

Crystal and Molecular Structure of a 1:1 Complex of a Chiral α -D-Glucosido-benzo-18-crown-6* and Potassium Thiocyanate

KINGA SUWIŃSKA

*Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01 224 Warsaw, Poland*

and

GIOVANNI DARIO ANDRETTI

*Institute of Structural Chemistry, University of Parma,
Via M. D'Azeglio 85, 43100 Parma, Italy*

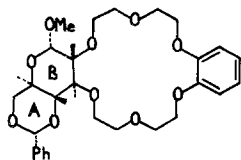
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Abstract. $C_{28}H_{36}O_{10}$. KSCN is monoclinic, space group $P2_1$ with $Z = 2$, $a = 10.390(3)$, $b = 8.959(7)$, $c = 16.377(7)$ Å, $\beta = 92.49(5)^\circ$. Final $R = 0.053$ for 1437 reflections measured at room temperature. The K^+ ion lies on the least-squares plane formed by the six oxygen atoms in the macrocyclic ring. The SCN^- ion was found on the same face of the macrocycle as the chiral glucopyranoside moiety.

Key words: Crystal structure, single crystal, chiral macrocycles, cyclic polyethers, glucopyranosides, complexation.

1. Introduction

Chiral crown polyethers are a subject of interest because of their possible use in the selective complexing of optically-active aminoacids or related compounds [1]. An attempt to crystallize a molecular complex of the chiral crown (I) and the methyl ester of L-phenylalanine (solution:



(I)

the thiocyanate salt of the methyl ester of L-phenylalanine and crown 1 : 1 mixture in acetone) yielded a few good looking crystals having cell dimensions very similar to those previously observed for the KI crystalline complex of the same macrocyclic ligand [2]. A crystal structure analysis showed that a complex with KSCN had been obtained.

*Methyl-4,6-O-benzylidene-2,3-O-(1,2-bis(ethoxyethoxy)benzenediyl)- α -D-glucopyranoside.

2. Experimental and Structure Determination

A single crystal with approximate dimensions of $0.3 \times 0.3 \times 0.4$ mm was selected for analysis. Accurate cell dimensions were determined by the least-squares method from the setting angles of 13 reflections centered on a Siemens AED diffractometer (Cu $K\alpha$). Crystal data are given in Table I. Intensities were collected in the ω - 2θ mode with a filtered Cu $K\alpha$ radiation $\lambda = 1.54178$ Å. 3211 reflections were recorded up to $\theta = 70^\circ$. The intensity of a standard reflection, monitored after each group of 30 reflections, showed no observable decay of the crystal during data collection. Data were corrected for Lorentz and polarization effects, but not for absorption and extinction.

Table I. Crystal data. Molecular formula: $C_{28}H_{36}O_{10} \cdot KSCN$, $M_r = 629.76$; monoclinic, space group $P2_1$

$a = 10.390(3)$ Å	$Z = 2$
$b = 8.959(7)$ Å	$F(000) = 664$
$c = 16.377(7)$ Å	$D_c = 1.373$ Mg m $^{-3}$
$\beta = 92.49(4)^\circ$	$\mu(\text{Cu } K\alpha) = 2.64$ mm $^{-1}$
$V = 1523$ Å 3	$\lambda = 1.54178$ Å

The structure was solved by tangent-formula refinement [3] applied to 100 reflections with $E > 2.07$. Ten of the 42 non-hydrogen atoms in the asymmetric unit were found in the best E map; the remaining 32 atoms were found, after two successive electron density maps, in their correct position ($R = 0.24$) [4]. Subsequent refinement was based on 1437 observations

