Crystal Structures of Complexes between Alkali-metal Salts and Cyclic Polyethers. Part V.[1] The 1:2 Complex formed between Potassium Iodide and 2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (Benzo-15-crown-5)

By **P. R. Mallinson** and **Mary R. Truter,*** A.R.C. Unit of Structural Chemistry (University College London), Inveresk House, 346 Strand, London WC2R 0HG

Potassium iodide forms a 1 : 2 complex with the cyclic polyether ' benzo-15-crown-5 '. The crystals are tetragonal with $a = b =$ 17·84(1), $c =$ 9·750(6) Å, Z = 4, space group $P4/n$. The crystal structure has been determined by the heavy-atom method and refined by full-matrix least-squares to a final R of 0·09 on 1603 diffractometer data. The complex cation has crystallographic symmetry $\bar{1}$, the potassium being ' sandwiched ' between two centrosymmetrically related ligand molecules. In each of these the five ether-oxygen atoms are approximately coplanar, the cation lying 1·67 Å away from this plane, so that the ten-co-ordination is an irregular pentagonal antiprism. The K–O distances range from 2·777(7) to 2·955(8) Å. Iodide ions occupy two sets of positions with 4 or $\bar{4}$ symmetry and the arrangement of complex cations and anions resembles the caesium chloride structure; there is no interaction between the anions and the metal.

CERTAIN naturally-occurring antibiotics show a high degree of cation specificity in metabolic behaviour[2] and the electrical properties of biological membranes in the presence of such antibiotics show an analogous ion-dependence.[3,4] The stability constants of their complexes with alkali-metal cations[5] have magnitudes in the order $Li^+ \ll Na^+,Cs^+ < Rb^+,K^+$; the same as that established in the biological and electrochemical experiments.

Simulation of the natural phenomenon in a simplified model may be achieved by utilizing the selective properties of cyclic polyethers for extracting alkali-metal salts across aqueous-nonpolar boundaries. Crystalline complexes have been isolated and the structures of four of these were reported in earlier parts of this series.[1,6-8] The first compounds[9] to be isolated had the stoicheio-

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[3] P. Mueller and D. O. Rudin, *Biochem. Biophys. Res. Comm.*, 1967, **26**, 398.

[4] Z. Stefanac and W. Simon, *Chimia*, 1966, **20**, 436; *Mikrochem. J.*, 1967, **12**, 125.

[5] L. A. R. Pioda, H. A. Wachter, R. E. Dohner, and W. Simon, *Helv. Chim. Acta*, 1967, **50**, 1373.

[6] D. Bright and M. R. Truter, *J. Chem. Soc.* (*B*), 1970, 1544.

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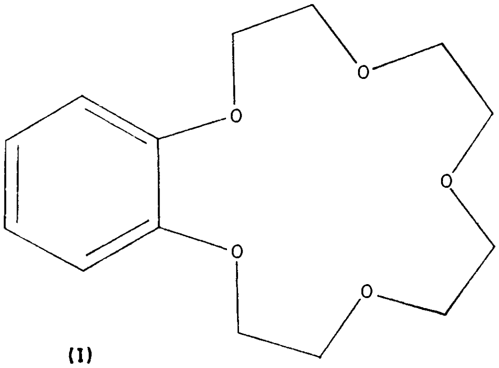
[8] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 341.

[9] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017; *Fed. Proc.*, 1968, **27**, 1305.

metry 1 : 1, *i.e.* one metal salt to one cyclic ether. For a particular cation the stability constant in methanol solution was found to be greatest when the metal fitted the centre of the ring. K^+ formed the strongest complexes by comparison at optimum size; this can be explained on an ionic model as the result of its not being so small as to be too strongly solvated for the ligand to compete, nor too large to induce a sufficiently strong ion–dipole interaction for complex formation.[10] Recently a metal–ligand ratio of 2 : 1 has been found in a dibenzo-24-crown-8 complex [11] and complexes of ratios 1 : 2 and 2 : 3 have been obtained [12] if the cation is too large to fit into the hole in the ring, *e.g.* K^+ and benzo-15-crown-5 (I), and stability constant measurements [10] showed K^+(cyclohexyl-15-crown-5)$_2$ exists in solution. We have determined the crystal structure of KI(benzo-15-crown-5)$_2$ for comparison with the 1 : 1 complex NaI(benzo-15-crown-5) [8] and with the 1 : 1 complex KI(dibenzo-30-crown-10) [1] in which the potassium is also ten-co-ordinate having the ligand wrapped round it in a similar way to the naturally occurring antibiotic nonactin.[13]


