# Crystal Structures of Complexes between Alkali-metal Salts and Cyclic Polyethers. Part III.[1] Aquo-(2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene)sodium Iodide

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The crystal structure of the title complex determined from three-dimensional diffractometer data. $Z = 4$ in an orthorhombic unit cell having $a = 12{\cdot}271$, $b = 9{\cdot}550$, $c = 15{\cdot}719$ Å, and space group $P2_12_12_1$. Full-matrix least-squares refinement based on 887 observations has led to $R$ 0·048 for the correct absolute configuration of the molecule.

The sodium ion is surrounded by a pentagonal pyramid of oxygen atoms. The base is formed by those of the cyclic ether with Na–O 2·35(1)—2·43(1) Å and the sodium ion is 0·75 Å from this plane towards the apical water molecule, Na–O 2·29(1) Å. The iodide ion does not interact with the sodium ion but may form hydrogen bonds to water molecules [O · · · I 3·47(1) and 3·51(1) Å], linking the complexes in chains along the $b$-axis of the crystal.

WHEN alkali-metal salts were first observed[2] to form complexes with macrocyclic ethers, sodium appeared to be preferred to potassium for an ether with a fifteen-membered ring containing five oxygen atoms while the larger ion, potassium, was preferred by an eighteen-membered ring containing six oxygen atoms. Crystal-structure determinations of complexes of dibenzo-18-crown-6 (I) with sodium salts showed that the sodium ion was approximately equidistant from all six coplanar

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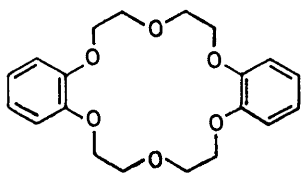
[1] Part II, M. A. Bush and M. R. Truter, *J. Chem. Soc.* (*B*), 1971, 1440.

[2] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

oxygen atoms with Na–O(mean) 2·7 (ref. 1) or 2·8 Å (ref. 3). These are at the high end of the range 2·2—2·7 Å usually considered [4] to represent interactions. We have determined the structure of the complex between sodium iodide and benzo-15-crown-5 (systematically named 2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene) to obtain comparable Na–O distances and discover the configuration of the molecule. A preliminary report has appeared.[5]



(I)

TABLE 1

Atomic co-ordinates ($\times 10^4$) and isotropic vibration parameters ($\times 10^2$) with estimated standard deviations in parentheses

| | $x/a$ | $y/b$ | $z/c$ | $B/\text{Å}^2$ |
|---|---|---|---|---|
| I | 0828(1) | 1921(1) | 1328(1) | * |
| Na | −2758(5) | 0612(6) | 2640(4) | 493(14) |
| O(6) | −0926(10) | 0231(11) | 2761(7) | 733(28) |
| O(1) | −3740(8) | 0421(11) | 3934(6) | 541(25) |
| C(2) | −4468(14) | −0757(19) | 4035(10) | 626(42) |
| C(3) | −4091(13) | −1863(18) | 3429(9) | 593(36) |
| O(4) | −4061(8) | −1299(10) | 2607(6) | 500(22) |
| C(5) | −3600(13) | −2198(19) | 1994(11) | 670(43) |
| C(6) | −3576(14) | −1490(18) | 1152(11) | 693(45) |
| O(7) | −2974(8) | −0247(11) | 1247(7) | 573(24) |
| C(8) | −3157(13) | 0767(18) | 0616(10) | 545(37) |
| C(9) | −2581(12) | 2026(19) | 0864(10) | 589(39) |
| O(10) | −3006(8) | 2540(11) | 1664(7) | 525(25) |
| C(11) | −2422(14) | 3660(18) | 2042(12) | 665(46) |
| C(12) | −2916(15) | 4015(21) | 2860(11) | 682(45) |
| O(13) | −2893(8) | 2751(11) | 3396(6) | 563(25) |
| C(14) | −3411(11) | 2787(16) | 4169(9) | 458(35) |
| C(15) | −3523(15) | 4035(21) | 4643(12) | 701(45) |
| C(16) | −4084(15) | 3920(20) | 5430(11) | 670(42) |
| C(17) | −4564(14) | 2768(20) | 5691(11) | 702(46) |
| C(18) | −4460(13) | 1546(17) | 5237(10) | 589(43) |
| C(19) | −3891(12) | 1576(17) | 4465(10) | 520(38) |
| H(1,2) † | −5205 | −0506 | 3902 | 550 |
| H(2,2) | −4474 | −1131 | 4608 | 550 |
| H(3,3) | −4562 | −2667 | 3440 | 550 |
| H(4,3) | −3375 | −2182 | 3590 | 550 |
| H(5,5) | −4007 | −3073 | 1964 | 550 |
| H(6,5) | −2864 | −2459 | 2146 | 550 |
| H(7,6) | −4320 | −1358 | 0975 | 550 |
| H(8,6) | −3258 | −2139 | 0738 | 550 |
| H(9,8) | −3907 | 0966 | 0527 | 550 |
| H(10,8) | −2872 | 0446 | 0062 | 550 |
| H(11,9) | −2699 | 2782 | 0419 | 550 |
| H(12,9) | −1816 | 1899 | 0872 | 550 |
| H(13,11) | −2418 | 4439 | 1670 | 550 |
| H(14,11) | −1686 | 3374 | 2142 | 550 |
| H(15,12) | −3669 | 4343 | 2775 | 550 |
| H(16,12) | −2545 | 4790 | 3130 | 550 |
| H(17,15) | −3258 | 4924 | 4429 | 550 |
| H(18,16) | −4134 | 4748 | 5779 | 550 |
| H(19,17) | −4996 | 2772 | 6184 | 550 |
| H(20,18) | −4705 | 0656 | 5463 | 550 |

