

## $(\beta\text{-Cyclodextrin})_2 \cdot \text{KI}_7 \cdot 9 \text{H}_2\text{O}$ . Spatial Fitting of a Polyiodide Chain to a Given Matrix

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Dedicated to Prof. Friedrich Cramer on the occasion of his 60th Birthday

**Abstract.**  $\alpha$ -Cyclodextrin, a torus shaped molecule with a 5 Å wide central cavity, forms a number of deep green, blue and black crystals when complexed with iodine/metal iodide. In contrast,  $\beta$ -cyclodextrin, having a 6 Å cavity produces only one type of reddish-brown crystal, no matter what metal iodide is used. The complex  $(\beta\text{-cyclodextrin})_2 \cdot \text{KI}_7 \cdot 9 \text{H}_2\text{O}$  displays space group  $P2_1$  (pseudo- $C2$ ) with cell constants  $a = 19.609(5)$ ,  $b = 24.513(7)$ ,  $c = 15.795(6)\text{Å}$ ,  $\beta = 109.50(2)^\circ$ ,  $Z = 4$ . The crystal structure was solved in  $C2$  on the basis of 3022 absorption corrected  $\text{CuK}\alpha$  (Ni-filter) X-ray intensities and refined by full matrix least squares to  $R = 17\%$ . This relatively high  $R$ -factor is due to many weak reflections (pseudo- $C2$ ) and considerable disorder exhibited by water and iodine. In the complex,  $\beta$ -cyclodextrin adopts a 'round' shape with  $\text{O}(2)\dots\text{O}(3)$  interglucose hydrogen bonds formed and all  $\text{O}(6)$  hydroxyls pointing away from the cavity. Two molecules are arranged head-to-head to produce a dimer, and dimers are stacked such that a slightly zigzagged cylinder with a 6 Å-wide cavity is formed. In the cavity described by each dimer, an  $\text{I}_7^-$  ion composed of  $\text{I}_2 \cdot \text{I}_3^- \cdot \text{I}_2$  units is located, with  $\text{I}_2$  and  $\text{I}_3^-$  perpendicular to each other.  $\text{K}^+$  ions and 9  $\text{H}_2\text{O}$  molecules are found in interstices between the  $\beta$ -cyclodextrin cylinders. This zigzag polyiodide contrasts with the linear form observed in the 5 Å wide  $\alpha$ -cyclodextrin channels. It explains differences in color of the crystals and suggests that  $\beta$ -cyclodextrin polyiodide is not a good model for blue starch-iodine.

**Key words:**  $(\beta\text{-cyclodextrin})_2 \cdot \text{KI}_7 \cdot 9 \text{H}_2\text{O}$ , zigzag and linear polyiodide,  $\text{I}_2 \cdot \text{I}_3^- \cdot \text{I}_2$ , starch-iodine model, crystal structure

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## 1. Introduction

Since the discovery of the starch-iodine reaction in 1814 [1], there have been many attempts to explain the deep blue color of the resulting complex [2–4]. A main obstacle in the investigation of this complex is the preparation of starch itself, of which only the linear portion, called amylose, produces the blue color whereas the branched amylopectin fraction yields a reddish complex. X-ray fiber diffraction analyses of starch-iodine suggested that the amylose molecule is screwed into a (left-handed) helix with six glucoses per 8 Å pitch, the so-called V-form. The iodine atoms are located in the  $\sim 5$  Å wide central cavity of the helix at an

equidistant spacing of 3.1 Å which, taken together with charge-transfer contacts to amylose oxygens, was considered responsible for ready charge delocalization along the polyiodide chain and thus explained the characteristic color. In order to simplify the system for detailed investigation in the 1950s, F. Cramer replaced amylose by the enzymatically degraded product cyclodextrin which, when cocrystallized with metal iodide/iodine produces deeply colored crystals with metallic luster. The spectroscopic properties of these crystals resembled those of the starch-iodine complex and thus indicated a good analogy [3,5].

