Structural Chemistry of Linear α-Cyclodextrin–Polyiodide Complexes. X-ray Crystal Structures of $(\alpha\text{-Cyclodextrin})_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$ and $(\alpha\text{-Cyclodextrin})_2 \cdot Cd_{0.5} \cdot I_5 \cdot 27H_2O$. Models for the Blue Amylose–Iodine Complex†

M. Noltemeyer and W. Saenger*

Contribution from the Max-Planck-Institut für Experimentelle Medizin, Abteilung Chemie, D-3400 Göttingen, West Germany.

Received April 5, 1979

Abstract: α-Cyclodextrin (α-CD, $C_{36}H_{60}O_{30}$) is an enzymatic degradation product of amylose (starch). It consists of six (1→4) linked glucoses and represents in its annular structure and overall dimensions one turn of the V_6 amylose helix. α-CD and starch are able to form inclusion complexes with a variety of guests. With metal iodides in aqueous solution, essentially black, channel-type complexes crystallize in which α-CD molecules stack like coins in a roll and in the tubular cavity polyiodide chains are embedded. Depending on the counterion, four different crystal types have been observed: the (pseudo)hexagonal $(\alpha\text{-CD})_2 \cdot KI_3 \cdot I_2 \cdot 12H_2O$ (form I), the triclinic $(\alpha\text{-CD})_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$ (form II), the hexagonal $(\alpha\text{-CD})_2 \cdot BaI_2 \cdot I_2 \cdot 12H_2O$ (form III), and the tetragonal $(\alpha\text{-CD})_2 \cdot Cd_{0.5} \cdot I_5 \cdot 27H_2O$ (form IV). While for forms I and III only packing of the molecules can be given, the structures of forms II and IV have been studied in detail. In these, countercations are located in interstices between α-CD stacks and coordinated with α-CD hydroxyls in the case of Li^+ (form II) but Cd^{2+} (form IV) is surrounded by water. This finding suggests that the observed polymorphism is due to different coordination schemes of cations. In complexes II and IV, α-CD molecules adopt a "relaxed" form with all O(5)–C(5)–C(6)–O(6) torsion angles (−)-gauche. They are linked head-to-head via H bonds to form dimers and each dimer accommodates five I atoms. Four of these are in fully occupied positions near planes defined by O(4) and C(6) atoms (diameter of cavity ~5.2 Å). The fifth I is where the O(2), O(3) rims of adjacent α-CD meet and, since the cavity there bulges to ~7 Å, this I is twofold disordered (in ratio 39/61 in II and 50/50 in IV). The polyiodide chain in II is interpreted as $(I_2 \cdot I_3^-)_n$ while it is $(I_5^-)_n$ in IV. Distances between I_2, I_3^-, or I_5^- units are 3.14–4.01 Å, which are in all cases smaller than the van der Waals distance 4.3 Å. The black or blue color effects are due mainly to I···I charge transfer and possibly to I···H but not to I···O interactions. Electrical conductivity is $10^{-6}\ \Omega\ cm^{-1}$ along and $10^{-10}\ \Omega\ cm^{-1}$ perpendicular to the polyiodide chains in these crystals. It is proposed that in the "blue starch–iodine complex" the polyiodide chain is as found in complex II or IV.

Introduction

Starch is a polymer consisting of α(1→4) linked glucoses. The glucoses in one particular form of amylose, V_6 amylose, are in C1 chair conformation and arranged into a left-handed helix with six glucoses per turn ,of about 8-Å pitch height. Owing to a channel-like, 5 Å wide cavity in the center of the helix,[1-3] amylose is able to form inclusion complexes with small organic molecules and with iodine, yielding the well-known "blue starch–iodine complex" (the "blue amylose–iodine complex", "iodine's blue").[4-9]

Amylose can be degraded by glucosyl transferases into cylic oligosaccharides consisting of six, seven, or eight glucoses, called hexa-, hepta-, and octaamylose, or α-, β-, and γ-cyclodextrin (α-, β-, and γ-CD).[10-13] In α-CD, one turn of the starch helix is reconstituted to form a conical structure with outer diameter 13.5 Å and an annular aperture of 5.2 Å, Figure 1. The height of the cone, around 8 Å, corresponds to the pitch of the amylose helix because both are determined by the dimensions of the glucose units. Further, the distances of the atoms from the molecular axis in α-CD and in the amylose helix are comparable within 0.1 Å on average.

α-CD may be interpreted as a projection of the amylose helix down its axis. The conformational angles at links between adjacent glucoses are similar in both molecules[14] and therefore the spatial relations of atoms lining the cavities in the amylose helix and in the α-CD torus resemble each other except that the helical turn in amylose is replaced by an annulus in α-CD.

Like amylose, α-CD is able to form inclusion complexes.[10-16] These complexes crystallize in "cage"- or "channel"-type structures, depending on the nature and on the size of the guest compounds.[17] When molecular iodine (I_2) is added to an aqueous solution of α-CD, a cage-type complex of composition $\alpha\text{-CD} \cdot I_2 \cdot 4H_2O$ crystallizes as reddish needles.[18] However, if iodide anions are present, nearly black crystals showing metallic luster are formed. They belong to the channel-type inclusion compounds and their habitus, colors, and space groups depend strongly on the counterion, Table I. These complexes are of particular interest in relation to the polymeric amylose–iodine complex, because the "infinite columns" of the stacked α-CD molecules mimic the amylose helix. The correspondence of matrix dimensions is obvious from the crystal data entered in Table I. Similarities in optical properties are indicated by the spectra displayed in Figure 2, where reflection and absorption spectra for amylose–iodine and for several α-CD–iodine complexes are compared. The "blue polyiodide compounds" are not restricted to amylose, α-CD, or cholanic acid as matrices but can be found with many low and high molecular weight organic compounds.[19,20]

For some 40 years no explicit description of the structure of the iodine chain in the amylose–iodine complex and iodine–amylose interactions has been available.[1,5,8,10] X-ray fiber diagrams indicated that the iodine atoms should be arranged in a linear and equidistant array at 3.1-Å separation.[8] The same distance was found in iodine-soaked stretched polymers used nowadays as polarization filters,[21] and in rotation photographs of crystalline α-CD–polyiodide inclusion complexes.[22]

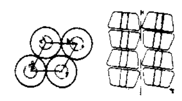
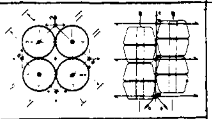
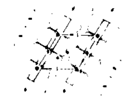
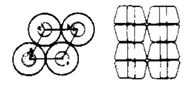
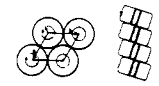
The nature of the blue color of amylose–iodine and of cyclodextrin–polyiodide complexes was studied by spectrophotometric investigations[1,23] and had been explained by the electron gas theory.[24] A quantum-mechanical treatment,[25] based on the twin chains of triiodide ions observed in the $(\text{benzamide})_2 \cdot HI_3$ complex,[26] indicated that the blue color might originate from the iodine chain per se. Assuming the existence of $(I_3^-)_n$ chains in amylose–iodine, electric conductivity measurements have been interpreted[27] and the one-

---

† Part 12 of the series "Topography of Cyclodextrin Inclusion Complexes". For part 11, see B. Klar, B. Hingerty, and W. Saenger, *Acta Crystallogr.*, in press.

0002-7863/80/1502-2710$01.00/0

Table I. Crystallographic Systematics of α-Cyclodextrin–Polyiodide Complexes

LATTICE TYPE CRYSTAL FORM	TRICLINIC II	TETRAGONAL IV	(PSEUDO)HEXAGONAL I	HEXAGONAL III	STARCH
HABITUS	HEXAGONAL PLATES OR RHOMBIC NEEDLES	RECTANGULAR NEEDLES	STOUT HEXAGONAL PRISMS	THIN HEXAGONAL PRISMS	–
COLOR/METALLIC LUSTER	DARK BROWN	DARK BROWN	BLUE-BLACK	BRONZE	DARK BLUE
DICHROISM	STRONG ∥ PRISM AXIS	STRONG ∥ PRISM AXIS	WEAK, ⊥ PRISM AXIS	STRONG, ∥ PRISM AXIS	STRONG, ∥ HELIX AXIS
CATIONS	Li^+, Na^+, Tl^+	H_3O^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}	K^+, Rb^+, Cs^+, NH_4^+	Ba^{2+}	K^+
SPACE GROUP	P1	$P4_22_12$	C222 or $P6_2$, $P6_222$, $P3_12$	P622	HEXAGONAL
CELL CONSTANTS (Å and °)	a=13.38, b=13.88 c=15.69 α=94.1, β=87.8 γ=120.0	a=b=19.93 c=30.88	a=15.80, b=27.37 c=40.20 or a=b=15.80, c=40.20, γ=120.0	a=b=13.71 c=17.04 γ=120.0	a=b=12.97 c=7.91 γ=120.0
PACKING					
CELL VOLUME (Å³)	2,673	12,234	17,384	2,774	1,152
DENSITY g/cm³)	1.72 (Li^+)	1.69 (Cd^{2+})	1.73 (Cs^+)	1.68	1.69-1.77
GENERAL COMPOSITION	$(\alpha\text{-CD})_2 \cdot MeI_3 \cdot I_2 \cdot 8H_2O$	$(\alpha\text{-CD})_2 \cdot MeI_5 \cdot 27H_2O$	$(\alpha\text{-CD})_2 \cdot MeI_3 \cdot I_2 \cdot 12H_2O$	$(\alpha\text{-CD})_2 \cdot BaI_2 \cdot I_2 \cdot 12H_2O$	$(C_6H_{10}O_5)_6 \cdot I_2 = (\alpha\text{-CD}) \cdot I_2$

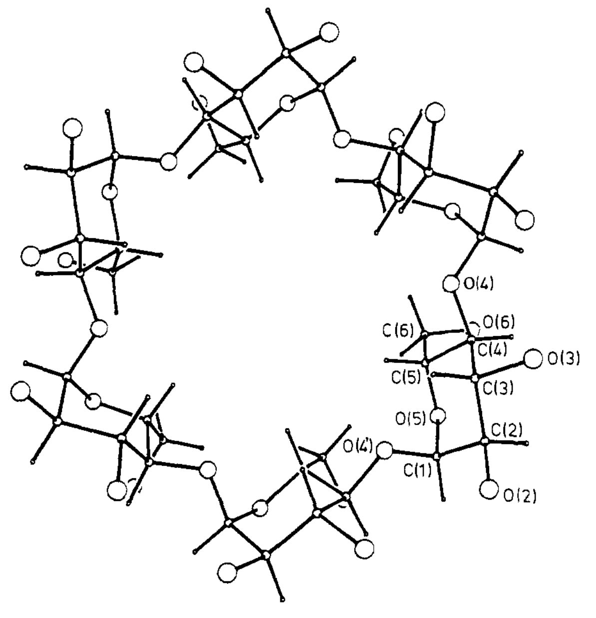


Figure 1. α-CD molecule drawn from the coordinates of $(\alpha\text{-CD})_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$ (molecule A). The wide O(2), O(3) side of the torus is toward the viewer, and, since the glucose mean planes are almost perpendicular to the paper plane, a view distance of 10 Å has been applied to reduce overlap. ○ = carbon; ◯ = oxygen; hydrogens (∘) have been included to show the hydrocarbon nature of the interior. In the text, atom names are followed by numbers 1–6 in order to indicate the glucose to which the respective atoms belong.

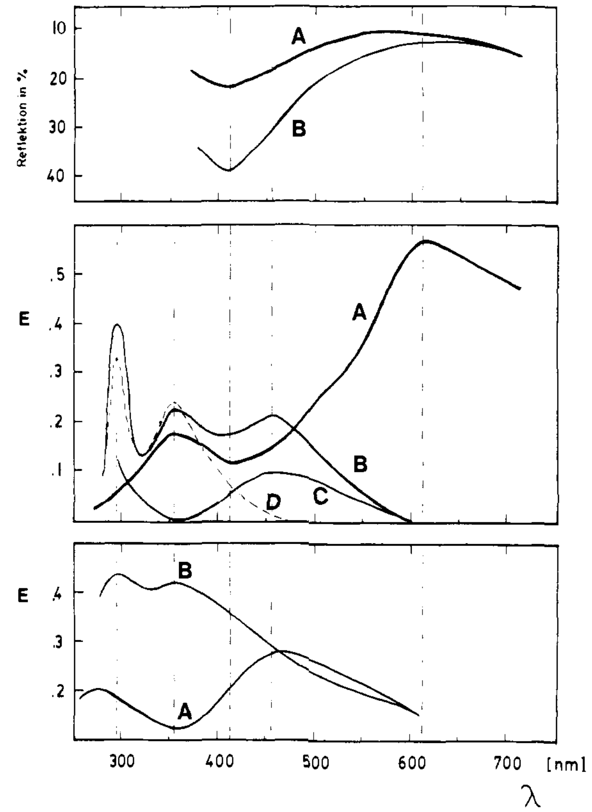


Figure 2. Comparison of spectra of systems containing I_2, I_3^-, and polyiodide, redrawn from ref 23, 76, and 77. Top: solid-state reflection spectra of polyiodide embedded into matrices of (A) α-CD and (B) cholanic acid. Middle: solution absorption spectra (A) of the blue amylose-iodine complex, (B) of I_2 and α-CD (without IO_3^-), (C) of I_2 and amylose (with IO_3^- to suppress I_3^- formation), (D) of I_3^- and α-CD. Bottom: solution absorption spectra of (A) I_2 and (B) I_3^-. Note that the absorption around 610 nm is only observed for polyiodide embedded into α-CD, cholanic acid, or amylose.

