b = 9.56–9.77 Å). In addition we also present for the first time two structures of the β phase (**1**.0.5acetone and **1**.0.5dimethoxyethane, b = 8.26–8.35).

Slow evaporation of an undried toluene solution of (**1**) resulted in the formation of (**1**.0.5H_2O) which contains half of one water molecule per CTV unit but no included toluene. The structure is closely related to the "CTVW" structure reported by Birnbaum *et al.*[6] which contained 0.16 water molecules per CTV, and Burlinson and Ripmeester have also reported the formation of a CTV-water complex of stoichiometry 1 : 0.35 prepared by this method. The observed stoichiometry may well depend simply upon the amount of water available in the toluene solvent at the time of crystallization. The crystallographic c axis in (**1**.0.5H_2O) is elongated by 1.15 Å whilst the β angle is increased by *ca.* 5.5° relative to CTVW, resulting in only a small increase in overall cell volume. Like the CTVW structure the water molecule resides on a general position and its occupancy was refined to the value reported here in the final stages of refinement. In both cases the water molecules reside in channels between the CTV units, divided into loose cavities by the methyl groups of the methoxy substituents. Water molecules are hydrogen bonded to their symmetry equivalents at a distance of 2.64 Å (*cf.* 2.78 Å for CTVW) and, importantly, there also exists weak hydrogen bonding interaction to the methoxy oxygen atoms of the CTV molecules: Ow...O(2) 3.13 Å, Ow...O(1) 3.39 Å. It should be noted that CTV is capable of acting as a hydrogen bond acceptor in this way but possesses only very weak hydrogen bond donor sites, hence precluding the possibility of hydrogen bonds between pairs of CTV molecules. A view of the packing in (**1**.0.5H_2O) is shown in Figure 2.

Slow cooling of an undried toluene solution of (**1**) results in the formation of a further water clathrate (**1**.0.5tol.0.5H_2O) which also contains a toluene molecule situated upon the crystallographic twofold axis in space-group *C2/c*. As with (**1**.0.5H_2O), the water molecule is weakly hydrogen bonded to the H-bond acceptor sites at the methoxy groups of the CTV molecule, Ow...O(3) 3.04 Å, Ow...O(4) 3.05 Å, and Ow...O(5)' 3.30 Å. In addition, short contacts also exist between the water molecule and the only possible CTV H-bond donor sites (the C-H bonds of the OMe group) on two neighboring CTV molecules: Ow...C(24)' 3.68 Å and Ow...C(26)" 3.42 Å, giving the water oxygen atom an approximately tetrahedral environment. Similar contacts were noted for the closely related "CTVBW" structure of composition CTV : 0.5 benzene : 0.5 water. The toluene molecules occupy the space formed by the OMe groups along the channels parallel to b in the structure with the plane of the toluene ring aligned in the b direction. An interesting static disorder also exists between the methyl group of the toluene and the water molecule such that the two occupy approximately the same position either side of the crystallographic twofold axis. In general the structure may be regarded as being related to that of (**1**.0.5H_2O) with the methyl group of the toluene occupying one of the water molecule sites, although there are no significant short contacts from the toluene to the CTV molecule. A stereoscopic view of the packing in (**1**.0.5tol.0.5H_2O) is shown in Figure 3. It is interesting to note that Burlinson and Ripmeester[3b] also reported a CTV-toluene clathrate of composition 1 : 0.5 produced by the slow cooling method and, as with guest-free CTV, assigned a structure incorporating two independent molecules in the asymmetric unit based on solid state NMR measurements. In the latter case the results of our x-ray structure investigation[5] revealed the presence of only one molecule in the asymmetric unit, as is also the case with (**1**.0.5tol.0.5H_2O). It is possible that the observed vari-

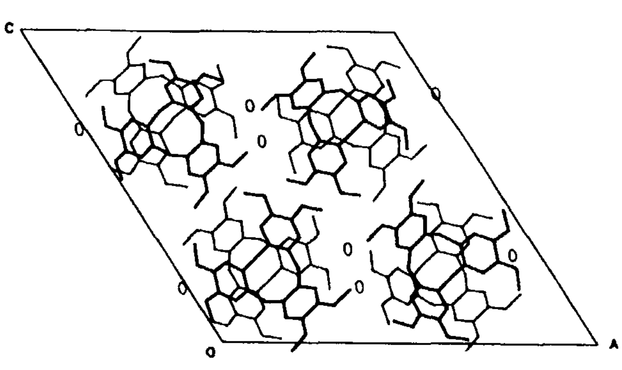

Figure 2 Crystal packing in the α phase complex (**1**.0.5H_2O) viewed down the b axis.