Cyclodextrins are a family of cyclic oligosaccharides consisting of six, seven or eight  $\alpha(1-4)$ -linked glucoses, and they are called  $\alpha$ -,  $\beta$ -,  $\gamma$ -cyclodextrins (CD) or cyclohexa-, hepta-, octaamylose, Figure 1. In its overall dimensions,  $\alpha$ -CD closely resembles the structure of one

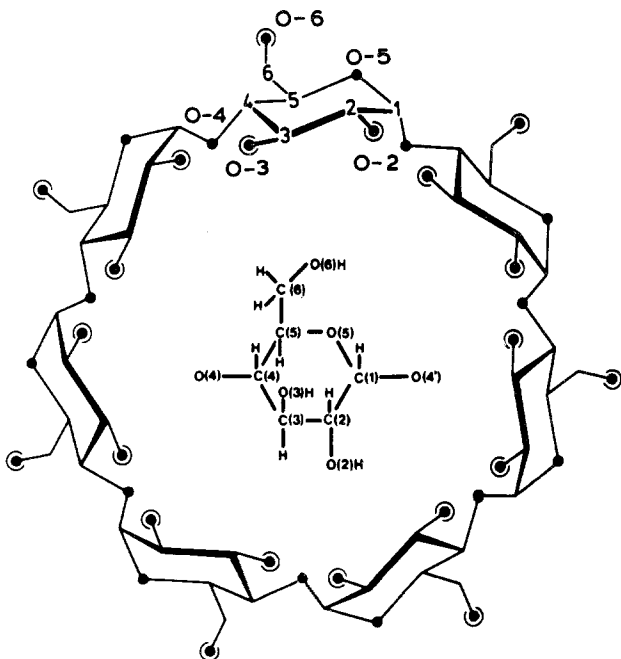


Fig. 1. Chemical structure and numbering scheme (insert) for  $\beta$ -cyclodextrin. Oxygen atoms marked by solid circles, hydroxyl groups by  $\odot$ .

turn of the amylose helix [6-8]. If  $\alpha$ -CD is crystallized with metal iodide/iodine, at least four different crystal forms can develop depending on the nature of the counterion [4, 9]. Two of these, the triclinic complex  $(\alpha\text{-CD})_2 \cdot \text{LiI}_3 \cdot \text{I}_2 \cdot 8 \text{H}_2\text{O}$  and the tetragonal complex  $(\alpha\text{-CD})_2 \cdot \text{Cd}_{0.5}\text{I}_5 \cdot 26 \text{H}_2\text{O}$ , have been investigated in detail by single crystal X-ray methods [4]. In both crystal structures,  $\alpha$ -CD molecules are arranged as head-to-head dimers which are stacked to produce cylinders. The 5 Å wide open central cavities of the CD's line up and provide channels in which polyiodide is embedded. The polyiodide in the  $\text{Li}^+$ -complex is best described as alternating  $\dots\text{I}_3^- \cdot \text{I}_2 \cdot \text{I}_3^- \cdot \text{I}_2 \dots$  units whereas with  $\text{Cd}^{2+}$ ,  $\text{I}_5^- \cdot \text{I}_5^- \cdot \text{I}_5^- \dots$  is obtained. The metal ions are not incorporated in these polyiodide chains but are located outside the  $\alpha$ -CD cylinders. Thus,  $\text{Li}^+$  is coordinated with O(2), O(3) hydroxyls of neighbouring  $\alpha$ -CD's whereas  $\text{Cd}^{2+}$  is surrounded only by water molecules. The different coordination schemes of the cations appear to produce the observed polymorphism of the  $\alpha$ -CD polyiodide complexes [4].

In contrast, the larger  $\beta$ -CD yields only one crystal form with a variety of metal ions. The space group is monoclinic  $P2_1$ , and the distribution of reflection intensities strongly suggests a superlattice with space group  $C2$ . This is indicated by very weak or totally absent reflections of type  $(h + k \text{ odd})$ , depending in part on the crystallization conditions but not, to our observation, on the nature of the metal ion. In this report, the structure of one of these complexes,  $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 9 \text{H}_2\text{O}$ , is described and compared with  $\alpha$ -CD polyiodide crystal structures.

## 2. Experimental

In general, crystals of  $\beta$ -CD polyiodide were grown from hot, concentrated aqueous solutions of  $\beta$ -CD containing metal iodide/iodine in up to 2-fold molar excess. These solutions were immersed in a Dewar filled with hot water in order to allow slow cooling. The resulting crystals are brown, in contrast to those obtained with  $\alpha$ -CD which are deep blue, green or black, and display metallic luster [4].

A crystal of the potassium salt with dimensions  $0.5 \times 0.1 \times 0.2$  mm was sealed together with some mother liquor in a quartz capillary and used for all X-ray work. Unit cell dimensions are  $a = 19.609(5)\text{\AA}$ ,  $b = 24.513(7)\text{\AA}$ ,  $c = 15.795(6)\text{\AA}$ ,  $\beta = 109.50(2)^\circ$ , space group is  $P2_1$  (superspace group  $C2$ ) as determined by precession photographs and diffractometer measurements and the number of formula units per unit cell is  $Z = 4$ . 7955 Intensity data were collected for space group  $P2_1$  up to  $\sin \theta = 0.766$  on a four circle diffractometer employing Ni-filtered  $\text{CuK}\alpha$  radiation and  $2\theta/\omega$  scan mode with stationary background counts. The data were corrected for the usual geometrical factors. Because the linear absorption coefficient of the crystals is  $\mu = 136.7 \text{ cm}^{-1}$  an empirical absorption correction was applied according to [10], with a ratio of maximum/minimum transmission in the performed  $\Phi$ -scan of 2.0.