dimensional metallic properties of these complexes have been considered,[28] questioned,[29] and withdrawn.[30] Alternatively, charge-transfer interactions between the iodine chain and oxygen atoms of the glucose units within the amylose molecule were taken into consideration to explain the color effects,[31-33] similar to solutions of iodine in organic solvents.[35-37] Complex formation is weakly cooperative,[38,39] in contrast to the strong

Table II. Relationships between Cell Constants a, b, c (Å) of Amylose–Iodine and Cell Constants of α-CD–Polyiodide Complexes

amylose–iodine AI	α-CD–polyiodide form I	form II	form III	form IV
$a_{\mathrm{AI}} \sim 13$ Å	$a_{\mathrm{I}} \sim 2c_{\mathrm{AI}}$	$a_{\mathrm{II}} \sim b_{\mathrm{II}} \sim a_{\mathrm{AI}}$	$a_{\mathrm{III}} = b_{\mathrm{III}} \sim a_{\mathrm{AI}}$	$a_{\mathrm{IV}} \sim a_{\mathrm{AI}}\sqrt{2}$
$c_{\mathrm{AI}} \sim 7.9$ Å	$c_{\mathrm{I}} \sim 3c_{\mathrm{AI}}$	$c_{\mathrm{II}} \sim 2c_{\mathrm{AI}}$	$c_{\mathrm{III}} > 2c_{\mathrm{AI}}$	$c_{\mathrm{IV}} \sim 4c_{\mathrm{AI}}$

Other Complexes of Amylose[a]

complex	ref	cell const, Å	lattice type	comparison with α-CD–polyiodide
amylose–water	2	$a = 12.97$	pseudo-hexagonal	$a \sim a_{\mathrm{II}}, a_{\mathrm{III}}$
		$b = 22.46$	ortho-rhombic	
		$c = 7.91$		$c \sim 0.5c_{\mathrm{II,III}}$
amylose–Me$_2$SO	2	$a = b = 19.17$	pseudo-tetragonal	$a \sim a_{\mathrm{IV}}$
		$c = 24.39$	ortho-rhombic	$c \sim 0.75c_{\mathrm{IV}}$
amylose–1-butanol	9	$a = 13.7$	pseudo-hexagonal	$a \sim a_{\mathrm{II}}$
		$b = 24.8$	ortho-rhombic	$b \sim a_{\mathrm{III}}$
		$c = 8.05$		$c \sim 0.5c_{\mathrm{II,III}}$

[a] These occur in similar crystal systems as observed for α-CD-polyiodide.

cooperativity postulated earlier.[40] Mössbauer spectra of amylose–iodine have been discussed on the basis of I_3^- [41,42] and in recent studies including resonance Raman data[43-45] a polyiodide structure consisting of I_5^- and I_3^-, I_2 units has been favored[46] (Mizuno and Tanaka (Nagoya), private communication).

In a variety of crystalline complexes of polyiodide ions with other small organic molecules zigzag chains of alternating iodine molecules and triiodide ions perpendicular to each other have been found.[47,48] The diffuse scattering in the diffraction pattern of the trimesic acid-HI_5 complex was interpreted to indicate the presence of a linear array of pentaiodide ions.[49] The constituents of all these structures, I_2, I_3^-, and I_5^-, were similar to those observed in complexes with inorganic cations which served in quantum-chemical calculations to elucidate the nature of the interiodine bonds involved.[50,51]

The aim of the work presented here has been to investigate the arrangement of iodine atoms in a linear array, to visualize the possible interactions of iodine with glucose units in the surrounding α-CD molecules, and to arrive at a model for the "blue starch iodine complex". A preliminary account has been published[52] and some further information is contained in ref 53.

Experimental Section

A. Preparation of Crystalline Complexes of Polyiodide with α-CD and with β-CD. Crystals of cyclodextrin–polyiodide complexes were grown from aqueous, hot, saturated solutions of α-CD (Corn Products Development, Englewood Cliffs, N.J.) containing 5×10^{-2} M metal iodide and iodine (Merck, Darmstadt) in excess with I^-/I_2 ratios exceeding 1.3/1. For β-CD, the concentrations used were a factor of 10 lower because β-CD is less soluble in water than α-CD. The hot solutions were filtered and distributed to a number of small test tubes, which were stoppered and immersed in a Dewar container filled with hot water, in order to allow them to cool down slowly. In most of the batches single crystals up to 2 mm in size grew overnight, which were identified and classified by habitus and X-ray diffraction pattern. From microcrystalline samples, X-ray powder diagrams were taken and compared with powder diagrams obtained from identified and then ground single crystals. Combustion and oxidimetric titration analyses were carried out on all crystalline samples. Data are given in ref 54.

B. Crystal Data. Crystalline α-CD–polyiodide complexes exist in four different lattice types depending on the kind of metal ion (Table I). In the cases of K^+, NH_4^+, and Ba^{2+} ions, two crystal forms were observed simultaneously, coexisting for some time in the same batch until the metastable form I for K^+, NH_4^+, or III (for Ba^{2+}) transformed into the stable form IV. Three of the observed crystal forms have been described previously by French[11] and termed I, II, and III (Table I). Form IV has not been reported earlier. In contrast to α-CD, the larger β-CD develops only one crystal form with a variety of metal polyiodide solutions.[54] All the crystalline α-CD–polyiodide complexes appear essentially black with brown, blue, or green luster and their dichroism is well developed while the β-CD–polyiodide complexes are only light brown and weakly dichroic. With α-CD as matrix, Table II shows obvious relationships between the reported cell constants of amylose complexes. The periods along the polyiodide chains (c axes in forms II, III, and IV and a axis in form I, Table II) are multiples of the helix pitch height, 7.9 Å. A similar correspondence can be seen in the lattice parameters vertical to the iodine chains. In the β-CD complex ($a = 19.58$ Å, $b = 24.44$ Å, $c = 15.75$ Å, $\beta = 109.3°$), this correspondence is only evident in the polyiodide c axis repeat but the other lattice dimensions and the optical properties discriminate these complexes as models for the amylose–iodine adduct.

C. Continuous Diffraction. The resolution of the diffraction patterns varied from crystal to crystal. For crystal forms II and IV it was usually better than 1 Å and for forms I and III it could be worse than 3 Å. The patterns from crystals with low resolution often showed continuous, diffuse diffraction streaks perpendicular to the orientation of the polyiodide chains. The distance between the streaks corresponds to 3.1 Å, resembling the situation in amylose–iodine fibers[9] or polarization foils.[21] The iodine is disordered with respect to the matrix structure, the average interiodine separation being 3.1 Å.

D. Data Collection. From each different crystal form one X-ray data set was collected using an automated STOE four-circle diffractometer in the $\omega/2\theta$ scan mode. Stationary background measurements were made on both sides of each reflection. A semiempirical absorption correction[55] was performed and data reduction included background, Lorentz, and polarization corrections. Reflections with $F_{\mathrm{obsd}} < 3\sigma$ were treated as unobserved.

E. Preliminary Conductivity Measurements. In contrast to the amylose–iodine pellets investigated by Peticolas,[27] the α-CD–polyiodide single crystals allow measurement of the anisotropy of electric conductivity. Suitable large crystals of forms I and IV were covered with silver/oil paste on opposite faces. They were fixed on a printed copper board and attached at the upper side to a copper foil. The resistance of the assembly was measured at ambient temperature, 21 °C. With respect to the crystal dimensions specific conductivities of about 10^{-6} Ω cm^{-1} along the iodine chains and 10^{-10} Ω cm^{-1} perpendicular to these were obtained. The values are in agreement with data measured by Labes[56] but should be regarded as preliminary because no precautions were taken to prevent AgI formation.

Results and Discussion

I. Triclinic Lattice (Crystal Form II), $(\alpha\text{-CD})_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$. The triclinic lattice, space group $P1$, was only observed in the presence of the cations Li^+, Na^+, and Tl^+. The unit cell is almost hexagonal with cell constants $a \sim b \neq c$, $\alpha \sim \beta \sim 90°$, $\gamma \sim 120°$, Table I. From the crystal density measured by floating a crystal in cyclohexane/methyl iodide and from the results of combustion and oxidimetric titration analyses of crystalline samples it was concluded that the asymmetric unit (the unit cell) contains two α-CD molecules enclosing five iodine atoms plus one Li^+ cation and about eight water molecules. In the Patterson synthesis the iodine atoms generate an equidistant (~3.1 Å) and linear vector distribution along the crystallographic c axis, leading to a model with a centrosymmetric iodine chain; 100 phases supplied by this heavy-atom model were used as starting reflections in MULTAN[57] to produce phases for the 500 strongest E's. An E map based on these data revealed the nonequidistant, asymmetric structure of the iodine chain. Conventional heavy-atom methods including all the reflection data allowed then the location of the C,O atoms of the α-CD and of water molecules. Full-matrix least-squares refinement carried out in blocks of 200 variables and using weights $1/\sigma^2(F)$ started at $R = 38\%$. Very slow convergence was achieved to $R = 13\%$ after iodine atoms were allowed to vibrate anisotropically and corrections for anomalous dispersion were applied. After anisotropic temperature factors were introduced for C and O atoms and data were corrected for secondary extinction ($g = -3.7 \times 10^{-6}$),[58] the Li^+ cation could be identified as a difference Fourier peak with reasonable coordination geometry to surrounding hydroxyl groups. Hydrogens could not be located but the positions of C–H hydrogens were calculated and introduced. The final R factor is 8.7% for all the 5600 data. The crystal density calculated from the composition $(\alpha\text{-CD})_2\cdot LiI_3\cdot I_2\cdot 8H_2O$, 1.72 g/cm^3, agrees with the measured density, 1.72 (2) g/cm^3. Atomic coordinates are given in Table III; temperature factors, structure amplitudes, and some structural data have been deposited. Some selected structural details of the α-CD molecules are given in Tables IV–VII.

Description of the Structure. A. General. The crystal structure of the complex $(\alpha\text{-CD})_2\cdot LiI_5\cdot 8H_2O$ presented in Figure 3 consists of head-to-head arranged dimers of α-CD molecules which are shifted laterally to each other by 1.1 Å. These dimers are stacked along the c axis with the α-CD molecules inclined by about 7° relative to the stack axis. Further, the matrix is composed of the Li^+ cations and of the eight hydration water molecules, all hydrogen bonded together with the α-CD hydroxyl groups to form a complicated yet systematic network. This matrix is penetrated by "endless" parallel channels in which the polyiodide chains are embedded.

B. Conformation of the α-CD Molecules. Both α-CD molecules in this complex are crystallographically independent and occur in a conformation considered as "relaxed" relative to the "strained" α-CD in the α-CD hexahydrate complex.[16] In contrast to all cage-type α-CD inclusion complexes,[16-18] the α-CD hexagon in this complex is more regular when conformation angles ϕ,ψ and mean planes comprising the O(4) atoms or the O(2), O(3) atoms as well as interglucose hydrogen bonds are compared using fundamental statistical measures (Table VI).[53] The glucoses are in the C1 chair conformation and the torsion angles O(5)–C(5)–C(6)–O(6) are all (−)-gauche; i.e., the C(6)–O(6) bonds point "away" from the centers of the α-CD molecules. Adjacent glucoses in the macrocycles are in such close proximity that interglucose hydrogen bonds between O(2) and O(3) hydroxyl groups can form.[16,53] Distances between glucoses 5, 6, and 1 of molecule A are in the range 3.1–3.3 Å and slightly beyond the accepted O···O hydrogen bonding distance, but could represent weak hydrogen-bonding interactions (van der Waals O–H···O is 3.6 Å). The overall shape of the α-CD molecules can be described as conical, with the wide side of the cone formed by the O(2), O(3) hydroxyls. This implies that the van der Waals diameter of the α-CD cavity near the O(4) plane, 5.2 Å, opens to 7.6 Å in the O(2), O(3) plane. Therefore, the channel-like cavity of the α-CD stack bulges where O(2), O(3) sides of head-to-head arranged α-CD molecules meet.