Table II. Atomic fractional coordinates for non-hydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) and isotropic thermal parameters (e.s.d.'s are in parentheses)

	x/a	y/b	z/c	(B_{eq}) (Å 2)
K	8236(2)	8097 ^a	7354(1)	5.64
S	4916(4)	4713(8)	6583(2)	13.85
C	6039(10)	5002(14)	7147(6)	5.28
N	6881(9)	5023(17)	7589(7)	9.64
C(1)	1322(9)	10185(12)	8133(6)	4.45
C(2)	205(9)	10724(12)	8450(6)	4.45
C(3)	-692(10)	11508(13)	7948(7)	5.61
C(4)	-465(11)	11801(14)	7138(7)	6.00
C(5)	662(12)	11305(13)	6838(7)	5.98
C(6)	1579(11)	10519(13)	7338(6)	5.54
C(7)	2240(8)	9235(12)	8627(5)	4.66
O(8)	1972(5)	9236(8)	9460(4)	4.68
C(9)	2773(8)	8155(14)	9912(5)	4.99
C(10)	4154(8)	8585(11)	9787(5)	4.03
C(11)	4414(8)	8688(11)	8883(5)	3.88
O(12)	3525(5)	9733(8)	8514(3)	4.19
O(13)	4963(6)	7461(7)	10147(4)	4.29
C(14)	6301(8)	7848(13)	10133(5)	4.45
C(15)	6654(8)	8032(13)	9204(5)	4.30
C(16)	5775(8)	9178(12)	8769(5)	4.53
O(17)	6604(5)	9157(7)	10543(3)	4.35
C(18)	6339(11)	8997(16)	11392(3)	5.81
O(19)	7965(5)	8495(7)	9135(3)	4.53
C(20)	8936(8)	7573(12)	9553(5)	4.45

TABLE II (continued)

	x/a	y/b	z/c	$(B_{eq}) (\text{\AA}^2)$
C(21)	7296(9)	6197(11)	9084(5)	4.25
O(22)	9976(5)	6614(8)	8390(3)	4.41
C(23)	10310(9)	5297(11)	7931(6)	4.59
C(24)	11167(9)	5837(12)	7250(5)	4.98
O(25)	10364(6)	6698(8)	6698(4)	4.97
C(26)	11002(10)	7396(12)	6065(6)	4.91
C(27)	12313(10)	7289(12)	5957(6)	5.54
C(28)	12801(10)	8087(16)	5291(6)	6.41
C(29)	12037(12)	8896(16)	4777(8)	7.38
C(30)	10697(11)	8969(14)	4868(6)	4.41
C(31)	10157(10)	8238(12)	5533(6)	4.97
O(32)	8892(6)	8218(9)	5708(3)	5.83
C(33)	8051(10)	9146(16)	5216(6)	6.84
C(34)	6718(10)	9101(17)	5546(6)	6.79
O(35)	6801(5)	9728(9)	6333(4)	5.72
C(36)	5604(10)	10137(15)	6625(6)	6.45
C(37)	5734(10)	10535(12)	7490(5)	5.28
O(38)	6083(5)	9211(8)	7931(3)	9.64
H(2)	1	1052	908	4.45
H(3)	-155	1195	822	4.54
H(4)	-118	1235	675	5.61
H(5)	91	1159	622	6.00
H(6)	246	1010	710	5.98
H(7)	213	810	842	5.54
H(9A)	255	815	1055	4.66
H(9B)	261	706	965	4.68
H(10)	434	965	1008	4.99
H(11)	429	763	857	4.03
H(14)	686	696	1040	3.88
H(15)	652	696	891	4.19
H(16)	593	1026	904	4.29
H(18A)	536	880	1156	4.45
H(18B)	694	809	1162	4.30
H(18C)	668	1003	1166	4.53
H(20A)	861	727	1015	4.35
H(20B)	981	823	932	5.81
H(21A)	839	566	887	4.53
H(21B)	983	543	947	4.47
H(23A)	1084	452	833	4.25
H(23B)	945	476	768	4.41
H(24A)	1195	651	751	4.59
H(24B)	1156	491	692	4.98
H(27)	1294	661	635	4.97
H(28)	1382	806	520	4.91
H(29)	1246	949	428	5.54
H(30)	1007	960	445	6.41
H(33A)	839	1028	526	7.38
H(33B)	805	879	459	6.41
H(34A)	603	970	515	4.97
H(34B)	643	795	559	5.83
H(36A)	520	1105	627	6.84
H(36B)	496	919	658	6.79
H(37A)	650	1134	756	5.72
H(37B)	486	1101	771	6.13

