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Inclusion chemistry of cyclotetraveratrylene

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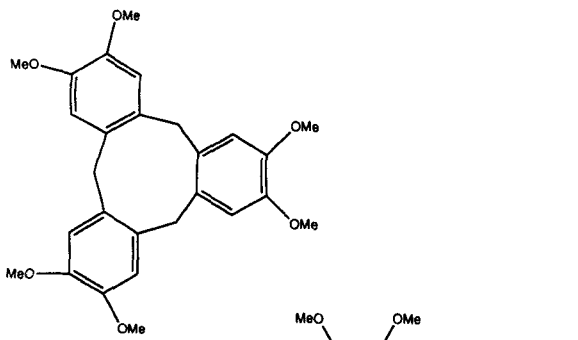
The structures of four crystalline inclusion compounds of cyclotetraveratrylene (2) (CTTV) containing either chloroform or methylene chloride have been determined by X-ray crystallography. The structures are of the channel inclusion type with solvent molecules ordering to maximize weak host-guest interactions involving the methoxy oxygen atoms of the CTTV hosts.

INTRODUCTION

The acid catalyzed condensation of veratrole (*o*-dimethoxybenzene) with formaldehyde has been shown to give either the cyclic trimer, cyclotriveratrylene (**1**) (CTV), or the analogous tetramer, cyclotetraveratrylene (**2**) (CTTV), depending upon the reaction conditions.[1] There is also some evidence that related reactions may give rise to pentameric and higher homologues. Compound (**1**), which adopts a rigid, shallow bowl conformation both in solution and the solid state,[2] has been extensively studied because of its propensity to form crystalline inclusion complexes with a variety of small, neutral guests.[3] In addition, compounds closely related to (**1**) are the prime building blocks in the synthesis of cryptophanes and other effective small molecule complexing agents.[4] In a previous paper[5] we have reported a number of X-ray crystal structure determinations of inclusion complexes of (**1**) and definitively characterized both the α- and β-phases formed by these materials in the solid state.[3a] We now extend our work to related host-guest compounds of (**2**) which, in contrast to (**1**), have been very little studied.[6]



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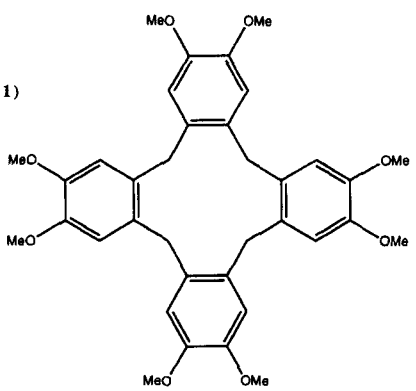

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*Corresponding author.

RESULTS AND DISCUSSION

Preparation of inclusion complexes of CTTV

Unlike (**1**) single crystals of inclusion complexes of CTTV could only be obtained from solutions of (**2**) in either chloroform or methylene chloride, with both the crystalline form and host : guest ratio highly dependent upon crystallization conditions. Slow evaporation of a solution of (**2**) in chloroform results in the formation of prismatic crystals of a complex containing four molecules of chloroform per CTTV unit (**2**.4$CHCl_3$-I). A very similar material is obtained from crystallization of CTTV from mixed chloroform/benzene solvent (1:1), although the complex (**2**.4$CHCl_3$-II) exhibits rather different unit cell parameters. Slow cooling of a chloroform solution of (**2**) gives, as the initial product, a third chloroform solvate (**2**.2$CHCl_3$) containing two chloroform

Table 1 Scope and properties of cyclotriveratrylene inclusion compounds

Solvent and technique[a]	*Guest(s)*	*Host : guest ratio*	*Unit cell dimensions a, b, c, α, β, γ (Å, °)*		*Physical properties & spacegroup*
Chloroform SE or SC (**2**.4$CHCl_3$-I)	chloroform	1:4	8.057(4) 13.448(5) 13.481(5)	60.87(3) 77.38(3) 76.64(3)	colorless prisms $P\bar{1}$
Chloroform/ benzene (1:1) SE (**2**.4$CHCl_3$-II)	chloroform	1:4	8.375(4) 11.335(5) 13.704(5)	82.39(4) 85.70(5) 75.90(5)	colorless plates $P\bar{1}$
Chloroform SC (**2**.2$CHCl_3$)	chloroform	1:2	19.024(5) 7.509(2) 14.554(5)	90.0 102.54(3) 90.0	thin colorless prisms $P2_1/n$
Methylene chloride (**2**.2CH_2Cl_2)	methylene chloride	1:2	18.998(2) 7.406(3) 14.307(5)	90.0 105.94(2) 90.0	colorless prisms $P2_1/n$