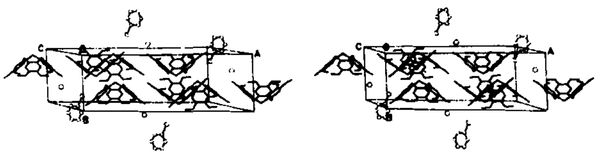

Figure 3 Stereoview of the crystal packing in the α phase complex (1.0.5tol.0.5H_2O).

able occupancies of solvent molecules, especially water, is responsible for the observation of more signals in the ^{13}C solid state NMR spectrum than expected on the basis of one molecule per asymmetric unit, especially since there would appear to be significant host-guest interactions.

Slow evaporation of a bromobenzene solution of (**1**) results in the bromobenzene inclusion complex (**1**.0.5bbz.0.5H_2O) which is isostructural with (**1**.0.5tol.0.5H_2O). The bromine atom and the water molecule are disordered across the mirror plane with short contacts Ow...O(3) 3.06 Å, Ow...O(4) 3.03 Å, Ow...O(5)' 3.46 Å. Also, the bromine atom exhibits contacts to the methoxy carbon atoms in the range of 3.69–3.88 Å.

Crystals were also obtained from a chloroform solution of CTV. Unlike toluene and bromobenzene, chloroform is capable of acting as a hydrogen bond donor and so in this case water is not included in the structure (**1**.2$CHCl_3$) in spite of the fact that the chloroform was undried. As with the previous structures the CTV molecules pack one within the other along the *b* axis giving rise to the characteristic α phase. Again, the chloroform molecules occupy channels between these CTV stacks with weak hydrogen bonds from the chloroform carbon atoms to the methoxy oxygen atoms C(28)...O(5) 3.22 Å, C(28)...O(6) 3.32 Å, C(29)...O(1) 3.26 Å, C(29)...O(2) 3.21 Å, Figure 4.

Unlike water and chloroform, acetone and DME are extremely weak hydrogen bond donors (as are CS_2 and butyric acidic if the acidic proton is taken up by bonding to a second acid molecule as indicated by the stoichiometry of the butyric acid complex reported by Cagoliti *et al.*,[3a] both of which form β phases) and yet can adequately fill the channels within the host lattice and may act as H-bond acceptors. The two isolated complexes incorporating these solvents belong to the β phase. Because of the lack of $XH_{solvent}...O_{methoxy}$ (X = O, CCl_3 *etc.*) interactions a different form of crystal packing is adopted such as to maximize the weak OCH_2-H...O_{solv} interactions from the methoxy groups of CTV to the H-bond acceptor solvent, *e.g.* the acetone complex, which incorporates one acetone molecule situated on a crystallographic twofold axis between two CTV molecules, exhibits short contacts between the carbonyl oxygen atom and methoxy carbon atoms, O(7)...C(25), C(25)' 3.07 Å (significantly shorter than the sum of the van der Waals radii) and O(7)...C(26), C(26)' 3.58 Å, Figure 5. It is interesting to note that this interaction apparently has an effect upon the O(4)-C(25) bond length which is appreciably shorter than all the values observed for the α phase structures: 1.379(8) Å, *cf.* 1.41(7) Å for free CTV and values of 1.413(8) to 1.45(1) for the range of α phase inclusion complexes described above. Also, significant distortions are observed for the OMe groups which are not associated with the solvent molecule. Most notably C(22) is positioned such as to minimize space within the channels along the *b* axis and hydrogen bond with neighboring methoxy oxygen atoms, resulting in a large out of ring plane distortion of 0.97 Å (torsion angle C(2)-C(3)-O(1)-C(22) 117.5°), whilst C(24) resides within the CTV cavity, C(9)-C(10)-O(3)-C(24) −30.8°. This may be compared to the maximum distortion in free CTV of 0.52 Å (torsion angle −24.6°). A stereoview of the crystal packing in (**1**.0.5acet) is given in Figure 6.