^a Not refined; fix the origin on the polar axis.

above threshold, $I_0 > 2\sigma(I_0)$. The isotropic full-matrix least-squares refinement of the heavy-atom model led to $R = 0.14$. Anisotropic refinement of this model converged at $R = 0.07$. At this stage all H atoms were introduced in calculated positions. The final R was 0.053 ($R_w = [\sum w(\Delta F)^2 / \sum w F_0^2]^{1/2} = 0.063$ where $w = 0.58 / (\sigma^2(F) + 0.001(F)^2)$). No attempt was made to refine the positions of the H atoms; only their thermal parameters were refined. Form factors for all atoms were taken from the *International Tables for X-ray Crystallography* [5]. In the final difference map, calculated after the last cycle, there were no peaks $> 0.25 \text{ e}\text{\AA}^{-3}$. The atomic coordinates are given in Table II.

3. Discussion of results

The distances and bond angles in the macrocyclic complex are given in Figure 1 and Table III.

Table III. Distances (Å) and angles (°) involving the potassium and thiocyanate ions (e.s.d.'s in parentheses)

S - C	1.479(11)	S - C - N	170.8(1.4)
N - C	1.112(14)	K...N - C	106.3(1.0)
K...N	3.124(14)		

Bond lengths in the benzene moiety in the macrocyclic ring range from 1.344 Å for a peripheral bond to 1.426 Å for the bond included into the macrocyclic ring. In the phenyl substituent dimensions are in the range of 1.364 - 1.417 Å. The C(sp^3) - O (1.401 - 1.449 Å, average 1.427 Å) and C(sp^3) - C(sp^3) (1.461 - 1.535 Å, average 1.507 Å) distances follow the trends usual for crown ether compounds [6 - 8]. The dimensions in the thiocyanate groups are abnormally short (S - C and C - N distances are 1.479 and 1.112 Å respectively) and very large thermal parameters are observed.

Torsion angles are shown in Table IV. The values for the torsion angles about C - O bond are close to 180° (values range from 156.1 to 180.0°) and those about C - C bonds are close

Table IV. Torsion angles (°) in the macrocyclic 18-membered ring (e.s.d.'s in parentheses)

		(★)
C(16) - C(15) - O(19) - C(20)	173.0(7)	173.7
C(15) - O(19) - C(20) - C(21)	81.0(9)	74.9
O(19) - C(20) - C(21) - O(22)	70.4(9)	69.9
C(20) - C(21) - O(22) - C(23)	180.0(7)	180.0
C(21) - O(22) - C(23) - C(24)	-174.6(7)	-171.2
O(22) - C(23) - C(24) - O(25)	-68.4(9)	-61.7
C(23) - C(24) - O(25) - C(26)	174.9(8)	174.4
C(24) - O(25) - C(26) - C(31)	180.0(8)	178.1
O(25) - C(26) - C(31) - O(32)	-1.0(1.3)	2.0
C(26) - C(31) - O(32) - C(33)	175.5(9)	175.8
C(31) - O(32) - C(33) - C(34)	-174.5(9)	-176.1
O(32) - C(33) - C(34) - O(35)	64.0(1.1)	65.5
C(33) - C(34) - O(35) - C(36)	163.4(9)	174.4
C(34) - O(35) - C(36) - C(37)	170.2(9)	172.8
O(35) - C(36) - C(37) - O(38)	-66.4(1.0)	-71.2
C(36) - C(37) - O(38) - C(16)	-156.1(8)	-156.9
O(37) - O(38) - C(16) - C(15)	-157.9(7)	-162.5
O(38) - C(16) - C(15) - O(19)	61.2(9)	64.1

★ Data for the complex with KI [2].

