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Structure of the inclusion complexes of heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin with indole-3-butyric acid and 2,4-dichlorophenoxyacetic acid ☆

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Abstract—The crystal structures of the complexes of heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin with indole-3-butyric acid and with 2,4-dichlorophenoxyacetic acid were studied by X-ray diffraction. The complexes crystallize in the monoclinic $P2_1$ space group. The host molecules are elliptically puckered and stacked along the *a* crystal axis, in a head-to-tail fashion, forming columns. One primary methoxy group of the host molecule of the complex with indole-3-butyric acid has the unusual trans–gauche conformation for permethylated CDs. All the secondary O-3–CH_3 methoxy groups, some secondary O-2–CH_3 and some primary methoxy groups pointing inwards the cavity enclose the indole or the 2,4-dichlorophenoxy moieties of the guest molecules inside the cavity, while the chains of the guests protrude between two adjacent host molecules of the columns. The mean planes of the indole and 2,4-dichlorophenoxy moieties of the guests are nearly perpendicular to the mean planes of the elliptical heptagons defined by the O-4*n* atoms of the hosts. The carboxyl group of the guests form hydrogen bonds with oxygen atoms of the host molecules or with the water molecules found in the space between the complexes of the same column.

Keywords: Heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin; Indole-3-butyric acid; 2,4-Dichlorophenoxyacetic acid; Crystal structures; Inclusion compounds; Auxins

1. Introduction

Auxins are plant hormones producing a growth response and therefore are known as plant growth regulators.[2] The first auxin found, and thoroughly studied since then, is the naturally occurring indole-3-acetic acid (IAA). In addition to naturally occurring plant growth regulators, more than 200 synthetic compounds are commercially available.[3] Indole-3-butyric acid (IBA) is an auxin promoting the root formation in cuttings. It has been considered for a long time as a synthetic auxin, but it has now been proven that it is also a naturally occurring one. Though it was found in maize and various dicots and is probably widespread in the plant kingdom,[4] its exact role in plants was only recently elucidated. A conversion of IBA to IAA occurs in plants, IBA being a slow release source for IAA[5] having also a strong rooting effect. The crystal structure and the physiological effects at the molecular level of IAA and of some of their derivatives have been studied,[6] but no simple correlation of their structural parameters with their bioactivity has been found.[6,7] 2,4-Dichlorophenoxyacetic acid (2,4-D) is a synthetic plant growth regulator causing many responses similar to those of natural auxins. As it is chemically very stable, it has been widely used commercially. Its auxin activity appears at low concentrations while at relatively higher concentrations it becomes phytotoxic.[8] It is used for the formation of somatic embryos[9,10] and usually in combination with naphthoxyacetic acid and IBA for callus initiation.

Cyclodextrins (cyclomaltosides, CDs) are oligosaccharides consisting of six, seven or eight α-(1 → 4)-linked

☆ Part IV in the series: Inclusion compounds of plant growth regulators in cyclodextrins. For Part III see Ref. 1.

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D-glucose residues called α-, β- or γ-cyclodextrins (α-, β- or γ-CD), respectively, having the ability to include a variety of molecules with suitable size and shape inside their cavity. They can be used in plant cell biotechnology acting as solubilizers, protecting agents for labile molecules and carriers.[11] Heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TRiMEB) presents an improved aqueous solubility and greater stability towards hydrolysis, both in solution and in the solid state.[12] Hence TRiMEB is used as carrier of pharmaceutical molecules.

In an ongoing study of inclusion compounds of plant growth regulators in CDs, we report here the crystal structures of the complexes of IBA and 2,4-D in TRiMEB.

2. Experimental

2.1. Crystallization

Aqueous solutions of IBA or 2,4-D (obtained from Serva or Fluka) were added to aqueous solutions of TRiMEB (purchased from Cyclolab) at a 1:1 host/guest mole ratio (concentrations = 0.02 M). After stirring the solutions for 1 h at 40 °C, they were maintained at 50 °C until white crystals of the complexes, suitable for X-ray data collection, were formed.