C. The Polyiodide Chain. The polyiodide chain follows the inclination of the matrix molecules, thereby adopting a slightly zigzag arrangement, Figure 3. The iodine atom located in the relatively spacious bulge between the O(2), O(3) sides of opposing α-CD molecules is twofold disordered at 69 and 31% occupancy (I(3)A and I(3)B, hatched in Figure 3). The remaining four well-ordered iodine atoms located within the cavities of the two α-CD molecules form I_2 units each of which is in bonding distance to one of the two disordered iodine sites (Figure 6). The latter cannot be occupied simultaneously as they are at only 1.79 Å from each other (van der Waals distance = 4.3 Å) and therefore each α-CD dimer accommodates two units $I_3^-\cdot I_2$ or $I_2\cdot I_3^-$ in the statistical occupancy ratio

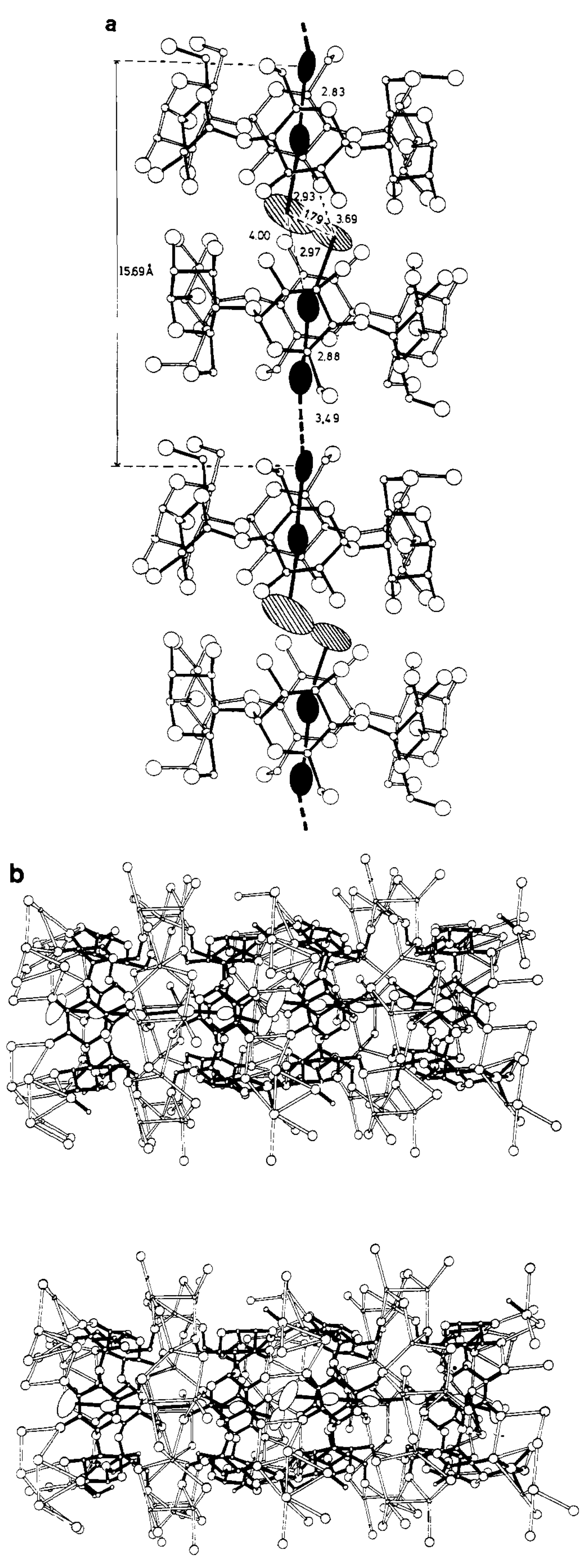


Figure 3. Pictorial description of the $(\alpha\text{-CD})_2\cdot LiI_3\cdot I_2\cdot 8H_2O$ complex. (a) A view of the polyiodide chain embedded into the α-CD matrix. Carbon and oxygen atoms are represented by small and large spheres; iodine atoms are shown as 50% probability ellipsoids.[78] The disordered (and partially occupied) iodine sites are indicated by hatching. (b) A stereodiagram illustrating hydrogen-bonding scheme and Li^+ coordination.[78]

Table III. Fractional Atomic Coordinates of $(\alpha\text{-CD})_2\cdot\text{LiI}_3\cdot\text{I}_2\cdot 8\text{H}_2\text{O}^a$

atom	*x*	*y*	*z*
I(1)	0.0247(2)	0.0224(2)	−0.6221(2)
I(2)	0.0034(2)	0.0150(2)	−0.4389(2)
I(3)A	−0.0307(12)	−0.0045(17)	−0.2513(7)
I(3)B	0.0679(15)	−0.0322(13)	−0.2036(7)
I(4)	0.0082(2)	−0.0255(2)	−0.0231(2)
I(5)	−0.0109(2)	−0.0250(2)	0.1572(2)
Li	−0.5169(38)	0.2373(38)	−0.1937(31)
(1)W	0.6636(14)	0.3207(15)	0.1791(14)
(2)W	−0.6719(11)	−0.3582(11)	0.1765(11)
(3)W	−0.3193(14)	0.3520(15)	0.3601(15)
(4)W	−0.6466(11)	−0.3169(12)	0.3562(11)
(5)W	−0.4860(10)	−0.5115(10)	0.2673(9)
(6)W	0.0076(10)	0.4724(10)	0.2747(9)
(7)W	−0.4654(10)	−0.0063(10)	0.2645(9)
(8)W	0.6457(9)	0.3195(10)	−0.2178(8)
O(2)1	0.3954(9)	−0.0952(9)	−0.1194(7)
O(3)1	0.1762(10)	−0.2816(10)	−0.1624(8)
O(4)1	0.0126(8)	−0.3196(8)	−0.0323(7)
O(5)1	0.2751(9)	−0.1738(9)	0.0869(8)
O(6)1	0.1189(10)	−0.3909(9)	0.1441(8)
O(2)2	0.4814(10)	0.3382(9)	−0.0906(7)
O(3)2	0.4669(10)	0.1312(9)	−0.1016(8)
O(4)2	0.3160(9)	−0.0186(8)	0.0197(7)
O(5)2	0.4080(8)	0.2540(9)	0.1283(7)
O(6)2	0.4578(13)	0.1298(12)	0.2256(9)
O(2)3	0.1253(8)	0.4410(10)	−0.1147(8)
O(3)3	0.3262(8)	0.4205(10)	−0.1010(7)
O(4)3	0.3095(8)	0.2825(8)	0.0256(7)
O(5)3	0.1245(8)	0.3856(9)	0.1075(7)
O(6)3	0.3026(10)	0.4365(10)	0.2217(8)
O(2)4	−0.3138(11)	0.0735(11)	−0.1769(9)
O(3)4	−0.0975(12)	0.2766(15)	−0.1491(12)
O(4)4	0.0072(8)	0.2795(8)	−0.0010(7)
O(5)4	−0.2897(9)	0.1115(9)	0.0546(8)
O(6)4	−0.1471(11)	0.3011(13)	0.1740(11)
O(2)5	−0.4408(10)	−0.3815(9)	−0.1949(8)
O(3)5	−0.4266(11)	−0.1667(10)	−0.1863(8)
O(4)5	−0.3014(8)	−0.0297(8)	−0.0424(7)
O(5)5	−0.4293(8)	−0.3109(8)	0.0337(7)
O(6)5	−0.4834(9)	−0.1588(10)	0.1330(8)
O(2)6	−0.0572(9)	−0.4514(9)	−0.1811(8)
O(3)6	−0.2671(10)	−0.4461(9)	−0.1945(7)
O(4)6	−0.3008(8)	−0.3310(8)	−0.0571(7)
O(5)6	−0.1410(9)	−0.4456(9)	0.0386(8)
O(6)6	−0.3480(10)	−0.4982(11)	0.1262(8)
C(1)1	0.3413(12)	−0.1052(12)	0.0282(11)
C(2)1	0.3204(14)	−0.1708(14)	−0.0595(13)
C(3)1	0.1979(12)	−0.2155(14)	−0.0819(11)
C(4)1	0.1260(11)	−0.2904(12)	−0.0132(10)
C(5)1	0.1532(12)	−0.2288(12)	0.0745(11)
C(6)1	0.0964(14)	−0.2981(14)	0.1482(12)
C(1)2	0.4154(12)	0.3117(12)	0.0563(10)
C(2)2	0.4706(13)	0.2784(13)	−0.0152(11)
C(3)2	0.4081(13)	0.1553(13)	−0.0391(10)
C(4)2	0.3950(12)	0.0944(12)	0.0430(10)
C(5)2	0.3438(14)	0.1335(14)	0.1143(12)
C(6)2	0.3460(16)	0.0881(14)	0.2028(12)
C(1)3	0.0801(12)	0.3905(12)	0.0338(11)
C(2)3	0.1766(13)	0.4402(14)	−0.0359(11)
C(3)3	0.2326(12)	0.3730(13)	−0.0472(10)
C(4)3	0.2729(13)	0.3619(14)	0.0390(11)
C(5)3	0.1773(14)	0.3185(14)	0.1053(11)
C(6)3	0.2229(15)	0.3271(16)	0.1979(12)
C(1)4	−0.3318(14)	0.0524(14)	−0.0224(13)
C(2)4	−0.2814(16)	0.1315(16)	−0.0976(15)
C(3)4	−0.1509(14)	0.1850(14)	−0.0900(12)
C(4)4	−0.1131(14)	0.2433(16)	0.0006(13)
C(5)4	−0.1695(13)	0.1575(14)	0.0635(11)
C(6)4	−0.1409(16)	0.2027(17)	0.1558(13)
C(1)5	−0.4188(13)	−0.3685(13)	−0.0403(11)
C(2)5	−0.4509(13)	−0.3256(14)	−0.1167(11)
C(3)5	−0.3792(14)	−0.2020(13)	−0.1207(11)
C(4)5	−0.3909(13)	−0.1467(13)	−0.0379(10)
C(5)5	−0.3587(13)	−0.1940(13)	0.0388(11)
C(6)5	−0.3746(15)	−0.1491(16)	0.1246(12)
C(1)6	−0.0690(13)	−0.4333(13)	−0.0291(11)
C(2)6	−0.1356(13)	−0.4693(11)	−0.1133(14)
C(3)6	−0.1921(13)	−0.4007(13)	−0.1233(11)
C(4)6	−0.2684(13)	−0.4142(12)	−0.0459(11)
C(5)6	−0.1946(13)	−0.3754(14)	0.0374(11)
C(6)6	−0.2590(14)	−0.3888(14)	0.1212(11)
O′(2)1	0.4347(9)	0.1071(9)	−0.2884(8)
O′(3)1	0.4142(11)	0.2977(11)	−0.2693(8)
O′(4)1	0.3095(8)	0.3326(8)	−0.4067(7)
O′(5)1	0.4268(9)	0.1632(9)	−0.5100(8)
O′(6)1	0.4907(12)	0.3656(11)	−0.5897(9)
O′(2)2	0.0809(8)	−0.3583(9)	−0.3457(8)
O′(3)2	0.2836(11)	−0.1440(10)	−0.3136(8)
O′(4)2	0.2999(7)	0.0128(8)	−0.4307(7)
O′(5)2	0.1588(9)	−0.2544(9)	−0.5577(7)
O′(6)2	0.3731(11)	−0.1076(10)	−0.6161(9)
O′(2)3	−0.3699(8)	−0.4415(9)	−0.3620(8)
O′(3)3	−0.1540(9)	−0.4252(10)	−0.3495(8)
O′(4)3	0.0020(8)	−0.2903(8)	−0.4717(7)
O(5)3	−0.2656(9)	−0.3932(9)	−0.5784(7)
O′(6)3	−0.1299(9)	−0.4486(10)	−0.6763(8)
O′(2)4	−0.4768(10)	−0.0803(10)	−0.3597(8)
O′(3)4	−0.4526(9)	−0.2775(9)	−0.3559(8)
O′(4)4	−0.3026(8)	−0.2841(8)	−0.4796(7)
O′(5)4	−0.3915(8)	−0.1070(8)	−0.5755(7)
O′(6)4	−0.4382(9)	−0.2985(9)	−0.6810(8)
O′(2)5	−0.1286(11)	0.3610(10)	−0.2928(9)
O′(3)5	−0.3250(9)	0.1525(10)	−0.3271(8)
O′(4)5	−0.2983(8)	0.0265(8)	−0.4692(7)
O′(5)5	−0.1139(8)	0.3144(8)	−0.5242(7)
O′(6)5	−0.2860(11)	0.1653(13)	−0.6492(10)
O′(2)6	0.3478(9)	0.4812(10)	−0.2683(8)
O′(3)6	0.1461(10)	0.4976(11)	−0.2832(8)
O′(4)6	0.0102(9)	0.3374(8)	−0.4168(7)
O′(5)6	0.3002(8)	0.4526(9)	−0.4978(7)
O′(6)6	0.1531(9)	0.4986(10)	−0.5954(8)
C′(1)1	0.4187(14)	0.1005(12)	−0.4457(12)
C′(2)1	0.4469(14)	0.1707(14)	−0.3592(12)
C′(3)1	0.3704(14)	0.2235(13)	−0.3471(11)
C′(4)1	0.3908(13)	0.2972(13)	−0.4237(11)
C′(5)1	0.3585(15)	0.2187(15)	−0.5057(12)
C′(6)1	0.3784(15)	0.2788(14)	−0.5860(12)
C′(1)2	0.0852(13)	−0.3173(13)	−0.4913(11)
C′(2)2	0.1570(12)	−0.2930(11)	−0.4111(9)
C′(3)2	0.2026(14)	−0.1707(14)	−0.3814(11)
C′(4)2	0.2773(12)	−0.0992(12)	−0.4582(10)
C′(5)2	0.2064(11)	−0.1372(11)	−0.5413(10)
C′(6)2	0.2847(15)	−0.0840(14)	−0.6143(11)
C′(1)3	−0.3311(12)	−0.3946(13)	−0.5074(11)
C′(2)3	−0.3036(12)	−0.4420(12)	−0.4342(11)
C′(3)3	−0.1763(12)	−0.3675(12)	−0.4129(11)
C′(4)3	−0.1125(12)	−0.3707(13)	−0.4927(11)
C′(5)3	−0.1448(12)	−0.3211(13)	−0.5672(10)
C′(6)3	−0.0958(14)	−0.3375(15)	−0.6571(12)
C′(1)4	−0.4046(18)	−0.0560(12)	−0.5033(10)
C′(2)4	−0.4635(13)	−0.1352(13)	−0.4349(11)
C′(3)4	−0.3954(12)	−0.1930(12)	−0.4162(10)
C′(4)4	−0.3831(13)	−0.2459(14)	−0.4968(11)
C′(5)4	−0.3275(13)	−0.1615(13)	−0.5692(11)
C′(6)4	−0.3254(14)	−0.2128(14)	−0.6553(11)
C′(1)5	−0.0735(13)	0.3621(13)	−0.4419(11)
C′(2)5	−0.1624(12)	0.3193(12)	−0.3776(10)
C′(3)5	−0.2259(12)	0.1904(12)	−0.3808(10)
C′(4)5	−0.2611(12)	0.1407(12)	−0.4699(10)
C′(5)5	−0.1608(12)	0.1952(12)	−0.5323(10)
C′(6)5	−0.1928(15)	0.1529(16)	−0.6275(13)
C′(1)6	0.3463(11)	0.4464(12)	−0.4211(10)
C′(2)6	0.3082(12)	0.4966(13)	−0.3492(10)
C′(3)6	0.1788(12)	0.4319(13)	−0.3383(11)
C′(4)6	0.1268(11)	0.4200(12)	−0.4270(10)
C′(5)6	0.1780(11)	0.3830(11)	−0.4997(10)
C′(6)6	0.1404(15)	0.3892(15)	−0.5872(12)

