The Crystal Structure of 1,4,7,14,17,20,28,35-Octaoxa[2^{3,29}.2^{18,34}][7.7]-orthocyclophane and its Multihydrated Complex with Potassium Chloride

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Crystal structures of a bridged crown ether (I), systematically named in the title, and its complex with potassium chloride (II) have been determined by X-ray diffraction. Observations were collected on a four-circle diffractometer. Compound (I) is monoclinic, a = 11.539(2), b = 9.558(3), c = 22.802(7) Å, β = 98.19(2)° with space group $P2_1/c$. Compound (II) crystallises with eight complex cations [K(I)]$^+$, eight chloride ions, and 44 water molecules in a monoclinic unit cell, a = 22.578(6), b = 17.162(5), c = 16.742(5) Å, β = 99.48(2)° and space group $I2/c$. Full matrix refinement of (I) led to an R value of 0.066 for 1 775 observed reflections. The molecule has no symmetry, the conformation of the portion from O(1) to O(7) is unusual, unfavourable torsion angles may be correlated with inter-, but not with intra-molecular O $\cdots$ HC contacts. Part of the structure exhibits disorder, one oxygen atom O(28) was allowed partial occupancy of two sites, and the benzene ring to which it is attached was allowed anisotropic vibration parameters as were all the oxygen atoms. The structure of (II) consists of complex cations which have a non-crystallographic plane of symmetry. Co-ordination about the potassium ion approximates to an end-capped trigonal prism, K–O distances to the capping atoms (CH$_2$–O–CH$_2$) average 2.687 Å, and those for the other atoms average 2.733 Å. There are no interactions between the anions or water molecules and the potassium ions, or the eight oxygen atoms of the ligand. The cations are packed, with contacts of normal van der Waals distances, to form channels parallel to the c axis of the crystal. In these channels chloride ions, mainly disordered over two sites, and water molecules, also disordered, form networks which cannot be uniquely determined. Full matrix refinement gave an R value of 0.104 for 2 138 observed reflections. In this the potassium ion and the carbon atoms of one benzene ring were allowed anisotropic vibration; the other atoms of the cation were allowed isotropic vibration parameters while the disordered atoms were all assumed to have mean square isotropic vibrations of 0.25 Å^2 and their occupation numbers were treated as parameters.

A RECENT advance by our group in systematic study of the co-ordination chemistry of alkali and alkaline earth metal cations has been the design and synthesis of novel macrobicyclic polyethers.[1] Like the cryptates[2] they can form complexes with alkali metal salts having high formation constants even in aqueous solution but, unlike the cryptates, there are no nitrogen atoms giving sensitivity to pH. Further compounds in the series have now been synthesised and their behaviour as ligands is under investigation.[3]

Characteristic features are that the compounds themselves are not soluble in water but are solubilised by alkali metal salts, and the complexes crystallise with large and non-stoicheiometric numbers of molecules of water of crystallisation; even if the crystals are dried over sodium hydroxide in a desiccator, or in an oven, they increase in weight while being weighed open to the atmosphere.

For a given molecule the i.r. spectra of (1 : 1) complexes with different salts are the same in the fingerprint region, and indicate a conformation different from that of the free molecule. As shown in a preliminary communication[4] stoicheiometries other than 1 : 1 are possible for large cations. The formation constants also showed that substitution of two methylene groups by a benzene ring did not lead to a decrease in formation constant unlike the usual behaviour of monocyclic crown ethers.[5] We reported there[4] the crystal structure of the complex of the title compound (I) with potassium chloride, and showed the formula to be KCl(I)nH$_2$O; the crystal contains discrete [K(I$^+$)]$^+$ cations and disordered columns of water molecules and anions in sites of partial occupation. The structure is consistent with the conformation of the complex cation being independent of the anion. We now report the full results for the structure analysis of the complex and, for comparison, the crystal structure of the uncomplexed molecule which, as expected, does not have the same conformation. In

fact it shows two conformations in the crystal, neither of which can be accurately determined because the crystal structure is a space average of them.

For both compounds observations were collected on the same instrument so the experimental details are reported for the free ligand with those of the complex in parentheses.

EXPERIMENTAL

Compound (I) was obtained from acetone as colourless needles, one of which, $0.15 \times 0.2 \times 0.45$ mm elongated along the b axis, was used for intensity measurements.

[It was difficult to find a good crystal of (II), the large rhombs tended to shatter when cut; a fragment $0.3 \times 0.1 \times 0.09$ mm (elongated parallel to the a axis) was mounted on the diffractometer and found to give good diffraction with a small mosaic spread.]

Unit cell dimensions and intensities were measured on an Enraf–Nonius CAD4 diffractometer with monochromated Mo-K_α radiation, $\lambda = 0.710\ 69$ Å (1 Å $\equiv 10^{-10}$ m).

Crystal Data.—(I), $C_{28}H_{30}O_8$, $M = 494.6$. Monoclinic, $a = 11.539(2)$, $b = 9.558(3)$, $c = 22.802(7)$ Å, $\beta = 98.19(2)°$, $U = 2\ 489(1)$ Å^3, $D_m = 1.32$ g cm^{-3}, $Z = 4$, $D_c = 1.32$ g cm^{-3}, $F(000) = 104\ 8$. Space group $P2_1/c$ uniquely determined.

[*Crystal Data.*—(II), $C_{28}H_{30}O_8$,KCl,nH$_2$O, $M = 659.2$ ($n = 5$). Monoclinic, $a = 22.578(6)$, $b = 17.162(5)$, $c = 16.742(5)$ Å, $\beta = 99.48(2)°$, $U = 6\ 398.7$ Å^3, D_m $1.35(1)$ g cm^{-3}, $Z = 8$, D_c ($n = 5$) 1.368, D_c ($n = 4.5$) 1.349 g cm^{-3}. Space group $I2/c$ or Ic from systematic absences (non-standard settings of $C2/c$ or Cc), $I2/c$ by structure analysis; equivalent positions $\pm(x,\ y,\ z;\ x,\ -y,\ \frac{1}{2} + z;\ \frac{1}{2} + x,\ \frac{1}{2} + y,\ \frac{1}{2} + z;\ \frac{1}{2} + x,\ \frac{1}{2} - y,\ z).$]

Unit cell dimensions were refined from 25[24] reflections. The crystal quality was tested and the scan width set to
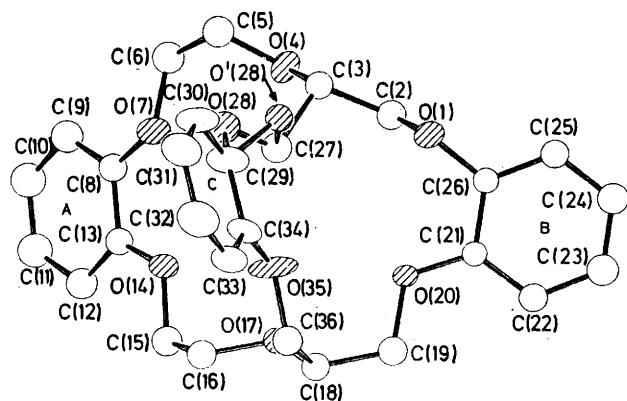

FIGURE 1 The designations of the atoms of the bicyclic compound in the cyclophane system. Letters A—c denote benzene rings. Hydrogen atom H(n) is attached to carbon C(n). The conformation is that of the uncomplexed molecule (I) showing alternative sites for O(28). Atoms subject to anisotropic refinement are shown as ellipsoids at the 30% confidence level by means of the program ORTEP [10]

$(0.8 + 0.35 \tan \theta)° [(1.0 + 0.35 \tan \theta)°]$. A prescan speed of $2°$ min^{-1} was used and weaker reflections collected for up to three times as long as strong ones; backgrounds were counted each side of the scan. Reference reflections $(11\bar{5})$ and $(1, 1, 11)$ $[(11\bar{4})$ and $(2\bar{2}6)]$ were measured every 2 h during the course of data collection; in 5 days [3 weeks] no

change was found. For (I) each reflection in the range $1 \leqslant \theta \leqslant 22°$ was scanned twice; 3 043 unique reflections were measured of which 1 775 had $|F_0| \geqslant 3\sigma_F$ and were considered ' observed '. [For (II) two quadrants, hkl and $h\bar{k}l$, were measured, each reflection in the range $1.5 < \theta < 22°$ being scanned once, after averaging 3 918 unique reflections were obtained of which 2 138 having $|F_0|->2\sigma_F$ were considered ' observed ']. While all unique reflections were used in SHELX to determine the approximate scale and E values for direct methods, only the ' observed ' were used for structure factor calculation and parameter refinement.