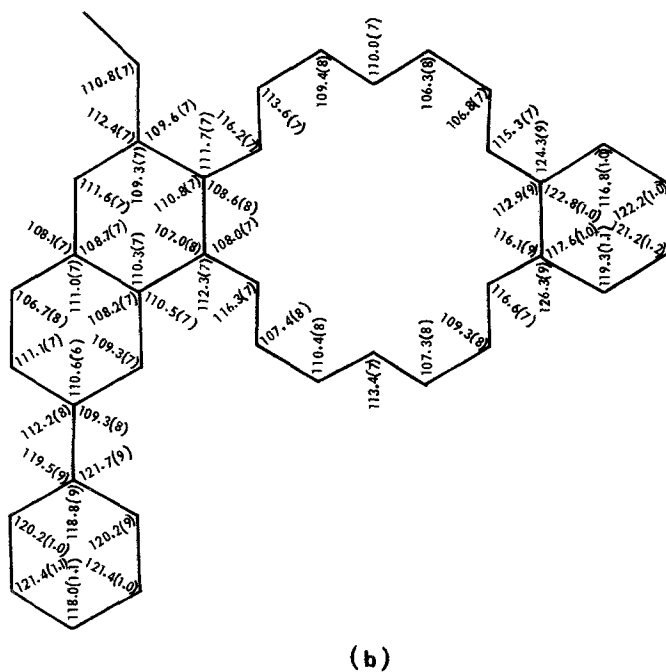
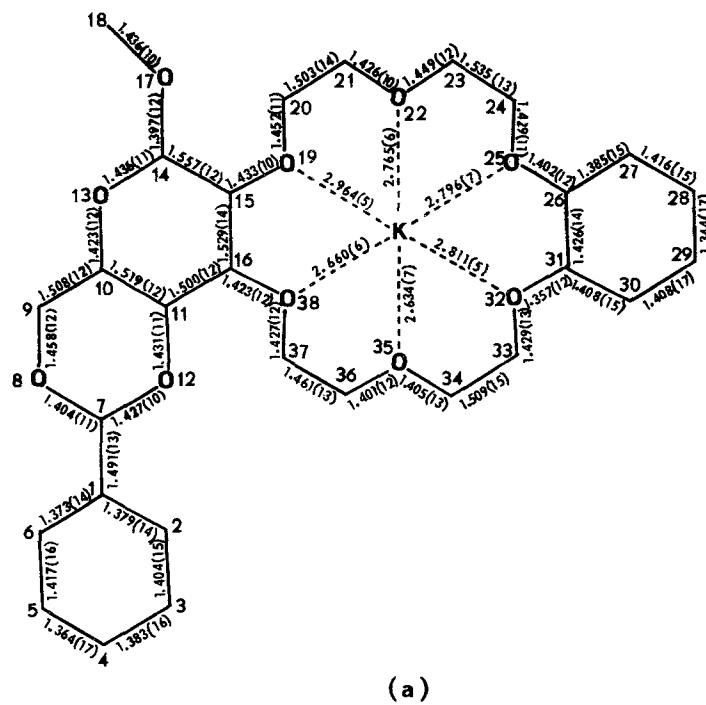


Fig. 1. (a) The numbering of the atoms and distances (Å) and (b) bond angles in the macrocyclic ligand (e.s.d.'s in parentheses). Dashed lines are K...O distances.

to 60° (values range from 61.2 to 70.4°). Observed antiplanar (180°) and synclinal (60°) conformations are energetically optimal in the aliphatic fragment of the macrocyclic ring. The aromatic rings are planar within $\pm 0.02(1)$ Å. The conformation of 1,3-dioxane (A) and pyranoside (B) rings is described by ring puckering coordinates [9]. The puckering amplitudes★ describe very slightly distorted chairs with $q_3 = 0.591(9)$ and $q_2 = 0.026(10)$ Å (ring (A)) and $q_3 = 0.602(9)$ and $q_2 = 0.038(10)$ Å (ring (B)). The total puckering amplitude $Q = 0.592(9)$ Å (ring (A)) and $Q = 0.603(9)$ Å (ring (B)) lies only slightly under the Q value of the ideal cyclohexane chair (0.63 Å for C – C 1.54 Å). The magnitude of the distortion is given by $\theta = 2.5(1.0)$ (ring (A)) and $3.6(9)^\circ$ (ring (B)) and the direction is described by Φ_2 (354(18) and 158(13)° for ring (A) and (B), respectively) which corresponds to a twist-boat conformation.

