Crystal Structures of Complexes between Alkali-metal Salts and Cyclic Polyethers. Part VI.[1][‡] Complex formed between Dicyclohexyl-18-crown-6, Isomer B, (Perhydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin) and Sodium Bromide

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A three-dimensional *X*-ray crystal structure analysis has been carried out on the title complex, $[Na(C_{20}H_{36}O_6)(H_2O)_2]Br$. Crystals are triclinic, space group $P\bar{1}$, with $a = 10{\cdot}32(1)$, $b = 11{\cdot}34(1)$, $c = 6{\cdot}67(1)$ Å, $\alpha = 116° 42'(6')$, $\beta = 109° 48'(5')$, $\gamma = 100° 10'(6')$. The sodium ion lies on a centre of symmetry, and is surrounded by an approximately planar ring of six oxygen atoms of one ligand. (Na–O 2·67—2·97 Å). The hexagonal bipyramidal arrangement about the sodium is completed by two water molecules, at 2·34 Å. The water molecules form hydrogen bonds to the bromide ion, resulting in an infinite chain structure.

1366 Intensities measured on a diffractometer were refined by full-matrix least-squares to *R* 0·046. All hydrogen atoms were located, except that involved in the hydrogen bond.

THE natural selectivity which biological systems show towards Na^+ and K^+ can be parallelled [2-6] by the series of cyclic polyethers, first synthesised by Pedersen.[7] Structure determinations have shown that the main feature in which the ' crown ' compounds differ from naturally occurring antibiotics is that the smaller ' crown ' compounds have their oxygen atoms arranged in a plane around the central ion,[8-12] leaving axial positions available for other interactions (solvent or anion), whereas the naturally occurring compounds

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‡ The systematic names of compounds in Parts I—IV in the present (Chem. Abs.) nomenclature are: 6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin (dibenzo-18-crown-6); 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (benzo-15-crown-5); and 6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo-[*b,q*][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontin (dibenzo-30-crown-10).

[1] (*a*) Part V, P. R. Mallinson and M. R. Truter, *J.C.S. Perkin II*, 1972, 1818; (*b*) for details see ref. 15 of ref. 1; (*c*) for details see ref. 16 of ref. 1.

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enclose the central atom in either an octahedral environment (enniatin B[13] or valinomycin[14]) or a cubic environment (nonactin[15]). A large cyclic polyether, dibenzo-30-crown-10, has been shown[12] to have sufficient flexibility to enclose the central metal-ion completely.

Stability constant measurements[16] for a series of macrocyclic polyethers show that the feature of total enclosure gives a particularly high ratio of selectivity of K^+ over Na^+. Experiments on the smaller ligands[17] indicate that a six-oxygen-membered ring would preferentially select K^+ over Na^+.

The crystal structure of this sodium ion complex, with a six-oxygen 18-membered ring is, therefore, a study of a complex formed by a selectively unfavourable environment. A preliminary account has appeared[18] and we now describe the analysis of the crystal structure of bisaquo(dicyclohexyl-18-crown-6)sodium bromide and compare it with those of the complexes formed between sodium bromide and thiocyanate with dibenzo-18-crown-6.[8,10]

EXPERIMENTAL

Plate-shaped crystals suitable for *X*-ray analysis were obtained from a solution of equimolecular quantities of dicyclohexyl-18-crown-6 (isomer B) and sodium bromide in ethanol–acetone, which was allowed to evaporate in air. Chemical analysis for C and H indicated $NaBr(L)(H_2O)_x$ $x = 1—2$. Calc. for $x = 1$: C, 48·7; H, 7·75%; for $x = 2$: C, 46·95; H, 7·80. Found: C, 47·9; H, 7·95%.