(I)

EXPERIMENTAL

Crystals of KI(benzo-15-crown-5)$_2$ were prepared by Fenton [14] following Pedersen's method.[12] Their i.r. spectrum showed that the band at 985 cm^{-1} in the free ligand was not present, indicating that both molecules were complexed to the metal.

Crystal Data.—$C_{28}H_{40}KIO_{10}$, $M = 702\cdot6$. Tetragonal, $a = b = 17\cdot84(1)$, $c = 9\cdot750(6)$ Å, $U = 3102$ Å^3, $D_c = 1\cdot51$, $Z = 4$, $D_m = 1\cdot52$, $F(000) = 1440$. Space group $P4/n$, from systematic absences. $\mu = 12\cdot41$ cm^{-1} for Mo-$K_{\alpha 1}$ radiation, $\lambda = 0\cdot70926$ Å (1 Å $\equiv 10^{-10}$m).

A single crystal, obtained by recrystallization from acetone, was cut and ground into an approximately spherical shape of diameter 0·25 mm and mounted * in a random orientation. 3745 Independent X-ray intensities were measured by 2θ scan from $2\theta_{\alpha 1} - 0\cdot5°$ to $2\theta_{\alpha 2} + 0\cdot5°$ on a Picker four-circle automatic diffractometer at room temperature (17°), using zirconium-filtered Mo-K_α radiation with attenuators. These comprised all possible reflections with $\sin\theta/\lambda \leqslant 0\cdot65$ Å^{-1}. 1603 Reflections had $I > 2\sigma(I)$; the remainder were considered unobserved. $\sigma^2(I) = C + (t_c/2t_b)^2(B_1 + B_2)$, where C is the total integrated count in time t_c, B_1 and B_2 are background counts, each obtained in time t_b, and $I = C - (t_c/2t_b)(B_1 + B_2)$. The intensities of three standard reflections, (2,6,0), (4,1,1), and (4,2,0) were measured together after every 50 observations. No reduction in intensity occurred during the period of data collection. The intensities were corrected [15] for Lorentz and polarization effects but not for absorption. The unit-cell parameters were determined [15] by least-squares refinement from diffractometer setting angles of 13 reflections.

Computation was carried out on an IBM 1130 computer at the Unit of Structural Chemistry, a CDC 6600 at the University of London Computer Centre, and an IBM 360 at the University College Computer Centre. The principal computer programmes used are listed in refs. 15 and 16.

Structure Determination.—The four potassium and four iodine atoms in the cell must occupy special positions to generate the space group symmetry. From the three-dimensional Patterson function it was deduced that three different kinds of position are involved; with the origin at a centre of symmetry the K^+ is in four-fold positions of symmetry $\bar{1}$ at $0,0,\frac{1}{2}$, *etc.*, the I^- in two sets of two-fold positions of symmetry, I(1) on $\bar{4}$ at $\frac{1}{4},\frac{3}{4},0$, *etc.* and I(2) on 4 at $\frac{1}{4},\frac{1}{4},z$, *etc.* with $z \approx +\frac{1}{6}$. This arrangement of the ions resembles that in CsCl. The carbon and oxygen atomic