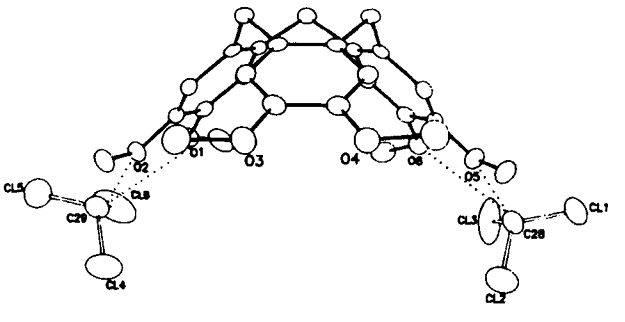

Figure 4 Intermolecular short contacts in (**1**.2$CHCl_3$).

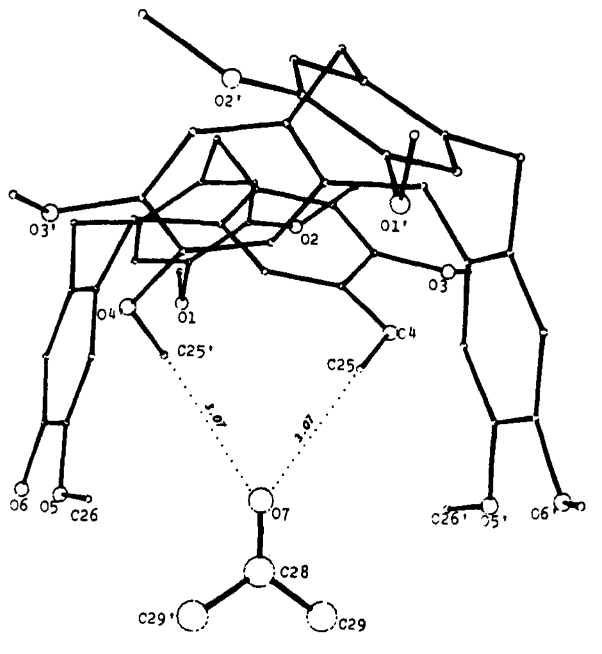

Figure 5 Intermolecular short contacts in (**1**.0.5acet).

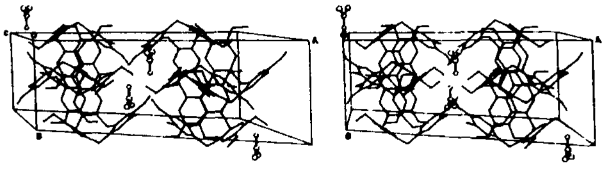

Figure 6 Stereoview of the crystal packing in the β phase complex (**1**.0.5acet).

Similar intermolecular interactions and rotations are observed in the DME complex (**1**.0.5dme) with short contacts O(7), O(7)'...C(22), C(22)' 3.26 Å, O(7), O(7)'...C(27), C(27)' 3.44 Å, Figure 7, and an out of plane distortion of 1.08 Å for C(24) resulting in that methyl group hydrogen bonding to the neighboring O(4) at 3.05 Å. In this case however there is no obvious shortening of any of the O-Me bonds, and hence it is the large out of plane rotations of the methoxy substituents which must be responsible for the change from the α to the β phase. This results in the stacking of CTV units along the *b* axis occurring in a significantly more slipped fashion such that the *b* axis length is reduced while the β angle is greatly increased. The change is geometry of one of the methoxy groups is therefore responsible for the additional absorptions in the methoxy region of the infrared spectra of the complexes.