Preliminary *X*-ray photographs showed that the crystal system was triclinic. A crystal *ca.* 0·8 × 0·15 × 0·4 mm cut from a larger crystal, was mounted along the *c* axis, and set on a Picker four-circle diffractometer by use of the centred positions of 14 reflections, having a mean 2θ value of 17°. Unit-cell constants, and their standard deviations were determined from a least-squares fit to the setting angles. The intensities of general reflections were measured out to $2\theta = 45°$ by the 2θ scan procedure, with Mo-K_α (Zr-filtered) radiation, with attenuators. Scans were run at the rate of 0·5° min^{-1} from $2\theta_{\text{calc.}}$ ($K_{\alpha1}$) $-0{\cdot}6$ to $2\theta_{\text{calc.}}$ ($K_{\alpha2}$) 0·6°. Stationary background counts of 20 s each were taken at the ends of each scan. Three reference reflections were measured after every 50 reflections, and were used to put the data on a common scale. Intensities were corrected for Lorentz and polarisation effects. Reflections for which $I \leqslant 2\sigma$ were removed from the data set, leaving 1510 independent reflections observed out of 1562 collected reflections.

Computation was carried out initially on an IBM 1130 computer with programmes of the *X*-RAY ARC system.[1b] Final refinement was carried out on the University College IBM 360/651 system.[1c]

Crystal Data.—$C_{20}H_{40}BrNaO_8$, $M = 511{\cdot}557$, Triclinic, $a = 10{\cdot}32(1)$, $b = 11{\cdot}34(1)$, $c = 6{\cdot}67(1)$ Å, $\alpha = 116°\ 42'(6')$, $\beta = 109°\ 48'(5')$, $\gamma = 100°\ 10'(6')$, $U = 603{\cdot}718$ Å^3, $D_m = 1{\cdot}43$, $Z = 1$, $D_c = 1{\cdot}406$, $F(000) = 270$. Space group $P\bar{1}$ (C_i, No. 2), Mo-K_α radiation, $\lambda(K_{\alpha1}) = 0{\cdot}7093$ Å, $\lambda(K_{\alpha2}) = 0{\cdot}7135$ Å (1 Å $\equiv 10^{-10}$ m); μ(Mo-K_α) = 18·6 cm^{-1}. No correction for absorption was made.

Structure Analysis.—The position of the bromide ion was assumed to be at the origin, and an electron-density map calculated on this assumption revealed the Na^+ ion at another crystallographic centre of symmetry ($\frac{1}{2}$,0,0). All the carbon and oxygen atom positions were immediately obtained from a subsequent electron-density map. Their designations are shown in Figure 1. Refinement started by using block-diagonal least-squares, with unit weights and scattering factors taken from ref. 19. Anisotropic vibration parameters were used for Br^-, Na^+, and O atoms. R was reduced from 0·25 to 0·074 in four cycles. Hydrogen atom co-ordinates were calculated assuming C–H 0·95 Å. All hydrogen atoms were subsequently located on a difference map, with the exception of the hydrogen atom located in the hydrogen bond between water and the bromide ion. Hydrogen atoms were included in the subsequent refinement, with scattering factors taken from ref. 20. Refinement was by full-matrix least-squares with a weighting scheme of the form: $F_o < 3{\cdot}0$, reflection rejected, $|F_o| < 126$, $\sqrt{w} = 1{\cdot}0$; $|F_o| > 126$, $\sqrt{w} = 126/F_o$, resulted in convergence at R 0·046, R' [$= (\Sigma w\Delta^2/\Sigma(wF_o)^2)^{\frac{1}{2}}$] = 0·030.

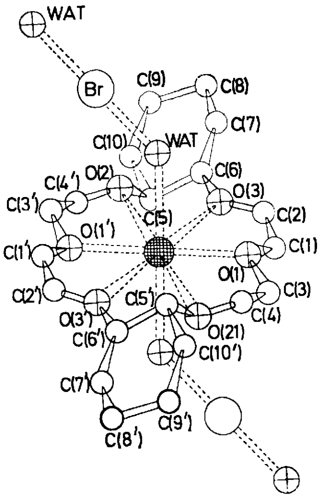

FIGURE 1 One molecule of the complex, showing the designations of the atoms, those with primes being related to those without by a centre of symmetry occupied by a sodium ion. The water molecules, WAT, are shown with an indication of hydrogen bonding to the bromide ion

A final electron-density difference map showed only random maxima between 0·4 and −0·4 eÅ^{-3}. Molecular parameters were computed using ORFFE,[1c] and torsion angles and planes through groups of atoms were calculated on the IBM 1130 computer. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20811 (14 pp., 1 microfiche).* Atomic co-ordinates and vibration parameters are listed in Table 1. The bond lengths and angles in the dicyclohexyl-18-

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

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crown-6 and some significant non-bonding distances are shown in Table 2, and the torsion angles in this ligand in Table 3. Table 4 gives the environment of the sodium ion, and Table 5 the planes through various groups of atoms.