Attempts to solve the crystal structure in space group  $P2_1$  on the basis of all 7955 measured data using transformed  $\beta$ -CD atomic coordinates from the pseudo-isomorphous complex  $\beta\text{-CD} \cdot 2,5\text{-diiodobenzoic acid}$  (space group  $C2$ , [11]) were unsuccessful. Although the positions of the iodine atoms could be located in principle from difference Fourier maps, the structure did not refine below an  $R$ -factor of 33% and positions of water of hydration molecules were not clearly indicated. In order to omit the many weak reflections of parity  $(h + k = \text{odd})$ , structure determination was then continued in the higher symmetry space group  $C2$ . Difference Fouriers were now easier to interpret and showed positions of cation  $\text{K}^+$ , of 9 water molecules, and of minor occupancy iodine atoms. After a series of full matrix least squares cycles and difference Fourier maps, refinement with isotropic carbon and O(4), O(5) atoms and with anisotropic I, water oxygens, O(2), O(3), and O(6) converged at  $R = 17\%$  for all 3022 data greater than  $\sigma$  (in space group  $C2$ ). Table I lists the final atomic coordinates of this crystal structure (since the refinement was carried out in blocks of 20 atoms, all  $y$  coordinates have standard deviations instead of assigning one  $y$  coordinate for origin fixation). Temperature factors, structure amplitudes and bonding geometry for the  $\beta$ -CD molecule are deposited with the British Library [21].

## 2. Results and Discussion

### 2.1. GEOMETRY of $\beta$ -CD MOLECULE

In this crystal structure the  $\beta$ -CD macrocycle adopts the circular round structure usually observed [11,12]. All the glucoses are in the  $\text{C1}$  chair form, torsion angles

Table I. Fractional atomic coordinates with standard deviations in parentheses. Occupational parameters are 1.0 except for I(1), 0.5; I(4), 0.82(9); I(5), 0.70(9); I(4)A, 0.17(8); I(5)A, 0.15(8); I(5)B, 0.14(9).

Atom	X	Y	Z
C(1)1	0.717(2)	0.174(1)	0.310(2)
C(2)1	0.697(2)	0.206(1)	0.387(2)
C(3)1	0.616(2)	0.199(1)	0.375(2)
C(4)1	0.566(2)	0.219(1)	0.282(2)
C(5)1	0.594(2)	0.188(1)	0.210(2)
C(6)1	0.554(2)	0.217(2)	0.115(3)
C(1)2	0.441(2)	0.250(2)	0.243(2)
C(2)2	0.405(2)	0.257(1)	0.312(2)
C(3)2	0.360(2)	0.201(1)	0.316(2)
C(4)2	0.312(2)	0.192(2)	0.221(2)
C(5)2	0.352(2)	0.187(1)	0.157(2)
C(6)2	0.302(3)	0.178(2)	0.058(3)
C(1)3	0.192(2)	0.140(2)	0.193(2)
C(2)3	0.158(2)	0.116(2)	0.255(2)
C(3)3	0.189(2)	0.063(1)	0.280(2)
C(4)3	0.163(2)	0.026(1)	0.198(2)
C(5)3	0.200(2)	0.049(1)	0.131(2)
C(6)3	0.174(3)	0.024(2)	0.040(3)
C(1)4	0.142(2)	-0.075(1)	0.195(2)
C(2)4	0.161(2)	-0.109(1)	0.281(2)
C(3)4	0.239(2)	-0.128(1)	0.303(2)
C(4)4	0.248(1)	-0.161(1)	0.222(2)
C(5)4	0.224(2)	-0.122(2)	0.140(2)
C(6)4	0.223(2)	-0.152(2)	0.056(3)
C(1)5	0.343(2)	-0.227(1)	0.228(2)
C(2)5	0.401(2)	-0.250(1)	0.319(2)
C(3)5	0.469(2)	-0.216(1)	0.338(2)
C(4)5	0.497(2)	-0.218(2)	0.266(2)
C(5)5	0.440(2)	-0.194(1)	0.176(2)
C(6)5	0.463(3)	-0.199(2)	0.098(3)
C(1)6	0.630(2)	-0.211(1)	0.280(2)
C(2)6	0.686(2)	-0.200(2)	0.372(2)
C(3)6	0.703(2)	-0.141(1)	0.386(2)
C(4)6	0.724(2)	-0.118(1)	0.309(2)
C(5)6	0.662(2)	-0.130(2)	0.218(3)
C(6)6	0.688(2)	-0.112(2)	0.141(3)
C(1)7	0.798(2)	-0.030(2)	0.318(3)
C(2)7	0.827(2)	0.003(1)	0.403(2)
C(3)7	0.773(2)	0.049(1)	0.410(2)
C(4)7	0.756(2)	0.083(1)	0.318(2)
C(5)7	0.730(2)	0.047(1)	0.237(2)
C(6)7	0.724(4)	0.084(3)	0.151(4)
O(4)1	0.496(1)	0.205(1)	0.272(1)
O(5)1	0.668(1)	0.195(1)	0.226(1)
O(4)2	0.269(1)	0.141(1)	0.227(1)
O(5)2	0.399(1)	0.235(1)	0.155(1)
O(4)3	0.192(1)	-0.028(1)	0.218(1)
O(5)3	0.169(1)	0.106(1)	0.112(2)
O(4)4	0.325(1)	-0.172(1)	0.243(1)
O(5)4	0.152(1)	-0.104(1)	0.120(1)
O(4)5	0.562(1)	-0.184(1)	0.287(1)