Table III *(Continued)*

$B(11)$ * 10000.	$B(22)$ * 10000.	$B(33)$ * 10000.	$B(12)$ * 10000.	$B(13)$ * 10000.	$B(23)$ * 10000.	$B(11)$ * 10000.	$B(22)$ * 10000.	$B(33)$ * 10000.	$B(12)$ * 10000.	$B(13)$ * 10000.	$B(23)$ * 10000.
91(2)	123(2)	141(2)	62(2)	1(1)	45(2)	621(32)	457(24)	118(8)	449(26)	147(14)	139(12)
108(2)	176(3)	129(2)	75(2)	5(2)	5(2)	128(2)	102(2)	132(2)	60(2)	17(2)	22(2)
822(34)	1469(50)	161(9)	722(36)	179(14)	59(17)	117(2)	101(2)	133(2)	59(2)	11(2)	33(2)

[a] Esd's in parentheses obtained from the least-squares correlation matrix. Occupational parameters are 1.0 except for I(3)A (0.69) and for I(3)B (0.31). Primed atoms belong to α-CD molecule B, unprimed atoms to molecule A. Anisotropic temperature factors for iodine atoms in the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Bond Distances and Angles in the Polyiodide Chains[c,d]

bond distances d, Å	$(\alpha\text{-CD})_2\cdot LiI_3\cdot I_2\cdot 8H_2O$				$(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$			
	d	$d-d_{cov}$[b]	p	d_{therm}	d	$d-d_{cov}$[b]	p	d_{therm}
I(1)-I(2)	2.882(5)	0.21	0.71	2.943	2.963(4)	0.29	0.66	3.018
I(2)-I(3)A	2.973(10)	0.30	0.65	3.269	3.144(9)	0.47	0.55	3.312
I(2)-I(3)B	4.005(15)	1.34	0.13	4.105				
I(3)A-I(3)B[a]	1.793(30)				1.282(19)			
I(3)A-I(4)	3.693(13)	1.02	0.28	3.912	3.168(9)	0.50	0.51	3.337
I(3)B-I(4)	2.926(13)	0.26	0.68	3.066				
I(4)-I(5)	2.832(5)	0.16	0.77	2.889	2.965(4)	0.30	0.66	3.018
I(5)-I(1)	3.486(5)	0.82	0.35	3.527	3.316(4)	0.65	0.43	3.354
mean (except a)	3.257	0.59	0.51		3.111	0.44	0.56	
range	1.08	1.18	0.64		0.35	0.36	0.23	
angles, deg								
I(1)-I(2)-I(3)A		176.8(5)				168.7(5)		
I(3)B-I(4)-I(5)		168.0(4)						
I(2)-I(3)A-I(4)						157.6(5)		

[a] Distances between disordered iodine positions. [b] d_{cov} is the covalent bond distance in I_2, 2.67 Å. [c] Tables IV–VII contain a selection of structural data for both α-CD–polyiodide complexes. For accurate bond distances and angles within the α-CD molecule, see ref 16. Individual bond distances and angles involving C and O are not given because the respective esd's (from the inverse refinement matrix) are, for the Li^+ complex, 0.025 Å for C–C, 0.022 Å for C–O, and 1.3° for C–C–O and C–O–C; for the Cd^{2+} complex, 0.029 Å for C–C, 0.025 Å for C–O, and 1.5° for C–C–O and C–O–C. [d] Esd's obtained from the least-squares correlation matrix are in parentheses. Bond orders p were taken from a diagram given by Wiebenga and Kracht.[51] Distances corrected for thermal motion d_{therm} were calculated using ref 81 and assuming the atoms to move independently. No further interpretations were based on these distances.

69/31. The interiodine distances in both I_3^- and I_2 units are lengthened beyond the ideal 2.9 Å in I_3^- and 2.67 Å in I_2, and similar to those observed in many inorganic polyiodide salts.[50,51] The lengthening of the covalent bonds is paralleled by a shortening of the nonbonded distances between adjacent I_2 units from the van der Waals 4.3 Å to only 3.7 Å, indicating charge-transfer interactions between I_3^- and I_2 units.

According to Slater and Mooney-Slater,[59,60] formation of I_3^- units $(I_1\text{-}I_2\text{-}I_3)^-$ can be visualized when distances d_1, $I_1\text{-}I_2$, and d_2, $I_2\text{-}I_3$, are plotted vs. distances D, $I_1\text{-}I_3$, Figure 4. Data for isolated, noninteracting I_3^- units lie on the curve in the range $D = 5.8\text{–}6.0$ Å. If data for the $(\alpha\text{-CD})_2\cdot LiI_3\cdot I_2\cdot 8H_2O$ complex are plotted, a bimodal distribution of points near $D = 5.8$ and around $D = 7.0$ is observed, corresponding to I_3^- units and to $I_2\cdot I_3^-$ interactions, respectively. The points entered in Figure 4 which do not lie close to the two branches of the curve indicate intrachain interactions (charge delocalization) between I_2 and I_3^- units.

Besides being asymmetric in their bond lengths, the I_3^- units in the α-CD complex are not strictly linear (168 and 177°). In general, strong deviations from centrosymmetry are explained by polarization effects exerted by the counterion, as in CsI_3.[50,51,59] The Li^+ cation in the present structure, however, is located outside the α-CD channels and more than 6 Å away from the I_3^- anions. Therefore, the influence of the electric field of Li^+ on the polyiodide chain can be neglected and we observe an unperturbed I_3^- moiety displaying an intrinsic asymmetry.[59]

Phenacetin·HI_5 is the only known structure where I_3^- and I_2 combine to form infinite chains of the type $(I_3^-\cdot I_2)_\infty$.[49] However, the polyiodide chain in this complex is zigzag with symmetrical I_3^- and I_2 units nearly perpendicular to each other.

Table V. Root Mean Square Displacement $\sqrt{\mu^2}$ (Å) of Iodine Atoms in Direction of Crystallographic Axes

atom	rmsd in direction					
	$(\alpha\text{-CD})_2\cdot LiI_3\cdot I_2\cdot 8H_2O$			$(\alpha\text{-CD})_2\cdot Cd_{0.5}I_5\cdot 27H_2O$		
	a	b	c	a	b	c
I(1)	0.22	0.27	0.43	0.22	0.27	0.33
I(2)	0.26	0.36	0.40	0.26	0.33	0.34
I(3)A	0.33	0.74	1.03	0.36	0.46	0.79
I(3)B	0.28	0.35	0.73			
I(4)	0.26	0.30	0.40	0.29	0.33	0.33
I(5)	0.25	0.28	0.41	0.22	0.25	0.33

D. Hydrogen Bonds between α-CD Molecules and Coordination of Li^+. In a "dimer" of head-to-head arranged α-CD molecules A and B, the O(2), O(3) sides are linked by direct hydrogen bonds O(2)···O′(3) and O′(2)···O(3) (Figure 5; unprimed and primed numbering refers to α-CD molecules A and B, respectively). There are also O(3)···O′(3) contacts between glucoses 3,6′, 4,5′, and 2,1′, and in these cases a clear distinction between the hydrogen bonds is not possible because we do not know the positions of the hydrogen atoms. The two glucoses 1 and 2′ form an O(2)···O(3) hydrogen bond; these four hydroxyl groups are further coordinated with the Li^+ cation in a square-pyramidal form, the apex of the pyramid being formed by water molecule W(8), Figure 3. Some of the O(2) and O(3) hydroxyl groups, especially those of molecule A, are also hydrogen bonded to O(2) and O(3) hydroxyl groups of α-CD molecules belonging to a neighboring stack.

Table VI. Torsion Angles ϕ and ψ to Describe Orientations of Glucoses about the Glucosidic Bonds, with Mean Values and Standard Deviations for Each Molecule[a]

				$(\alpha\text{-CD})_2\cdot\mathrm{LiI_3\cdot I_2\cdot 8H_2O}$		$(\alpha\text{-CD})_2\cdot\mathrm{Cd_{0.5}\cdot I_5\cdot 27H_2O}$	
ϕ	m	n		A	B	A	B
	1	2		172.2	165.6	166.8	160.3
	2	3		165.4	169.2	167.3	168.1
	3	4		166.4	165.0	162.5	159.6
	4	5		165.0	169.1		
	5	6		166.7	156.0		
	6	1		171.8	164.1		
	mean, deg			167.9	164.8	165.5	162.7
	standard deviation, deg			2.9	4.4	2.2	3.9
	range, deg			7.2	13.2	4.8	8.5
Ψ	m	n	l				
	1	2	3	−177.1	−166.8	−166.2	−160.8
	2	3	4	−169.2	−167.9	−175.6	−171.4
	3	4	5	−167.7	−168.8	−168.1	−166.4
	4	5	6	−171.3	−171.0		
	5	6	7	−165.5	−167.1		
	6	1	2	−169.1	−168.4		
	mean, deg			−170.0	−168.3	−170.0	−166.2
	standard deviation, deg			4.0	1.5	4.4	4.7
	range, deg			11.6	4.2	9.4	10.6

[a] ϕ, $O(4)_n\cdots C(1)_n-O(4)_m\cdots C(4)_m$; ψ, $C(1)_n-O(4)_m-C(4)_m\cdots O(4)_l$. Angles (deg) are given. Average esd's (from the inverse matrix): for the Li^+ complex, 1.7°; for the Cd^{2+} complex, 2.1°. Standard deviations obtained from $s = [1/(n-1)\sum_{j=1}^{n}(x-\bar{x})^2]^{1/2}$ with $\bar{x} = 1/n\sum_{j=1}^{n}x_j$.

Table VII. Data to Describe the Hexagon Formed by O(4) Atoms[a]

	$(\alpha\text{-CD})_2\cdot\mathrm{LiI_3\cdot I_2\cdot 8H_2O}$		$(\alpha\text{-CD})_2\cdot\mathrm{Cd_{0.5}I_5\cdot 27H_2O}$	
	A. Sides of Hexagon (Å)			
	A	B	A	B
O(4)1-O(4)2	4.23	4.36	4.34	4.21
O(4)2-O(4)3	4.21	4.20	4.24	4.35
O(4)3-O(4)4	4.19	4.24	4.22	4.32
O(4)4-O(4)5	4.31	4.28		
O(4)5-O(4)6	4.16	4.35		
O(4)6-O(4)1	4.29	4.17		
mean	4.23	4.27	4.27	4.27
standard deviation	0.05	0.07	0.05	0.07
range	0.15	0.19	0.12	0.14
	B. Angles in Hexagon (deg)			
O(4)1-O(4)2-O(4)3	117.7	122.5	122.7	119.5
O(4)2-O(4)3-O(4)4	120.6	117.9	116.1	121.2
O(4)3-O(4)4-O(4)5	120.9	120.9	121.1	119.2
O(4)4-O(4)5-O(4)6	119.8	119.9		
O(4)5-O(4)6-O(4)1	118.0	119.2		
O(4)6-O(4)1-O(4)2	122.8	119.1		
mean	120.0	119.9	120.0	120.0
standard deviation	1.7	1.5	2.8	0.9
range	5.1	4.6	6.6	2.0
	C. Diagonals of Hexagon (Å)			
O(4)1-O(4)4	8.31	8.54	8.45	8.68
O(4)2-O(4)5	8.53	8.42	8.34	8.64
O(4)3-O(4)6	8.53	8.65	8.84	8.50
mean	8.46	8.54	8.54	8.61
standard deviation	0.10	0.09	0.21	0.08
range	0.22	0.23	0.50	0.18
	D. Deviation of O(4) Atoms from Least-Squares O(4) Plane (Å)			
O(4)1	0.07	0.02	0.01	0.01
O(4)2	−0.08	0.01	0.05	−0.09
O(4)3	0.03	0.03	−0.07	0.08
O(4)4	0.01	−0.09		
O(4)5	−0.02	0.12		
O(4)6	−0.02	−0.08		
standard deviation	0.05	0.08	0.05	0.07
range	0.14	0.21	0.12	0.17

[a] Average esd's are 0.022 Å and 1.3° for Li^+ complex, and 0.025 Å and 1.5° for the Cd^{2+} complex.

The situation is quite different for the hydrogen bonding between O(6) hydroxyl groups of adjacent α-CD molecules within the same stack. Hydrogen bonding is not direct, O(6)···O′(6), but mediated by one or by two water molecules, O(6)···H_2O···O(6)′ and O(6)···H_2O···H_2O···O(6)′, in alternating sequence, Figures 3 and 5. The "two-water" hydrogen bonds involve water molecules W(1), W(2) and W(3), W(4) linking O(6) hydroxyls of vertically related glucoses, i.e., O′(6)6···W(1)···W(2)···O(6)3; O′(6)5···W(3)···W(4)···O(6)4. The four remaining O(6)···H_2O···H_2O···O′(6) links involve the same water molecules W(1), W(2), W(3), W(4) in translation-equivalent positions. For the "one-water" hydrogen bonds a cross relation is observed, W(5) bonding to O′(6)6 and O(6)4, W(6) to O′(6)4 and O(6)6, and W(7) to O′(6)5 and O(6)5; the other O(6) pairs are linked by translation-equivalent water molecules W(5), W(6), and W(7). The use of translation-equivalent water molecules in both "one-water" and "two-water" hydrogen bonds implies the above-mentioned two-dimensional extension of the hydrogen-bonding scheme (see stereoplot Figure 3b).