TABLE 1

(*a*) Fractional atomic co-ordinates (× 10^4), with standard deviations in the least significant digits in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Br	0	0	0
Na	5000	0	10000
WAT	3452(6)	0002(8)	11890(14)
O(1)	2866(4)	−0132(4)	6154(7)
O(2)	5167(4)	−2493(4)	9205(7)
O(3)	2711(4)	−2840(4)	5480(7)

(*b*) Anisotropic vibration parameters (× 10^4) 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}
Br	0549(6)	0633(6)	0567(6)	0322(5)	0291(5)	0374(5)
Na	0642(25)	1110(33)	0784(27)	0552(24)	0514(23)	0675(27)
WAT	0848(40)	1914(66)	1398(54)	0881(42)	0840(40)	1232(54)
O(1)	0344(22)	0397(22)	0602(26)	0166(19)	0202(20)	0241(21)
O(2)	0386(23)	0459(24)	9442(24)	0319(19)	0124(19)	0247(20)
O(3)	0490(24)	0503(24)	0423(23)	0272(20)	0212(20)	0295(20)

(*c*) Fractional atomic co-ordinates and isotropic vibration parameters (× 10^4). Hydrogen atoms are numbered according to the carbon atoms to which they are bonded

	x/*a*	*y*/*b*	*z*/*c*	*U*/Å^2
C(1)	1562(7)	−1412(6)	4479(11)	0476(15)
C(2)	2004(7)	−2658(7)	3506(12)	0513(16)
C(3)	2506(6)	1103(6)	7011(11)	0444(15)
C(4)	3910(6)	2390(6)	8544(11)	0457(15)
C(5)	4068(6)	−3878(6)	7248(10)	0402(14)
C(6)	3346(6)	−3902(6)	4876(10)	0414(14)
C(7)	2236(7)	−5381(7)	2687(12)	0490(16)
C(8)	1019(7)	−5952(7)	3179(12)	0514(16)
C(9)	1748(7)	−5896(7)	5624(12)	0552(17)
C(10)	2887(7)	−4331(6)	7848(11)	0453(15)
H(1A)	0954(53)	−1361(50)	2754(91)	0449(148)
H(1B)	1121(45)	−1439(44)	5635(79)	0274(127)
H(2A)	1064(54)	−3587(51)	2272(89)	0391(140)
H(2B)	2707(57)	−2446(53)	2657(97)	0593(167)
H(3A)	2221(54)	1076(51)	8417(94)	0547(156)
H(3B)	1873(52)	1145(51)	5333(93)	0498(159)
H(4A)	−4430(51)	−2342(48)	2545(87)	0398(142)
H(4B)	−3757(53)	−3339(52)	1007(90)	0470(153)
H(5)	4405(54)	−4718(52)	6632(92)	0475(156)
H(6)	4092(57)	−3527(53)	4535(92)	0534(164)
H(7A)	2664(56)	−6207(53)	2441(94)	0556(166)
H(7B)	1896(61)	−5342(58)	1406(108)	0597(180)
H(8A)	0192(62)	−7139(59)	1499(105)	0672(182)
H(8B)	0506(49)	−5262(47)	3287(83)	0324(136)
H(9A)	2170(63)	−6717(60)	5505(104)	0781(195)
H(9B)	0976(66)	−6273(60)	6127(108)	0729(189)
H(10A)	3430(44)	−4442(41)	9466(77)	0199(116)
H(10B)	2519(61)	−3620(60)	8394(106)	0701(189)
H(WAT)	3496(113)	−0204(118)	2920(191)	1791(455)

TABLE 2

Bond lengths (Å) and bond angles (°) in the ligand, with standard deviations in the least significant digits in parentheses

(*a*) Bond lengths

O(1)–C(1)	1·415(6)	C(9)–C(10)	1·503(8)
C(1)–C(2)	1·492(8)	C(10)–C(5)	1·524(8)
C(2)–O(3)	1·399(7)	C(5)–O(2)	1·409(6)
O(3)–C(6)	1·437(6)	O(2)–C(4′)	1·418(6)
C(6)–C(7)	1·498(8)	C(4)–C(3)	1·472(8)
C(7)–C(8)	1·513(8)	C(3)–O(1)	1·427(6)
C(8)–C(9)	1·513(8)	C(5)–C(6)	1·488(7)

Mean C–C 1·484, cyclohexyl 1·510, C–O 1·417.