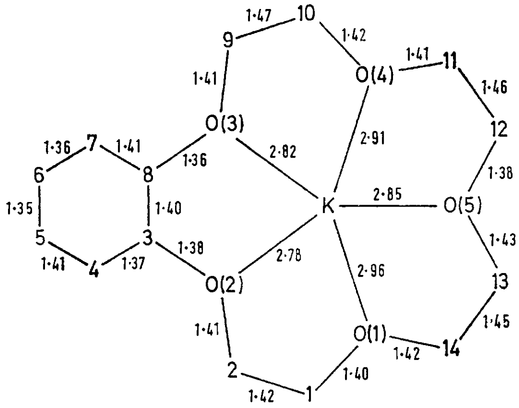


FIGURE 1 Diagram of one molecule of benzo-15-crown-5 showing the oxygen atoms designated O(n) and the carbon atoms as numbers, n, corresponding to C(n); of these C(3)—(8) inclusive form the benzene ring and C(1), C(2), and C(9)—(14) inclusive are in CH_2 groups. Bond lengths, (Å), are shown, standard deviations in the K–O bonds are 0·007—0·008 Å and in the others 0·01—0·02 Å

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* On a support designed by R. H. B. Mais and P. G. Owston, Imperial Chemical Industries Ltd.

[10] H. K. Frensdorff, *J. Amer. Chem. Soc.*, 1971, 600.

[11] D. E. Fenton, M. Mercer, N. S. Poonia, and M. R. Truter, *Chem. Comm.*, 1972, 66.

[12] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1970, **92**, 386.

[13] B. T. Kilbourn, J. D. Dunitz, L. A. R. Pioda, and W. Simon, *J. Mol. Biol.*, 1967, **30**, 559; M. Dobler, J. D. Dunitz, and B. T. Kilbourn, *Helv. Chim. Acta*, 1969, **52**, 2573.

[14] D. E. Fenton, 1970, personal communication.

[15] X-RAY ARC: IBM 1130 Program System for Crystallography, compiled by B. L. Vickery, D. Bright, and P. R. Mallinson; including least-squares program BLOK by B. L. Vickery, Fourier program FODAP by A. Zalkin and D. Bright, Picker setting program PICK 3 by W. C. Hamilton and D. Bright, data reduction program PRED by B. L. Vickery and P. R. Mallinson, mean planes program MPLN (NRC 22) by M. E. Pippy and F. R. Ahmed, intermolecular contacts program BANGL by D. Bright.

[16] IBM 360 and CDC 6600: Full-matrix least-squares program NUCLS by R. J. Doedens and J. A. Ibers; interatomic distances and errors ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy.

positions were obtained by the heavy-atom method. Two centrosymmetrically related ligand molecules ' sandwich ' each K^+ ion. The atom designations are shown in Figures 1 and 2.

Structure factors at this stage gave R 0·40 for the observed reflections, which was reduced to 0·135 after four cycles of refinement of scale, positional, and isotropic thermal parameters.[15] For the anisotropic refinement hydrogen atom positions were estimated from the molecular geometry assuming a C–H bond length of 1·084 Å for the benzo-hydrogens and 1·073 Å for the alkyl hydrogens. These were included in the calculations but not refined. The function minimised was $R' = \Sigma w(|F_o| - |F_c|)^2 = \Sigma w\Delta^2$. A weighting scheme was used in which $\sqrt{w} = 1/\{0{\cdot}5\sigma(F_o) + 1{\cdot}0 + 0{\cdot}005|F_o|\}$ if $|F_o| < 16$, and $\sqrt{w} = 1/\{0{\cdot}5\sigma(F_o) + 0{\cdot}005|F_o| + 0{\cdot}0001|F_o|^2\}$ if $|F_o| > 16$. This gave similar average values of $w\Delta^2$ for various ranges of $|F_o|$ and of $\sin\theta/\lambda$. Twenty reflections had $|F_o|$ appreciably $<|F_c|$, the agreement being consistently bad as the refinement progressed, presumably due to faulty measurement. These were removed from the data. Atomic scattering factors for C, O, and H were taken from ref. 17, and for K^+ and I^- from ref. 18. Anomalous scattering corrections were applied for I^-, the values of $\Delta f'$ and $\Delta f''$ being taken from ref. 19. The constraints on the iodine thermal parameters imposed by the special positions are $\beta_{11} = \beta_{22}$, and $\beta_{12} = \beta_{13} = \beta_{23} = 0$. After seven cycles of full-matrix anisotropic refinement[16] of the overall scale, positional, and anisotropic thermal parameters, R was 0·076. In the later cycles oscillations of the atomic positions were damped by halving the shifts.