Table I. Continued

Atom	X	Y	Z
O(5)5	0.378(1)	-0.226(1)	0.158(2)
O(4)6	0.731(1)	-0.056(1)	0.325(1)
O(5)6	0.649(1)	-0.187(1)	0.212(1)
O(4)7	0.701(1)	0.120(1)	0.321(1)
O(5)7	0.782(1)	0.001(1)	0.241(1)
O(6)1	0.565(2)	0.272(1)	0.115(2)
O(6)2	0.251(2)	0.220(2)	0.034(2)
O(6)3	0.099(2)	0.023(2)	-0.002(2)
O(6)4	0.174(2)	-0.198(1)	0.038(2)
O(6)5	0.483(2)	-0.254(2)	0.082(2)
O(6)6	0.751(2)	-0.144(1)	0.138(2)
O(6)7	0.792(3)	0.101(2)	0.155(2)
O(2)1	0.455(1)	0.268(1)	0.395(1)
O(3)1	0.599(1)	0.229(1)	0.445(1)
O(2)2	0.743(1)	0.187(1)	0.474(1)
O(3)2	0.320(1)	0.209(1)	0.377(1)
O(2)3	0.184(1)	0.154(1)	0.338(2)
O(3)3	0.153(1)	0.039(1)	0.344(2)
O(2)4	0.147(1)	-0.079(1)	0.346(1)
O(3)4	0.253(1)	-0.167(1)	0.378(1)
O(2)5	0.364(1)	-0.247(1)	0.385(1)
O(3)5	0.524(1)	-0.240(1)	0.420(1)
O(2)6	0.670(1)	-0.223(1)	0.443(1)
O(3)6	0.762(1)	-0.128(1)	0.468(1)
O(2)7	0.843(1)	-0.030(1)	0.482(1)
O(3)7	0.802(1)	0.080(1)	0.479(1)
I(1)	0.500(0)	0.006(0)	1.000(0)
I(2)	0.402(0)	0.985(0)	0.108(0)
I(4)	0.528(1)	0.007(1)	0.331(1)
I(5)	0.616(1)	-0.011(1)	0.506(1)
K	0.457(1)	0.343(1)	0.085(2)
I4A	0.408(2)	1.000(3)	0.314(2)
I5A	0.602(2)	0.055(1)	0.509(2)
I5B	0.564(2)	0.927(1)	0.501(2)
OW1	0.500(0)	0.437(2)	1.000(0)
OW2	1.000(0)	0.118(3)	1.000(0)
OW3	0.914(2)	0.012(2)	0.179(2)
OW4	0.108(2)	0.892(1)	0.805(3)
OW5	0.090(2)	0.846(2)	0.491(7)
OW6	0.365(4)	0.664(2)	0.065(3)
OW7	0.590(3)	0.654(2)	0.550(7)
OW8	0.430(4)	0.656(1)	0.616(4)
OW9	0.512(4)	0.516(4)	0.355(7)

O(6)–C(6)–C(5)–O(5) are in the *gauche* range and direct O(6) hydroxyls ‘away’ from the center of the molecule. The other side of the macrocycle is formed by O(2),O(3) hydroxyls which display interglucosidic O···O distances averaging 2.85 Å. These distances are suitable for hydrogen bonding, which has been investigated in detail in the  $\beta$ -CD · 11 H<sub>2</sub>O complex [13].