Computer programs were the CAD4 processing [6] and the SHELX suite [7] for structure determination and refinement run on the ICL system 4 of Rothamsted Experimental Station, while for molecular geometry the X-RAY ARC programs [8] for the IBM 1 130 were used. Scattering factors were calculated using the analytical approximation coefficients given in Table 2.2B of ref. 9 for K$^+$, Cl$^-$, C, H, and O (water molecules also being treated as O).

Structure Determination of (I).—A multisolution direct methods program gave one set of signs for the 346 E values greater than 1.2 and all the non-hydrogen atoms appeared in the corresponding E map.

The numbering adopted in both compounds is shown in Figure 1 which depicts the configuration of the molecule in (I). Refinement with isotropic vibration parameters gave R 0.14. An electron density difference map showed features attributable to hydrogen atoms in geometrically likely positions and also a peak, 3 eÅ^{-3}, close to O(28) and out of the plane of ring c, the atoms of which appeared to be undergoing very anisotropic vibration, the main displacement being normal to the plane of the ring. Experiments with CPK models involving rotation about the bonds C(3)–C(27) and C(18)–C(36) indicated that several conformations were possible, two of which resulted in approximately parallel displacement of atoms O(28) $\cdots$ O(35) inclusive along the normal to ring c. Various possibilities were examined in successive least squares refinements; the best approximation to the electron density distribution was found by allowing anisotropic vibration for atoms C(27) and C(29)— C(36) inclusive and partial occupation of two sites for O(28) designated O(28) and O'(28) as shown in Figure 1. As these two sites correspond to different orientation of the bonds about C(27) there are two hydrogen atoms corresponding to O(28), H(27A) and H(27B), and two corresponding to O'(28), H(27C) and H(27D). The occupation number of O(28) was a parameter, those of O'(28) and the hydrogen atoms of C(27) being adjusted accordingly. Hydrogen atoms were fixed at 0.98 Å from the corresponding carbon atom in geometrically calculated positions, their isotropic vibration parameters were linked in groups, i.e. on ring A, on ring B, on ring c, on CH$_2$ groups [other than C(27)] while for H(27A—D) a fixed value 0.09 Å^2 was used. Refinement was considered complete when the largest shift in a parameter was less than 0.04 of the corresponding standard deviation. R Was then 0.066, R' with unit weights was 0.062, and there was a uniform distribution of R' in $|F_0|$ or sin θ/λ. In the final electron density difference map the largest peak was 0.6 eÅ^{-3} and the deepest ' hole ' 0.3 eÅ^{-3}; every peak was within 0.8 Å of at least one of the atoms so there was no evidence for any solvent molecule.

In the full matrix refinement, as might be expected, the occupation number of O(28) was highly correlated with the isotropic vibration parameters of O(28) and O'(28); the

other correlation coefficients greater than 0.5 were for $O(35)$, U_{13} being correlated with U_{11} and U_{33}.

Atomic co-ordinates and vibration parameters are in Table 1; those for hydrogen atoms have been deposited in Supplementary Publication No. SUP 22903 (37 pp.) * with the Tables of structure factors.

Structure Determination of (II).—Systematic absences corresponded to space groups $I2/c$ or Ic (non-standard settings of $C2/c$ and Cc). A three-dimensional Patterson synthesis revealed one set of peaks corresponding to an atom at $0.4,0,-0.1$ and sufficient peaks in the Harker section at $V = 0$ to suggest the presence of a two-fold axis. As K^+ and Cl^- have nearly the same scattering powers, a more complicated synthesis was expected corresponding to two independent heavy atoms and vectors between them. Direct methods yielded a solution with one most electron-dense atom; the E statistics corresponded to a centric distribution.

This one atom was used to phase a Fourier synthesis despite a high R value, 0.54, and the electron density map clearly showed eight oxygen atoms of the bicyclic molecule round the heavy atom, now identified as the potassium ion. One cycle of isotropic refinement and a difference synthesis revealed the remaining atoms of the cationic complex, shown in Figure 2. Isotropic refinement yielded R 0.18, and a difference synthesis showing seven peaks at *ca.* 3 eÅ^{-3} and many smaller ones in positions which corresponded to hydrogen atoms of the complex cation.

Inclusion of the hydrogen atoms led to smooth refinement of the parameters of the cationic complex, but difference synthesis did not reveal any peak which could be assigned to the chloride ion; a number of peaks did appear, *ca.* 1 Å apart and with heights ranging from 1.1 to 2.6 eÅ^{-3}. It was clear that these represented sites partially occupied by
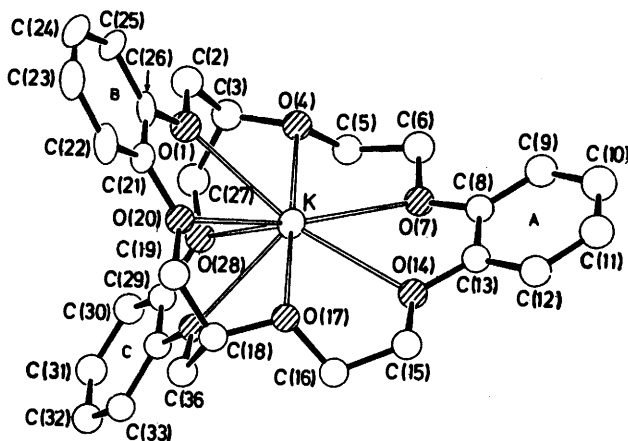

FIGURE 2 The complex cation in (II) showing the observed conformation with the ellipsoids at the 30% confidence level for the potassium and the carbon atoms of ring B

water molecules and by chloride ions; the problem then became one of refining the parameters of the atoms of the complex cation and obtaining the best representation of the electron density in the disordered sites, in the knowledge that these aspects are not independent, and that the number of parameters which could be handled by the SHELX programs is 319, quite as many as can be determined from 2 138 observations. For the complex cation possible

anisotropic vibration was checked. In one cycle the anisotropic vibration parameters of the oxygen atoms and the potassium ion were determined; the former were nearly isotropic and assumed to be so subsequently. Next the carbon atoms of the benzene rings were allowed anisotropic vibration; only for ring B were they significantly different from those for isotropic vibration so final refinement allowed anisotropic parameters for K^+ and for ring B. The small

TABLE 1

(a) Atomic co-ordinates (fractional $\times$ 10^4) for (I), the macrobicyclic compound. Isotropic vibration parameters U_{iso} (Å^2 $\times$ 10^3). Here and throughout the paper the standard deviations in the least significant digits are in parentheses

Atom	x	y	z	U_{iso}
O(1)	6 016(4)	4 415(4)	4 344(2)	
C(2)	5 228(5)	5 299(7)	3 981(3)	53(2)
C(3)	3 986(5)	5 024(7)	4 113(3)	46(2)
O(4)	3 285(4)	5 979(4)	3 744(2)	
C(5)	2 085(6)	6 016(8)	3 837(3)	61(2)
C(6)	1 324(6)	6 119(7)	3 259(3)	62(2)
O(7)	1 447(4)	4 847(5)	2 943(2)	
C(8)	890(5)	4 745(7)	2 378(3)	50(2)
C(9)	−50(6)	5 575(8)	2 141(3)	64(2)
C(10)	−540(7)	5 366(9)	1 557(3)	76(2)
C(11)	−121(7)	4 420(8)	1 210(4)	73(2)
C(12)	842(6)	3 564(7)	1 436(3)	60(2)
C(13)	1 319(5)	3 719(7)	2 027(3)	47(2)
O(14)	2 213(4)	2 294(5)	2 315(2)	
C(15)	2 617(6)	1 762(7)	2 002(3)	56(2)
C(16)	3 339(5)	835(7)	2 437(3)	53(2)
O(17)	4 434(3)	1 475(4)	2 631(2)	
C(18)	5 271(5)	555(7)	2 942(3)	48(2)
C(19)	6 385(5)	1 371(7)	3 088(3)	53(2)
O(20)	6 250(3)	2 491(4)	3 495(2)	
C(21)	7 228(5)	3 205(6)	3 726(3)	38(2)
C(22)	8 332(5)	2 976(7)	3 581(3)	50(2)
C(23)	9 291(6)	3 741(7)	3 856(3)	61(2)
C(24)	9 143(6)	4 723(7)	4 271(3)	59(2)
C(25)	8 049(5)	4 952(7)	4 427(3)	50(2)
C(26)	7 089(5)	4 223(6)	4 154(3)	40(2)
C(27)	3 682(6)	3 504(6)	3 946(3)	
O(28)	2 854(7)	2 869(7)	4 248(3)	60(3)
O'(28)	3 710(12)	2 925(13)	4 576(6)	44(5)
C(29)	3 166(7)	1 512(7)	4 525(3)	
C(30)	2 607(7)	1 204(7)	5 001(3)	
C(31)	2 601(7)	−134(8)	5 216(3)	
C(32)	3 181(7)	−1 144(8)	4 960(4)	
C(33)	3 759(7)	−853(7)	4 490(3)	
C(34)	3 759(6)	472(6)	4 260(3)	
O(35)	4 274(5)	839(5)	3 783(2)	
C(36)	4 839(6)	−167(7)	3 466(3)	55(2)