TABLE 2 (*continued*)

(*b*) Angles

C(1)–O(1)–C(3)	111·5(5)	C(3)–C(4)–O(2)	109·6(6)
C(3)–O(1)–Na	112·0(3)	O(2)–C(5)–C(10)	113·2(5)
C(1)–O(1)–Na	116·6(4)	C(6)–C(5)–O(2′)	108·7(5)
C(4)–O(2)–C(5)	113·9(5)	C(6)–C(5)–C(10)	108·4(6)
C(4′)–O(2)–Na	113·7(4)	O(3)–C(6)–C(5)	105·9(5)
C(5′)–O(2)–Na	126·7(4)	O(3)–C(6)–C(7)	114·2(6)
C(2)–O(3)–C(6)	115·3(5)	C(5)–C(6)–C(7)	110·8(4)
C(2)–O(3)–Na	107·9(4)	C(6)–C(7)–C(8)	112·6(6)
C(6)–O(3)–Na	111·3(3)	C(7)–C(8)–C(9)	108·5(6)
O(1)–C(1)–C(2)	109·0(6)	C(8)–C(9)–C(10)	109·7(6)
C(1)–C(2)–O(3)	109·6(6)	C(9)–C(10)–C(5)	109·8(6)
O(1)–C(3)–C(4)	108·2(5)		

(*c*) Non-bonding ligand distances

C(6) · · · C(9)	2·887(8)	O(1) · · · O(2′)	2·810(5)
C(6) · · · C(10)	2·411(8)	O(1) · · · WAT	3·593(7)
C(7) · · · C(9)	2·455(9)	O(2) · · · WAT	3·702(7)
C(7) · · · C(10)	2·862(9)	O(3) · · · WAT	3·713(8)
C(8) · · · C(10)	2·517(9)		

Environment of the water molecule

Br–WAT–HWAT	115·6
HWAT–WAT–Na	115·9
Br–WAT–Na	128·6

TABLE 3

Torsion angles (°)

(*a*) In the cyclic ether ring

O(1)–C(1)–C(2)–O(3)	70·1
C(1)–C(2)–O(3)–C(6)	−173·2
C(2)–O(3)–C(6)–C(5)	178·3
O(3)–C(6)–C(5)–O(2)	−59·5
C(6)–C(5)–O(2)–C(4′)	−170·9
C(5)–O(2)–C(4′)–C(3′)	159·8
O(2)–C(4′)–C(3′)–O(1′)	65·8
C(4)–C(3)–O(1)–C(1)	−174·7

(*b*) In the cyclohexyl ring

C(5)–C(6)–C(7)–C(8)	58·6
C(6)–C(7)–C(8)–C(9)	−55·8
C(7)–C(8)–C(9)–C(10)	55·6
C(8)–C(9)–C(10)–C(5)	−60·6
C(9)–C(10)–C(5)–C(6)	61·3
C(10)–C(5)–C(6)–C(7)	−60·4

TABLE 4

Environment of the sodium ion

(*a*) Bond lengths (Å)

Na–WAT	2·346(5)
Na–O(1)	2·676(4)
Na–O(2)	2·682(4)
Na–O(3)	2·967(4)
Br–WAT	3·350(5)

(*b*) Bond angles (°)

O(1)–Na–O(2)	116·7(1)
O(1)–Na–O(3)	60·7(1)
O(2)–Na–O(3)	56·7(1)
O(1)–Na–WAT	91·1(2)
O(2)–Na–WAT	94·6(2)
O(3)–Na–WAT	87·8(2)
Br–WAT–Na	128·9(3)

RESULTS

Description of the Structure.—The sodium atom is at a crystallographic centre of symmetry, with the ligand oxygen atoms approximately coplanar (Table 5). A view of the molecule as a whole is shown in Figure 1. The Na–O(ether) distances range from 2·67 to 2·97 Å (Table 4) while the Na–O(water) distance is 2·35 Å. In the crystal the complex cations and bromide anions may be held in chains along the *a* axis by O–H · · · Br hydrogen bonds;