a) SE=slow evaporation, SC=slow cooling

molecules per CTTV unit. Further cooling however, gives (**2**.4$CHCl_3$-I). Slow evaporation of a methylene chloride solution of (**2**) gives a further 1:2 complex (**2**.2CH_2Cl_2) which is structurally similar to (**2**.2$CHCl_3$). The complexes prepared, along with host : guest stoichiometry and other relevant data, are summarized in Table 1. The formation of stable inclusion complexes of (**2**) with chlorinated methanes has been reported earlier[6] and materials of 1:2 stoichiometry, prepared under similar conditions to (**2**.2$CHCl_3$) and (**2**.2CH_2Cl_2), have been characterized by solid state ^{13}C NMR spectroscopy. In that study an unstable benzene inclusion compound was also reported but no data could be obtained.

Structure determinations of CTTV complexes

i) Structure of the CTTV molecule

A representative view of the crystallographically determined structure of the CTTV molecule is given in Fig. 1, along with the atom numbering scheme adopted for all

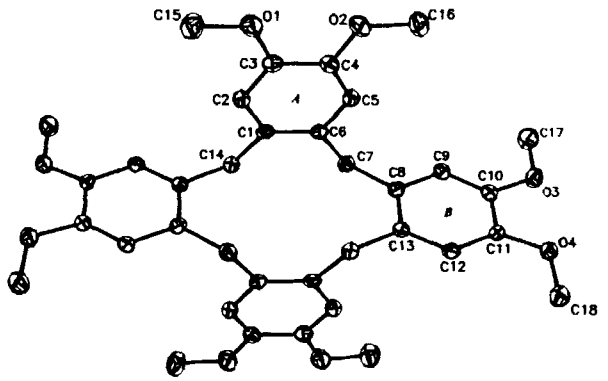

Figure 1 Representative view of the X-ray crystal structure of the CTTV molecule (**1**) showing the atom numbering scheme adopted.

four CTTV structures. Representative bond lengths and angles are given in Tables 2 and 3. In each case the macrocycle resides upon an inversion center with only two aromatic rings in the asymmetric unit. This is consistent with the results of Burlinson and Ripmeester[6] who surmised the presence of only half a molecule per asymmetric unit from the relative simplicity of the solid state ^{13}C NMR spectra of (**2**.2$CHCl_3$) and (**2**.2CH_2Cl_2). In contrast to the rigid crown conformation of CTV, the CTTV molecule adopts a characteristic "sofa" conformation in the solid state with the horizontal and vertical rings inclined at an angle of *ca.* 86° to one another, Fig. 2. This conformation has been suggested to be the most stable form of (**2**) by dynamic ^1H NMR analysis in solution.[7] In the solid state the molecule is distorted from the ideal C_{2h} symmetry as a consequence of unfavourable H...H interactions between hydrogen atoms on adjacent methylenic bridges. These hydrogen atoms were located experimentally in the final stages of refinement of the structure of (**2**.4$CHCl_3$-I) and approach one another at a distance of 2.05 Å ($H(1)_{C(7)}$...$H(1)_{C(14)}$) resulting in strain in the cyclododecatetraene ring system (*e.g.* angles at C(1) and C(6) are opened up to 121.4(7)° and 122.9(7)° av). Like CTV, the angles subtended at the methylene carbon atoms C(7) and C(14) (114.7(7)° av) suggest a lack of homoaromaticity in the molecule as a whole and repulsion between the constituent six-membered rings. This repulsion, however, serves to bring the methylenic hydrogen atoms closer together and, as a consequence of the need to minimize these two opposing repulsive interactions, a twisted conformation is adopted with endocyclic torsion angles C(2)-C(1)-C(6)-C(5) *etc.* *ca.* 2°.