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

Atom	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
O(1)	53(3)	45(3)	50(3)	11(2)	10(2)	2(2)
O(4)	44(3)	35(3)	95(4)	6(3)	17(2)	8(2)
O(7)	66(3)	49(3)	62(3)	14(2)	10(2)	−5(2)
O(14)	53(3)	54(3)	56(3)	9(2)	2(2)	−17(2)
O(17)	40(2)	44(3)	60(3)	−2(2)	6(2)	−12(2)
O(20)	37(2)	40(3)	69(3)	3(2)	9(2)	−21(2)
C(27)	70(5)	28(4)	72(5)	−6(4)	18(4)	5(4)
C(29)	118(7)	23(4)	80(6)	−6(4)	42(5)	2(4)
C(30)	121(7)	42(5)	74(6)	−7(4)	58(5)	−6(5)
C(31)	111(7)	54(5)	62(5)	−16(4)	27(5)	6(5)
C(32)	114(7)	41(5)	74(6)	−7(4)	21(5)	22(5)
C(33)	85(6)	28(4)	66(5)	1(4)	16(4)	1(4)
C(34)	81(5)	23(4)	52(4)	−8(3)	18(4)	−2(4)
O(35)	146(5)	29(3)	90(4)	14(3)	78(4)	−1(3)

departure from isotropic vibration suggests that the cations are not disordered and, in particular, that they truly have the space group symmetry $I2/c$. This space group was retained in treatment of the disordered atoms; co-ordinates

could only be obtained reliably from difference maps, as shown by attempted refinement, so these were fixed. If all the peaks were treated as oxygen, with occupation numbers fixed at 0.5 and their isotropic vibration parameters allowed

TABLE 2

(a) Atomic co-ordinates (fraction $\times 10^4$) for the complex with potassium chloride. W represents a water molecule, A and B distinguish alternative sites; the last column is the site occupation number. Isotropic vibration parameters U_{iso} ($\text{Å}^2 \times 10^3$)

Atom	x	y	z	U_{iso}
K	3 298(1)	−675(1)	1 318(2)	
O(1)	2 934(4)	−843(5)	2 034(5)	69(2)
C(2)	2 508(6)	−226(7)	1 902(7)	75(4)
C(3)	2 565(5)	207(7)	1 158(7)	69(4)
O(4)	3 156(3)	524(4)	1 276(4)	61(2)
C(5)	3 288(5)	1 047(7)	666(7)	65(3)
C(6)	3 888(5)	1 403(7)	954(7)	72(4)
O(7)	4 332(3)	774(4)	978(4)	63(2)
C(8)	4 925(5)	954(7)	1 240(6)	57(3)
C(9)	5 141(6)	1 689(7)	1 470(7)	75(4)
C(10)	5 747(6)	1 796(8)	1 718(8)	89(4)
C(11)	6 133(6)	1 206(7)	1 744(7)	84(4)
C(12)	5 937(6)	451(7)	1 520(7)	72(4)
C(13)	5 315(5)	333(7)	1 267(6)	58(3)
O(14)	5 066(3)	−385(4)	1 035(4)	62(2)
C(15)	5 458(5)	−1 045(6)	1 074(7)	65(3)
C(16)	5 082(5)	−1 736(6)	825(7)	61(3)
O(17)	4 703(3)	−1 871(4)	1 410(4)	56(2)
C(18)	4 358(5)	−2 567(7)	1 327(6)	59(3)
C(19)	4 059(5)	−2 645(7)	2 052(7)	68(4)
O(20)	3 674(3)	−1 992(4)	2 088(4)	61(2)
C(21)	3 318(6)	−1 978(8)	2 693(7)	
C(22)	3 349(7)	−2 517(8)	3 301(8)	
C(23)	2 971(9)	−2 424(11)	3 864(9)	
C(24)	2 578(8)	−1 804(13)	3 823(10)	
C(25)	2 553(6)	−1 277(9)	3 221(8)	
C(26)	2 923(6)	−1 359(8)	2 647(7)	
C(27)	2 389(5)	−230(7)	355(7)	75(4)
O(28)	2 852(3)	−800(4)	295(4)	63(2)
C(29)	2 732(5)	−1 355(6)	−307(7)	55(3)
C(30)	2 236(5)	−1 297(7)	−935(7)	68(4)
C(31)	2 158(6)	−1 898(7)	−1 487(7)	71(4)
C(32)	2 537(5)	−2 504(7)	−1 458(7)	65(3)
C(33)	3 034(5)	−2 563(7)	−837(6)	57(3)
C(34)	3 112(5)	−1 969(6)	−267(6)	53(3)
O(35)	3 586(3)	−1 958(4)	381(4)	55(2)
C(36)	3 955(5)	−2 636(7)	517(7)	65(3)
ClA	−1 122	280	6 286	250 0.59
ClB	−1 054	61	7 205	250 0.41
W(1)A	763	873	5 894	250 0.62
W(1)B	657	692	6 538	250 0.47
W(2)A	473	1 370	3 623	250 0.37
W(2)B	472	1 346	2 895	250 0.62
W(3)A	461	1 389	4 861	250 0.88
W(3)B	−16	1 391	4 318	250 0.24
W(4)A	−907	543	4 586	250 0.55
W(4)B	−732	396	5 350	250 0.43
W(5)A	−1 092	956	3 100	250 0.53
W(5)B	−978	915	3 881	250 0.49
W(6)	126	729	7 199	250 (0.50)

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

Atom	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
K	50(2)	61(2)	65(2)	1(1)	8(1)	7(1)
C(21)	64(9)	73(9)	42(8)	−24(7)	10(7)	3(8)
C(22)	90(11)	96(11)	56(9)	−51(9)	−2(9)	18(9)
C(23)	123(16)	130(16)	43(9)	−81(10)	14(11)	1(13)
C(24)	91(14)	168(19)	60(11)	−71(13)	42(10)	−39(13)
C(25)	68(10)	120(12)	39(7)	−37(8)	23(7)	−10(9)
C(26)	68(10)	72(10)	45(8)	−45(7)	0(7)	3(8)

to vary, it became clear that the two peaks of highest electron density corresponded to fractional chloride ions Cl(A) and Cl(B). In the next cycle of refinement, the appropriate scattering factors were used for these two

TABLE 3

(a) Bond lengths (Å)

	(I)	(II)		(1)	(II)
C(23)−C(24)	1.361(9)	1.38(2)	C(21)−C(26)	1.404(8)	1.38(2)
C(24)−C(25)	1.378(8)	1.35(2)	C(23)−C(22)	1.398(9)	1.38(2)
C(25)−C(26)	1.380(8)	1.38(2)	C(22)−C(21)	1.378(8)	1.37(2)
C(26)−O(1)	1.381(7)	1.36(1)	C(21)−O(20)	1.380(7)	1.39(1)
O(1)−C(2)	1.419(7)	1.42(1)	O(20)−C(19)	1.440(7)	1.43(1)
C(2)−C(3)	1.529(8)	1.48(2)	C(19)−C(18)	1.500(8)	1.49(1)
C(3)−O(4)	1.415(7)	1.43(1)	C(18)−O(17)	1.419(7)	1.42(1)
O(4)−C(5)	1.431(7)	1.43(1)	O(17)−C(16)	1.417(7)	1.42(1)
C(5)−C(6)	1.480(8)	1.49(1)	C(16)−C(15)	1.492(9)	1.48(1)
C(6)−O(7)	1.430(8)	1.47(1)	C(15)−O(14)	1.434(7)	1.43(1)
O(7)−C(8)	1.360(7)	1.37(1)	O(14)−C(13)	1.372(7)	1.38(1)
C(8)−C(9)	1.390(9)	1.38(2)	C(13)−C(12)	1.389(8)	1.41(2)
C(9)−C(10)	1.385(8)	1.38(2)	C(12)−C(11)	1.416(9)	1.40(2)
C(10)−C(11)	1.337(10)	1.33(2)	C(13)−C(8)	1.399(8)	1.38(1)
C(3)−C(27)	1.530(8)	1.53(1)	C(18)−C(36)	1.522(8)	1.51(1)
C(27)−O(28)	1.393(9)	1.45(1)	C(36)−O(35)	1.416(7)	1.43(1)
O(28)−C(29)	1.465(9)	1.38(1)	O(35)−C(34)	1.358(7)	1.39(1)
C(29)−C(30)	1.372(9)	1.41(1)	C(34)−C(33)	1.372(9)	1.39(1)
C(30)−C(31)	1.369(10)	1.38(2)	C(33)−C(32)	1.369(9)	1.40(1)
C(31)−C(32)	1.353(10)	1.34(1)	C(29)−C(34)	1.392(9)	1.35(1)
C(27)−O'(28)	1.533(14)				
O'(28)−C(29)	1.487(14)				