2.2. X-ray data collection

Data were collected on chosen single crystals of both inclusion complexes, sealed in Linderman glass capillaries, on a Syntex $P2_1$ diffractometer upgraded by Crystal Logic[13] and attached to a Rigaku rotating anode generator, using CuKα radiation monochromatized by a graphite single crystal, according to the $\theta/2\theta$ mode at the temperature of 293(2) K. Lorenz and polarization corrections were applied to the intensity data; $2\theta_{max}$ was less than 95° (IBA/TRiMEB) or 95.02° (2,4-D/TRiMEB).

2.3. Structure solution and refinement

The structure of IBA/TRiMEB has been solved by a Patterson vector search method and Fourier recycling with DIRDIF99,[14] using the coordinates of the macrocycle of the ethyl laurate/TRiMEB complex.[15] The same process has been applied to solve the structure of 2,4-D/TRiMEB, using the coordinates of the macrocycle of IBA/TRiMEB, as attempts to solve it by isomorphous replacement of the coordinates of this macrocycle failed. Sequential difference electron density ($\Delta\rho$) maps gave the positions of the remaining non-hydrogen atoms of the hosts, and those of the guests and the water molecules as well. The refinement, based on F^2 proceeded by using full-matrix least squares with the SHELXL-97 program.[16] The relatively small number of observations [reflections/parameters ratios = 6.7 (IBA/TRiMEB) or 6.08 (2,4-D/TRiMEB)] allowed an anisotropic refinement of the non-disordered oxygen atoms only. The geometry of the guest molecules was optimized by fitting the atomic positions into the maxima of a $\Delta\rho$ map using the molecular graphics program 'O'.[17] After this optimization, all the atoms of IBA were kept at constant positions and those of the phenyl group of 2,4-D were considered as forming an ideal hexagon. Calculated positions of hydrogen atoms linked to carbon atoms of the host molecules have been used with C–H distances of 0.96, 0.97 and 0.98 Å for the primary, secondary and tertiary hydrogen atoms, and their thermal parameters have been set at $1.2 \times U_{iso}$ of the isotropic thermal parameters of the corresponding C-atoms. Extinction correction was applied in IBA/TRiMEB. Fourteen (IBA/TRiMEB) or 29 (2,4-D/TRiMEB) reflections exhibiting poor agreement were given zero weight during the final refinement cycles. The refinement converged to $R_1 = 0.1053$ and 0.1342 (IBA/TRiMEB) and $R_1 = 0.0927$ and 0.1335 (2,4-D/TRiMEB) for observed and all reflections, respectively. Details concerning the experimental data of both crystal structures are given in Table 1.

3. Results and discussion

The atomic numbering of the guest molecules is given in Scheme 1. Top and side views of the complexes are given in Figures 1 (IBA/TRiMEB) and 2 (2,4-D/TRiMEB), along with the numbering scheme of the host molecules, C-*mn* and O-*mn* denoting the *m*th atom within the *n*th glycosidic residue of the host molecule.

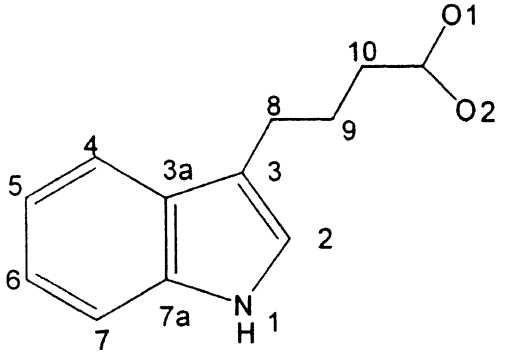
3.1. Conformation of the TRiMEB molecule

The non-H atoms of the host molecules of both structures exhibit a thermal motion similar to those of the guests. Some geometric features of the host molecules of both structures are given in Table 2. All the pyranose rings have the usual $^4C_1$ conformation, as it is indicated by the Cremer–Pople puckering parameters Q and θ.[18,19] Note that it has been observed one pyranose ring with the $^0S_2$ skew-boat conformation in the *m*-iodophenol/TRiMEB complex[20,21] and another one, having the $^1C_4$ inverted chair conformation, in monohydrated TRiMEB.[22,23]