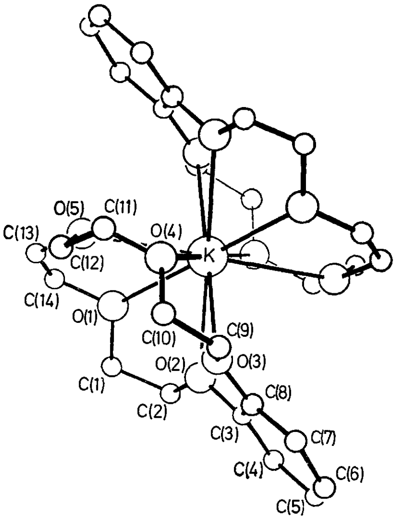

FIGURE 2 The complex cation

At this stage C(13) and C(14) had mean-square vibration amplitudes in the a^* direction of 0·25 Å^2 and the C–C bond length was anomalously short at 1·24 Å, with the O–C–C angles large at 123 and 126°. These atoms are presumably disordered, although no peaks corresponding to alternative positions were found in a high-resolution difference map. The C(13) and C(14) positions were adjusted so as to leave the C(13)–C(14) torsion angle unchanged but alter the bond length to 1·45 Å, the mean value of the C(9)–C(10), C(11)–C(12), and C(1)–C(2) lengths. C(13) and C(14) were then assigned isotropic temperature factors of 8 Å^2, equivalent to $U = 0{\cdot}10$ Å^2, which were not subsequently refined. This adjustment increased R to 0·092. Two further cycles brought this to the final value of 0·090 for the 1603 observed reflections. In the final cycle all shifts were $<0{\cdot}34\sigma$. The nine cycles of anisotropic refinement had reduced $\Sigma w\Delta^2$ from $0{\cdot}173 \times 10^5$ to $0{\cdot}300 \times 10^4$ (on relative scale) with a change of only $0{\cdot}002 \times 10^4$ in the final cycle. The final standard deviation of an observation of unity weight was 1·4, indicating that the weighting scheme gave a fair estimation of absolute weights.

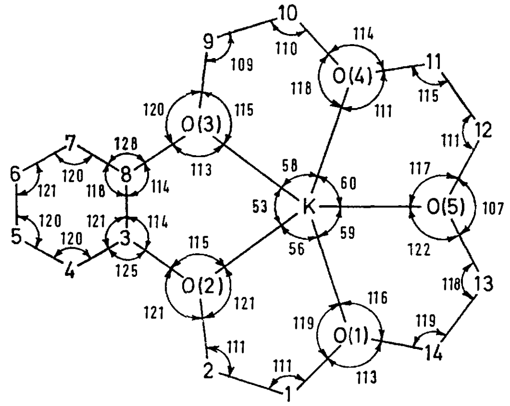

FIGURE 3 Bond angles; the designations of the atoms are as in Figure 1. Standard deviations are 0·2 O–K–O, 0·6—0·7 K–O–C, and 1° for C–C–O, C–O–C, and C–C–C

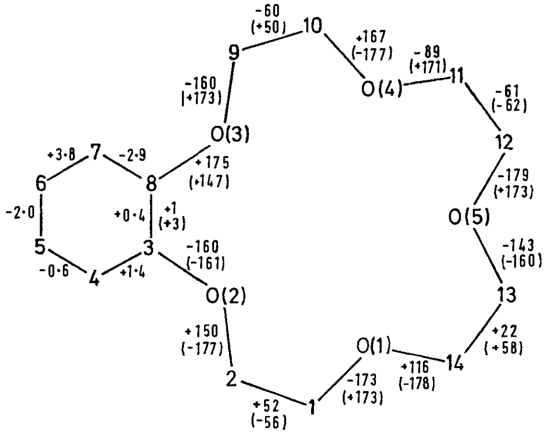

FIGURE 4 Torsion angles: values in parentheses are the corresponding ones in (benzo-15-crown-5)(H_2O)NaI;[8] both are for a molecule complexed to a metal ion above the plane of the paper