(b) Bond angles (°). Estimated standard deviations are in parentheses except for bond angles of compound (II) which range from 0.8 to 1.4°

|				Bond angle abc	
a	b	c	d	(I)	(II)
C(21)−C(26)−O(1)−C(2)				120.4(5)	117
C(25)−C(26)−O(1)−C(2)				119.3(5)	123
C(26)−O(1)−C(2)−C(3)				115.1(5)	120
O(1)−C(2)−C(3)−O(4)				108.9(5)	111
O(1)−C(2)−C(3)−C(27)					
C(2)−C(3)−O(4)−C(5)				104.1(5)	107
C(27)−C(3)--O(4)−C(5)				112.0(5)	114
C(2)−C(3)−C(27)−O(28)				107.6(5)	117
C(2)−C(3)−C(27)−O'(28)					
O(4)−C(3)−C(27)−O(28)					
O(4)−C(3)−C(27)−O'(28)					
C(3)−O(4)−C(5)−C(6)				114.2(5)	116
O(4)−C(5)−C(6)−O(7)				109.4(5)	108
C(5)−C(6)−O(7)−C(8)				107.6(6)	107
C(9)−C(8)−O(7)−C(6)				124.4(6)	125
C(6)−O(7)−C(8)−C(13)				118.1(5)	118
O(7)−C(8)−C(13)−O(14)				115.7(6)	115
C(8)−C(13)−O(14)−C(15)				114.7(5)	117
C(12)−C(13)−O(14)−C(15)				125.0(6)	123
C(13)−O(14)−C(15)−C(16)				117.8(5)	118
O(14)−C(15)−C(16)−O(17)				108.6(5)	107
C(15)−C(16)−O(17)−C(18)				109.9(5)	199
C(16)−O(17)−C(18)−C(19)				113.7(5)	117
C(16)−O(17)−C(18)−C(36)					
O(17)−C(18)−C(19)−O(20)				106.8(5)	108
C(36)−C(18)−C(19)−O(20)				115.4(6)	116
O(17)−C(18)−C(36)−O(35)				113.4(5)	113
O(35)−C(36)−C(18)−C(19)				108.6(5)	109
C(18)−C(19)−O(20)−C(21)				111.1(5)	109
C(22)−C(21)−O(20)−C(19)				124.9(6)	124
C(19)−O(20)−C(21)−C(26)				117.5(4)	118
O(20)−C(21)−C(26)−O(1)				116.5(5)	115
C(3)−C(27)−O(28)−C(29)				116.1(6)	108
C(3)−C(27)−O'(28)−C(29)				97.9(7)	
C(30)−C(29)−O(28)−C(27)				114.7(7)	122
C(27)−O(28)−C(29)−C(34)				117.0(6)	118
C(30)−O(29)−O'(28)−C(27)				112.0(8)	
C(27)−O'(28)−C(29)−C(34)				107.6(9)	
O(28)−C(29)−C(34)−O(35)				123.4(6)	117
O'(28)−C(29)−C(34)−O(35)				117.0(8)	
C(29)−C(34)−O(35)−C(36)				117.5(6)	115
C(33)−C(34)−O(35)−C36				124.7(6)	123
C(34)−O(35)−C(36)−C(18)				121.3(5)	118
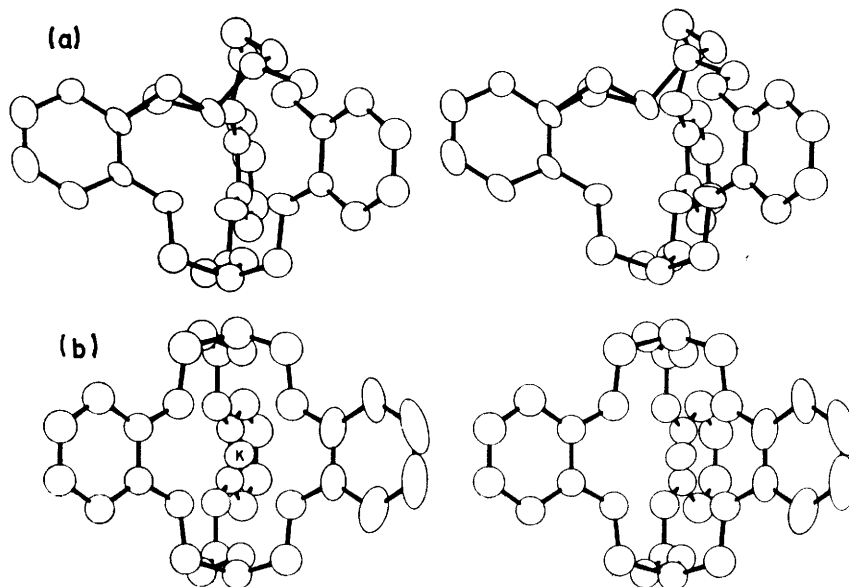
FIGURE 3   Stereopairs of (a) the uncomplexed molecule (I) and (b) the complex cation in (II)
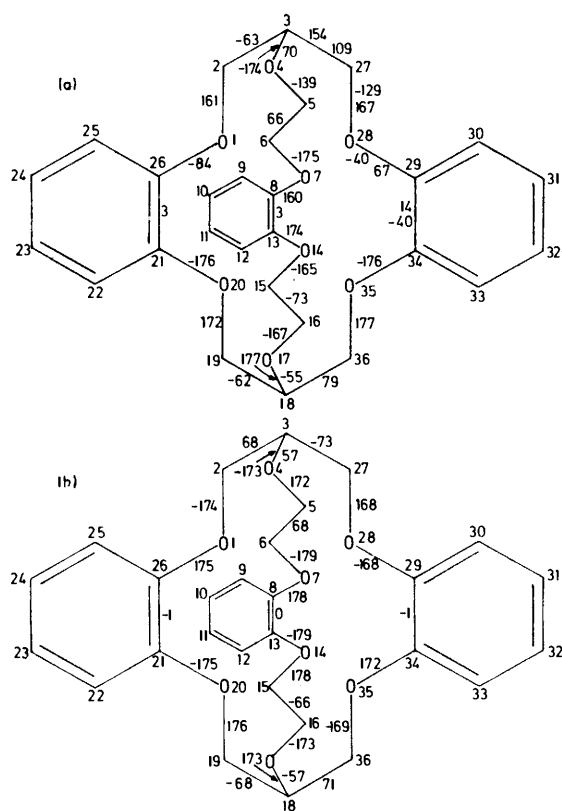

FIGURE 4   Torsion angles in the bicyclic compounds (a) in (I) and (b) in the complex cation in (II).   For clarity the values shown have been rounded to the nearest integer; estimated standard deviations range from 0.4° at 180° to 1.0° at 0° in (a) and similarly from 0.9° to 2.5° in (b).   In (a) angles involving O(28) are above or to the left of those involving O'(28).   It is not possible to show all those involving the bridgehead carbon atoms C(3) and C(18); those depicted are in the 14-crown-4 ring; additional angles are O(1)–C(2)–C(3)–O(4) 178° (a) −61° (b);   O(4)–C(3)–C(27)–O(28)   −92° (a) 53° (b);   O(4)–C(3)–C(27)–O'(28)   −137° (a);   O(17)–C(18)–C(36)–O(35)   −44° (a) −55° (b); and O(17)–C(18)–C(19)–O(20) 65° (a) 61° (b)

atoms.   The U_{iso} values for the oxygen atoms of the water molecules were very different and a better model was obtained by assuming the same isotropic vibration parameter for all and allowing the occupation numbers to vary. For Cl(A) and Cl(B) occupation numbers were constrained to add up to unity, for the water molecules W(1)—W(5) inclusive those for (A) and (B) were allowed to vary independently, and that of W(6), which is close to the two-fold axis, was fixed at 0.5.   The co-ordinates of W(6) refined to a position off the two-fold axis.   The implications of the disorder and the space group ambiguity are discussed later.

Table 2 gives the final atomic parameters corresponding to an R value of 0.104 (a smaller value can be obtained with more parameters for the disordered atoms but the physical significance of these is questionable).   The disordered columns were fixed and a final cycle of refinement of the cation gave the maximum shift in a parameter 0.06 of the corresponding standard deviation;   correlation coefficients >0.5 were found for several parameters of C(23) and between its co-ordinates and those of C(24).   The weighted R' value   was   0.117, w being $3.47/(\sigma^2_{(F)}$ counting $+ 0.000\ 6|F|^2)$.   The structure factor Tables and the parameters for hydrogen atoms are in SUP 22903.

RESULTS AND DISCUSSION

The compound was synthesised by bridging a dibenzo-14-crown-4 diol,[1] corresponding to the benzene rings B and C with O(4) and O(17) as the two hydroxy oxygen atoms.   In the systematic numbering, the bridge which includes a benzene ring consists of atoms 5—16.   Figure 3 shows stereopairs of the molecule in (I) and the cation in (II).