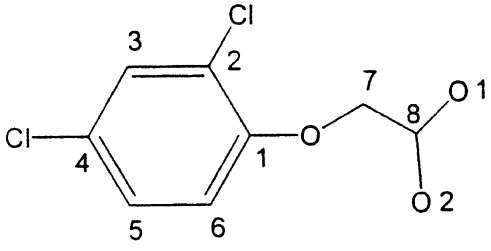
The heptagons of the glucosidic O-4*n* atoms are seriously puckered (see Table 2) having an elliptical shape, the distortions being due to the absence of O-3$n\cdots$O-2$(n+1)$ H-bonds between the vicinal glucosidic residues. In both structures, the long axis of the ellipse passes near the O-45 atom and the middle of the line formed by the O-41 and O-42 atoms. The ranges of the values of the Φ = O-5$(n+1)$–C-1$(n+1)$–O-4*n*–C-4*n* and

Table 1. Experimental details

	IBA/TRiMEB	2,4-D/TRiMEB
Chemical formula	$C_{63}H_{112}O_{35}\cdot C_{11}H_{10}NO_2\cdot(H_2O)_{0.37}$	$C_{63}H_{112}O_{35}\cdot C_8H_6O_3Cl_2\cdot(H_2O)_2$
Formula weight	1695.92	1646.65
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1$
Unit cell dimensions	$a = 11.411(7)$ Å	$a = 11.68(2)$ Å
	$b = 28.629(7)$ Å, $\beta = 111.91(2)°$	$b = 28.23(5)$ Å, $\beta = 112.63(7)°$
	$c = 15.069(4)$ Å	$c = 15.02(3)$ Å
Volume (Å^3)	4567(3)	4571(14)
Z, calculated density (Mg/m^3)	2, 1.183	2, 1.196
Absorption coefficient (mm^{-1})	0.805	1.321
Radiation type, λ	CuKα, 1.5418 Å	CuKα, 1.5418 Å
Crystal size (mm)	0.2×0.6×0.7	0.2×0.4×1.0
θ range for data collection	3.09–49.97°	3.19–47.5°
Limiting indices	$-10 \leqslant h \leqslant 11$, $-28 \leqslant k \leqslant 16$,	$-10 \leqslant h \leqslant 9$, $-25 \leqslant k \leqslant 25$,
	$-14 \leqslant l \leqslant 12$	$-14 \leqslant l \leqslant 9$
Reflections collected/unique/observed	4766/4593/3314	4080/3844/2804
Completeness to θ	49.97°, 93.6%	47.51°, 89.1%
Data/restraints/parameters	4593/0/689	3844/25/671
Goodness-of-fit on F^2	1.321	1.061
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.1063$, $wR_2 = 0.2813$	$R_1 = 0.0927$, $wR_2 = 0.2420$
R indices (all data)	$R_1 = 0.1342$, $wR_2 = 0.3146$	$R_1 = 0.1335$, $wR_2 = 0.2880$
$(\Delta/\sigma)_{max}$	0.117	0.007
Extinction coefficient	0.0025(6)	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^3)	0.340, −0.319	0.281, −0.312
Flack parameter	0.35 (0.61)	0.57 (0.14)



indole-3-butyric acid



2,4-Dichlorophenoxyacetic acid

Scheme 1.

Ψ = C-1(n + 1)–O-4n–C-4n–C-3n angles are similar to those observed in other TRiMEB complexes.[23]

The tilt angles, in both structures, vary widely and their maximum values are those of the VI pyranose rings, 49.2(9)° (IBA/TRiMEB) and 42.1° (2,4-D/TRiMEB). The mean planes of C-26, C-36, O-56 and C-56 atoms form angles of 59.0(3)° (IBA/TRiMEB) and 62.5° (2,4-D/TRiMEB) with the corresponding mean planes of the O-4n atoms. Therefore, residue VI of the host molecules of both complexes are the most inclined to the mean planes of the O-4n atoms creating openings in the truncated cones of both host molecules, where the chains of the guests are accommodated, while their carboxyl groups exit from the macrocycles towards the free space between two adjacent complexes linked by the a axis.