TABLE 5

Planes through various groups of atoms. Equations are in the form $lX + mY + nZ - p = 0$, where X, Y, and Z are co-ordinates in Å; X is along the a axis, Y in the (ab) plane, and Z along the c^* axis. Deviations (Å) of atoms from the planes are given in square brackets

Plane (1): O(1)—(3), O(1′)—(3′)

$$0{\cdot}8477X + 0{\cdot}3066Y - 0{\cdot}4328Z = -0{\cdot}8694$$

[O(1) 0·127(7), O(2) 0·132(4), O(3) −0·123(4), O(1′) −0·127(7), O(2′) −0·132(4), O(3′) 0·123(4), Na − 0·000, C(1) −0·364(6), C(2) 0·330(6), C(3) − 0·423(6), C(4) 0·224(6), C(5) −0·042(6), C(6) 0·566(6), C(7) 0·487(6), C(8) − 0·933(6), C(9) − 1·600(6), C(10) − 1·487(6), H(5) 0·329(60), H(6) 1·440(60)]

Plane (2): C(6), C(7), C(9), C(10)

$$-0{\cdot}8702X + 0{\cdot}4780Y - 0{\cdot}1189Z = -5{\cdot}9067$$

[C(6) −0·009(7), C(9) 0·008(8), C(9) −0·008(8), C(10) 0·008(8), C(5) − 0·713, C(8) 0·682, H(5) − 1·591 ax., H(6) − 0·385 eq., O(2) − 0·780, O(3) 1·294]

Plane (3): C(7)—(9)

$$0{\cdot}3839X - 0{\cdot}7623Y - 0{\cdot}5210Z = 5{\cdot}617$$

Plane (4): C(5), C(6), C(10)

$$0{\cdot}3040X - 0{\cdot}7802Y - 0{\cdot}5466Z = 4{\cdot}265$$

[H(5) 0·941 ax., H(6) −0·109 eq., O(2) − 1·114, O(3) − 1·240]

Dihedral angles (°) between planes

(1)—(2)	122·7	(2)—(3)	129·5
(1)—(3)	71·5	(2)—(4)	124·9
(1)—(4)	75·2	(3)—(4)	4·9

Br · · · O is 3·350 Å, which is the sum of the van der Waals' radii. As the bromide ion is on a centre of symmetry the O–H · · · Br · · · H–O angle is 180° in contrast with *ca.* 110° found in NaBr(dibenzo-18-crown-6)$(H_2O)_2$.[10] Although all the other hydrogen atoms were located unequivocally, that in the O–H · · · Br bond could not be detected in the final difference-Fourier map. Disappearance of the hydrogen atom taking part in a hydrogen bond is not uncommon, but it is not proof of the existence of such a bond. However, the geometry of Br, WAT, HWAT, and Na (Table 2) is consistent with the Na^+ and Br^- ions lying in the plane of the water molecule with a hydrogen bond from water to bromine.

The complexed 18-membered ring maintains very similar bond lengths and angles (Table 2) to those reported previously for the dibenzo-derivatives,[8,10] irrespective of variation in the substituent ring type.

The mean aliphatic C–C distances of the macrocycle are 1·484 Å, and in the cyclohexyl ring are 1·510 Å. Both are shorter than the average distance (1·537 Å) [21] normally quoted. This shortening has also been observed in other crystal structures of cyclic polyethers. It is difficult, at this stage, to be certain if this is a genuine shortening of the bond for chemical reasons, or an artefact of the assumptions made in the crystallographic programme system. Although, as the mean C–O bond lengths, and bond lengths in the aromatic rings [21] are normal, the former is more likely. A tetrahedral environment about all carbon atoms is maintained, except at C(5) and C(6), where some reflection of steric strain in the ligand would be expected. The torsion angles in Table 3 show no marked differences from those of other cyclic polyether complexes. The torsion angles about the C–C aliphatic bonds are *ca.* 60°, corresponding to the *gauche* configuration, C–C–O–C torsion angles are in agreement with the observation [8,10] that these are usually close to 180° in the 18-crown-6-type complexes.