Structure determination of the CTC-DMF-water complex

Demethylation of CTV to give the hexaol CTC is readily accomplished through the use of BBr_3.[12] Apart from a reduction in the steric bulk of the trimeric unit on going to CTC, the demethylated molecule is also a strong H-bond donor in contrast to the parent species, and might be expected to display supramolecular interactions with a wide range of guests. Hyatt *et al.*[9] have already prepared a range of CTC inclusion complexes with H-bond acceptors such as acetone, DMSO *etc.*, Table 2. It is noteworthy that in each case host-guest stoichiometries range from 1 : 2 to 1 : 3 rather than values of less than 1 seen in the majority of examples of CTV complexes. These workers have crystallographically characterized a 1 : 2 complex of CTC with 2-propanol (**3**.2prop), a guest which is capable both of hydrogen bond donation and acceptance. For comparison we have attempted to obtain crystals of inclusion complexes of CTC containing only an H-bond acceptor. However, in attempting to obtain crystals of the 1 : 3 *N,N*-dimethylformamide (DMF) complex reported by these workers,[8] we instead obtained the mixed guest species (**3**.2dmf.$2H_2O$) which contains two DMF molecules and two adventitious water molecules per CTC unit.

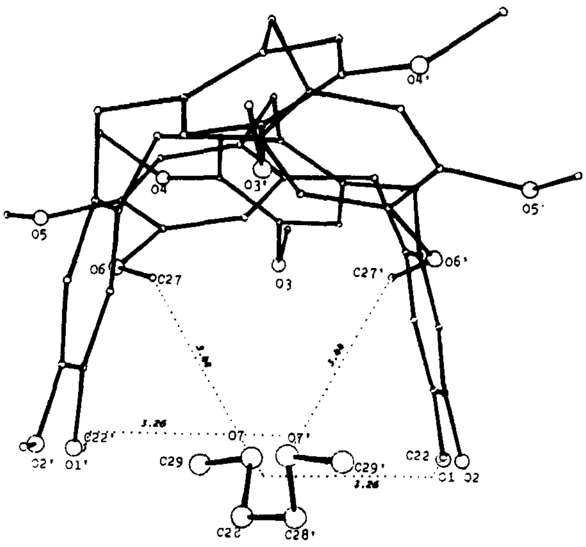

Figure 7 Intermolecular short contacts in (**1**.0.5dme).

Unsurprisingly, the present structure of the CTC molecule itself is not significantly different to that reported by Hyatt *et al.* for (**3**.2prop). Because of the electron withdrawing nature of the hydroxy substituents there is apparently much less π-π repulsion between the aromatic decks of the molecule and hence the angles at C(7), C(14) and C(21) are approximately equal; 111.6(4)°, 112.1(4)° and 115.1(5)°, although the fact that the values are still significantly greater than in CNT reflects strain in the nine-membered ring, as do the enlarged angles at the sp^2 carbon atoms within the ring. More interestingly, however, the packing within the crystal is radically different to that observed for (**3**.2prop). In the 2-propanol structure the CTC molecules stack back-to-back with each CTC layer separated by a layer of the guest molecules. This results in hydrogen bonds between CTC molecules within a layer but not between layers. The crystal packing in (**3**.2dmf.$2H_2O$) is also arranged in a layer structure, but one in which one chain of CTC molecules faces another which is offset from it by half a molecule along the *a* direction. As a result the structure exhibits a smooth channel made up of the cavities of the CTC molecules into each of which is inserted a DMF molecule which accepts hydrogen bonds from the hydroxyl functionalities, O(2)...O(7) 2.637(5) Å, and from a water molecule external to the channel, O(7)...Ow(2) 3.031(6) Å (the atom numbering scheme adopted is the same as that for CTV hence O(7) and O(8) belong to

Table 2 Inclusion compounds of cyclotricatechylene (CTC)[a]

Guest molecules	*Host : guest ratio*
N,N-dimethylformamide	1 : 3.1
N-methylpyrrolidone	1 : 3.0
N,N-dimethylacetamide	1 : 3.1
Dimethylsulfoxide	1 : 3.0
Water	1 : 3.0
Hexamethylphosphoramide	1 : 3.0
Acetone	1 : 2.0
2-Propanol	1 : 2.0

a) taken from ref. 8.