3.1.1. Conformation of the methoxy groups of the host molecule of IBA/TRiMEB. The O-62–C-92 and the C-74 groups are disordered over two sites (occupancies 0.70 and 0.30). The O-63 atom of the O-63–C-93 group is also disordered over two sites (occupancies 0.60 and 0.40). Attempts to find more than one site for the C-93 group failed, though its thermal parameter is high indicating a possible disorder. The primary methoxy groups of residues I, II (site A), IV and VII have the gauche–gauche conformation pointing outwards the cavity, those of the residues II (B site), III (both sites) and V have gauche–trans conformation pointing inwards, and those of residue VI has the trans–gauche conformation, pointing also inwards the cavity. To our knowledge, it is the first time that a trans–gauche conformation is observed in a TRiMEB complex.[24] However, it has been observed in the crystal structures of heptakis(2,3,6-tri-*O*-propanoyl)-β-CD,

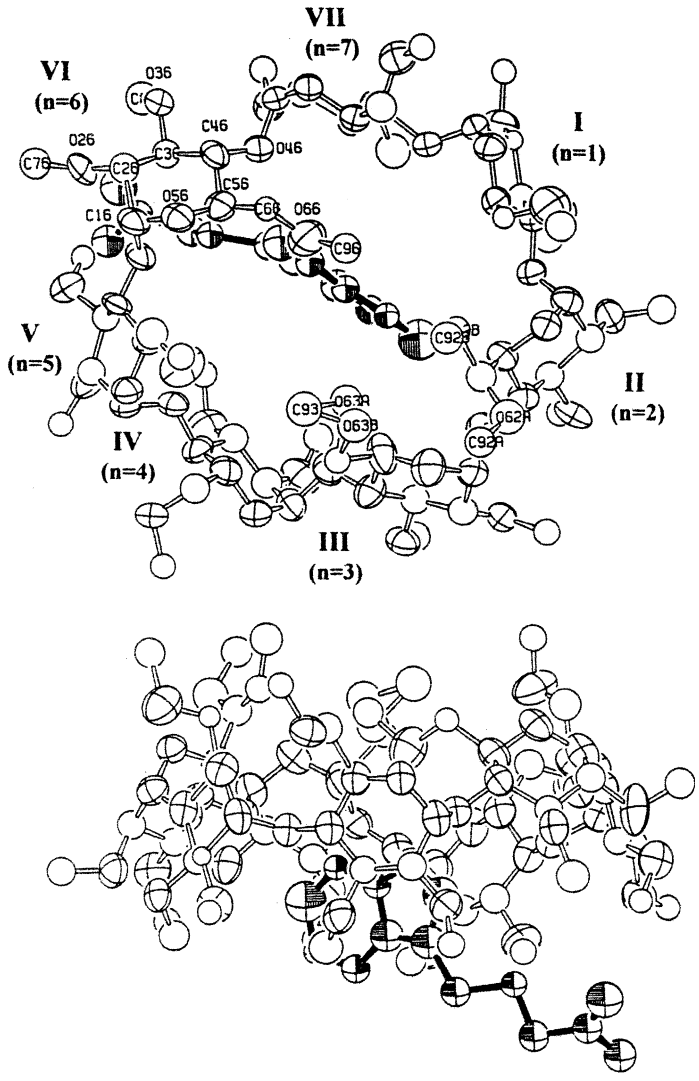


Figure 1. Front and side views of IBA/TRiMEB. C-*mn* and O-*mn* denote the *m*th atom within the *n*th glycoside residue.

heptakis(2,3,6-tri-*O*-acetyl)-β-CD and heptakis(2,3,6-tri-*O*-butanoyl)-β-CD molecules.[25] All the O-2*n*–C-7*n* groups point outwards the cavity, except the O-24–C-74 group pointing inwards like all the O-3*n*–C-8*n* secondary groups. Therefore, the primary groups orientated inwards close the opening of the primary side of the host molecule and the secondary ones reduce the opening of the wide side of the host cavity, enclosing inside it the indole moiety of the guest molecule.

3.1.2. Conformation of the methoxy groups of the host molecule in the 2,4-D/TRiMEB complex. The O-66–C-96 group is disordered over two positions (occupancies 0.50). The C-91 and C-93 methyl groups are also disordered over two sites (occupancies of their major sites 0.77 and 0.78). The C-74 methyl group is disordered over three sites (occupancies 0.30, 0.50 and 0.20). The primary groups of the residues I, II, IV and VII have the gauche–gauche conformation pointing outwards the cavity, while the residues III, V and VI (both sites) have the gauche–trans conformation pointing inwards (Table 2). All the groups O-3*n*–C-8*n* point inwards the cavity, while all the other O-2*n*–C-7*n* groups point outwards. Therefore, both apertures are limited and the TRiMEB cavity has a bowl shape where the 2,4-dichlorophenoxy moiety is entrapped.