The dihedral angle between the plane of the oxygen atoms in the ring, and the plane of the cyclohexyl ring is 122·7° (Table 5). The cyclohexyl ring is in the usual chair form, H(5) and H(6) being identified as axial and equatorial, respectively. Torsion angles for the cyclohexyl ring are all satisfactorily within the ideal range, *ca.* 60°. The dihedral angles between planes (3) and (4) (Table 5) of the cyclohexyl ring, show some slight departure from ideality, presumably caused by adaptation to the ligand requirement.

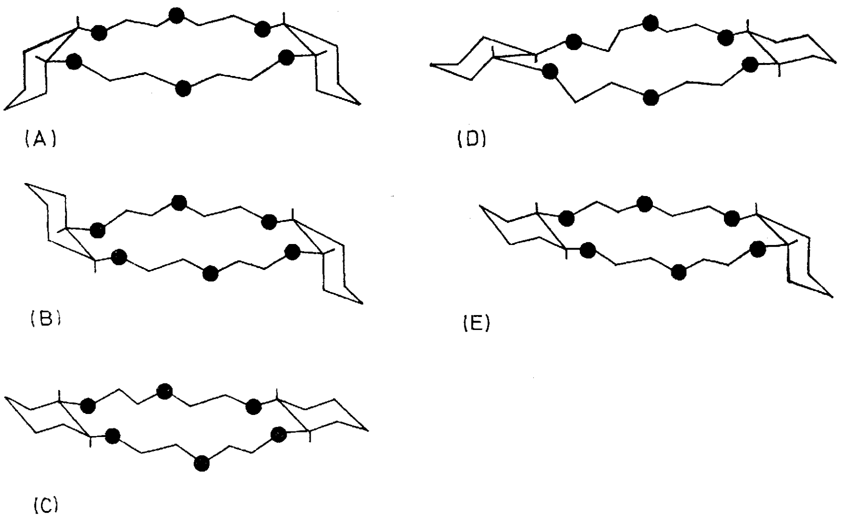

FIGURE 2 The five theoretical isomers available for dicyclohexyl-18-crown-6. Isomers A and B are the only two so far isolated. A, Isomer A (ref. 21), *cis-syn-cis* (*meso*); B, Isomer B (present work; ref. 22), *cis-anti-cis* (*dl*); C, *trans-syn-trans* (*meso*); D, *trans-anti-trans* (*dl*); E, *trans-anti-cis* (*dl*)

DISCUSSION

Dicyclohexyl-18-crown-6 is made by hydrogenation of the benzo-analogue so there is a possibility of *cis–trans* isomerism at the two bridge bonds. In the *trans*-isomer both oxygen substituents are equatorial for complex formation, in the *cis*-isomer one substituent is axial, and the other equatorial. In theory, five isomers,

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[21] *Chem. Soc. Special Publ.*, No. 18, 1960.

which are not interconvertible by conformational change, are possible. These are shown diagramatically in Figure 2. The two isomers which have so far been isolated have been previously referred to as isomer A (m.p. 61—62 °C) and isomer B (m.p. 69—70 °C).[16,22,23]

The n.m.r. evidence on the conformation of isomers A and B was not conclusive. ^{1}H n.m.r.[22b] suggested both isomers were *trans* (C and D, Figure 2). ^{13}C n.m.r.[24b] suggested both isomers were *cis* (A and B, Figure 2). The n.m.r. evidence eliminated isomer E.[22b,24b,25] The distinction between the spectroscopically similar pairs has been resolved by *X*-ray crystallography, isomer A being identified [24] as being in the *cis-syn-cis* form; and the present work identifies isomer B[18] as being the *cis-anti-cis* form. In solution, even in the presence of sodium, the cyclohexyl ring flips from one conformation to another.[25] This is consistent with the substituents in the bridge bonds being *cis*. Oxygen atoms which are axial and equatorial may chelate to a metal, and remain attached while the 'flipping' produced equatorial and axial alternatives for each oxygen.

The main factor affecting the formation of macrocyclic ether complexes with alkali metals is the radius of the cation and the diameter of the 'hole' as found from space-filling models * and confirmed by crystal-structure analyses.