The least-squares plane through the six oxygen atoms in the macrocycle and their deviations are presented in Table V. The K^+ cation lies in this plane. The dihedral angle between r.m.s.

Table V. Least-squares plane and atomic deviations (Å) for the six oxygen atoms in the macrocyclic ring (e.s.d.'s in parentheses).

$-5.5127 X - 7.5170 Y - 1.5914 Z = -11.9080$	
O(19)	-0.322(6)
O(22)	0.102(7)
O(25)	0.094(7)
O(32)	-0.080(8)
O(35)	-0.162(8)
O(38)	0.369(7)
K^a	0.111

^a Atom not included in the least-squares calculation.

planes defined by glucopyranoside atoms (C(7) to C(16)) and the six macrocycle oxygen atoms is 31°. The thiocyanate anion lies on the same side of the macrocyclic ring as the sugar moiety (Figure 2) and forms with the macrocyclic ring an angle of 55°. The $K^+ \dots O$ distances are in the range of 2.634 – 2.964 Å (average 2.772 Å) and are longer than those found in the KI complex of the same macrocyclic ligand, except for the $K^+ \dots O(35)$ distance which is shorter (the average $K^+ \dots O$ distance in the KI complex is 2.746 Å). The equation of least-squares plane for all eighteen atoms in the macrocyclic ring is: $-4.4149 X - 7.6192 Y - 4.7716 Z = -13.4805$, $\Sigma \Delta^2 = 7.247 \text{ Å}^2$, $\langle \Delta^2 \rangle^{1/2} = 0.574 \text{ Å}$; the ring is less planar than that found in the KI complex ($\Sigma \Delta^2 = 3.309 \text{ Å}^2$, $\langle \Delta^2 \rangle^{1/2} = 0.429 \text{ Å}$). C – C – O bond angles within the aliphatic part of the macrocyclic ring are confined to a range of 106.3 – 113.6° (average 108.7°); C – O – C bond angles may be classified in two groups: angles at O(22) and O(35) equal to 110.0 and 113.4° respectively, which are in agreement with those observed in other macrocyclic compounds. The remaining C – O – C angles are larger being in the range of 115.3 – 116.6° (average 116.1°); the same was observed in the KI complex.

The packing of the molecules is shown in Figure 3. All intermolecular distances are longer than or approximately equal to the sums of the corresponding van der Waals radii.

★ Puckered monocyclic rings are oriented, following [9], with respect to a unique mean plane and the up and down positions of the various atoms are related to the out-of-plane distance, q_i = puckering amplitude, and to the angular position with respect to the points of an ideal polygon.