3.2. The guest molecules

3.2.1. Indole-3-butyric acid. The indole moiety is planar within 0.032 Å, being almost perpendicular to the mean plane of the O-4*n* atoms forming an angle of 83.13(7)° with it. The butyric chain lies nearly on the indole mean plane, as the C-3a–C-3–C-8–C-9 and C-3–C-8–C-9–C-10

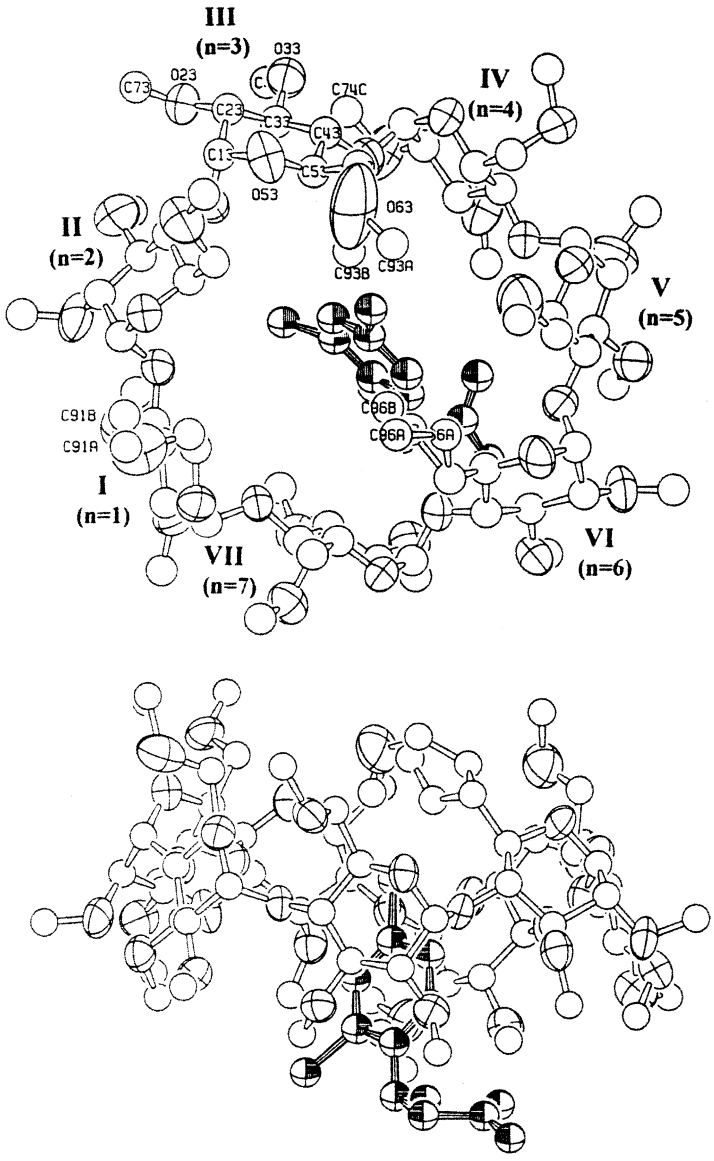


Figure 2. Front and side views of 2,4-D/TRiMEB. C-*mn* and O-*mn* denote the *m*th atom within the *n*th glycoside residue.

torsion angles are 153.32(1)° and −171.86(1)°. The O-1 atom of the carboxyl group is hydrogen bonded with the O-31 atom of a vicinal host molecule (distance O-1···O-31 = 2.663 Å; angles C–O-1···O-31 = 125.1°, O-1···O-31–C-31 = 129.6°; symmetry code: $1-x$, $0.5+y$, $1-z$). The N atom forms also a hydrogen bond with the O-66 atom of the host molecule (distance N···O-66 = 3.099 Å; angles C-66–O-66···N = 126.8°, O-66···N–C-2 = 125.1°, O-66···N–C-7A = 123.8°).