In the present compound, the mean Na–O(ether) distance is 2·775 Å, and in the three dibenzo-18-crown-6 compounds it is 2·774 Å [8,10] compared with the usual range 2·2—2·5 Å. This lengthening appears to explain the lower stability constant found for sodium than for potassium complexes in 18-membered polyether rings.[16]

Cyclohexyl-15-crown-5 gives approximately the same values of the stability constants for Na^+ in a 1 : 1 complex, and K^+ in a 2 : 1 ligand to K^+ complex; [16] crystal-structure determination has been carried out on benzo-15-crown-5 complexes and the bond distances found to be optimum in both cases, *viz.* 2·35—2·43 Å for Na [11] and 2·78—2·96 Å for K [1,12] owing to the change in M^+ : ligand ratio. If the same distances are obtained in the cyclohexyl compound (and saturation has produced no change in those for the 18-membered rings) the similarity in stability constant may result from both sets of M–O distances being optimum.

Differences in stability caused by substitution or changes in the anion/solvent cannot be interpreted by simple electrostatic theory, because the bond distances remain the same. Changing the solvent can even change the selectivity, *e.g.* from tetrahydrofuran (Na > K) to oxetan (K > Na).[26] Further discussion of this subject would require consideration of both thermodynamics and theoretical interpretation of the bonding, possibly on the basis of lone-pair interactions. Although, at present, a systematic set of crystal structures of those compounds whose stability constants have been measured is not available, in order to check the possibility of correlation between lone-pair orientations and stability constants we have calculated the orientation of the lone pairs of the oxygen atoms in five 18-membered cyclic ether complexes on the assumption: (*a*) that with the two carbon atoms they complete tetrahedra, or (*b*) that one is coplanar with the carbon atoms and the other normal to this plane. Calculated electronegativities [27] of the lone pairs suggest that (*b*) would be slightly more stable than (*a*). Corresponding to these the metal might be (a) along the projection of a tetrahedral lone-pair, 'tetrahedral,' (b) along the extension of the bisector of C–O–C, 'trigonal,' (c) somewhere between (a) and (b) 'intermediate,' or (d) normal to both C–O bonds '*p*-type.' These are illustrated in Figure 3. Simple perturbation theory [28] favours (d) which is rarely found, purely electrostatic bonding should favour (b) and, as recent calculations show,[29] even non-bonding lone pairs of electrons are effective at distances of *ca.* 1 Å from the atom. From the results in Table 6 comparing O–M directions with (a_1), (b), and (a_2) it can be seen that the intermediate state (*c*) is the most common, and further that four (*b*)–O–M angles are found, 23, 32, 41, and 14°, giving respectively the sub-divisions (1), (2), (3), and (4).

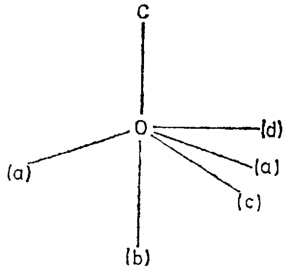

FIGURE 3 Possible directions from an ether oxygen atom to a metal. (a) tetrahedral, (b) trigonal, (c) intermediate, and (d) *p*-type. The carbon–carbon bond is normal to the plane of the paper. The angles in Table 6 show the deviation of the state (c) from the ideals (a) and (b)

The radius of potassium is about the same as that of barium, for which the structure of the complex with dicyclohexyl-18-crown-6, isomer A, was determined.[24]

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* From ref. 16.

	Hole diam./Å	Ion diam./Å
14-crown-4	1·2—1·5	Li^+ 1·36
15-crown-5	1·7—2·2	Na^+ 1·94
18-crown-6	2·6—3·2	K^+ 2·66
		Ba^{2+} 2·68
21-crown-7	3·4—4·3	Rb^+ 2·94
		Cs^+ 3·34

[22] (*a*) H. K. Frensdorff, *J. Amer. Chem. Soc.*, 1971, **93**, 4684; (*b*) E. C. Brame, unpublished work, quoted in ref. 22.

[23] R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, *J. Amer. Chem. Soc.*, 1971, **93**, 1619.

[24] (*a*) N. Kent Dalley, D. E. Smith, R. M. Izatt, J. J. Christensen, *J.C.S. Chem. Comm.*, 1972, 90; (*b*) Quoted in ref. 23 as D. Grant, personal communication.