There is no discernible symmetry in the free molecule. In the complex a non-crystallographic plane of symmetry passes through the potassium ion and the midpoints of two bonds in each benzene ring, C(8)–C(13), C(10)–C(11), C(21)–C(26), C(23)–C(24), C(29)–C(34), and C(31)–C(32).   In Table 3 the bond lengths and bond angles have been arranged to display this and to facilitate

comparison between compounds (I) and (II). Figure 4 shows the torsion angles in (I) and the cation in (II).

In (I) the average aromatic C–O distance [excluding O(28)] is 1.366 Å, average aliphatic C–O [excluding O(28)] is 1.424 Å, and the aliphatic C–C bond is 1.509 Å, the usual short value for carbon atoms separating two oxygen atoms. In (II) the corresponding averages are, respectively, 1.38, 1.43, and 1.50 Å with deviations indicating that the values for the e.s.d. in Table 3 are realistic. The only possible significant difference, excluding O(28), between the bond lengths in (I) and (II) is that C(2)–C(3) is 0.053 Å, 3.2 σ, longer in (I).

In the free molecule the distance between the oxygen atoms on the same benzene rings O(1) ··· O(20) and O(28) ··· O(35) are 2.71 and 2.84 Å respectively, both longer than in the complex while the O(7) ··· O(14) 'bite' is the same, 2.57 Å. The change in conformation affects one half of the molecule, as shown by the torsion angles in Figure 4. About six bonds there are changes in

TABLE 4

Mean planes through various groups of atoms in Å. Equations of the planes are in the form $lx' + my' + nz' + d = 0$ where x', y' and z' are co-ordinates with respect to orthogonal axes a' and b' parallel to the crystallographic a and b axes and c' perpendicular to both

			l	m	n	d
A	Benzene ring atoms C(8)—C(13)	I	0.681	0.676	−0.281	−1.721
		II	−0.271	−0.189	0.944	1.293
B	Benzene ring atoms C(21)—C(26)	I	0.063	−0.698	0.714	−4.310
		II	0.615	0.548	0.567	−4.815
C	Benzene ring atoms C(29)—C(34)	I	0.751	0.205	0.637	−8.347
		II	0.659	0.499	−0.563	−3.251
D	(i). O(1), O(20), O(35)	I	0.533	−0.530	0.660	−7.184
	(ii). O(1), O(20), O(28), O'(28), O(35)		0.334	−0.520	0.786	−7.245

Oxygen atoms in the co-ordination polyhedron in II

D	O(1), O(20), O(28), O(35)	0.763	0.639	0.091	−4.015
E	O(7), O(28), O(14), O(35)	−0.227	−0.129	0.965	0.782
F	O(1), O(7), O(20), O(14)	0.261	0.260	0.929	−4.330
G	O(1), O(7), O(28)	−0.640	0.767	−0.046	5.148
H	O(14), O(20), O(35)	−0.639	0.767	−0.046	7.717
I	O(1), O(4), O(7), O(14) O(17), O(20)	0.258	0.264	0.930	−4.180

Direction cosines

(a) O(4) ··· O(17)	0.643	−0.765	0.041
(b) O(1) ··· O(20)	0.643	−0.765	0.035
(c) O(7) ··· O(14)	0.637	−0.770	0.036
(d) O(28) ··· O(35)	0.634	−0.771	0.056

Deviations (10^3 Å) of atoms from the planes; those in italics were not included in calculation of the equations

		I	II			I	II
(A)	C(8)	8(7)	−3(11)	(B)	C(21)	0(6)	0(13)
	C(9)	7(7)	1(12)		C(22)	4(7)	3(14)
	C(10)	−13(8)	1(13)		C(23)	−1(7)	−4(19)
	C(11)	3(8)	−1(12)		C(24)	−6(7)	2(14)
	C(12)	12(7)	−1(16)		C(25)	11(6)	1(14)
	C(13)	−17(6)	3(10)		C(26)	−8(6)	2(13)
	K	*1 262(2)*			*K*		*1 018(2)*
	O(7)	*27(4)*	*−10(7)*		*O(1)*	*89(4)*	*28(8)*
	O(14)	*−75(4)*	*9(7)*		*O(20)*	*39(4)*	*18(7)*
	C(6)	*482(7)*	*18(12)*		*C(2)*	*−1 136(7)*	*−85(12)*
	C(15)	*−240(7)*	*48(12)*		*C(19)*	*149(7)*	*−89(12)*

TABLE 4 (continued)

			I(Dii)					I(Dii)
(C)	C(29)	−4(8)	−1(11)	(D)	O(1)	114(4)	−6(8)
	C(30)	9(8)	7(12)		O(28)	−497(7)	6(7)
	C(31)	−7(8)	−9(12)		O(35)	285(5)	−6(7)
	C(32)	−1(8)	3(12)		O(20)	−253(4)	6(7)
	C(33)	6(7)	4(11)		O'(28)	351(13)	
	C(34)	−4(7)	−5(11)		*K*		*1 935(2)*
	K		*557(2)*				
	O(28)	*−333(7)*	*−16(7)*				
	O(35)	*−45(6)*	*−11(7)*				
	C(27)	*156(7)*	*−285(12)*				
	C(36)	*−124(7)*	*−192(11)*				
	O'(28)	*804(13)*					

(E)	O(7)	13(7)	(F)	O(1)	−1(8)	(I)	O(1)	+123
	O(28)	−13(7)		O(7)	1(7)		O(4)	−239
	O(14)	−13(7)		O(20)	1(7)		O(7)	122
	O(35)	13(7)		O(14)	−1(7)		O(14)	108
	K	*1 104(2)*		*K*	*−387(2)*		O(17)	−227
				O(4)	*−368(7)*		O(20)	113
				O(17)	*−331(7)*			

Angles (°) between normals to planes. Observed values are in the lower left hand corner; ideal values for a trigonal prism (Figure 5) are in the upper right hand corner for compound II in italics.

	(A)	(B)	(C)	(Di)
			I	
(B)	51.0			
(C)	61.7	69.4		
(Di)	100.4	29.1	45.1	
(Dii)	110.2	19.1	50.4	13.5

	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
					II			
(A)		*60*	*60*	*90*	*30*	*30*	*90*	*90*
(B)	74.6		*60*	*30*	*90*	*30*	*90*	*90*
(C)	36.5	68.9		*30*	*30*	*90*	*90*	*90*
(D)	104.0	29.4	39.5		*120*	*120*	*90*	*90*
(E)	4.4	70.3	40.8	99.7		*120*	*90*	*90*
(F)	40.8	33.9	102.8	116.8	143.6		*90*	*90*
(G)	89.1	90.0	89.2	89.8	90.1	89.4		*180*
(H)	90.9	90.1	90.8	90.1	89.9	89.5	179.9	
(I)	40.8	33.9	102.8	116.7	143.6	0.29	89.7	89.7

Angles between the normal to plane (G) and the O ··· O vectors (a) 0.0, (b) 0.9, (c) 0.7, (d) 1.4°.

kind, *trans* or *gauche*; these are C(26)–O(1), C(2)–C(3), C(3)–C(27), C(27)–O(28), O(28)–C(29), and O(4)–C(5). These alter the intramolecular oxygen atom separations; O(4) is 3.58 Å from O(1), 2.81 from O(7), and 5.25 from O(28), while O(17) remains more nearly equidistant from O(14), O(20), and O(35) at 2.91, 2.83, and 2.73 Å, respectively.

Although some torsion angles in (I) differ from the ideal values 60 or 180° there is no evidence for intramolecular C–H ··· O hydrogen bonding [excluding the disordered H(27) or O(28)]. The shortest H ··· O distance is O(14) ··· H(16B) 2.48 Å.

Planes of the benzene rings with the deviations of the catechol oxygen atoms and of the neighbouring carbon atoms are given in Table 4. The oxygen and attached carbon atoms are significantly out of these planes in (I) but, except for C(27) and C(36), not in the complex (II). Plane (D) comprises the four oxygen atoms of the parent 14-crown-4: because of the disorder in (I), we have calculated the plane (Di) for three oxygen atoms and also (Dii) including both positions for O(28). In both (I) and (II) the benzene rings B and C are not equally inclined to this plane.