## 2.2. STRUCTURAL CHARACTERISTICS OF $\beta$ -CD CHANNELS

As depicted in Figure 2,  $\beta$ -CD molecules are stacked like coins in a roll, the stacks running parallel to the crystallographic  $c$ -axis. Their cavities line up to produce channels which, however, are not uniform. They display separation into dimeric units consisting of a head-to-head arrangement of  $\beta$ -CD molecules facing each other with their O(2),O(3) sides and connected by hydrogen bonds between O(2),O(3) hydroxyls.

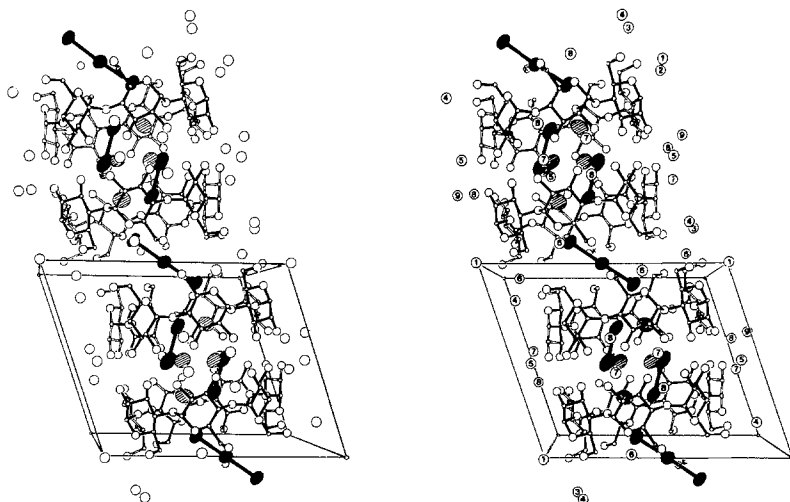


Fig. 2. Stereo view of the crystal structure of  $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 9 \text{H}_2\text{O}$  along the  $b$ -axis, with  $a$ -axis horizontal and  $c$ -axis up. The unit cell ( $1/2$  in  $a$ ,  $1$  in  $b$  and  $1$  in  $c$ ) is outlined, water molecules indicated by numbered circles and potassium ions by K. Iodine atoms with full occupancy drawn solid, these with partial occupancy shaded. In the  $\beta$ -cyclodextrin molecules, small spheres represent carbon atoms and larger spheres oxygens.

Adjacent  $\beta$ -CD dimers are linked by hydrogen bonds between O(6) hydroxyls. These are, however, not as well juxtaposed as O(2),O(3) hydroxyls and show a translational shift along the  $a$ -axis of about  $2 \text{ \AA}$ , leading to a slightly bent appearance of the  $\beta$ -channel. This bend is only obvious when looking along  $b$ . In a view along the  $a$ -axis, Figure 3, the  $\beta$ -CD stack is straight because now the space-group diads run perpendicular to the stack and produce the symmetrical, linear form.

Adjacent  $\beta$ -CD stacks are linked by the nine water molecules of hydration *via* hydrogen bonding, see Table II. The  $\text{K}^+$ -cation is fourfold coordinated by two water molecules and by two O(6) hydroxyl groups in a near-tetrahedral arrangement. It is located between the  $\beta$ -CD dimers and outside the  $\beta$ -CD stacks. Such a molecular packing, with cations outside the cyclodextrin annuli, has also been observed with  $\alpha$ -CD polyiodide complexes containing  $\text{Li}^+$  and  $\text{Cd}^{2+}$  as counterions.

## 2.3. POLYIODIDE STRUCTURE

The polyiodide chain consists of discrete  $\text{I}_7^-$ -units which can be formulated as  $\text{I}_2 \cdot \text{I}_3^- \cdot \text{I}_2$ . These units are shaped into a Z-like structure, Figures 2 and 4. The central  $\text{I}_3^-$  ion (I(2) – I(1) – I(2)) is slightly bent ( $160.2(5)^\circ$ ) yet symmetric because its I(1) atom is located on a crystallographic diad. The I(1) – I(2) distance,  $3.003(7) \text{ \AA}$ , is longer than expected for