DMF molecules, whilst Ow denotes a water oxygen atom). Ow(2) is itself associated with the CTC molecule, O(1)...Ow(2) 2.697(6) Å, O(4)...Ow(2) 3.011(6) Å. The remaining DMF and water molecules are both external to the CTC cavities. The methyl groups of the DMF occupy spaces between the hydrophobic regions of the CTC fragments whilst the carbonyl functionality and the water molecule are again hydrogen bonded to the hydroxyl groups: O(6)...O(8) 2.660(6) Å, O(1)...Ow(1) 2.789(6) Å, O(5)...Ow(1) 2.840(6) Å. The two water molecules are also associated with one another Ow(1)...Ow(2) 2.779(5) Å.

This layered packing arrangement (Fig. 8) is highly reminiscent of that found for the calix[4]arene sulfonates and other organic clays[13] in which the crystal consists of alternating hydrophobic and hydrophilic layers. In this case the hydroxyl functionalities along with the water molecules comprise the hydrophilic layer whilst the back-to-back bases of the CTC units along with the -NMe_2 section of DMF form the hydrophobic layer. There is also an additional hydrophobic phase actually within the face-to-face cavities of the bowlic macrocycles in which a second -NMe_2 fragment resides.

CONCLUSIONS

This comprehensive survey has confirmed that the CTV molecule may form two distinct crystalline phases. The α phase is obtained in the presence of H-bond donor solvents and results in a longer *b* axis as a result of regular stacking of CTV units in the *b* direction. In the presence of H-bond acceptor solvents with little H-bond donor ability, the β phase is formed which results from major out of ring plane rotation of at least one methoxy group to give a slipped packing along the *b* axis and significant changes in the 1040-840 cm^{-1} region of the infrared spectrum of the inclusion complex relative to the α phase. These observations are supported by the fact that of the two inclusion complexes formed with acetone both are of the β type,[3a] whereas all complexes incorporating water adopt the α phase. In the case of solvents of no particular H-bond donor/acceptor ability adventitious water is incorporated into the lattice in varying ratios according to the "wetness" of the solvent.

The interesting contrast between the structure of the CTC-DMF-water complex reported herein and the previously known 2-propanol complex confirms the predic-