The main change from the uncomplexed to the complexed form is that in the former five oxygen atoms,

O(4), O(7), O(14), O(17), and O(20) are on a fairly open face while, in the complexed form, O(1) is, as shown in plane (I), also in this more open face. An open face is also found in other uncomplexed molecules in this series as described in the following paper [11] which gives
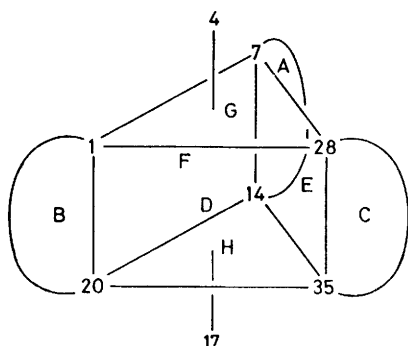

FIGURE 5 An end-capped trigonal prism; numbering of the corners corresponds to the oxygen atoms in (II), letters on loops to the benzene rings

the comparison between (I) and a molecule having CH_2 groups instead of a benzene ring at C(8) and C(13).

Co-ordination of the Potassium Ion.—As shown in Figure 2, co-ordination is solely by eight oxygen atoms of the ligand; these are arranged approximately in an end-capped trigonal prism shown in Figure 5 with the

K^+, O, and benzene rings differs from that of D_{3h} symmetry in that the line joining O(4)–K–O(17) does not pass through the mid-point of the triangular faces. In Table 4 the observed angles between the plane normals are contrasted with ideal values from a trigonal prism with D_{3h} symmetry as in Figure 5. These deviations are all such that K, O(4), and O(17) lie sufficiently close to plane (F), and benzene rings A and B are at such angles to it as to make that part of the molecule, atoms (1)—(26) inclusive, comparable with complexes of dibenzo-18-crown-6,[12] and the tetramethyl substituted derivatives [13] noticeably in the torsion angles (Figure 4), *trans* about C–O, *gauche* about CH_2–CH_2. This comparison is also shown in plane (I), through the six oxygen atoms and suggests that the caesium ion in the 1 : 2 complex [4] could be sandwiched between two six-oxygen faces. This finding also reinforces a point made by Coxon and Stoddart,[14] who synthesised molecules $RC(CH_2OCH_2$-$CH_2OCH_2CH_2OCH_2)_3CR$ which proved disappointing as ligands, *i.e.* the need to base a molecule on units having only two carbon atoms between the oxygen atoms as Pedersen [15] found in his original crown ethers. However, the six oxygen atoms differ from coplanarity by significant amounts, and we regard the end-capped trigonal prism as a useful description.

In their molecular orbital treatment of eight co-

TABLE 5

Co-ordination of the potassium ion; the ordering of the atoms demonstrates the pseudosymmetry of Figure 5

K–O(a) distance		O(a)–K–O(b) angles (°) (standard deviation 0.2°)							
O(a)	Å	O(b)	O(1)	O(7)	O(28)	O(35)	O(14)	O(20)	O(17)
O(4)	2.690(8)		61.1	62.4	62.6	118.6	118.7	117.6	178.2
O(1)	2.728(8)			120.9	63.8	89.5	163.7	56.6	118.0
O(7)	2.740(8)				103.4	133.0	56.3	163.6	118.0
O(28)	2.741(7)					56.1	131.9	89.8	118.5
O(35)	2.740(7)						103.4	62.6	62.5
O(14)	2.735(8)							120'9	61.8
O(20)	2.709(8)								61.4
O(17)	2.684(7)								

Bond angles K–O–C(°)

[O]	[C]		[O]	[C]	
(1)	(2)	116.0(7)	(20)	(19)	117.2(6)
(1)	(26)	121.3(8)	(20)	(21)	121.6(7)
(4)	(3)	107.4(6)	(17)	(18)	107.2(6)
(4)	(5)	106.8(6)	(17)	(16)	107.2(6)
(7)	(6)	115.1(6)	(14)	(15)	116.1(6)
(7)	(8)	118.6(6)	(14)	(13)	117.6(6)
(28)	(27)	118.6(6)	(35)	(36)	117.5(6)
(28)	(29)	123.9(6)	(35)	(34)	124.4(6)

corners numbered to correspond to the oxygen atoms in (II). The triangular faces are formed by O(1), O(7), O(28) and O(20), O(14), O(35). These, as shown in Table 4, are parallel to one another and normal to the planes (D)—(F) of the rectangular faces while the atoms O(4) and O(17) cap the ends. The twist angle between faces (G) and (H) is 0.5° (*cf.* 0° for a trigonal prism and 60° for a trigonal antiprism).

Bond lengths and angles involving potassium are in Table 5 which shows that the K–O distances to the oxygen atoms on the aromatic rings average 2.733 Å, while those to the capping atoms O(4) and O(17) are significantly shorter, 2.687 Å. The pairs of oxygen atoms on the benzene rings form the prism edges; the system

ordination, Burdett *et al.*[16] showed that, while this geometry is favoured on electronic grounds, it is sterically very unfavourable. The minimum energy geometry is found theoretically if the angles subtended at the centre between the capping atoms and the atoms of a triangular face are 58°; this corresponds to the set of angles O(4) to O(1), O(7), O(28) or O(17) to O(20), O(14), O(35) which, as Table 5 shows, range from 61.1 to 62.6°. The theory also predicts that the end-capping position should be occupied by the more electronegative (or better σ electron acceptor) ligand; as an oxygen atom between two aliphatic carbon atoms is more electronegative than one attached to a benzene ring, the prediction is borne out in this example.

The complex is one example of toleration by d° cations of the higher energy possibilities for eight coordination in regular discrete polyhedra. Other examples are the hexagonal bipyramid in some complexes of

TABLE 6

Selected intermolecular distances in (I) including all O $\cdots$ H and C $\cdots$ H distances less than 3.0 Å and H $\cdots$ H distances less than 2.6 Å

a	b		a $\cdots$ b	b $\cdots$ a
C(10)	H(23)	3.20	I	II
C(10)	H(22)	3.00	I	II
C(9)	H(22)	2.73	I	II
C(8)	H(22)	3.00	I	II
C(12)	H(6B)	2.81	VII	VIII
O(1)	H(3)	2.59	III	III
O(1)	C(3)	3.56	III	III
O(1)	H(32)	2.63	IV	IV
O(1)	C(32)	3.57	IV	IV
C(21)	H(32)	2.95	IV	IV
C(26)	H(31)	2.67	IV	IV
O(4)	H(33)	2.78	V	VI
O(4)	C(33)	3.48	V	VI
H(5B)	C(32)	2.99	V	VI
H(5B)	H(32)	2.78	V	VI
H(5B)	C(33)	3.09	V	VI
H(5B)	H(33)	2.95	V	VI
C(34)	H(10)	3.12	VII	VIII
O(28)	H(10)	2.89	VII	VIII
C(29)	H(10)	2.90	VII	VIII
C(24)	H(12)	3.19	I	II
C(25)	H(12)	3.31	I	II
H(24)	H(12)	3.03	I	II
H(25)	H(30)	2.31	III	III
H(25)	C(30)	3.16	III	III
C(25)	H(30)	3.11	III	III
H(25)	O(28)	2.98	III	III
H(25)	O'(28)	2.98	III	III
C(24)	H(24)	2.97	IX	IX
H(24)	H(24)	2.50	IX	IX
C(21)	H(16A)	2.79	I	II
C(23)	H(15A)	3.06	I	II
C(24)	H(15A)	2.96	I	II
C(25)	H(15A)	3.06	I	II
O(20)	H(16A)	2.93	I	II
H(2B)	H(16A)	2.52	I	II
O(7)	H(23)	2.87	X	XI
H(9)	C(13)	2.97	VIII	VII
H(9)	O(14)	2.81	VIII	VII
C(13)	H(19B)	2.88	I	II

Roman numerals give the position of atoms related to those of the crystal chemical unit, x, y, z in Table 1

I	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	VI	$x, y - 1, z$
II	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$	VII	$-x, -\frac{1}{2} + y, \frac{1}{2} - z$
III	$1 - x, 1 - y, 1 - z$	VIII	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
IV	$1 - x, -y, 1 - z$	IX	$2 - x, 1 - y, 1 - z$
V	$x, y + 1, z$	X	$x - 1, y, z$

In the designations of hydrogen atoms A and B distinguish those attached to the same carbon atom.

18-crown-6 derivatives (*e.g.* ref. 12), and the cube in complexes of nonactin.[17] The cube is a particular case of an end-capped trigonal antiprism. The sodium complex [18] of the [222] cryptand, $N(CH_2CH_2OCH_2 CH_2OCH_2CH_2)_3N$ is close to the general case having a linear N $\cdots$ Na $\cdots$ N system with the twist angle between two triangles of oxygen atoms of 45.8° while in complexes of the larger cations potassium,[19] rubidium, and caesium,[20] the angle is 22.5, 14.4, and 15.3°, respectively, nearer that for the end-capped trigonal prism. This change in twist angle is accompanied by a diminu-

tion in the metal–nitrogen relative to the metal–oxygen distance.

Changes in conformation between the complexed (cryptate) and uncomplexed cryptand [21] differ from those for (I); there are changes about the three central CH_2–CH_2 bonds [the equivalents in (I) being fixed as benzene rings] and about the C–O bonds. Angles involving the bridgehead nitrogen atoms are unchanged.