3.2.2. 2,4-Dichlorophenoxyacetic acid. The 2,4-D guest molecule is disordered over two positions (occupancies 0.78 and 0.22) (Fig. 3). The mean planes of the 2,4-dichlorophenyl moieties are nearly perpendicular to the heptagon of the O-4*n* atoms, forming dihedral angles of 77.5(4)° (site A) or 86.9(8)° (site B) with it. They are orientated along the lines passing through the C-13 and O-56 atoms (site A) or the C-12 and O-46 atoms (site B). A short hydrogen bond is formed between the O-1 atom of the carboxyl group of both sites and the O-W2 water molecule (distances O-1A···O-W2 = 2.590 Å and O-1B···O-W2 = 2.657 Å; angles C-8–O-1A···O-W2 = 105.0° and C-8–O-1B···O-W2 = 104.0°).

3.3. Crystal packing

Both complexes crystallize in the monoclinic $P2_1$ space group, unlike all the TRiMEB complexes reported so far crystallizing in the $P2_12_12_1$ space group. The complexes are stacked along the shortest axis *a* of the unit cell, in

Table 2. Conformational characteristics of the host molecules

Residue	I ($n = 1$)	II ($n = 2$)	III ($n = 3$)	IV ($n = 4$)	V ($n = 5$)	VI ($n = 6$)	VII ($n = 7$)
IBA/TRiMEB							
Q (Å)	0.55	0.60	0.54	0.51	0.54	0.57	0.55
θ (°)	3.01	5.48	3.08	3.99	9.92	3.78	4.81
D (Å)	4.39	4.33	4.49	4.29	4.30	4.49	4.38
Φ_h (°)	123.5	122.7	138.1	124.1	115.7	140.0	125.8
D_K (Å)	5.28	5.11	4.54	5.12	5.36	4.58	4.94
Φ_K (°)	49.9	52.9	55.0	48.3	50.5	56.2	50.5
d (Å)	−0.193	−0.490	0.421	0.369	−0.666	0.058	0.501
τ	15.6	−31.8	−38.4	15.5	−28.9	49.2	10.7
t	75.5	60.8	66.8	77.1	61.5	59.0	81.7
d_H	3.24	3.38	3.66	3.58	3.48	3.56	3.34
τ_1	−74.5	−81.5 (site A) 73.5 (site B)	95.4 (site A) 61 (site B)	−81.1	63	134.4	−69.3
τ_2	52	34 (site A) −171.1 (site B)	−147.2 (site A) 178.6 (site B)	43.2	−176.6	−102.5	53.7
C	gg	gg gt	gt gt	gg	gt	tg	gg
Φ	105(1)	105(1)	85(2)	109(1)	107(1)	87(1)	108(1)
Ψ	142(1)	139(1)	98(2)	155(1)	148(1)	93(1)	144(1)
2,4-D/TRiMEB							
Q (Å)	0.54	0.56	0.59	0.54	0.56	0.56	0.55
θ (°)	4.54	5.16	11.40	6.66	6.18	11.90	2.57
D (Å)	4.39	4.27	4.47	4.35	4.19	4.53	4.36
Φ_h (°)	125.5	122.1	135.5	127.4	117.2	135.6	127.8
D_K (Å)	5.18	5.17	4.66	4.97	5.31	4.76	4.88
Φ_K (°)	50.3	51.2	55.2	49.9	48.9	56.1	51.2
d (Å)	0.201	0.434	−0.413	−0.302	0.631	−0.118	−0.434
τ	12.6	26.1	−33.4	18.0	30.9	42.1	10.5
t	75.9	66.4	69.5	75.6	58.5	62.5	82.1
d_H	3.06	3.30	3.60	3.64	3.35	3.54	3.23
τ_1	−66	−78.4	69	−76	70	65.3 (site A) 115 (site B)	−69.5
τ_2	57	43	−171	48	−174.2	−171 (site A) −121 (site B)	55.9
C	gg	gg	gt	gg	gt	gt gt	gg
Φ	111(2)	107(2)	85(2)	113(2)	102(2)	82(2)	114(1)
Ψ	135(2)	137(2)	98(2)	157(2)	138(2)	101(2)	139(1)