In common with the structure of CTV[2] and other *o*-dimethoxybenzene derivatives, an alternating pattern of

Table 2 Bond lengths for the CTTV molecule in the representative complex (**2**.2$CHCl_3$)

Atoms		*Distance*	*Atoms*		*Distance*
O(1)	—C(3)	1.372(7)	O(1)	—C(22)	1.420(8)
O(2)	—C(4)	1.390(7)	O(2)	—C(23)	1.412(8)
O(3)	—C(10)	1.382(7)	O(3)	—C(24)	1.421(8)
O(4)	—C(11)	1.375(7)	O(4)	—C(25)	1.413(8)
O(5)	—C(17)	1.383(7)	O(5)	—C(26)	1.435(8)
O(6)	—C(18)	1.363(7)	O(6)	—C(27)	1.418(8)
C(1)	—C(2)	1.389(8)	C(1)	—C(6)	1.369(8)
C(1)	—C(21)	1.532(8)	C(2)	—C(3)	1.402(8)
C(3)	—C(4)	1.390(8)	C(4)	—C(5)	1.364(8)
C(5)	—C(6)	1.428(8)	C(6)	—C(7)	1.521(8)
C(7)	—C(8)	1.518(8)	C(8)	—C(9)	1.408(8)
C(8)	—C(13)	1.385(8)	C(9)	—C(10)	1.379(8)
C(10)	—C(11)	1.396(8)	C(11)	—C(12)	1.370(8)
C(12)	—C(13)	1.422(8)	C(13)	—C(14)	1.516(8)
C(14)	—C(15)	1.505(8)	C(15)	—C(16)	1.431(8)
C(15)	—C(20)	1.374(8)	C(16)	—C(17)	1.375(8)
C(17)	—C(18)	1.397(8)	C(18)	—C(19)	1.398(8)
C(19)	—C(20)	1.392(8)	C(20)	—C(21)	1.532(8)
Cl(1)	—C(28)	1.70(1)	Cl(1)*	—C(28)	1.81(2)
Cl(2)	—C(28)	1.72(1)	Cl(2)*	—C(28)	1.83(2)
Cl(3)	—C(28)	1.711(9)	Cl(3)*	—C(28)	1.70(2)
Cl(4)	—C(29)	1.74(1)	Cl(4)*	—C(29)	1.88(2)
Cl(5)	—C(29)	1.69(1)	Cl(5)*	—C(29)	1.73(2)
Cl(6)	—C(29)	1.66(1)	Cl(6)*	—C(29)	1.72(2)

Table 3 Selected interbond angles for the CTTV molecule in the representative complex (**2**.2$CHCl_3$)