Intermolecular Contacts.—In Tables 6 and 7 'selected'

TABLE 7

Selected intercationic contacts in (II) including all O $\cdots$ H and C $\cdots$ H distances <3.0 Å and H $\cdots$ H distances <2.6 Å

a	b		a $\cdots$ b	b $\cdots$ a
O(7)	H(15B)	2.83		
C(8)	H(15B)	3.37		
C(8)	H(16A)	2.78		
C(11)	C(33)	3.49		
C(11)	C(34)	3.48		
C(12)	H(16A)	3.28		
C(13)	H(16A)	2.65	I	I
O(14)	H(16A)	2.89		
C(31)	H(11)	3.28		
C(32)	H(11)	3.10		
C(33)	H(11)	3.07		
C(34)	H(11)	3.20		
H(16A)	H(16A)	2.58		
C(10)	H(6B)	3.00		
C(11)	H(6B)	3.06		
H(10)	H(6B)	2.96		
H(11)	H(6B)	3.06		
C(16)	H(19B)	3.25	II	II
O(17)	H(19B)	2.87		
C(18)	H(19B)	3.20		
O(20)	H(15A)	2.85		
C(21)	H(15A)	2.81		
C(24)	H(19A)	3.25		
C(25)	H(19A)	3.25		
C(22)	C(25)	3.64		
C(23)	C(26)	3.62		
C(22)	C(26)	3.60		
C(24)	H(36B)	3.28	III	III
H(24)	H(36B)	2.45		
C(24)	O(20)	3.62		
C(24)	C(21)	3.63		
H(24)	C(33)	3.17		
H(24)	C(34)	3.07		
H(24)	O(35)	3.17		
C(29)	H(23)	2.92		
H(32)	H(32)	2.57	IV	IV
C(32)	H(32)	2.89	IV	IV
C(33)	H(5A)	2.96	IX	V
H(32)	H(5A)	2.78	IX	V
H(5A)	C(24)	2.99	VI	XIV
H(5A)	H(24)	2.55	VI	XIV

Roman numeral superscripts relate the atomic positions to those of the crystal chemical unit in Table 2, at x, y, z

I	$1 - x, -y, -z$	VIII	$\frac{1}{2} + x, \frac{1}{2} + y, -\frac{1}{2} + z$
II	$1 - x, y, \frac{1}{2} - z$	IX	$\frac{1}{2} - x, -\frac{1}{2} + y, -z$
III	$\frac{1}{2} - x, -\frac{1}{2} - y, \frac{1}{2} - z$	X	$\frac{1}{2} + x, -\frac{1}{2} + y, -\frac{1}{2} + z$
IV	$\frac{1}{2} - x, -\frac{1}{2} - y, -\frac{1}{2} - z$	XI	$\frac{1}{2} + x, -\frac{1}{2} - y, z$
V	$\frac{1}{2} - x, \frac{1}{2} + y, -z$	XII	$1 - x, -1 - y, -z$
VI	$x, -y, -\frac{1}{2} + z$	XIII	$x, -1 - y, -\frac{1}{2} + z$
VII	$\frac{1}{2} + x, \frac{1}{2} - y, z$	XIV	$x, -y, \frac{1}{2} + z$

In the designations of hydrogen atoms A and B distinguish those attached to the same carbon atom.

intermolecular, or intercationic, distances are given; all those less than the quoted limits are included. Those outside the limits have been selected, *e.g.* both a carbon atom and its attached hydrogen atom, to make the end-
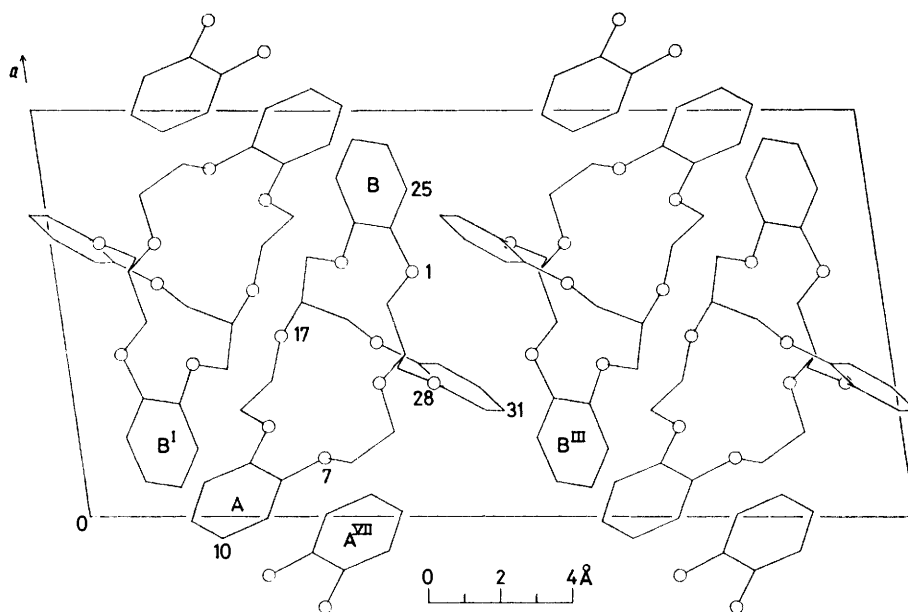
FIGURE 6   The structure of (I) in projection along the b axis.   The Roman numeral superscripts refer to the equivalent positions defined in Table 6; those not displayed here are IV, beneath III; V and VI are respectively above and below the crystal chemical unit; II is beneath I, VIII is above VII
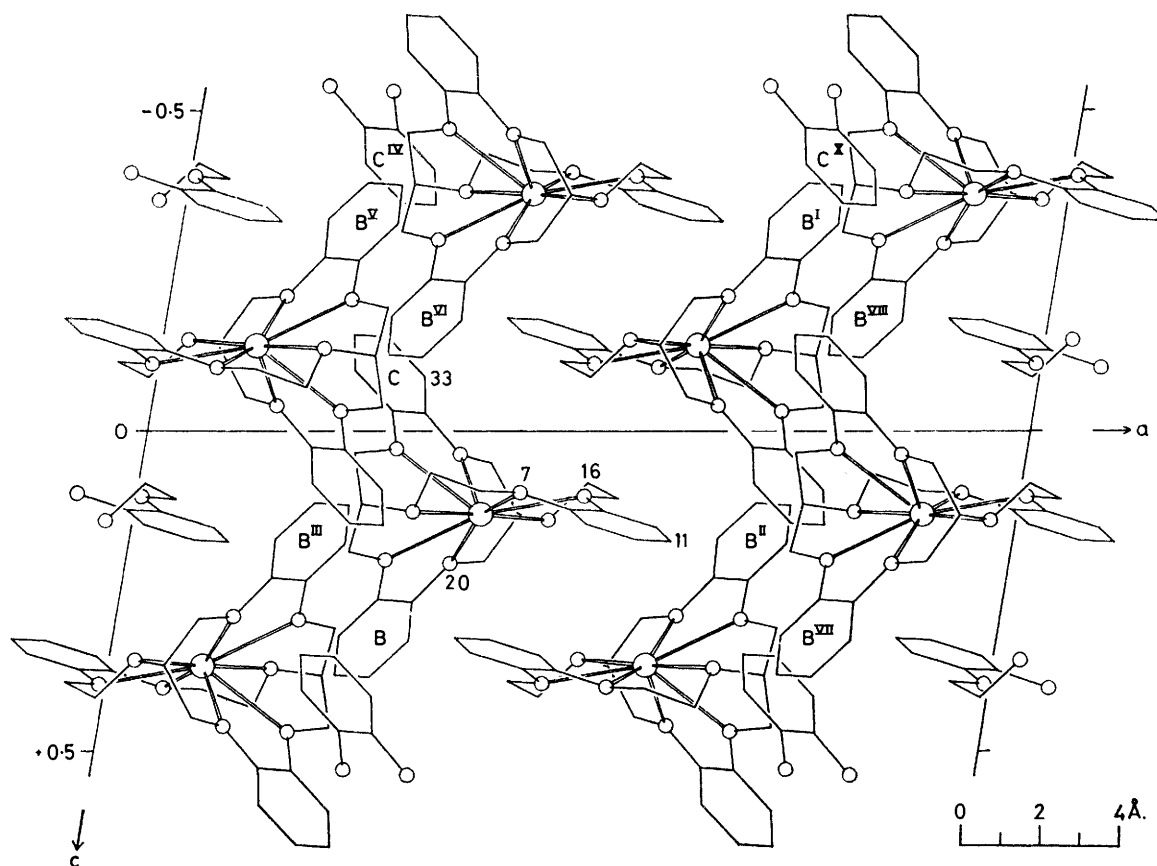

FIGURE 7   The cationic columns in (II) shown in projection down the b axis for the cations having the potassium between $y = -\frac{1}{2}$ and $+\frac{1}{2}$.   Roman numeral superscripts are defined in Table 7; those not shown here are IX one cell below V, X one cell below VIII, XI below VII, XII below I, and XIII below VI

on or side-on nature of the contact clear. For each benzene ring the possible contacts to be considered are (a) parallel stacking with another ring at *ca.* 3.5 Å, or (b) ' meshing ' from hydrogen of another ring or from a CH$_2$ group characterised by the hydrogen being equidistant from several ring carbon atoms and the donor C–H approximately normal to the ring. Both stacking or meshing contacts can appear on either side of a ring. An aromatic hydrogen atom may be meshed into a ring

other contacts. The second face of ring c is in contact with H(5B) in relation VI and H(10) in relation VII. Two of its hydrogen atoms contact oxygen atoms, see above.