[25] E. W. Randall and E. D. Rosenberg, 1971, personal communication.

[26] K. H. Wong, K. Konizer, and J. Smid, *J. Amer. Chem. Soc.*, 1970, **92**, 666.

[27] J. Hinze, M. A. Whitehead, and H. H. Jaffe, *J. Amer. Chem. Soc.*, 1963, **85**, 148.

[28] R. C. Hoffman, 1971, personal communication.

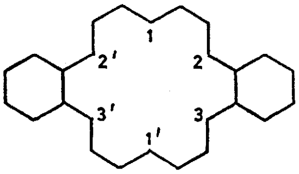
[29] M. A. Robb, W. J. Haines, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, 1973, **95**, 42.

For both potassium and sodium this isomer has a higher stability constant in water and in methanol than does isomer B.[16] The difference in lone-pair orientation is that two are trigonal for isomer A, but none for isomer B (Table 6).

The complexes formed by sodium bromide and sodium thiocyanate with dibenzo-18-crown-6 show a marked shift of orientation of the sodium ion relative to the lone pairs as the anion–solvent interaction shifts from NCS to either water or water–bromide (Table 6). It may also be noted that the benzene rings are not coplanar with the six oxygen atoms in the dibenzo-18-crown-6 complexes, and in all cases bend away from the direction occupied by the free lone pairs of electrons on the catechol oxygen atoms.

TABLE 6

Lone-pair orientations for substituted 18-crown-6 (numbers in brackets refer to crystallographic numbering in original ref.)



Dev. (°) from calc. direction of lone pairs

	Tetrahedral (1)	Tetrahedral (2)	Trigonal	Bond class
(i) Na-H_2O-H_2O Dicyclohexyl-18-crown-6 Isomer B				
O(1)[O(1)]	99	12	43	Intermediate (3)
O(1′)[O(1′)]	99	12	43	Intermediate (3)
O(2)[O(2)]	77	33	23	Intermediate (1)
O(2′)[O(3)]	105	4	51	Tetrahedral
O(3)[O(2′)]	77	33	23	Intermediate (1)
O(3′)[O(3′)]	105	4	51	Tetrahedral
(ii) Ba-CNS Dicyclohexyl-18-crown-6 [a]				Isomer A
O(1)[O(2)]	87	22	32	Intermediate (2)
O(1′)[O(2)]	87	22	32	Intermediate (2)
O(2)[O(5)]	109	1	55	Tetrahedral
O(2′)[O(5)]	109	1	55	Tetrahedral
O(3)[O(12)]	61	48	6	Trigonal
O(3′)[O(12)]	61	48	6	Trigonal
(iii) (B) Na-H_2O-Br Dibenzo-18-crown-6 [b]				
O(1)[O(4)]	109	2	55	Tetrahedral
O(1′)[O(17)]	101	8	47	Tetrahedral
O(2)[O(14)]	78	32	23	Intermediate (1)
O(2′)[O(20)]	96	13	42	Intermediate (3)
O(3)[O(7)]	77	32	23	Intermediate (1)
O(3′)[O(1)]	92	19	39	Intermediate (3)
(iv) (A) Na-H_2O-H_2O Dibenzo-18-crown-6 [b]				
O(1)[O(4)]	108	1	54	Tetrahedral
O(1′)[O(17)]	112	3	57	Tetrahedral
O(2)[O(14)]	82	27	27	Intermediate (2)
O(2′)[O(20)]	68	41	14	Intermediate (4)
O(3)[O(7)]	83	26	29	Intermediate (2)
O(3′)[O(1)]	76	33	21	Intermediate (1)
(v) Na-NCS Dibenzo-18-crown-6 [c]				
O(1)[O(5)]	127	18	72	Outside tetrahedron
O(1′)[O(2)]	123	14	68	Outside tetrahedron
O(2)[O(6)]	69	40	15	Intermediate (4)
O(2′)[O(4)]	77	32	23	Intermediate (1)
O(3)[O(1)]	78	31	24	Intermediate (1)
O(3′)[O(3)]	76	33	22	Intermediate (1)

[a] N. Kent Dalley, 1971, personal communication. [b] Ref. 10. Ref. 8.

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