Atoms			*Angle*	*Atoms*			*Angle*
C(3)	-O(1)	-C(22)	116.8(5)	C(4)	-O(2)	-C(23)	116.7(5)
C(10)	-O(3)	-C(24)	117.7(5)	C(11)	-O(4)	-C(25)	117.2(5)
C(17)	-O(5)	-C(26)	116.6(5)	C(18)	-O(6)	-C(27)	117.2(5)
C(2)	-C(1)	-C(6)	120.8(6)	C(2)	-C(1)	-C(21)	116.1(6)
C(6)	-C(1)	-C(21)	123.0(6)	C(1)	-C(2)	-C(3)	120.5(6)
O(1)	-C(3)	-C(2)	124.7(6)	O(1)	-C(3)	-C(4)	116.4(6)
C(2)	-C(3)	-C(4)	118.8(6)	O(2)	-C(4)	-C(3)	114.9(6)
O(2)	-C(4)	-C(5)	124.6(6)	C(3)	-C(4)	-C(5)	120.5(6)
C(4)	-C(5)	-C(6)	120.9(6)	C(1)	-C(6)	-C(5)	118.3(6)
C(1)	-C(6)	-C(7)	125.0(6)	C(5)	-C(6)	-C(7)	116.7(6)
C(6)	-C(7)	-C(8)	115.6(5)	C(7)	-C(8)	-C(9)	117.0(5)
C(7)	-C(8)	-C(13)	123.8(6)	C(9)	-C(8)	-C(13)	119.2(6)
C(8)	-C(9)	-C(10)	121.3(6)	O(3)	-C(10)	-C(9)	124.3(6)
O(3)	-C(10)	-C(11)	116.0(6)	C(9)	-C(10)	-C(11)	119.7(6)
O(4)	-C(11)	-C(10)	115.6(6)	O(4)	-C(11)	-C(12)	124.6(6)
C(10)	-C(11)	-C(12)	119.8(6)	C(11)	-C(12)	-C(13)	121.1(6)
C(8)	-C(13)	-C(12)	119.0(5)	C(8)	-C(13)	-C(14)	124.0(5)
C(12)	-C(13)	-C(14)	117.0(5)	C(13)	-C(14)	-C(15)	114.9(5)
C(14)	-C(15)	-C(16)	116.5(5)	C(14)	-C(15)	-C(20)	125.5(5)
C(16)	-C(15)	-C(20)	118.0(6)	C(15)	-C(16)	-C(17)	121.1(6)
O(5)	-C(17)	-C(16)	124.7(6)	O(5)	-C(17)	-C(18)	114.9(6)
C(16)	-C(17)	-C(18)	120.5(6)	O(6)	-C(18)	-C(17)	117.1(6)
O(6)	-C(18)	-C(19)	124.5(6)	C(17)	-C(18)	-C(19)	118.4(6)
C(18)	-C(19)	-C(20)	121.3(6)	C(15)	-C(20)	-C(19)	120.8(6)
C(15)	-C(20)	-C(21)	123.3(6)	C(19)	-C(20)	-C(21)	115.8(5)
C(1)	-C(21)	-C(20)	109.1(4)				
Cl(1)	-C(28)	-Cl(2)	110.2(6)	Cl(1)*	-C(28)	-Cl(2)*	103(1)
Cl(1)	-C(28)	-Cl(3)	112.1(6)	Cl(2)	-C(28)	-Cl(3)	108.6(6)
Cl(1)*	-C(28)	-Cl(3)*	111(1)	Cl(2)*	-C(28)	-Cl(3)*	105(1)
Cl(4)	-C(29)	-Cl(5)	108.6(6)	Cl(4)*	-C(29)	-Cl(5)*	104(1)
Cl(4)	-C(29)	-Cl(6)	107.6(7)	Cl(5)	-C(29)	-Cl(6)	110.6(7)
Cl(4)*	-C(29)	-Cl(6)*	108(1)	Cl(5)*	-C(29)	-Cl(6)*	120(1)

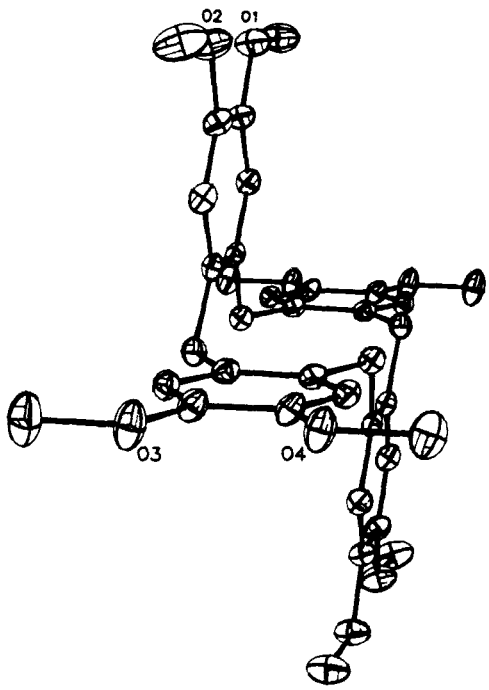

Figure 2 Sofa conformation of the CTTV molecule in the solid state.

short and long bonds is observed within the six-membered rings indicating partial localization of the π-electrons. Unlike CTV, however, the methoxy substituents are all essentially coplanar with the benzenoid rings (maximum deviation 0.11 Å), consistent with the increased Me-Me non-bonded distances caused by the sofa conformation of CTTV.

ii) Crystal packing and host-guest interactions

In our previous work[5] upon CTV (**1**) it was demonstrated that the inclusion of small guest molecules and the resulting crystal structure is strongly influenced by (often weak) hydrogen bond donor/acceptor interactions involving the methoxy oxygen atoms of the macrocycle, as well as the need to minimize free space within the crystal. Such interactions are also found to be the dominating feature of the inclusion chemistry of CTTV although it is unfortunate that, as yet, no structures have been obtained with strong hydrogen bond donor guests.