For ring A contacts from one side are from H(22) and H(23) of ring B^{I}; on the other H(6B)^{VII}. Its hydrogen atoms H(10) and H(12) mesh into rings C^{VIII} and B^{II}. Ring B receives a mesh contact from H(12^{I}) and on the same side contacts from H(16A) and H(15A) in relation
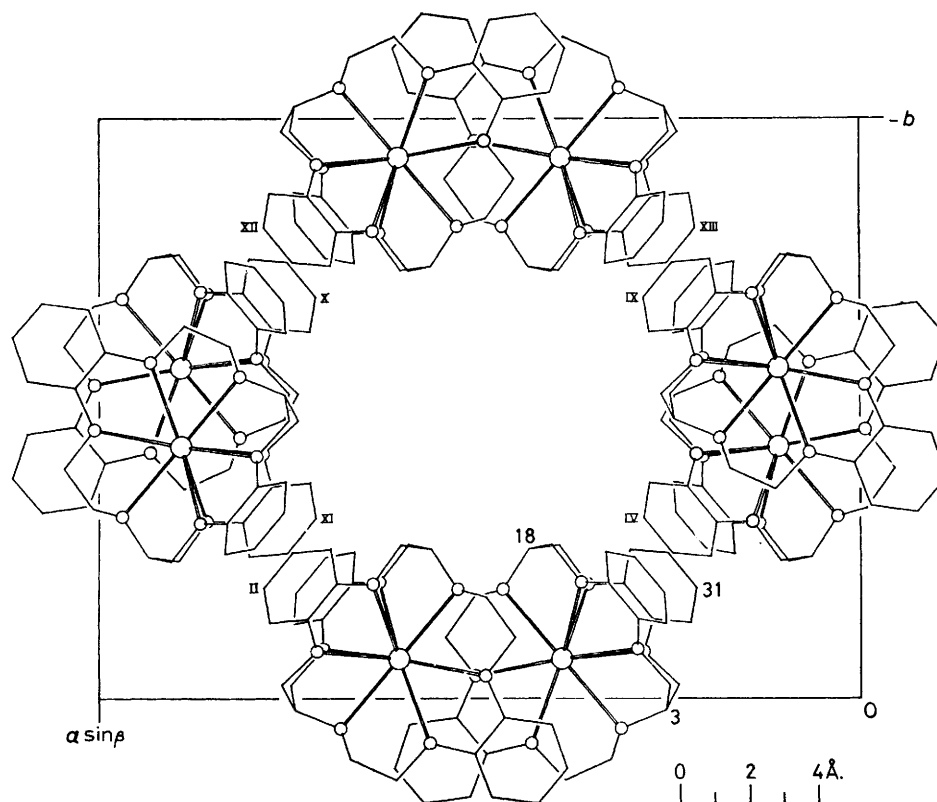
FIGURE 8   The structure of the cationic columns of II in a projection down the *c* axis showing the eight potassium ions having $-1 < y < 0$ so that only two cations overlap each of the projected points at 0, $\frac{1}{2}$; $\frac{1}{2}$, 0; 1, $\frac{1}{2}$, and $\frac{1}{2}$, 1. At each of these points there is overlap from a further two cations in the neighbouring unit cells. The spaces available for columns of water molecules and anions are visible at 0,0,*z* and $\frac{1}{2}$,$\frac{1}{2}$,*z*. The Roman numeral designations are defined in Table 7

or in contact with an oxygen atom. For both compounds the packing will be described in these terms.

Figure 6 shows the packing of (I). There are intermolecular C–H ··· O contacts, with angles at hydrogen of *ca.* 160°; these are H(3) ··· O(1^{III}), H(32) ··· O(1^{IV}) [so that O(1) is in two contacts about centres of symmetry separated by one translation along the *b* axis], and H(33) ··· O(4^{VI}) in the molecule in the next cell along *b*; the lengths exceed the sum of the van der Waals' radii.

As shown in Table 4, the normals to the planes of the three benzene rings A—c are at *ca.* 60°. Stacking is not important in this structure; the only such contact is from ring c to the one related to it by a centre of symmetry at $\frac{1}{2}$,0,$\frac{1}{2}$ (relation IV) and this gives rise to contacts from C(34) to C(32) and C(33) of 3.8 Å; although not representing a strong attraction it sterically prevents

I, there are no significant contacts on the other side; from H(30) of ring C^{III} there is a relatively close 2.31 Å contact to H(25) edge on and a similar one H(24) ... H(24)^{IX} across the centre of symmetry at 1,$\frac{1}{2}$,$\frac{1}{2}$.

The structure of (II) consists of complex cations which are arranged as shown in Figures 7 and 8 to form channels, along the crystallographic ' *c* ' axis, in which the water molecules and chloride ions occupy disordered sites. There is a superficial resemblance to an anion exchange resin but the cation columns are not polymers, consisting of discrete entities held, presumably, by van der Waals' forces; there is no evidence for efficient packing or strong inter-' molecular ' forces, as shown by the distances of various contacts given in Table 7. These have been arranged for ease of comparison with the packing diagrams with categories of types of contact. From the benzene ring A, nearest contacts are across a

centre of symmetry at $\frac{1}{2},0,0$ (relation I) to the hydrogen atoms of the CH_2 groups, (15) and (16); on the other side are the contacts to the hydrogen atom (6B) of the molecule across the two-fold axis, (relation II), and H(11) fits into one side of ring c^I. The nearest to the stacking of aromatic rings is from ring B to the one related by a centre of symmetry at $\frac{1}{4},-\frac{1}{4},\frac{1}{4}$ (III), on the other side of the ring in a contact from H(15A) in relation II, and H(24) meshes into one side of ring c in relation III. Ring c is contacted on one side by H(11^I) on the other by H(24^{III}); the centrosymmetrical relation at $\frac{1}{4},-\frac{1}{4},-\frac{1}{4}$ (relation IV) gives an abutment at H(32).

Comparison of Tables 6 and 7 shows that the minimum contacts of a given kind are longer between the cations of (II) than between the neutral molecules of (I).

The only neighbours within 4 Å of the potassium ion are two hydrogen atoms H(12) and H(15A) at 3.85 and 3.51 Å; both are in the complex cation in relation II.

Columns of Disordered Water Molecules and Chloride Ions.—In (II) the scattering attributable to one chloride ion and 4—5 water molecules per asymmetric unit cannot be precisely defined; this results in a high R factor and relatively large standard deviations even in the co-ordinates of the atoms of the cation. The best representation of the electron density we could obtain is shown by the parameters of Cl and of water molecules W(1)—W(5), each of which may occupy one of two mutually exclusive sites designated A and B, and of W(6) at 0.6 Å from a two-fold axis with occupation number 0.5. The occupation numbers were parameters; the sum of those of Cl(A) and Cl(B) was constrained to 1; there was no constraint for W(1)—W(5) and the refined values for A plus B are close to unity. A more detailed description includes a diagram in SUP 22903 together with a Table showing the distances of water molecules and chloride ions to the cations; none is less than the sum of the van der Waals' radii. There are more than sufficient potential hydrogen bonded contacts within the columns to accommodate all the hydrogen atoms.

While the presence of a large amount of water is inconvenient from the point of view of a crystal structure analysis, it may be an indication that the structure found resembles that in solution. A similar channel of disordered water molecules and chloride ions along a two-fold axis was found in a basic chromium acetate compound [22] $[OCr_3(CH_3COO)_6^-,3H_2O]^+Cl^-,6H_2O$. Chang and Jeffrey attributed the disorder to the channel being surrounded by hydrophobic groups so that tetrahedral contacts could not be formed. Other crystals containing complexed alkali metal cations with ' organic ' exteriors and networks of hydrogen bonded water molecules and anions have been described. One sodium ion between two molecules of 12-crown-4 (1,4,7,10-tetraoxacyclododecane) forms the cation in $NaCl(12\text{-crown-4})_2,5H_2O$ [23] and in $NaOH(12\text{-crown-4})_2,8H_2O$.[24] The cations form layers between which are layers of ordered networks of water and anions.

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