RESULTS

Atomic co-ordinates and thermal parameters with their estimated standard deviations are given in Tables 1 and 2. For the hydrogen atoms an isotropic temperature factor with $B = 7{\cdot}0$ Å^2, equivalent to $U = 0{\cdot}09$ Å^2, was used. The observed and calculated structure factors for the 1603 observed reflections are listed in Supplementary Publication No SUP 20456 (11 pp., 1 microfiche).* Bond lengths and angles are in Figures 1 and 3. The standard deviations were

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[17] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 202—206.

[18] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[19] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

Table 1

Fractional atomic co-ordinates ($\times 10^4$). Numbers in parentheses are the standard deviations in the least significant digits, unless the co-ordinate was not refined. Hydrogen atoms are designated by the numbers of the carbon atoms to which they are attached.

	x/a	y/b	z/c
I(1)	2500	7500	0
I(2)	2500	2500	1746(2)
C(1)	6705(7)	3848(7)	6127(17)
C(2)	6737(7)	3880(6)	4670(15)
C(3)	6674(5)	4882(6)	2988(12)
C(4)	7055(6)	4515(6)	1968(13)
C(5)	7295(6)	4913(8)	802(13)
C(6)	7143(6)	5650(7)	692(11)
C(7)	6738(5)	6019(6)	1670(13)
C(8)	6507(5)	5644(5)	2870(11)
C(9)	5990(6)	6715(6)	4028(13)
C(10)	5847(6)	6930(6)	5457(13)
C(11)	5139(8)	6569(7)	7404(15)
C(12)	5545(9)	5990(9)	8168(14)
C(13)	5712	4767	8655
C(14)	5937	4057	8053
O(1)	5979(5)	3990(5)	6600(8)
O(2)	6425(4)	4558(4)	4185(9)
O(3)	6143(4)	5937(4)	3971(8)
O(4)	5219(4)	6525(4)	5973(8)
O(5)	5294(5)	5281(4)	7832(8)
K	5000	5000	5000
H(1)	6971	3338	6535
H(1)	7103	4308	6500
H(2)	6431	3376	4314
H(2)	7320	3787	4301
H(4)	7232	3915	2080
H(5)	7565	4605	−71
H(6)	7370	5952	−203
H(7)	6611	6627	1487
H(9)	6474	7058	3633
H(9)	5517	6897	3391
H(10)	5723	7557	5493
H(10)	6337	6856	6044
H(11)	4529	6413	7647
H(11)	5241	7080	7801
H(12)	5586	6055	9288
H(12)	6167	5972	7854
H(13)	5733	4810	9604
H(13)	6360	4999	8272
H(14)	5183	3919	8212
H(14)	6105	3753	8734

Table 2

Anisotropic vibration parameters, ($\times 10^3$) Å^2, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + U_{22}k^2b^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + U_{33}l^2c^{*2})]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	79(1)	79(1)	157(2)	0	0	0
I(2)	63(1)	63(1)	75(1)	0	0	0
C(1)	77(9)	70(8)	107(12)	13(7)	−5(9)	19(8)
C(2)	83(9)	59(7)	94(11)	23(6)	12(8)	22(7)
C(3)	44(6)	60(7)	67(8)	3(5)	8(6)	3(6)
C(4)	44(6)	64(7)	84(9)	7(5)	−6(6)	−7(7)
C(5)	62(8)	96(10)	62(9)	2(7)	5(6)	−12(8)
C(6)	65(8)	80(9)	52(7)	−7(6)	10(6)	−11(7)
C(7)	54(6)	75(7)	54(7)	−4(5)	−13(6)	15(7)
C(8)	42(5)	55(6)	56(8)	−5(5)	−5(5)	8(5)
C(9)	74(8)	45(6)	77(9)	−5(5)	−1(6)	8(6)
C(10)	67(8)	61(7)	74(9)	−18(6)	−10(7)	−3(6)
C(11)	148(13)	74(9)	64(9)	16(8)	5(9)	−14(8)
C(12)	142(13)	117(12)	60(9)	2(10)	−31(9)	−23(9)
C(13)	101					
C(14)	101					
O(1)	119(7)	106(6)	44(5)	14(5)	−13(5)	15(5)
O(2)	75(5)	64(5)	101(7)	22(4)	42(5)	34(5)
O(3)	69(5)	50(4)	80(6)	11(4)	19(4)	9(4)
O(4)	82(5)	62(5)	53(5)	−2(4)	−5(4)	−10(4)
O(5)	132(7)	69(5)	57(6)	15(5)	−19(5)	−3(4)
K	42(2)	47(2)	47(2)	−4(1)	−2(2)	1(2)