In the case of both crystal modifications of (**2**.4$CHCl_3$), the four guest molecules are included within an extensive channel network and effectively surround each CTTV molecule in such a way as to maximize Cl_3C-H...O interactions. In both structures one pair of chloroform molecules exhibits close contacts C(19)...O(3), O(4) of 3.19, 3.26 Å (**2**.4$CHCl_3$-*I*) and 3.15, 3.24 Å (**2**.4$CHCl_3$-II) suggesting a weak, bifurcated hydrogen bond as observed for the related 1:2 CTV complex, with the chloroform...oxygen vector out of the plane of the nearest CTTV benzenoid ring (Fig. 3). In the case of (**2**.4$CHCl_3$-II), the remaining molecules of chloroform exhibit a much more asymmetric mode of hydrogen bonding as a consequence of the steric shielding effects of the vertical aromatic ring, with a single significant contact C(20)...O(2) 3.31 Å. The C(20)...O(2) vector remains out of the aromatic ring plane, however. In the case of the type I crystal modification, a closer approach of C(20) to the sterically crowded equatorial plane of the CTTV molecule is attained by aligning the C(20)...O vector with the plane of the rings to give a second type of bifurcated hydrogen bond C(20)...O(1), O(2) 3.41 and 3.19 Å, Fig. 4. Solution π-π stacking effects in the mixed benzene/chloroform solvent may well mitigate against the formation of this apparently stronger hydrogen bond in the type II complex.

In the case of (**2**.2$CHCl_3$) and (**2**.2CH_2Cl_2), there are no host-guest interactions involving the sterically crowd-

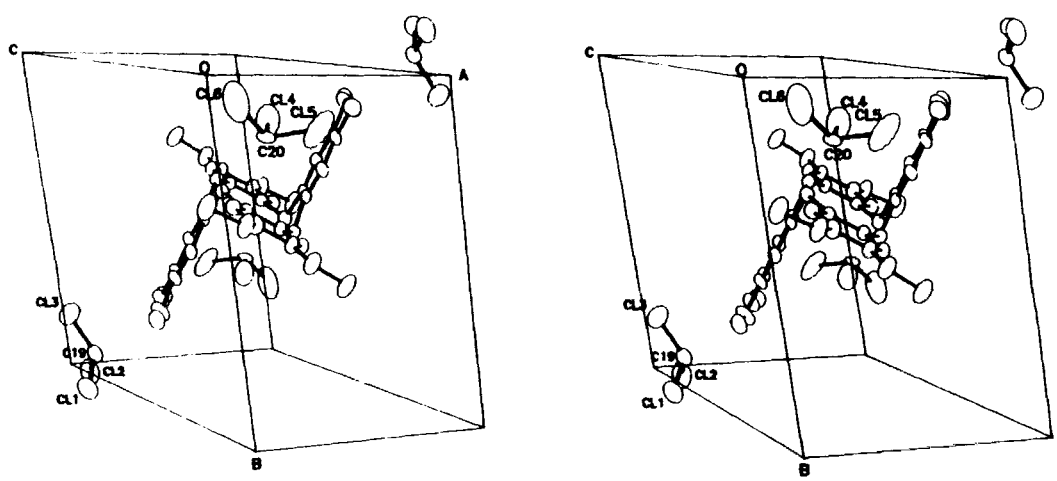

Figure 3 Stereoview of the host-guest interactions in the chloroform inclusion complex (**2**.4$CHCl_3$-II).