II. Tetragonal Lattice (Crystal Form IV), $(\alpha\text{-CD})_2\cdot\mathrm{Cd_{0.5}\cdot I_5\cdot 27H_2O}$. This lattice with space group $P4_22_12$ is formed when H_3O^+, K^+, NH_4^+, and cations of the second group of the periodic system or other divalent cations like Zn^{2+} or Cd^{2+} are present.

The Patterson function for the Cd^{2+} complex indicated equidistant peaks spaced at 3.1 Å along the 4_2 axis. In analogy with the previously described Li^+ complex and from symmetry requirements of space group $P4_22_12$ it was obvious that the α-CD molecules are arranged coaxially with the crystallographic c axis, that they have twofold (4_2) symmetry, and further that the asymmetric unit must contain two crystallographically independent half-α-CD molecules. Because heavy atoms were in special positions and therefore did not contribute in the phasing of general reflections, this crystal structure was solved by trial and error methods using one half-α-CD molecule placed in a translational position relative to the polyiodide chain as derived from the Li^+ complex. This α-CD half was rotated about the 4_2 axis in steps of 5°, structure factors and Fourier maps were computed, and the "correct" position of this fragment was indicated when the other half-α-CD in the asymmetric unit could be recognized.

At the beginning of the refinement, the R factor was 45%. Least-squares cycles with anisotropic temperature factors for iodine only and weights $1/\sigma^2(F)$ reduced the R factor to 22% and converged until it was found that the iodine atom near the O(2), O(3) sides of adjacent α-CD molecules is twofold disordered (50/50). Also, some of the hydration water molecules are disordered and most of them display high thermal motion. After correction of secondary extinction effects[58] ($g = -1.8 \times 10^{-8}$) and anisotropic refinement of all atoms, the R factor converged at 9.3%. The calculated density corresponding to $(\alpha\text{-CD})_2\cdot\mathrm{Cd_{0.5}\cdot I_5\cdot 27H_2O}$, 1.69 g/cm^3, agrees with the observed density, 1.70 g/cm^3. Atomic coordinates are given in Table VIII; temperature factors and structure amplitudes have been deposited together with bond angles, bond lengths, and torsion angles. For selected structural details, see Tables IV–VII.

Description of the Structure. A. General. As in the $(\alpha\text{-CD})_2\cdot\mathrm{LiI_5\cdot 8H_2O}$ complex, the α-CD molecules are again in a head-to-head arrangement forming dimers, but here the α-CD molecules are rotated relative to each other by 13° such that glucoses of adjacent α-CD molecules are staggered, al-

Table VIII. Fractional Atomic Coordinates of $(\alpha\text{-CD})_2{\cdot}Cd_{0.5}{\cdot}I_5{\cdot}27H_2O$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
I(1)	0.0000(0)	0.5000(0)	0.0876(1)	C(2)2	−0.2825(10)	0.5482(9)	0.2069(7)
I(2)	0.0000(0)	0.5000(0)	0.1835(1)	C(3)2	−0.2334(9)	0.4877(8)	0.2135(6)
I(3)	0.0283(6)	0.4847(12)	0.2832(3)	C(4)2	−0.2346(19)	0.4452(19)	0.1719(11)
I(4)	0.0000(0)	0.5000(0)	0.3840(1)	C(5)2	−0.2116(11)	0.4897(11)	0.1307(6)
I(5)	0.0000(0)	0.5000(0)	0.4801(1)	C(6)2	−0.2147(12)	0.4561(11)	0.0893(7)
Cd	0.5000(0)	−0.5000(0)	0.1248(3)	C(1)3	−0.0544(9)	0.7606(9)	0.1651(7)
W(1)	0.4655(0)	0.4405(0)	0.0624(11)	C(2)3	−0.1043(11)	0.7671(10)	0.2043(7)
W(2)	0.4643(29)	0.4336(27)	0.1828(14)	C(3)3	−0.1376(10)	0.7007(9)	0.2103(6)
W(3)	0.4027(21)	0.5699(23)	0.1173(15)	C(4)3	−0.1696(9)	0.6814(8)	0.1669(6)
W(4)	0.4556(19)	−0.3574(22)	0.0066(15)	C(5)3	−0.1183(9)	0.6748(9)	0.1327(7)
W(5)	0.3862(21)	−0.3998(22)	0.2086(14)	C(6)3	−0.1439(10)	0.6593(9)	0.0848(6)
W(6)	0.3438(18)	0.4205(18)	0.0429(16)	O′(2)1	0.0013(8)	0.8011(6)	0.3305(4)
Cd*	0.0000(14)	0.0000(14)	0.1169(9)	O′(3)1	0.1409(7)	0.7497(7)	0.3308(4)
W(1)*	0.0883(19)	0.0070(20)	0.1615(12)	O′(4)1	0.1573(7)	0.6502(6)	0.3930(3)
W(2)*	0.0840(21)	0.8888(21)	0.1108(18)	O′(5)1	0.0294(6)	0.7557(7)	0.4418(4)
W(3)*	0.0578(9)	0.0880(8)	0.0845(6)	O′(6)1	0.1452(7)	0.7445(7)	0.4955(5)
W(4)*	0.1196(10)	0.1848(10)	0.0362(9)	O′(2)2	−0.2519(7)	0.6434(7)	0.3292(4)
W(5)*	0.0950(14)	−0.0250(16)	0.0378(9)	O′(3)2	−0.1393(7)	0.7357(7)	0.3246(5)
W(6)*	0.1357(14)	−0.1352(15)	0.0000(9)	O′(4)2	−0.0447(6)	0.7118(6)	0.3901(4)
W(7)*	0.0957(20)	−0.1103(16)	0.2283(22)	O′(5)2	−0.2013(6)	0.6516(6)	0.4422(4)
W(8)*	0.2111(19)	−0.2568(25)	0.0396(14)	O′(6)2	−0.1274(8)	0.7460(8)	0.4942(6)
W(9)*	0.4018(18)	−0.4178(44)	0.2527(12)	O′(2)3	−0.2581(7)	0.3495(6)	0.3301(5)
O(2)1	−0.2099(6)	0.3099(6)	0.2453(4)	O′(3)3	−0.2757(6)	0.4950(8)	0.3286(4)
O(3)1	−0.0782(6)	0.2458(7)	0.2453(4)	O′(4)3	−0.2031(6)	0.5616(5)	0.3956(4)
O(4)1	0.0065(6)	0.2881(5)	0.1776(4)	O′(5)3	−0.2320(7)	0.3983(6)	0.4425(4)
O(5)1	−0.1631(6)	0.3100(6)	0.1306(4)	O′(6)3	−0.2716(6)	0.5021(8)	0.4980(5)
O(6)1	−0.0799(7)	0.2393(8)	0.0755(5)	C′(1)1	−0.0097(11)	0.7717(9)	0.4070(6)
O(2)2	−0.2787(7)	0.5909(6)	0.2443(4)	C′(2)1	0.0429(11)	0.7893(11)	0.3683(7)
O(3)2	−0.2618(6)	0.4445(6)	0.2459(4)	C′(3)1	0.0892(9)	0.7282(10)	0.3617(7)
O(4)2	−0.1821(6)	0.3973(6)	0.1788(4)	C′(4)1	0.1242(9)	0.7107(10)	0.4030(6)
O(5)2	−0.2585(7)	0.5480(6)	0.1287(4)	C′(5)1	0.0703(9)	0.6981(10)	0.4418(5)
O(6)2	−0.2789(9)	0.4280(9)	0.0820(5)	C′(6)1	0.1043(10)	0.6880(10)	0.4822(6)
O(2)3	−0.0676(6)	0.7845(7)	0.2432(4)	C′(1)2	−0.2300(10)	0.6236(10)	0.4043(6)
O(3)3	−0.1904(6)	0.7088(6)	0.2421(4)	C′(2)2	−0.2220(9)	0.6702(10)	0.3661(6)
O(4)3	−0.1920(6)	0.6099(6)	0.1751(4)	C′(3)2	−0.1450(11)	0.6809(10)	0.3590(6)
O(5)3	−0.0879(6)	0.7406(6)	0.1281(4)	C′(4)2	−0.1124(10)	0.7128(10)	0.3995(7)
O(6)3	−0.1918(7)	0.7058(7)	0.0711(4)	C′(5)2	−0.1269(9)	0.6588(9)	0.4380(6)
C(1)1	−0.1967(9)	0.3305(9)	0.1679(6)	C′(6)2	−0.1010(12)	0.6828(12)	0.4800(7)
C(2)1	−0.1743(8)	0.2871(8)	0.2065(6)	C′(1)3	−0.2281(9)	0.3577(9)	0.4075(7)
C(3)1	−0.1003(8)	0.2972(9)	0.2142(6)	C′(2)3	−0.2643(10)	0.3896(10)	0.3679(7)
C(4)1	−0.0669(9)	0.2717(9)	0.1685(6)	C′(3)3	−0.2347(10)	0.4598(9)	0.3597(6)
C(5)1	−0.0899(10)	0.3182(10)	0.1358(7)	C′(4)3	−0.2397(8)	0.5014(10)	0.4028(5)
C(6)1	−0.0649(10)	0.3028(10)	0.0872(6)	C′(5)3	−0.2009(11)	0.4625(9)	0.4386(6)
C(1)2	−0.2588(9)	0.5913(9)	0.1684(6)	C′(6)3	−0.2062(11)	0.4978(12)	0.4828(6)

B(11) * 10000.	*B*(22) * 10000.	*B*(33) * 10000.	*B*(12) * 10000.	*B*(13) * 10000.	*B*(23) * 10000.	*B*(11) * 10000.	*B*(22) * 10000.	*B*(33) * 10000.	*B*(12) * 10000.	*B*(13) * 10000.	*B*(23) * 10000.
38(1)	27(1)	24(0)	−2(1)	0(0)	0(0)	47(1)	53(1)	24(1)	4(1)	0(0)	0(0)
51(1)	43(1)	23(0)	−10(1)	0(0)	0(0)	25(1)	31(1)	24(0)	1(1)	0(0)	0(0)
139(9)	283(13)	28(1)	77(9)	7(2)	8(4)						

[a] Esd's given in parentheses. Atomic sites are fully occupied except for I(3), 0.5; W(5), 0.5; W(6)*, 0.5; W(9)*, 0.89; Cd, 0.18; Cd*, 0.07. Primed atoms refer to α-CD molecule B, unprimed atoms to molecule A. Anisotropic temperature factors for iodine atoms in the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

lowing an even shorter *c* axis repeat than observed for the Li^+ complex. The α-CD stacks and the "endless" channels containing the polyiodide are strictly linear owing to the operation of the 4_2 symmetry axis (Figure 6). Compared with the hexagonally dense packed stacks in the triclinic Li^+ complex, the stacks in this tetragonal complex are arranged in a square array (see "packing" in Table I) leaving large spaces between them. These are filled by 27 hydration water molecules per asymmetric unit. The Cd^{2+} cations occupy special positions on twofold axes.

B. Conformation of the α-CD Molecules. In general, the geometry of the α-CD molecules is similar to that observed for the Li^+ complex but conformational angles describing the geometry of the α-CD macrocycle are even more narrowly distributed about their mean, Table VII.[19]

C. The Polyiodide Chain. As with the triclinic Li^+ complex, five iodine atoms are accommodated within one α-CD dimer. Four of these iodine atoms are located on the 4_2 axis and the one near the O(2),O(3) sides of the dimer is disordered (50/50). The disordered sites are only 0.9 Å away from this axis and therefore cannot be occupied simultaneously. The repeat distance along the chain, 15.44 Å, is the shortest of all the structures listed in Table I and the I···I distances indicate that the iodine atoms are spaced even more equidistantly than in the Li^+ complex.

In contrast to the Li^+ complex, where I_3^- and I_2 units in the polyiodide chain are clearly indicated, the situation in the Cd^{2+} complex allows two interpretations. First, as in the Li^+ structure, one disordered iodine anion could be linked covalently to an I_2 unit to form a slightly bent (175°) I_3^- anion and the

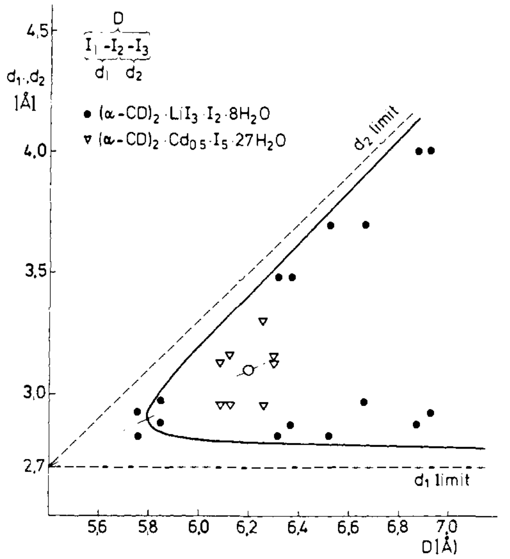


Figure 4. Diagram[59,60] correlating interatomic distances d_1 (I_1-I_2) and d_2 (I_2-I_3) with the overall distance D (I_1-I_3) in triiodides I_1-I_2-I_3^-. Data for isolated triiodides are located *on* the curve while data points for triiodides interacting with adjacent iodine units lie *off* the curves. The circle (○) marks the 3.1-Å interiodine distance postulated for equidistant polyiodide in the α-CD matrix.[22] Dots (●) represent data for $(\alpha\text{-CD})_2\cdot LiI_3\cdot I_2\cdot 8H_2O$, with the I_3^- units at D = 5.76 and 5.85 Å, while combination of intra- and intermolecular distances is at $D \sim 6.3$ Å. Triangles (▽) are for $(\alpha\text{-CD})_2\cdot Cd_{0.5}\cdot I_5\cdot 27H_2O$.