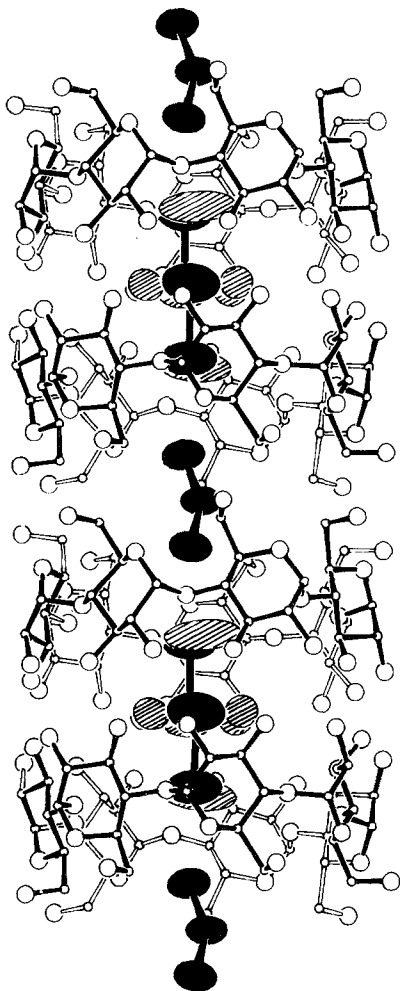


Fig. 3. View of the crystal structure along the  $a$ -axis. The  $b$ -axis is horizontal and  $c$ -axis up. Water of hydration molecules and potassium ions are omitted for the sake of clarity. For iodine and cyclodextrin atoms, see legend to Figure 2. Note straight, cylinder-like appearance of the  $(\beta\text{-CD})_2 \cdot \text{KI}_7$  complex. Bonds closer to viewer drawn solid.

an undisturbed  $\text{I}_3^-$  unit which has an I – I separation of  $2.9 \text{ \AA}$ . A similar lengthening is found for the  $\text{I}_2$  units (I(4) – I(5)) where the I – I distance,  $2.77(2) \text{ \AA}$ , is longer than the ideal value of  $2.67 \text{ \AA}$  for an isolated  $\text{I}_2$  molecule. In the Z-shaped  $\text{I}_7^-$  ion, the  $\text{I}_2$  and  $\text{I}_3^-$  units are nearly perpendicular to each other ( $99.6(3)^\circ$ ) and separated by  $3.61(1) \text{ \AA}$ , the distance between I(2) and I(4) (see Figure 4). This distance is much shorter than the sum of van der Waals radii,  $4.3 \text{ \AA}$ , and suggests that  $\text{I}_2$  and  $\text{I}_3^-$  units are bonded to each other utilizing  $p_y$  and  $p_z$  orbitals [14]. Within the  $\beta\text{-CD}$  channel, each  $\text{I}_7^-$  ion has as neighbours two  $\text{I}_7^-$  ions at a shortest distance of  $4.50(3) \text{ \AA}$  between I(5) atoms; i.e., the separation is slightly beyond the van der Waals contact. Between the  $\text{I}_7^-$  ions, therefore, there is no obvious bonding, in contrast to the linear polyiodide chains in  $\alpha\text{-CD}$  channels where distances between  $\text{I}_2$ ,  $\text{I}_3^-$  and  $\text{I}_5^-$  units are considerably shorter than  $4.3 \text{ \AA}$ , suggesting charge delocalization along the polyiodide chain.

Table II. Possible O–H···O hydrogen bonding contacts <3.15 Å and coordination around potassium ion. Distances in Å units.

<i>A</i>	<i>B</i>	<i>A...B</i>
OW1	O(6)3	2.87(5)
	O(6)3	2.88(5)
OW2	O(6)3	3.04(6)
	O(6)3	3.04(6)
OW3	O(6)3	2.73(5)
	O(5)7	3.08(5)
	O(6)7	3.15(6)
OW4	O(6)6	2.78(4)
OW5	O(3)6	2.84(5)
	O(2)1	2.96(9)
	O(3)1	2.97(6)
OW6	O(6)2	2.67(7)
	O(5)5	3.04(6)
	O(6)7	2.79(8)
	O(6)5	3.02(7)
OW7	O(2)5	2.68(6)
	O(3)7	2.95(7)
OW8	O(2)3	2.57(9)
	O(3)5	2.83(5)
OW9	O(3)3	2.89(9)
K	OW4	2.74(5)
K	OW1	2.93(4)
K	O(6)1	2.67(4)
K	O(6)4	2.84(3)

In the Z-shaped  $I_7^-$  ion of the  $\beta$ -CD complex, the central  $I_3^-$  unit is located on a crystallographic diad and *between* two  $\beta$ -CD dimers near their O(6) rim. The two  $I_2$  units attached to the central  $I_3^-$ , on the other hand, are included *within* the cavities of these two  $\beta$ -CD molecules and close to the O(2),O(3) rims. This implies that each  $\beta$ -CD dimer accommodates two  $I_2$  units whereas the  $I_3^-$  unit is located between and partially outside the dimers. Stacking of the  $(\beta\text{-CD})_2 \cdot I_7^-$  complexes parallel to the *c*-axis produces the channel-type architecture described in Figures 2 and 3.