calculated [16] from those in the co-ordinates in Table 1 with allowance for correlation and for the σ values of the cell dimensions. Torsion angles of the ring bonds are in Figure 4. Figure 5 is a projection of the structure along [001].

DISCUSSION

The complex cation has ten oxygen atoms in an irregular pentagonal antiprism configuration around the potassium. It possesses crystallographic symmetry $\bar{1}$, with approximate symmetry $2/m$, because each ligand molecule has an approximate mirror plane perpendicular to the oxygen plane. The deviations from symmetry $2/m$ are shown most sensitively by the torsion angles of the ring bonds (Figure 4). The cation in the 1 : 2 KI complex is 1·67 Å from the mean plane of the oxygens, as compared with 0·75 Å in the 1 : 1 complex NaI(benzo-15-crown-5). The largest deviation p_i of an oxygen atom from this plane is 0·126(7) Å, the value of $\chi^2 = \sum_i[p_i^2/\sigma^2(p_i)]$ being 925. The benzo-group is nearly coplanar with the oxygens, the greatest deviation being C(6) 0·11(1) Å. The benzo-group atoms themselves show no significant deviation from coplanarity. The alkyl carbons are all on the opposite side of this plane to the cation, whereas in the corresponding sodium iodide complex two alkyl carbons are on the same side of the oxygen plane as the cation.[8]

Figure 4 shows the torsion angles of the polyether bonds in both the sodium iodide and potassium iodide complexes. These are similar except for two sets of four bonds from O(3) to C(11) and from O(2) to C(14). Hence the conformation differs from that of the Na^+ complex in the positions of C(10) and C(1). The torsion angles round the benzene ring, ideally zero, give an estimate of the experimental error which agrees with the figure 2—3° calculated for the estimated standard deviation in torsion angles in other cyclic ether complexes.[7]

The stereogram (Figure 6) shows the directions of the O–K bonds and of the oxygen lone-pairs, trigonal or tetrahedral, which make the smallest angles with the respective bond directions. For each oxygen–potassium bond there is an oxygen lone-pair in a direction inclined not more than 21° to the bond direction. The C–O–C bond angles at O(2) and O(3), the catechol oxygens, are 121 and 120° respectively, so trigonal co-ordination might be expected. In the case of O(2) it is the sp^2 lone-pair which is closest to the bond direction. However, for the O(3)–K bond one of the sp^3 lone-pairs is closer. O(1), O(4), and O(5) are nearly tetrahedrally co-ordinated (C–O–C bond angles 113, 114, and 107°) and these all have one of their sp^3 lone-pair directions closest to the O–K bond.

The five O–K bond lengths (Figure 1 and Table 4) are all significantly different from one another, ranging from 2·777(7)—2·955(8) Å. The two shortest are those from the catechol oxygens. The lengths compare with 2·85—2·93 Å in KI(dibenzo-30-crown-10).[1] Only two of the five O–K–O angles in the asymmetric unit do not