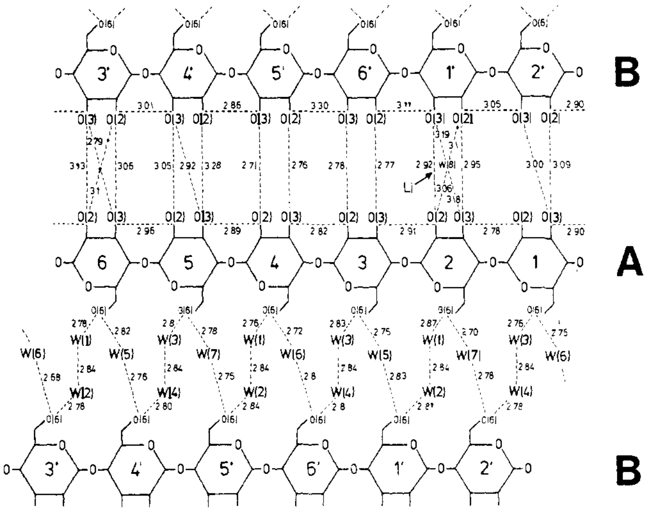


Figure 5. Hydrogen-bonding scheme in $(\alpha\text{-CD})_2\cdot LiI_3\cdot I_2\cdot 8H_2O$. Distances < 3.1 Å are indicated; average esd's are 0.02 Å. Glucoses are numbered according to Table III; primed and unprimed numbers belong to α-CD molecules B and A, respectively. For a description of this scheme, see text. Further intermolecular hydrogen bonding contacts (Å) from α-CD molecules A and B to translationally equivalent α-CD and to water molecules are for molecule A O(2)1-O′(3)5, 3.1; O(2)2-O′(3)6, 2.82; O(3)2-O′(2)4, 3.04; O(2)3-O(3)6, 3.05; O(2)4-O′(3)2, 3.04; O(2)5-W(8), 3.08; O(2)5-O(2)6, 2.78; O(3)5-O′(2)1, 3.1; O(2)6-O(2)5, 2.81; O(3)6-O′(2)2, 2.82. For molecule B: O′(3)1-O(2)6, 2.91; O′(2)5-O′(2)6, 2.81; O′(2)6-O′(2)5, 2.78; O′(3)6-W(8), 2.85. The α-CD molecule A is thus more involved in hydrogen bonding than molecule B.

remaining two iodine atoms in the repeating unit could represent I_2. Second, and this is the case we prefer, a nearly linear I_5^- unit can be visualized with the disordered iodine as central atom. In the complex $N(CH_3)_4\cdot I_5$,[61] a V-shaped I_5^- anion forms with an angle of 95° at the central atom and with distances of 3.17 Å from the central atom and 2.81 Å from the terminal iodine atoms. Comparable distances of 3.17 and 3.13 Å are observed from the disordered, central iodine I(3) in the Cd^{2+} complex while the distances to the terminal atoms, 2.96 and 2.95 Å, are significantly longer than in the V-shaped I_5^-. The very short 3.31-Å separation between the I_5^- units which is not found in the latter allows extensive charge delocalization leading to a widening of the I-I distance from 2.67 Å (in I_2) to 2.95 and 2.96 Å, respectively.

The interpretation as I_5^- is in agreement with the entries in Figure 4. For a hypothetical I_3^- unit in the Cd^{2+}-polyiodide chain (with D at 2.95 + 3.13 = 6.08 Å and 2.96 + 3.17 = 6.13 Å) we do not find the d_1 and d_2 values located on the curve which has been established for many I_3^- units. Rather they are close to the hypothetical equidistance point $d_1 = d_2 = 3.1$ Å,[22] indicating strong interactions between iodine atoms along the polyiodide chain.

D. Hydrogen Bonds between α-CD Molecules and Coordination of Cd^{2+}. The 13° rotation of opposing α-CD molecules A and B allows not only the hydroxyl groups to interlock such that hydrogen bonds O(2)···O′(2) and O(3)···O′(3) form (Figures 6 and 7), but also at the O(6) side, opposing α-CD molecules to give direct O(6)···O′(6) hydrogen bonds. Hydrogen bonds continue from the O(6) side to water molecules W(2)*, W(3), W(4), W(5)*, W(6), and W(8)* and from the O(2), O(3) side to W(1), W(2), W(5), W(7), and W(9); see legend to Figure 7. In contrast to the Li^+ complex, the Cd^{2+} cations are not in direct contact with the α-CD hydroxyls but are surrounded by hydration shells.

The two cation sites Cd and Cd* are located on the twofold axes parallel to c and passing through $x = y = 0.0$ and $x = y = 1/2$ with z values near $1/8$, $3/8$, $5/8$, $7/8$, etc., and related in pairs by diads in the a, b plane at $z = 0$. The site Cd is octahedrally coordinated by water molecules W(1), W(2), and W(3) while site Cd* is surrounded irregularly by six waters W(1)*, W(2)*, and W(3)*. Both sets of water molecules are completed by the operations of the diads.

It is remarkable that the hydration shells are formed by fully occupied water sites while the occupation of the Cd sites is only fractional. Obviously, the cages formed by the coordinated water molecules are stable even if the relatively small cations are statistically absent. Refinement yielded site occupancies 0.073 for Cd and 0.052 for Cd*. Since the crystallographic multiplicity is two for each Cd side, there is (0.073 + 0.052) × 2 = 0.25 Cd^{2+} cation per asymmetric unit or 0.5 Cd^{2+} per α-CD dimer, allowing one negative charge per five iodine atoms.

Because the tetragonal complex forms in the presence of a broad variety of cations (Table I) we infer that the interstices between the α-CD stacks are wide enough to accommodate different cations and even different types of coordination shells. Therefore this arrangement represents the more general structural type for α-CD-polyiodide adducts while the triclinic complex is restricted to cations Li^+, Na^+, and Tl^+, which are able to interact with α-CD hydroxyl groups.

III. Pseudohexagonal, Orthorhombic Lattice (Crystal Form I), $(\alpha\text{-CD})_2\cdot MeI_3\cdot I_2\cdot 12H_2O$. This complex is formed with group 1 cations K^+, NH_4^+, Rb^+, and Cs^+ and has the general composition $(\alpha\text{-CD})_2\cdot MeI_3\cdot I_2\cdot 12H_2O$. Crystals grown with K^+ and NH_4^+ are metastable and convert within a few days into the tetragonal form.

The crystals were described as hexagonal[11,54] but it is more likely that they exist in the orthorhombic space group $C222$ with $a' = a_{\text{hex}}$, $b' = b_{\text{hex}}\sqrt{3}$, $c' = c_{\text{hex}}$, Table I. R-factor calculations between diffractometer-measured, symmetry-equivalent reflections showed that Laue group mmm is much better satisfied than $\bar{3}$, $3m1$, $6/m$, or $6/mmm$. Further, the scintillation counter detected high-order reflections $00l$ with $l = 3n$ which appeared absent on photographs.

The Patterson function applied to the data in space group $C222$ indicates iodine chains arranged along the a axis and again in $z = 1/3$ parallel to the b_{hex} axis according to the pseudo-6_2 operation ("packing" in Table I). The lengths of the

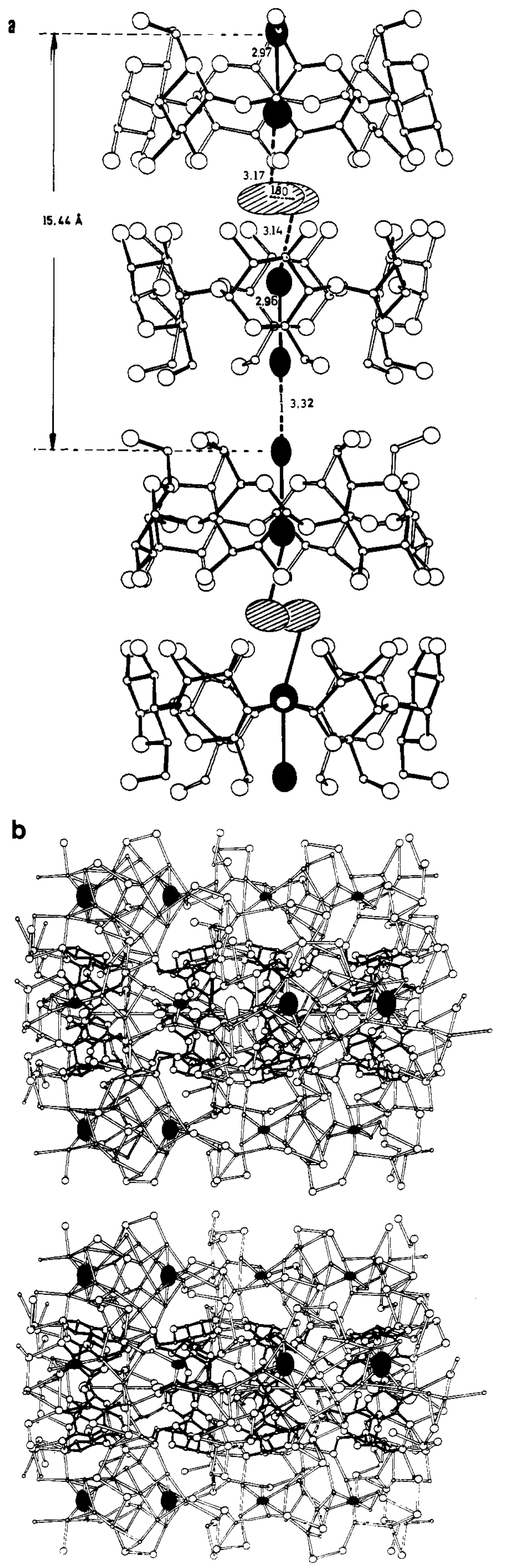


Figure 6. Description of $(\alpha\text{-CD})_2{\cdot}Cd_{0.5}{\cdot}I_5{\cdot}27H_2O$. (a) A view of the polyiodide chain embedded into the α-CD matrix. Disordered (and partially occupied) iodine sites are indicated by hatching. (b) Stereodiagram; iodine and Cd atoms indicated by filled-in probability ellipsoids.[78]

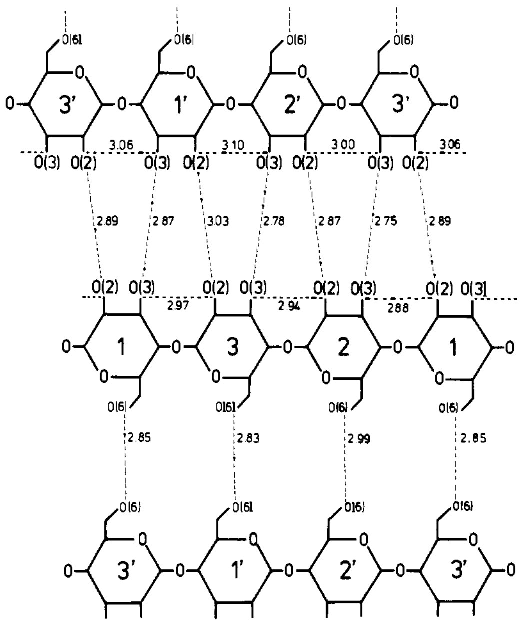


Figure 7. Hydrogen-bonding scheme in $(\alpha\text{-CD})_2{\cdot}Cd_{0.5}{\cdot}I_5{\cdot}27H_2O$. Distances < 3.1 Å indicated; average esd's are 0.02 Å. Note that glucoses of α-CD molecules A and B (primed numbers) are staggered relative to each other in this case but eclipsed in the Li^+ complex, Figure 3. Further intermolecular hydrogen bonds (Å) are for α-CD molecule A O(3)1-W(7)*, 2.77; O(2)2-W(9)*, 2.73; O(2)2-W(5), 2.89; O(2)2-W(7)*, 2.67; O(3)2-W(5), 2.87; O(3)2-W(9)*, 2.85; O(6)1-W(2)*, 2.78; O(6)1-W(8)*, 2.86; O(6)3-W(4)*, 2.82; O(6)2-W(3), 2.70. For molecule B: O(2)1-W(2), 2.76; O(3)3-W(1), 2.73; O(6)1-W(6), 2.79; O(6)2-W(8)*, 2.79; O(6)2-W(4), 2.77; O(6)3-W(4)*, 2.83; O(6)3-W(5)*, 2.91.

axes $a_{\text{hex}} = b_{\text{hex}} = 15.8$ Å suggest that similar α-CD dimers exist as in the two structures described above. The dimers form again endless stacks, but these are oriented in sheets parallel to the *a*, *b* plane and adjacent sheets are rotated by 120° relative to each other through the operation of the pseudo-6_2 axis. The dichroism of the crystals is not well developed because the polyiodide chains occur in three orientations. Another peculiar feature of this pseudohexagonal complex is that the counterion Cs^+ (or else) seems to be in direct contact with the iodine chain. This is indicated by a prominent Patterson peak found at the $Cs^+{\cdots}I$ distance (1.69 + 2.15 = 3.84 Å) from the origin in *w* direction and many other peaks show up on the plane $w = 3.8$ Å. The spatial requirements of such ion pairs allow that they are located within the channel near the O(2), O(3) bulges.

It is well known that simple polyiodide salts are preferentially formed with the larger cations Cs^+ or NR_4^+ rather than with Li^+, Na^+, and NH_4^+.[50] This tendency for direct cation-polyiodide contact might be a prerequisite for the formation of the pseudohexagonal lattice.