Q and θ = Cremer–Pople parameters; D = O-4$n\cdots$O-4$(n+1)$ distances; Φ_h = O-4$(n-1)\cdots$O-4$n\cdots$O-4$(n+1)$ angles; D_K = distances of the approximate centre K of the O-4n heptagon from the O-4n atoms; Φ_K = the O-4$n\cdots$K$\cdots$O-4$(n+1)$ angle; d = deviations of the O-4n atoms from their least-squares plane; τ = tilt angles between the optimum O-4n plane and the mean plane atoms O-4$(n-1)$, C-1n, C-4n, O-4n; t = angles between the mean plane formed by the C-2n, C-3n, C-5n and O-5n atoms with the optimum O-4n plane; d_H intramolecular O-3$n\cdots$O-2$(n+1)$ distances; torsion angles τ_1 = O-5n–C-5n–C-6n–O-6n and τ_2 = C-4n–C-5n–C-6n–O-6n; C = Conformation of the primary chain; Φ = O-5$(n+1)$–C-1$(n+1)$–O-4n–C-4n; Ψ = C-1$(n+1)$–O-4n–C-4n–C-3n.

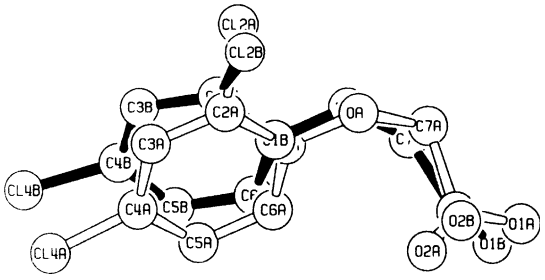


Figure 3. The two sites of the disordered 2,4-dichlorophenoxyacetic acid molecule.

a head-to-tail mode, linked by the lattice translation (Fig. 4). Though the cell dimensions of the two crystal structures are very nearly the same and the complexes are stacked along the a crystal axis, it seems that they are not isomorphous since their orientations towards the crystal axes appear to be different (Fig. 4). The mean planes of the O-4n atoms of both structures are nearly perpendicular to the ac plane, the corresponding angles being 89.2° (IBA/TRiMEB) and 84.1° (2,4-D/TRiMEB), and they form similar angles with the ab plane, 65.5° (IBA/TRiMEB) and 65.1° (2,4-D/TRiMEB) but their angles with the bc plane are quite different, 2.7° (IBA/TRiMEB) and 48.0° (2,4-D/TRiMEB). That is why it was impossible to solve the 2,4-D/TRiMEB structure by isomorphous replacement using the coordinates of IBA/TRiMEB. Nevertheless, a replacement of the b and c axes of the 2,4-D/TRiMEB by $-b$ and $-(a+c)$ provides