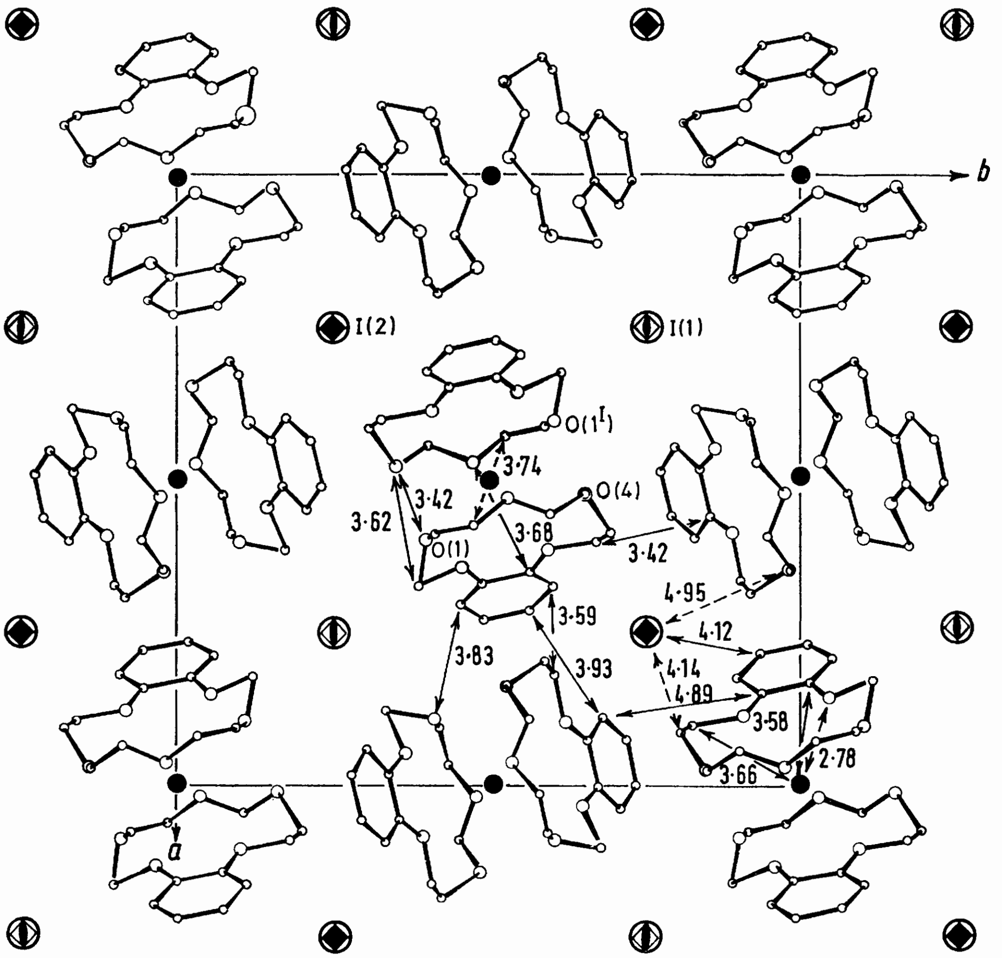

FIGURE 5 Projection of the structure down [001]. The designations of a few atoms are shown. Distances (Å) between atoms are shown along arrows connecting the atoms. Broken lines indicate translation ±1 along *c*. Filled circles represent potassium ions on centres of symmetry

differ significantly, O(4)–K–O(5) and O(1)–K–O(5). The smallest O–K–O angle for which the oxygens are in different halves of the ' sandwich ' is 71°, O(1)–K–O(4^{I}) and the largest is 180°, between each pair of centrosymmetrically related oyygens.

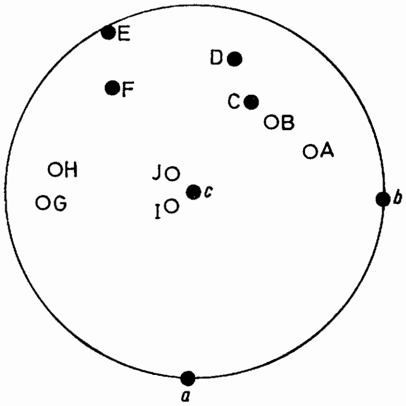

FIGURE 6 Stereogram showing the crystallographic axes, O–K bond directions, and the oxygen sp^3 or sp^2 orbital directions which make the smallest angles with the respective bond direction. Poles A and B represent O(1) sp^3 and O(1)–K; C and D O(2) sp^2 and O(2)–K; E and F O(3) sp^3 and O(3)–K; G and H O(4) sp^3 and O(4)–K; I and J O(5) sp^3 and O(5)–K