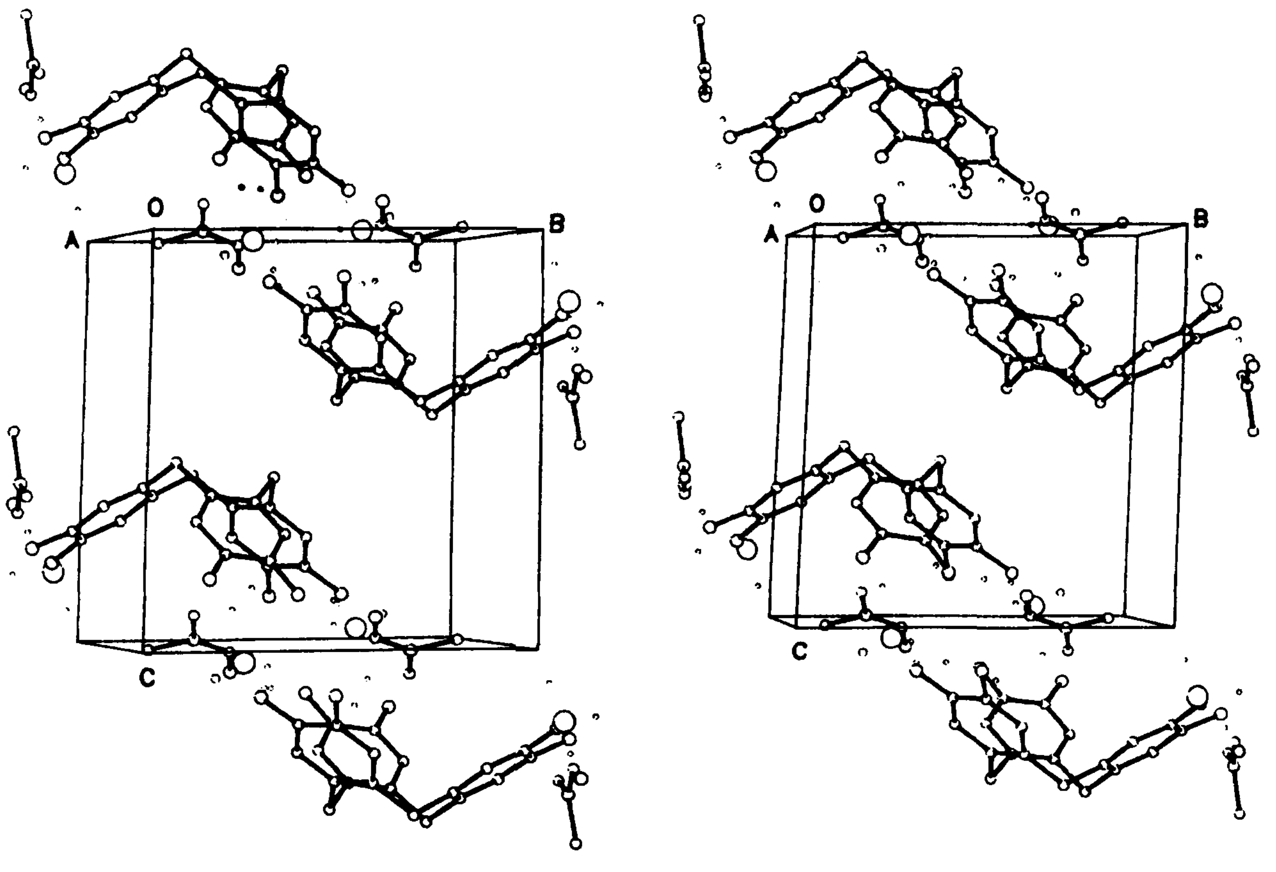

Figure 8 Stereoview of the bilayer packing arrangement in the CTC complex (3.2dmf.$2H_2O$).

tion of Hyatt *et al.*[9] that CTC may well exhibit an even more interesting and extensive host guest chemistry that CTV. Once again the two existing CTC structures highlight the fact that both electronic as well as steric properties of guest molecules must be considered if the driving forces behind supramolecular assemblies are to be fully understood.

EXPERIMENTAL SECTION

CTV was synthesized according to the method of Robinson[14] as detailed previously.[5] Demethylation of CTV to give CTC was accomplished with BBr_3 according to the method of Lindsey.[12] Colorless or pale yellow crystals of CTV and CTC inclusion complexes were grown either by slow evaporation of concentrated solutions of the host molecules within stoppered tubes with small slits cut at the top, or by slow cooling of the warm mother liquor. Crystals were mounted in thin-walled glass capillaries. Final lattice parameters were obtained from the least-squares refinement of the angular settings of 25 accurately centered reflections on an Enraf-Nonius CAD4 diffractometer. Data were collected by the θ-2θ scan technique as described previously.[15] Lattice, data collection, and refinement parameters are given in Table 3. Intensity data were corrected for Lorentz and polarization effects but absorption corrections were considered unnecessary. Structure solution was accomplished with the aid of the SHELXS-86 program[16] and structures were refined using the SHELX-76 system.[17] In each case all non-hydrogen atoms were refined anisotropically except