IV. Hexagonal Lattice, Form III, $(\alpha\text{-CD})_2{\cdot}BaI_2{\cdot}I_2{\cdot}12H_2O$. Crystallization of α-CD with Ba^{2+}-polyiodide usually yields the tetragonal form but in some cases tiny hexagonal or trigonal columns with cell constants $a = b = 13.7$, $c = 17.0$ Å, and possible space group *P*622 were observed (Table I). The composition of the crystals is $(\alpha\text{-CD})_2{\cdot}BaI_2{\cdot}I_2{\cdot}12H_2O$.[54]

The unit cell dimensions and the minimum set of symmetry operations indicate that again two α-CD molecules are positioned head-to-head. The relatively long period of 17.04 Å could be explained by rotations of C(6)-O(6) bonds toward the center of the inclusion channels with (+)-gauche torsion angles O(5)-C(5)-C(6)-O(6), as observed in the potassium acetate complex[59] with $2c = 16.60$ Å. This arrangement would allow interactions between O(6) hydroxyl groups and polar inclusion guests like water molecules, iodine atoms, or Ba^{2+} cations.

The Patterson function contains all the heavy-atom vectors lying on the *w* axis. The vector distribution along this axis is nearly continuous, indicating considerable disorder of the heavy atoms. Since no discrete peaks were found off the *w* axis, the Ba^{2+} cations might be incorporated into the iodine arrangement.

V. The Monoclinic β-CD–Polyiodide Complex. β-CD consists of seven glucose units and cocrystallizes with many different polyiodide salts in only one tan-brown needle form exhibiting weak dichroism. The crystals have unit cell constants a = 19.58 Å, b = 24.44 Å, c = 15.75 Å, β = 109.3° and belong to space group $C2$ or to $P2_1$. They are isomorphous with the β-CD–diiodobenzoic acid complex solved recently.[63] The structure of the β-CD·NaI_3·$8H_2O$ complex has been determined in detail and will be reported elsewhere.[64] The polyiodide chain consists of (disordered) I_3^- and I_2 units and is not linear but zigzag owing to the larger diameter of the channels (7 Å) in the β-CD matrix. However, as in the α-CD–polyiodide complexes, the β-CD molecules are packed as dimers in a head-to-head arrangement.

Conclusions

A. Intermolecular Forces between the Iodine Chain and the α-CD Matrix Indicate Specificity. Correlations with Amylose. In α-CD inclusion complexes thus far investigated, no host–guest specificity was recognized and the only requirement for inclusion seemed to be the mutual geometrical fit of the two partners.[12-16] We observe, however, that in both α-CD–polyiodide complexes the well-ordered iodine atoms are located near planes defined by the O(4) and C(6) atoms of the surrounding α-CD molecules. Since similar positions are also occupied by I_2 in the α-CD cavity in the cage-type complex α-CD·I_2·$4H_2O$,[18] it appears that specific iodine···α-CD interactions come into play.

It is certain that this interaction cannot be attributed to charge transfer, dipole–dipole, or van der Waals forces between iodine and oxygen as postulated for the "blue amylose–iodine compound".[1,6] The reason is that the shortest I···O separations, I···O(4), from 4.1 to 4.4 Å, are 0.6 Å longer compared to the expected van der Waals distance, 3.55 Å, and even 1.4 Å longer than observed in the charge-transfer complex dioxane·I_2.[37] However, contacts between the easily polarizable iodine and the C(3)–H, C(5)–H methine groups flanking the O(4) oxygens in a square array, 3.24–4.03 Å, are not shorter than the van der Waals distance H···I, 3.3 Å, and thus H···I dispersion forces as in solutions of iodine in hydrocarbons are the main contributors to the stabilization of the α-CD–polyiodide complexes.

The postulated interactions between amylose hydroxyls and iodine,[33,34] already a matter of discussion,[65] can also be ruled out for the α-CD–polyiodide complexes. We find that the O–H···I distances are comparable to or longer than the theoretical, nonbonded O–H···I separation of 4.3 Å, the shortest distances in the Li^+ complex corresponding to this value while all the other distances in the Li^+ and Cd^{2+} complexes exceed 5 Å. In general, hydrogen bond type interactions I···H–O appear improbable because the difference in electronegativity of the I and H atoms, $\Delta EN = 0.4$, is considerably less than, for instance, the difference between H and O in O–H···O bonds, $\Delta EN = 1.4$. It should be noted that this discussion discriminates sharply between these complexes and adducts formed by metal ions (M^+) and crown ethers or ionophore antibiotics where ion–dipole forces M^+···O play the paramount role and other contributions can be neglected.

Comparing the α-CD channel type crystal structures, we find two principal kinds of stacks. In the case of polyiodide, the described head-to-head dimers are produced with O(6) hydroxyls pointing away from the channel axis (O(5)–C(5)–C(6)–O(6) at (−)-gauche). If, however, potassium acetate,[62] methyl orange, or benzenesulfonate[66,67] are included, channel-type structures are formed with α-CD molecules stacked in head-to-tail mode and O(6) hydroxyls turned more toward the channel (O(5)–C(5)–C(6)–O(6) at (+)-gauche) and hydrogen bonded with the guest molecules and with O(2), O(3) hydroxyls of contiguous α-CD.

This finding suggests that the preferred head-to-head α-CD dimers containing I_2·I_3^- or I_5^- units are formed even in solution. These dimers crystallize into the crystal types entered in Table I, depending on the counterion. The association into dimers is only observed in the presence of I_3^- because with I_2 alone α-CD crystallizes in the cage-type structure consisting of individual α-CD·I_2 units.[18]

Why do α-CD and starch form complexes with polyiodides and with small organic molecules; i.e., what is the driving force for the inclusion process? As discussed in ref 14, hydrophobic, dipole–dipole, and dispersion interactions between guest and α-CD molecule have been proposed as well as release of strain energy and formation of hydrogen bonds within the α-CD itself and expulsion of "activated water" from the α-CD cavity. These driving forces are all intrinsically related with the annular structure of α-CD and we can assume that they also apply to amylose–guest adduct formation, the main feature being the favorable geometry of one turn of the amylose helix.[38]

B. Building Principles of Polyiodide Chains. Earlier investigators had proposed that the polyiodide chains in amylose[6,9] and in α-CD channels of the hexagonal crystal form III consist of linearly arranged, equidistantly spaced iodine atoms at 3.1-Å separation.[22] Since this value was obtained mainly from distances between diffuse streaks on X-ray photographs, it is obvious that disorder phenomena had been reported. In the (α-CD)$_2$·LiI_3·I_2·$8H_2O$ complex, however, the interiodine distances vary from 4.1 to 2.9 Å (average 3.17 Å), while in the Cd^{2+} complex these distances are more confined, between 2.95 and 3.31 Å (average 3.104 Å). Apparently, these average values are very close to the 3.1-Å separation and we conclude that in some of the previously published structures involving amylose and α-CD matrices linear, equidistant polyiodide chains did not in fact exist.

As discussed by Wiebenga and co-workers,[50,51] the interiodine bonds are brought about by interactions involving, in the case of 180° angles, $5p_x$ orbitals, while $5p_y$ and $5p_z$ are used if zigzag polyiodides are formed. The other two orbitals not involved in p_x bonding can contribute to π_y and π_z interactions, while the 5s orbital is believed not to be promoted to participate in bonding (for possible sp^3d hybridization, see ref 50 and 51). The interiodine bonds in I_3^- units are generally unequal and I_3^- adopts an intrinsically bent shape[59] which is also found in the Li^+ and Cd^{2+} polyiodides. We must note that in the latter structures the influence of the electric field of the cation is negligible and that I_3^-, I_2, and I_5^- units unperturbed by external fields are observed.

According to Wiebenga and Kracht,[51] interiodine separations can be correlated with bond orders. A comparison for the two polyiodide chains in the Li^+ and Cd^{2+} complexes is described in Table IV. While bond orders in the Li^+-polyiodide range from 0.35 to 0.77, they are more narrowly distributed in the Cd^{2+}-polyiodide, 0.43–0.67. In both cases, the bond orders indicate that the iodine atoms within the units (I_2·I_3^- and I_5^-) interact strongly and that the interaction is also considerable between the units.

In an unperturbed system of noninteracting, linearly arranged I_2 and I_3^- units, the repeat distance would be 2.67 (I_2) + 4.3 (van der Waals) + 5.8 (I_3^-) + 4.3 Å (van der Waals) = 17.07 Å. In agreement with the α-CD polyiodides, the "classical" polyiodide structures (Table IX), which all contain I_2, I_3^-, or I_5^- units, display repeat distances in the range 15.23–15.69 Å (except benzamide·HI_3). This shortening of the "unperturbed" 17.07-Å distance by almost 2 Å indicates that, even between polyiodides consisting of only a few units, a certain degree of polymerization exists. In this connection it is of interest that the 15.5-Å interiodine repeat distance for an $I_2 \cdot I_3^-$ or I_5^- building block corresponds to the repeat distance of one α-CD dimer or of two turns of the amylose helix. Thus the polyiodide chains are preformed fo fit into the cavity offered by the α-CD or V_6 amylose template.

C. Stoichiometry of Iodine/Iodide in the α-CD Channels and in the Amylose Helix. Density measurements of crystalline material allow us, in conjunction with unit cell constants, to deduce the number of atoms within the cell. Table I shows that densities for polyiodide complexes of α-CD and of amylose are comparable, suggesting that the I/glucose ratios are similar. In solution, titration experiments established an I/glucose ratio for amylose saturated with iodine of $\frac{1}{3}$[68] and in the crystalline Li^+ and Cd^{2+} complexes we observe I/glucose ratios of $\frac{5}{12}$ (=1.25/3). These data are in good agreement if we consider that the amylose helix, in solution, will have bends and kinks and therefore will display a slightly lower I content than the ideal α-CD matrices. The ratio I^-/I_2 or the factor b in $I_2 \cdot I_b^-$ [38,39] is ½ in the α-CD polyiodide crystals investigated. In amylose–polyiodide, this ratio was found to vary from nearly 0 to 1.0, depending on experimental conditions, above all on the iodide concentration. This finding appears to contradict our results but in fact does not. As a model for $b = 0$ we can consider the $\alpha\text{-CD} \cdot I_2 \cdot 4H_2O$ complex,[18] where one iodine molecule occupies one α-CD ring or, in amylose, one turn of six glucoses. An intermediate case with $b = 0.5$ is found in the Li^+ and Cd^{2+} complexes. These crystal structures are ordered and the length of the channel in one α-CD dimer accommodates one $I_3^- \cdot I_2$ unit. In general, this particular 1:1 ($b = 0.5$) stoichiometry for $I_3^-:I_2$ seems not only to be favored by the crystalline α-CD matrix but it is the only one leading to ordered arrays with an infinite n in the formula $(I_2 \cdot I_3^-)_n$. When I_3^-/I_2 ratios exceed 1.0, $I_3^- \cdots I_3^-$ repulsion will break the $(I_2 \cdot I_3^-)_n$ chain; also for ratios smaller than 1.0, triiodide ions would be omitted, resulting in holes along the polyiodide chain. Both effects produce disordered matrix/host structures giving rise to diffuse X-ray diffraction lines with 3.1-Å separation. The case for $b = 1$ or exclusively I_3^- is verified in the double chains of the $(\text{benzamide})_2\text{–}HI_3$ and caffeine $\cdot H_2O \cdot HI_3$ complexes and in the single chain of tetra-*n*-butylammonium$\cdot I_3^-$. In these complexes, the average I–I distance within the triiodide units is about "normal", 2.93 Å (Herbstein, Kaftory, Kapon, and Saenger, in preparation) and the repeating unit of the triiodide chains is about 9.6 Å. The latter does not agree with the *c* axis repeat of the α-CD stack or of the amylose helix and suggests that, owing to this structural incompatibility, this type of polyiodide chain will not be preferred in starch-like matrices.

D. Color and Spectra. Crystalline structures containing molecular iodine, triiodide, or pentaiodide as isolated units such as the complexes amylose$\cdot I_2$, $\alpha\text{-CD} \cdot I_2 \cdot 4H_2O$, $(\text{xanthotoxin})_2 \cdot KI_3$,[69] methylene blue$\cdot I_3$,[70] and many inorganic salts, as well as solutions of iodine/iodide in water (also with α-CD present), ethers, and alcohols exhibit only brown or reddish colors. In $\alpha\text{-CD} \cdot I_2 \cdot 4H_2O$, charge-transfer interactions between iodine and hydroxyl oxygens or adjacent α-CD have been established, but even there the crystals are only light brown and easily distinguishable from the nearly black crystals of the α-CD–polyiodide series.

The latter, and similarly colored crystalline complexes of $(\text{phenacetin})_2 \cdot HI_5$,[47] benzamide$\cdot HI_3$,[26] and theobromine$\cdot H_2I_8$,[48] all display polymerized iodine structures. There are many more "blue" iodine compounds with unknown structure, formed by poly(vinyl alcohol), methylcellulose, trimethylstarch, lithocholic acid, carbethoxyhydrindan, *O*-oxychalcon, benzylidene phthalide, coumarin, acetoin, basic lanthan acetate, praseodynium acetate,[19,20] and also frozen solutions of iodine–iodide in water.[71] All these complexes and solutions of iodine in hydrocarbons as well are not "blue" in the liquid phase but in colloid or crystalline state where host lattices hold the polyiodide units together, presumably at angles near 180 or 90°. For production of the typical blue color, the contacts of iodine atoms to atoms of solvents or the host matrices obviously do not play a role, but rather interiodine charge transfer has to be involved. In this context, the amylose helix can be considered as a one-dimensional crystalline array which stabilizes polyiodide chains even in aqueous solution.