TABLE 3

Deviations (Å) of the atoms from the plane through the oxygen atoms

Equation of the plane:

$$-0{\cdot}852x - 0{\cdot}294y - 0{\cdot}433y + 14{\cdot}000 = 0$$

O(1) +0·03, O(2) +0·08, O(3) −0·12, O(4) +0·13, O(5) −0·12, K +1·67, C(1) −0·80, C(2) −0·25, C(3) +0·04, C(4) +0·08, C(5) −0·00, C(6) −0·11, C(7) −0·10, C(8) −0·06, C(9) −0·32, C(10) −0·82, C(11) −0·38, C(12) −1·01, C(13) −0·83, C(14) −0·55]

The bond lengths and angles in the ligand are similar to those found previously in cyclic ether complexes but dimensions depending upon the atoms C(13) and C(14) must be excluded from the discussion. The mean aromatic C–C bond length, 1·38(1) Å is not significantly different from that in benzene, the aliphatic C–C bonds show the shortening found in other cyclic ethers [1,6-8] and the C(sp^2)–O bonds are shorter than the C(sp^3)–O bonds. The only remarkable bond angles are the four C–C–O angles involving aromatic carbon atoms; angles endocyclic to the polyether ring are equal, mean 114·3(6)°, while the mean of the exocyclic ones, also equal, is 126·5(6)°. The polyether ring clearly imposes some distortion on the trigonal configuration of C(3) and C(8), although there is no significant deviation from coplanarity of their bonds. This has been found in both complexed and uncomplexed macrocyclic ethers derived from catechol.[1,6-8]

TABLE 4

Environment of the potassium ion

(*a*) Bond lengths (Å), O(*n*)–K

O(1)–K	2·955(8)	O(4)–K	2·908(7)
O(2)–K	2·777(7)	O(5)–K	2·855(8)
O(3)–K	2·821(7)		

(*b*) Bond angles (°), O(*n*)–K–O(*m*). $O(1^{I})$ *etc.* are related to O(1) *etc.* by the inversion centre at K

	O(1)	O(2)	O(3)	O(4)	O(5)
O(1)					
O(2)	55·7(2)				
O(3)	97·0(2)	53·5(2)			
O(4)	108·6(2)	103·7(2)	57·6(2)		
O(5)	59·2(2)	99·1(2)	96·1(2)	59·7(2)	
$O(1^{I})$	180·0				
$O(2^{I})$	124·3(2)	180·0			
$O(3^{I})$	83·0(2)	126·5(2)	180·0		
$O(4^{I})$	71·4(2)	76·3(2)	122·4(2)	180·0	
$O(5^{I})$	120·8(2)	80·9(3)	83·9(2)	120·3(2)	180·0

Intermolecular Contacts.—The shortest distances (Figure 5) between atoms in different molecules or between the two ligand molecules belonging to the same cation are CH · · · CH 3·93, CH · · · CH_2 3·59, CH · · · C 4·89, CH · · · O 3·83, CH_2 · · · CH_2 3·74, CH_2 · · · C 3·42, CH_2 · · · O 3·62, C · · · O 3·68, and O · · · O 3·42 Å. These are consistent with intermolecular forces of the van der Waals' type, and it therefore seems possible that such packing forces relate the two halves of the cation ' sandwich ' with the spherical potassium ion occupying a space with no covalent character in the bonding. The shortest contacts which it makes are CH_2 · · · K 3·66, C · · · K 3·58, and O · · · K 2·78 Å.

The iodide anions occupy the spaces between the complex cations, situated at van der Waals' distances from them, *viz.* CH · · · I 4·12, CH_2 · · · I 4·14, and O · · · I 4·95 Å. There is no interaction between K^+ and I^-. All other intermolecular contacts (not involving hydrogen) are >5·0 Å.

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