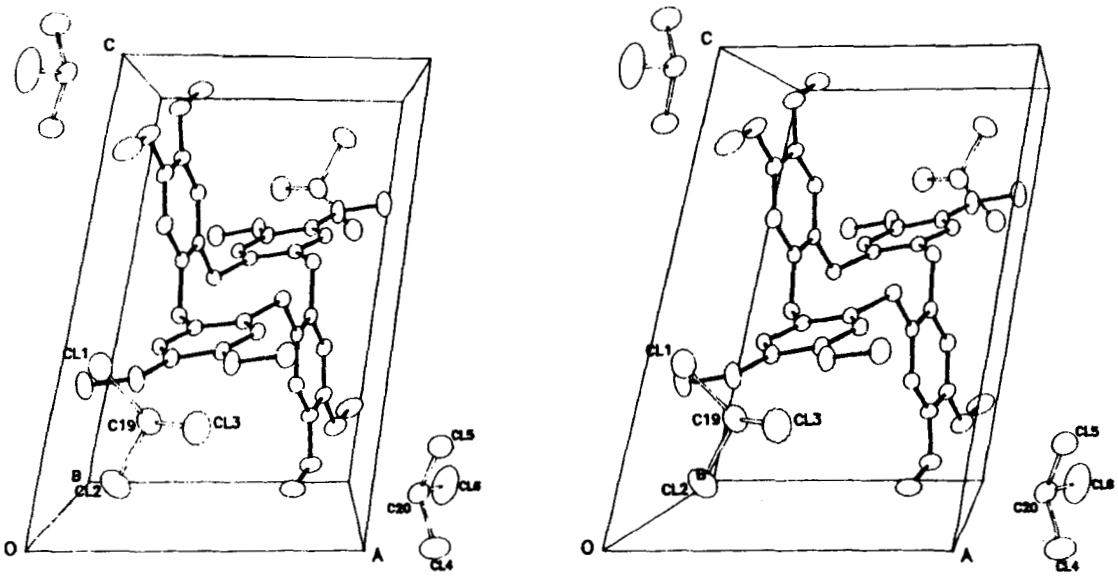

Figure 4 Stereoview showing intermolecular short contacts in (**2**.4$CHCl_3$-I).

ed equatorial plane of the CTTV molecule. Instead, the solvent molecules, which are arranged in layers between CTTV units, adopt the bifurcate mode of hydrogen bond interaction seen at the axial methoxy substituents in both forms of (**2**.4$CHCl_3$), C(19)...O(3), O(4) 3.32, 3.17 Å (**2**.2$CHCl_3$), C(19)...O(3), O(4) 3.28, 3.36 Å (**2**.2CH_2Cl_2). It is interesting to note that the availability of a second guest hydrogen atom in the case of the methylene chloride complex has no shortening effect upon the bifurcate C(19)...O(3), O(4) hydrogen bond. Instead, an additional long interaction to a neighbouring CTTV molecule is formed, C(19)...O(2)′ 3.44 Å, Fig. 5.

CONCLUSIONS

This study has demonstrated that, like the wide range of inclusion complexes of the analogous CTV molecule, CTTV is capable of complexing extensive arrays of guest molecules. As with CTV, crystal packing is dominated by the formation of weak, bifurcate hydrogen bond interactions to the methoxy oxygen atoms of the host. Both CTV and CTTV may thus be regarded as hosts of essentially pure H-bond acceptor character in contrast to the organometallic cluster $[Mn(CO)_3(\mu_3\text{-}OH)]_4$[8], for example, which forms a wide range of host guest complexes acting purely as a H-bond donor.

In the case of CTTV, the shape of the host results in the formation of open channel-like cavities between CTTV molecules rather than the cage structure observed in the case of CTV. This may well be a contributing factor in the relatively poor stability and limited range of inclusion complexes of CTTV so far observed.

EXPERIMENTAL SECTION

CTTV was synthesized according to the method of White and Gesner.[7] In a typical run veratryl alcohol (80 cm^3) was warmed in a dry box with glacial acetic acid