However, the situation is slightly more complicated because only the iodine atoms of the central  $I_3^-$  unit show full occupancy (1.0) whereas I(4) is filled to only 0.82(9) and I(5) to 0.70(9). Besides these positions, there are minor occupancies with factors 0.15(8) to 0.14(9), which display some short distances to iodine atoms I(2),I(4) and I(5), i.e. they are mutually exclusive (if one site is occupied, the other is not, and *vice versa*). Since the refinement of the low occupancy iodine sites was accompanied with difficulties and therefore bond distances and angles are somewhat uncertain, we refrain here from any further interpretation.



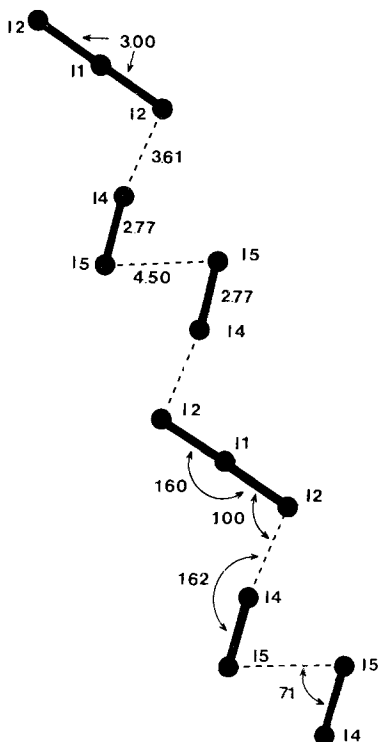


Fig. 4. Geometry of the polyiodide chain in the  $(\beta\text{-CD})_2 \cdot \text{KI}_7$  complex. Distances in Å units, angles in  $(^\circ)$ . Diads are vertical to paper plane and pass through I1 and halfway between I5 atoms. There is clear indication of  $\text{I}_7^-$  built up of  $\text{I}_2 \cdot \text{I}_3^- \cdot \text{I}_2$ . The  $\text{I}_3^-$  and  $\text{I}_2$  units are only separated by 3.61 Å. This is much shorter than expected from van der Waals radii (4.3 Å) and suggests bonding through iodine  $p_z$  orbitals. On the other hand, individual  $\text{I}_7^-$  units are 4.5 Å away and not in bonding contact. In this drawing, only fully occupied iodine positions are shown, partially occupied ones as indicated in Figures 2 and 3 have been omitted for clarity.

#### 2.4. LINEAR AND ZIGZAG POLYIODIDE CHAINS IN CHANNELS FORMED BY $\alpha\text{-CD}$ AND $\beta\text{-CD}$ - A COMPARISON

In the crystal structure described here and in the earlier reported polyiodide complexes of  $\alpha\text{-CD}$ , the matrices embedding the iodine atoms are comparable chemically, yet the channels formed by the cyclodextrin cavities display different widths: 4.7–5.2 Å in  $\alpha\text{-CD}$  and 6.0–6.4 Å in  $\beta\text{-CD}$  [15]. The difference between  $\alpha$ - and  $\beta$ -CD cavity widths of about 1.2 Å appears small, but if we consider that the  $\beta$ -CD dimers in the stack are displaced by about 2 Å, a considerable variation compared with the linear or near-linear channels formed by  $\alpha\text{-CD}$  molecules becomes apparent. These differences in  $\alpha\text{-CD}$  and  $\beta\text{-CD}$  channel structure explains why in  $\alpha\text{-CD}$  channels, the polyiodide chain is virtually linear whereas in the  $\beta\text{-CD}$  channel with slightly bent appearances it is Z-shaped.

The latter form is, in general, preferred by polyiodide units. Such zigzagged polyiodides are observed in the crystal structures of tetraethylammonium hepta-iodide [16], in phenacetin penta-iodide [17], and in (theobromine) $_2 \cdot \text{H}_2\text{I}_8$  [18]. The polyiodide molecules in each of these complexes consist of  $\text{I}_3^-$  units, the terminal atoms of which are linked to  $\text{I}_2$  units such that near perpendicular ( $90^\circ \pm 10^\circ$ ) entities are formed. Whereas in (theobromine) $_2 \cdot \text{H}_2\text{I}_8$  two U-shaped  $\text{I}_3^- \cdot \text{I}_2 \cdot \text{I}_3^-$  segments are bonded to a central  $\text{I}_2$  molecule to form an S-shaped

$[I_3^- \cdot I_2]_3 \cdot I_3^-$ , the other two polyiodide complexes display Z-shaped  $I_2 \cdot I_3^- \cdot I_2$  units, just as is found in the  $(\beta\text{-CD})_2 \cdot I_7^-$  inclusion compound. On the basis of this particular, preferred geometry of the polyiodide chain, the I – I bond can be defined as *p*-bonding with preferential involvement of  $p_y$  and  $p_z$  orbitals resulting in the formation of angles near  $90^\circ$ . If steric restrictions occur, this kind of polyiodide structure can be forced into a linear arrangement where only  $p_x$ -type orbitals are engaged [14].