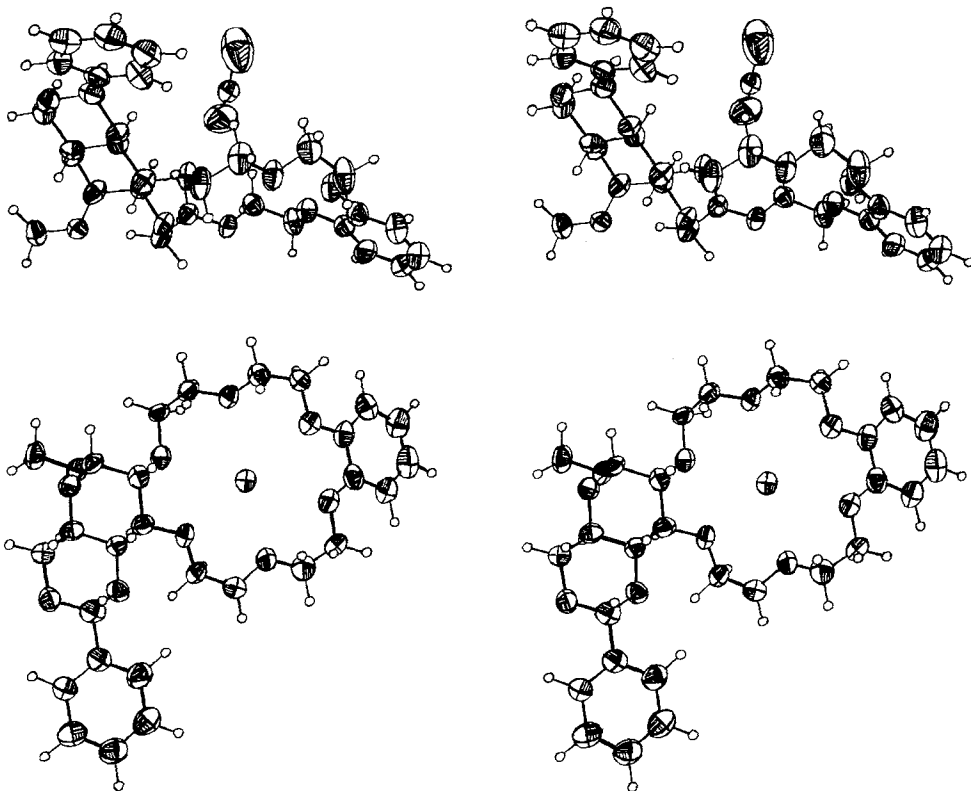


Fig. 2. Top: stereoview along *a* direction in the mean plane (K^+ cation omitted). The vibration ellipsoids are drawn at the 50% probability level [10]. Bottom: molecular stereoview in the direction normal to its mean plane (SCN^- anion omitted).

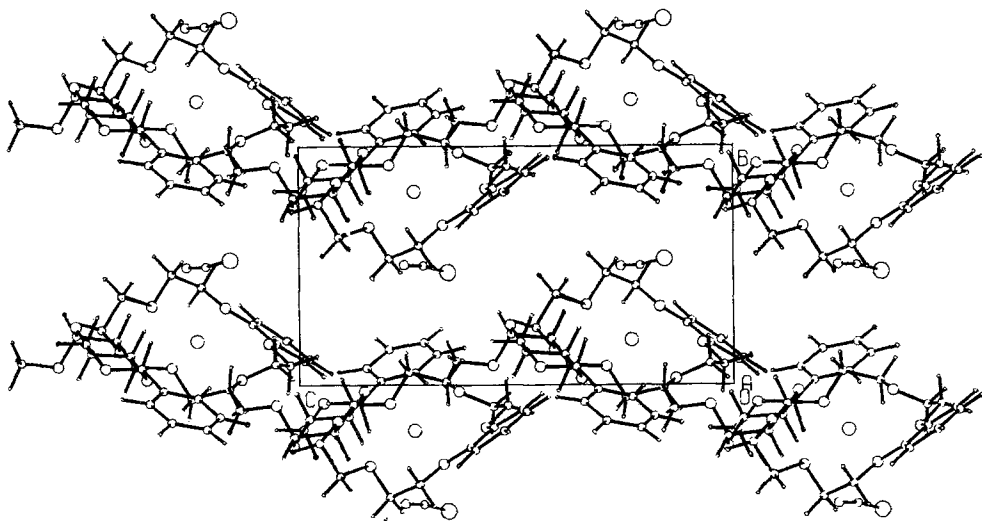


Fig. 3. The packing of the crown- K^+ complex and the SCN^- counterions.

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Supplementary Data relevant to this article have been deposited with the British Library Lending Division, and copies may be ordered from there, quoting Sup. No. 90074.