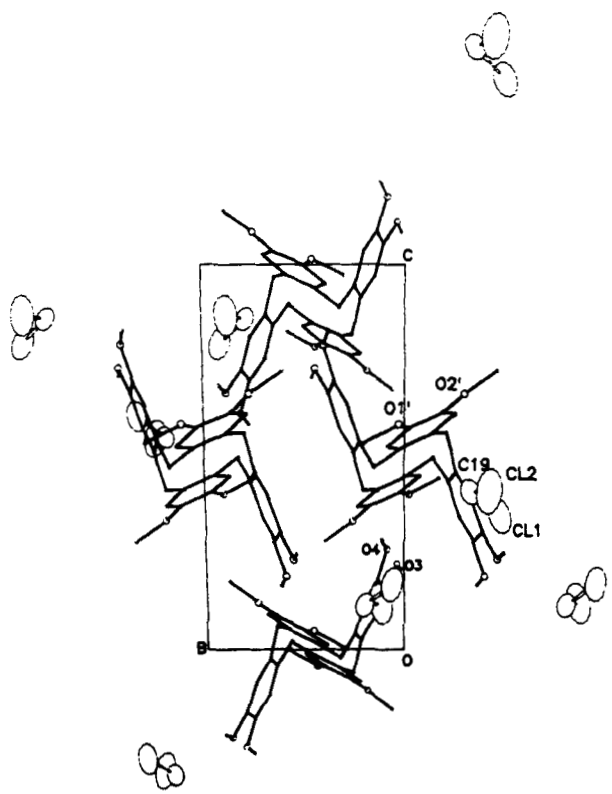

Figure 5 Environment of the methylene chloride guest molecules in (**2**.2CH_2Cl_2).

Table 4 Crystal data and summary of data collections

	Compound	
	(2.4CHCL$_3$-I)	*(2.4CHCl$_3$-II)*
Mol. Wt.	1078.23	1078.23
Space group	$P\bar{1}$	$P\bar{1}$
cell constants		
a, Å	8.057(4)	8.375(4)
b, Å	13.448(5)	11.335(5)
c, Å	13.481(5)	13.704(5)
α, °	60.87(3)	82.39(4)
β, °	77.38(3)	85.70(5)
γ, °	76.64(3)	75.90(5)
V, Å^3	1236	1249
molecules/unit cell	1	1
D_c, g cm^{-3}	1.45	1.43
μ_c, cm^{-1}	7.16	7.09
radiation	Mo Kα	Mo Kα
cryst dimens, mm	0.20x0.15x0.15	0.22x0.15x0.08
scan width, °	0.70 + 0.20 tan θ	0.75 + 0.20 tan θ
decay of stds	2%	<2%
2θ range, °	2 - 42	2 - 44
no. reflcns collcd	2530	3068
no. of obsd refls	2162	1726
no. of params	346	295
R	0.068	0.106
R_w	0.070	0.107
	Compound	
	(2.2CHCl$_3$)	*(2.2CH$_2$Cl$_2$)*
Mol. Wt.	839.47	770.58
Space group	$P2_1/n$	$P2_1/n$
cell constants		
a, Å	19.024(5)	18.998(3)
b, Å	7.509(2)	7.406(2)
c, Å	14.554(5)	14.307(4)
β, °	102.54(3)	105.94(2)
V, Å^3	2024	1936
molecules/unit cell	2	2
D_c, g cm^{-3}	1.37	1.32
μ_c, cm^{-1}	4.72	3.58
radiation	Mo Kα	
cryst dimens, mm	0.22x0.20x0.10	0.25x0.20x0.10
scan width, °	0.80 + 0.20 tan θ	0.70 + 0.20 tan θ
decay of stds	2%	<2%
2θ range, °	2 - 44	2 - 44
no. reflcns collcd	2811	2678
no. of obsd refls	1410	1089
no. of params	286	226
R	0.046	0.078
R_w	0.046	0.078

(200 cm^3) and sulfuric acid (0.2 cm^3) at 90°C for 15 minutes resulting in the formation of a mixture of trimer and tetramer. Pure CTTV was obtained (as its chloroform solvate) by fractional crystallization from benzene/chloroform (1:1). Colorless crystals of CTTV 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.[9] Lattice, data collection and refinement parameters are given in Table 4. Intensity data were corrected for Lorentz and polarization effects but absorption corrections were considered unnecessary. Structure solution was accomplished with the aid of the SHELX86 program[10] and structures were refined using the SHELX system.[11] In each case all non-hydrogen atoms were refined with anisotropic thermal parameters. In the case of (**2**.4CHCl$_3$-I) and (**2**.2CHCl$_3$) some disorder of the chloroform guests was noted and was resolved in terms of two sets of chlorine atom positions, occupancies refined to 50% each (**2**.4CHCl$_3$-I), 75%/25% (**2**.2CHCl$_3$). 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 additional bond lengths and angles are available upon request from the authors.

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