Table 3 Crystal data and summary of data collections

	Compound (**1**.0.5H_2O)	(**1**.0.5tol.0.5H_2O)	(**1**.0.5bbz.0.5H_2O)
Mol. Wt.	459.54	504.10	538.05
Space group	*C2/c*	*C2/c*	*C2/c*
cell constants			
a, Å	24.375(5)	32.736(8)	32.700(7)
b, Å	9.690(5)	9.657(5)	9.559(4)
c, Å	24.267(6)	24.368(6)	24.437(7)
β, °	123.49(2)	135.70(2)	135.21(2)
V, $Å^3$	4780.5	5380.2	5381.7
molecules/unit cell	8	8	8
D_c, g cm^{-3}	1.28	1.24	1.33
μ_c, cm^{-1}	0.96	0.93	8.80
radiation	Mo Kα		
cryst dimens, mm	0.15 × 0.22 × 0.15	0.20 × 0.10 × 0.10	0.20 × 0.20 × 0.10
scan width, °	0.80 + 0.20 tan θ		
decay of stds	2%	<2%	<2%
2θ range, °	2–40	2–42	2–40
no. reflcns collcd	3201	3330	2759
no. of obsd refls	1374	1486	1171
no. of params	307	228	188
R	0.065	0.074	0.054
R_w	0.071	0.075	0.055

	Compound (**1**.2$CHCl_3$)	(**1**.0.5acet)	(**1**.0.0.5dme)
Mol. Wt.	689.29	479.58	495.60
Space group	P_1/n	*C2/c*	*C2/c*
cell constants			
a, Å	16.702(5)	32.948(8)	33.315(10)
b, Å	9.766(4)	8.351(3)	8.259(4)
c, Å	20.468(4)	30.090(8)	31.064(9)
β, °	92.64(2)	141.76(2)	142.35(3)
V, $Å^3$	3335.3	5125.1	5222.9
molecules/unit cell	4	8	8
D_c, g cm^{-3}	1.37	1.24	1.26
μ_c, cm^{-1}	5.52	0.93	0.95
radiation	Mo Kα		
cryst dimens, mm	0.15 × 0.22 × 0.12	0.15 × 0.25 × 0.15	0.20 × 0.20 × 0.10
scan width, °	0.80 + 0.20 tan θ	0.70 + 0.20 tan θ	0.75 + 0.20 tan θ
decay of stds	< 2%	< 2%	< 2%
2θ range, °	2–42	2–42	2–40
no. reflcns collcd	4283	2950	2824
no. of obsd refls	2869	2306	1069
no. of params	424	407	220
R	0.067	0.048	0.054
R_w	0.073	0.045	0.055

Table 3 (Continued)

	Compound ($3.2dmf.2H_2O$)
Mol. Wt.	549.59
Space group	$P\bar{1}$
cell constants	
a, Å	10.614(1)
b, Å	11.289(1)
c, Å	12.108(1)
α, °	92.33(1)
β, °	99.53(1)
γ, °	95.88(1)
V, $Å^3$	1420.0
molecules/unit cell	2
D_c, g cm^{-3}	1.28
μ_c, cm^{-1}	1.05
radiation	Mo Kα
cryst dimens, mm	0.15 × 0.20 × 0.25
scan width, °	0.75 + 0.20 tan θ
decay of stds	3.5%
2θ range, °	2–46
no. reflcns collcd	3955
no. of obsd refls	1990
no. of params	352
R	0.054
R_w	0.056

in the cases of ($1.0.5tol.0.5H_2O$), ($1.0.5bbz.0.5H_2O$) and (1.0.5dme) where the paucity of observed data only allowed anisotropic refinement of the methoxy substituents in the case of ($1.0.5tol.0.5H_2O$), the bromine and oxygen atoms in the case of ($1.0.5bbz.0.5H_2O$) and for (1.0.5dme), the methoxy substituents and DME molecule. For ($1.0.5H_2O$) the occupancy of the water molecule was allowed to refine freely to a value of 0.5 and was then fixed in the final stages. In the case of ($1.0.5tol.0.5H_2O$) and ($1.0.5bbz.0.5H_2O$) the water molecule and methyl substituent or bromine atom positions were fixed at values of 0.5. For ($1.2CHCl_3$) the chloroform molecules were found to be disordered with two sets of chlorine atom positions, occupancies refined to 80% and 20%. Where possible, hydrogen atoms were located in the final stages of difference Fourier synthesis and their positional coordinates refined. Hydrogen atom which could not be located were included in idealized positions (C–H 1.0 Å) and allowed to ride on the atoms to which they were attached. In all cases hydrogen atoms were assigned a fixed isotropic temperature factor. Final tables of positional and thermal parameters and bond lengths and angles are available upon request from the authors.

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