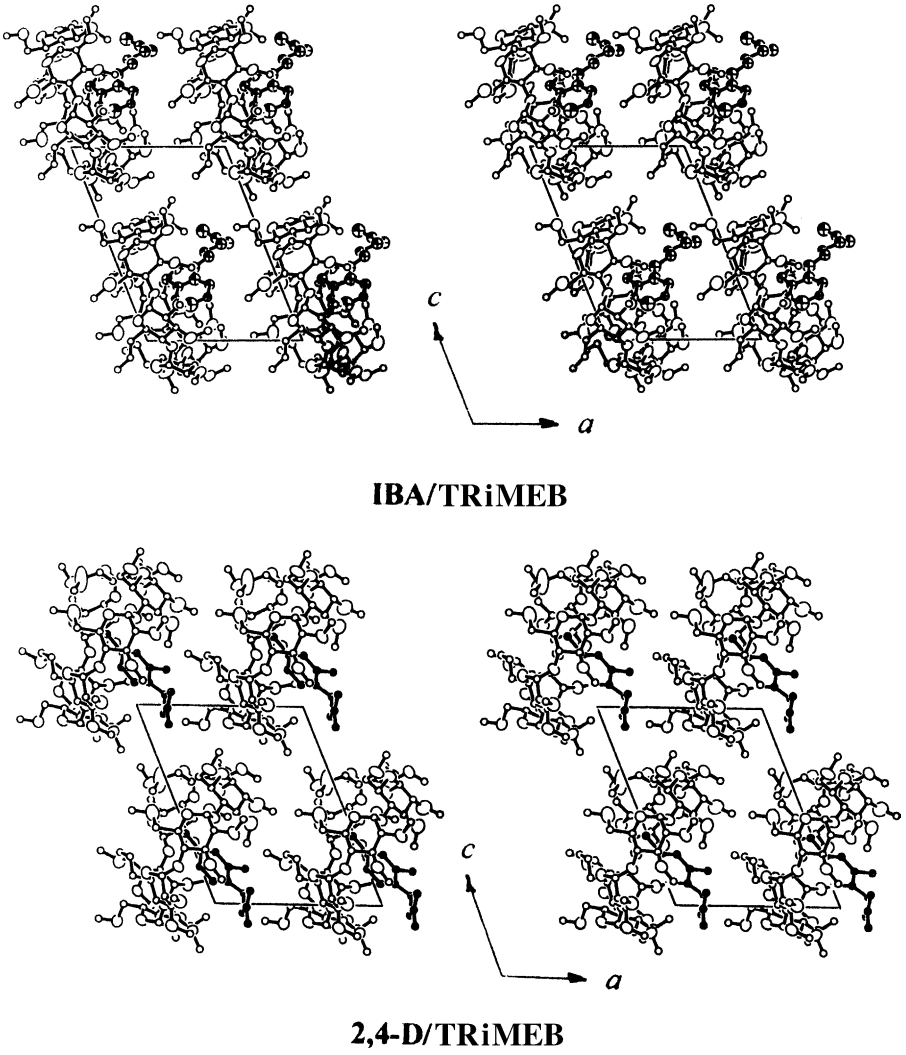


Figure 4. Stereo-diagrams of the two complexes view down the *b* axis.

another unit cell identical to that of IBA/TRiMEB and an isomorphous crystal packing, the angle between the O-4*n* mean plane of the 2,4-D/TRiMEB and the plane defined by the *b* and $(a+c)$ axes being now 6.1°. This discrepancy is due to a different choice of axes during the initial manipulations of the data collection of 2,4-D/TRiMEB because the moduli of the $(a+c)$ and *c* vectors are almost equal, and the angle formed by the *a* and $-(a+c)$ axes is about the same with the angle β.

The crystal packing of our structures has some common features with that of three TRiMEB complexes of 1,7-dioxaspiro[5.5]undecane,[26] methylcyclohexane[27,28] and (L)-menthol[29] (Table 3). All three crystallize in the $P2_12_12_1$ space group and have similar cell dimensions. Their *a* axes are about the same and their *c* axes are about the double to the *c* axes of the unit cells of our structures, while the complexes stack also along the *a* axis. As both sides of the host cavities are nearly closed

Table 3. Cell dimensions and space groups of some TRiMEB complexes

Guest	*a*	*b*	*c*	β	Space group	Reference
(L)-Menthol	11.060(3)	26.138(6)	29.669(6)		$P2_12_12_1$	29
1,7-Dioxaspiro[5.5]undecane	10.936(7)	25.53(2)	29.64(4)		$P2_12_12_1$	26
Methylcyclohexane	11.149(2)	25.664(2)	29.427(5)		$P2_12_12_1$	27
Methylcyclohexane	11.043(4)	25.333(4)	29.132(2)		$P2_12_12_1$	28
IBA	11.411(7)	28.629(7)	15.069(4)	111.91(2)	$P2_1$	This work
2,4-D	11.68(2)	28.23(5)	15.02(3)	112.63(7)	$P2_1$	This work

by the methoxy groups isolating the guest molecules inside, the stacking has not the form of a channel, as in a class of native β-CD complexes,[30] but of a column (Fig. 4). Antiparallel columns linked by the twofold *b* axis form the crystal packing, as in the three TRiMEB complexes mentioned above.[26–29] Therefore, the two structures presented in this report and these three orthorhombic structures stack in the same mode.

Only one water molecule is found in the asymmetric unit of IBA/TRiMEB with a short occupancy factor, 0.39, and lie at a distance of 2.90 Å from the O-57 atom. There exist two water molecules in 2,4-D/TRiMEB forming H-bonds with the O-31 atom of an adjacent host molecule (distance O-31···O-W2 = 2.719 Å, angle C-31–O-31···O-W2 = 111.5°, symmetry code: $-x$, $-0.5+y$, $-z$), between them (O-W1···O-W2 = 2.813 Å) and with the carboxyl group of the guest.

Supplementary material

Full crystallographic details, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Center, deposition no. CCDC 213747 (IBA/TRiMEB) and CCDC 194126 (2,4-D/TRiMEB). These data may be obtained, on request, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 1223 336408; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.

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