Table IX. Comparison of "Periods" of $(I_2 \cdot I_3)^-$ Units in Several Polyiodides[a]

anion	complex [ref]	period, Å
I_5^-	$(\alpha\text{-CD})_2 \cdot Cd_{0.5} \cdot I_5 \cdot 27H_2O$	15.44
$(I_2 \cdot I_3^-)_n$	$(\alpha\text{-CD})_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$	15.69
I_5^- disordered	(trimesic acid)$\cdot HI_5$ [46]	15.50
I_5^-	phenacetin$\cdot HI_5$ [44]	15.66
I_7^-	$N(C_2H_5)_4 \cdot I_7$ [79]	15.41
I_8^-	CsI_4 [80]	15.49
I_9^-	$N(CH_3)_4 \cdot I_9$ [47]	15.42/15.23/ 15.47/15.66
I_{16}^{4-}	$(\text{theobromine})_2 \cdot H_2I_8$ [45]	15.39/15.50/ 15.40/15.43
	av	15.48
compare with the chain composed exclusively of I_3^-		
$(I_3^-)_n$	$(\text{benzamide})_2 \cdot HI_3$ [26]	16.39

[a] These periods were obtained by adding up five successive interiodine distances of a polyiodide. In some cases, more than one interpretation is possible.

Raman spectroscopy should be an ideal method for investigating polyiodide structures. Spectra of amylose–polyiodide complexes do not show an absorption band at 212 cm^{-1} characteristic for an undistorted I_2 molecule.[43-45] The conclusions given in ref 43, namely, that in these complexes the polyiodide consists exclusively of I_3^-, do not agree with our study. We have rather to assume that the I_2 units interact with I_3^-, giving rise to perturbed I_2 which does not absorb at this energy. This interpretation is in line with recent resonance Raman spectra (ref 46; Mizuno and Tanaka, Nagoya University, private communication) and ^{129}I-Mössbauer investigations.[46] It could be demonstrated that in starch–iodine a mixture of I_3^-/I_2 and I_5^- (Mizuno and Tanaka) or predominantly I_5^- [46] exists and that the exclusive occurrence of I_2 or of I_3^- units can be ruled out safely.

E. Influence of Counterions. In analogy to the α-CD–polyiodide complexes we conclude that in amylose–iodine complexes countercations will not be incorporated into the amylose helix but bound to the outside either directly to amylose hydroxyls or via water molecules depending on their coordination affinity. It has been observed by titration studies that the absorption spectrum of amylose–iodine indeed depends on the counterion.[72] The micelle formation found in concentrated amylose–iodine solutions[32,73-75] will be facilitated by cations located between the amylose helices and from the influence of the cations on the packing of α-CD stacks it is to be assumed that the structures of the amylose–iodine micelles as well are determined by cation$^+$–[amylose$\cdot$polyiodide]$^-$ interactions.

Acknowledgment. The authors are indebted to Dr. Philip C. Manor for initial studies on the α-CD–polyiodide complexes and to J. A. Hamilton[60] for sending β-CD coordinates which were used to solve the β-CD–polyiodide crystal structure. They are grateful to the Deutsche Forschungsgemeinschaft for financial support of this work, a collaborative project with Professor H. Herbstein, Haifa, on organic iodine complexes. All calculations were carried out using the UNIVAC 1108 of the Gesellschaft für Wissenschaftliche Datenverarbeitung, Göttingen.

Supplementary Material Available: Bond lengths, bond angles, and torsion angles (Table 1), close contacts between iodine and atoms in the host matrix (Table 2), comparison of distances of nearest atoms from molecular axes in α-CD and amylose (Table 3), anisotropic temperature factors for Li^+ complex (Table 4), anisotropic temperature factors for Cd^{2+} complex (Table 5), structure factor listing for Li^+ complex (Table 6), and structure factor listing for Cd^{2+} complex (Table 7) (45 pages). Ordering information is given on any current masthead page.

References and Notes

(1) W. Banks and C. T. Greenwood, Eds. "Starch and Its Components", Edinburgh University Press, 1975.
(2) W. T. Winter and A. Sarko, *Biopolymers*, **13**, 1447–1460, 1461–1482 (1974).
(3) B. Zaslow, V. G. Murphy, and A. D. French, *Biopolymers*, **13**, 779–790 (1974).
(4) C. de Claubry, *Ann. Chim.* (*Paris*), **90**, 87–95 (1814).
(5) J. Holló and J. Szejtli in "Starch and Its Derivatives", 4th ed., Chaucer Press, England, 1968, pp 203–247.
(6) C. S. Hanes, *New Phytol.*, **36**, 189–239 (1937).
(7) K. Freudenberg, E. Schaaf, G. Dumpert, and T. Ploetz, *Naturwissenschaften*, **27**, 850–853 (1939).
(8) R. E. Rundle and D. French, *J. Am. Chem. Soc.*, **65**, 558–561, 1707–1710 (1943).
(9) R. E. Rundle and F. C. Edwards, *J. Am. Chem. Soc.*, **65**, 2200–2203 (1943).
(10) D. French, *Adv. Carbohydr. Chem.*, **12**, 189–260 (1957).
(11) F. Cramer, "Einschlussverbindungen", Springer-Verlag, Heidelberg, 1954.
(12) J. A. Thoma and L. Stewart in "Starch-Chemistry and Technology", Vol. 1, R. L. Whistler and E. F. Paschall, Eds., Academic Press, New York, 1965, pp 205–249.
(13) M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry", Springer-Verlag, New York, 1978.
(14) A. D. French and V. G. Murphy, *Polymer*, **18**, 489–494 (1977); *Cereal Foods World*, **22**, 61–63, 66–67 (1977); *Carbohyd. Res.*, **27**, 391–406 (1973).
(15) F. Cramer and F. M. Henglein, *Chem. Ber.*, **90**, 2561–2575 (1957).
(16) W. Saenger in "Environmental Effects on Molecular Structure and Properties", B. Pullman, Ed., D. Reidel, Dordrecht, Holland, 1976, pp 265–305.
(17) R. K. McMullan, W. Saenger, J. Fayos, and D. Mootz, *Carbohydr. Res.*, **31**, 37–46 (1973).
(18) R. K. McMullan, W. Saenger, J. Fayos, and D. Mootz, *Carbohydr. Res.*, **31**, 211–227 (1973).
(19) G. Barger and C. Eaton, *J. Chem. Soc.*, **125**, 2407–2414 (1924).
(20) K. H. Meyer, *Adv. Colloid Sci.*, **1**, 143–182 (1942).
(21) C. D. West, *J. Chem. Phys.*, **19**, 1432 (1951).
(22) H. v. Dietrich and F. Cramer, *Chem. Ber.*, **87**, 806–817 (1954).
(23) J. A. Thoma and D. French, *J. Am. Chem. Soc.*, **82**, 4144–4147 (1960).
(24) F. Cramer and E. Herbst, *Naturwissenschaften*, **39**, 256 (1952).
(25) M. B. Robin, *J. Chem. Phys.*, **40**, 3369–3377 (1964).
(26) J. M. Reddy, K. Knox, and M. B. Robin, *J. Chem. Phys.*, **40**, 1082–1089 (1964).
(27) W. L. Peticolas, *Nature* (*London*), **197**, 898–899 (1963).
(28) R. Bersohn and I. Isenberg, *J. Chem. Phys.*, **35**, 1640–1643 (1961).
(29) G. M. Olson and R. A. Berg, *J. Chem. Phys.*, **48**, 1426–1427 (1968).
(30) I. Isenberg and R. Bersohn, *J. Chem. Phys.*, **48**, 1427 (1968).
(31) H. Murakami, *J. Chem. Phys.*, **22**, 367–374 (1954).
(32) B. Pfannemüller, H. Meyerhöffer, and R. C. Schulz, *Makromol. Chem.*, **121**, 147–158 (1969).
(33) C. T. Greenwood and H. Rossotti, *J. Polym. Sci.*, **27**, 481–488 (1958).
(34) J. Holló and J. Szejtli, *Stärke*, **9**, 109–112 (1957); *Period. Polytech.*, **2**, 25–37 (1958).
(35) R. N. Hazeldine, *J. Chem. Soc.*, 4145–4151 (1954).
(36) D. L. Glusker and H. W. Thompson, *J. Chem. Soc.*, 471–479 (1955).
(37) O. Hassel, *Science*, **170**, 497–502 (1970).
(38) F. W. Schneider, C. O. Cronan, and S. K. Podder, *J. Phys. Chem.*, **72**, 4563–4568 (1968).
(39) C. L. Cronan and F. W. Schneider, *J. Phys. Chem.*, **73**, 3990–4004 (1969).
(40) R. S. Stein and R. E. Rundle, *J. Chem. Phys.*, **16**, 195–207 (1948).
(41) M. J. Potasek, P. G. Debrunner, W. H. Morrison, Jr., and D. N. Hendrickson, *J. Chem. Phys.*, **60**, 2203–2206 (1974).
(42) B. S. Ehrlich and M. Kaplan, *J. Chem. Phys.*, **51**, 603–606 (1969).
(43) T. Tasumi, *Chem. Lett.*, **1**, 75–78 (1972).
(44) A. G. Maki and R. Fowlers, *Spectrochim. Acta, Part A*, **23**, 867–880 (1967).
(45) W. Kieler and H. J. Bernstein, *J. Raman Spectrosc.*, **1**, 417–431 (1973).
(46) R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3215–3217 (1978).
(47) F. H. Herbstein and M. Kapon, *Nature* (*London*), *Phys. Sci.*, **239**, 153–154 (1972).
(48) F. H. Herbstein and M. Kapon, *J. Chem. Soc., Chem. Commun.*, 677–678 (1975).
(49) F. H. Herbstein and M. Kapon, Abstracts, IXth International Congress on Crystallography, Kyoto, Japan, 1972, No. VI-3.
(50) E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Adv. Inorg. Chem. Radiochem.*, **3**, 133–169 (1961).
(51) E. H. Wiebenga and D. Kracht, *Inorg. Chem.*, **8**, 738–746 (1969).
(52) M. Noltemeyer and W. Saenger, *Nature* (*London*), **259**, 629–632 (1976).
(53) M. Noltemeyer, Ph.D. Thesis, Universität Göttingen, 1977.
(54) F. Cramer, U. Bergmann, P. C. Manor, M. Noltemeyer, and W. Saenger, *Justus Liebigs Ann. Chem.*, 1169–1179 (1976).
(55) A. C. T. North, D. C. Phillips, and F. S. Matthews, *Acta Crystallogr., Sect. A*, **24**, 351–359 (1968).
(56) M. M. Labes, U.S. Department of Commerce, National Technical Information Service, Springfield, Va., 1973.
(57) P. Main, G. Germain, and M. M. Woolfson, "MULTAN, a System of Computer Programs for the Solution of Non-Centrosymmetric Structures", York, Louvain, 1970.
(58) G. H. Stout and L. H. Jensen, "X-ray Structure Determination", Macmillan, New York, 1968.
(59) R. C. L. Mooney Slater, *Acta Crystallogr.*, **12**, 187–196 (1959).
(60) J. C. Slater, *Acta Crystallogr.*, **12**, 197–200 (1959).
(61) J. Brockema, E. F. Havinga, and E. H. Wiebenga, *Acta Crystallogr.*, **10**, 596 (1957).
(62) A. Hybl, R. E. Rundle, and D. E. Williams, *J. Am. Chem. Soc.*, **87**, 2779–2788 (1965).
(63) J. A. Hamilton, M. N. Sabesan, L. K. Steinrauf, and A. Geddes, *Biochem. Biophys. Res. Commun.*, **73**, 659–664 (1976).
(64) M. Noltemeyer, G. Weber, and W. Saenger, to be published.
(65) H. Rossotti, *J. Polym. Sci.*, **36**, 557–558 (1959).
(66) K. Harata, *Bull. Chem. Soc. Jpn.*, **49**, 1493–1501 (1976).
(67) K. Harata, *Bull. Chem. Soc. Jpn.*, **49**, 2066–2072 (1976).
(68) R. R. Baldwin, R. S. Bear, and R. E. Rundle, *J. Am. Chem. Soc.*, **66**, 111–115 (1944).
(69) M. Kapon and F. H. Herbstein, *Nature* (*London*), **249**, 439–440 (1974).
(70) H. Endres, G. Jeromin, and H. J. Keller, *Z. Naturforsch. B*, **32**, 1375–1378 (1977).
(71) E. Kontos, Ph.D. Thesis, Columbia University, New York, 1959.
(72) T. J. Painter, *J. Chem. Soc., Perkin Trans. 2*, 215–228 (1976).
(73) J. Szejtli and S. Augustat, *Stärke*, **18**, 38–52 (1966).
(74) J. Szejtli, M. Richter, and S. Augustat, *Biopolymers*, **5**, 5–16 (1967).
(75) H. Bittiger and E. Husemann, "Solution Properties of Natural High Polymers", *Chem. Soc., Spec. Publ.*, **No. 23**, 159.
(76) J. A. Thoma and D. French, *J. Am. Chem. Soc.*, **80**, 6142–6146 (1958).
(77) A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842–1843 (1951).
(78) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(79) E. E. Havinga and E. H. Wiebenga, *Acta Crystallogr.*, **11**, 733–737 (1958).
(80) E. E. Havinga, K. H. Boswijk, and E. H. Wiebenga, *Acta Crystallogr.*, **7**, 487–490 (1954).
(81) W. Busing and H. A. Levy, ORFFE, Report ORNL-TM-306, Oak Ridge, Tenn., 1962.