Utilization of the different iodine orbitals in I – I bonding obviously has an influence on the length of the respective bond between  $I_2$  and  $I_3^-$  units. In the above mentioned polyiodide complexes with zigzag or bent polyiodide ions formed with  $\beta\text{-CD}$ , tetraethylammonium, theobromine, and phenacetin the I – I separation in the  $I_2$  units is 2.74 to 2.77 Å, in the  $I_3^-$  units 2.9–3.0 Å and between these units 3.42–3.61 Å, with  $\beta\text{-CD}$  at the upper end of this

Table III. Iodine bonding geometry. Atoms designated A, B are only partially occupied. Distances in Å units. Angles in ( $^\circ$ ).

I(1) – I(2)	3.00(1)
I(2) – I(4)A	3.24(3)
I(2) – I(4)	3.61(1)
I(4) – I(4)A	2.28(3)
I(4) – I(5)	2.77(2)
I(4) – I(5)A	2.95(3)
I(4) – I(5)B	3.21(3)
I(5) – I(5)	4.50(3)
I(5) – I(5)A	1.64(4)
I(5) – I(5)B	1.83(4)
I(5) – I(4)A	3.06(4)
I(5)A – I(5)B	3.23(4)
I(5)B – I(5)B	2.50(7)
I(2) – I(1) – I(2)	160.2(5)
I(1) – I(2) – I(4)	99.6(3)
I(4) – I(5) – I(5)	70.6(4)

range. As Table III shows, the corresponding distances in linear polyiodide chains formed with  $\alpha\text{-CD}$  as the matrix are quite different. This holds especially if the data for the  $\text{Cd}^{2+}$ -complex are considered where the polyiodide chain is forced into linearity because it is arranged along a crystallographic  $4_2$  axis. In this case, the I – I distances in  $I_2$  and  $I_3^-$  units are significantly lengthened with respect to values found in zigzag chains whereas distances between these units are shortened to 3.14 Å to 3.32 Å, about 1 Å shorter than the van der Waals distance between iodine atoms. These differences suggest that, along the linear polyiodide chains, considerable charge delocalization occurs, giving rise to the observed spectroscopic properties of the crystals and to electronic conductivity along the polyiodide chains [4].

Linear polyiodide of this form also occurs in the blue starch–iodine complex where the diameter of the channel provided by the starch helix resembles the dimensions of the  $\alpha\text{-CD}$  cavity. The overall geometry of the polyiodide chains in  $\alpha\text{-CD}$  and amylose complexes is comparable because average I – I distances, 3.14 Å to 3.18 Å in the former and 3.1 Å in the latter, agree well and spectroscopic properties are similar [19]. The linearity of the polyiodide appears to be dependent on the dimensions of the given matrix. If the matrix only allows

exclusive formation of linear polyiodide, the otherwise preferred bent or zigzagged molecule straightens out in order to satisfy spatial requirements. This happens in the V-amylose helix or in  $\alpha$ -CD channels. With  $\beta$ -CD, the available space is wider and therefore the polyiodide forms a Z-like structure and disintegrates into separate  $I_7^-$  units. There is essentially no charge delocalization along the iodine chain in the  $\beta$ -CD channel as observed in the linear polyiodide in  $\alpha$ -CD and consequently the spectroscopic properties of these complexes are different.

With the even larger cavity in  $\gamma$ -CD (7.5 Å to 8.3 Å diameter) [15], one would expect again Z-shaped polyiodide molecules, comparable to those observed in the  $\beta$ -CD complex. Small crystals obtained by slow cooling of a hot, aqueous solution of  $\gamma$ -CD with  $KI/I_2$  in fact display a brown color reminiscent of the  $(\beta\text{-CD})_2 \cdot KI_7 \cdot 9 H_2O$  crystals. The space group is probably tetragonal, as found for the  $\gamma$ -CD-*n*-propanol complex [19] and we assume that the polyiodide within the  $\gamma$ -CD channel is statistically disordered due to the fourfold symmetry axis, as observed in the *n*-propanol complex.

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