* Anisotropic vibration parameters ($\times 10^4$) for the iodide ion in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| I | 87(1) | 181(2) | 67(1) | 5(1) | −5(1) | −4(1) |

† Hydrogen atom parameters were not refined. The number after the comma, in the atom labelling, is the number of the carbon atom to which the hydrogen is attached.

Colourless crystals of the complex were obtained [6] by reaction between sodium iodide and the cyclic ether in methanol. The i.r. spectrum had a strong peak at 3490 cm$^{-1}$ with shoulders at 3430 and 3570 cm$^{-1}$ which suggested the presence of hydroxy-groups; elemental analysis and preliminary *X*-ray measurements were consistent with a formula unit NaI($C_{14}H_{22}O_5$)$H_2O$. There are four such units in the orthorhombic unit cell. All the atoms of one were located by conventional Fourier methods and atomic parameters were refined by least-squares to give the values in Table 1; for the hydrogen atoms the co-ordinates were calculated from the positions of the oxygen and carbon atoms.

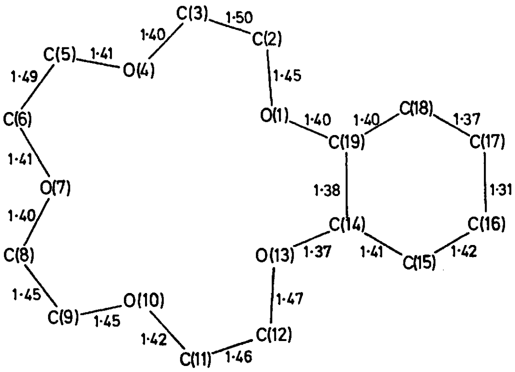


FIGURE 1 One molecule of benzo-15-crown-5 showing the designations of the atoms; for clarity hydrogen atoms have been omitted. C(15)—(18) have one and the other carbon atoms have two hydrogen atom substituents. Bond lengths (Å) all have estimated standard deviations of 0·02 Å. The water molecule, not shown, is designated O(6)

The numbering of the atoms of the ligand and the bond lengths are shown in Figure 1. Bond angles and torsion angles are given in Table 2. Figure 2 shows the structure as a whole consisting of iodide ions and complex cations in which each sodium ion is surrounded by the five oxygen atoms of the ligand and one water molecule.

The arrangement of oxygen atoms forming the solvation sphere around the sodium ion may be described as a distorted pentagonal pyramid, the base of which is formed by the ether oxygen atoms. The variations among the Na–O(ether) distances are statistically significant (Table 3), but all are much shorter than in the dibenzo-18-crown-6 derivatives.[1,3] The five oxygen atoms are not quite coplanar (Table 4), and the sodium ion is 0·75 Å from their mean plane towards the water molecule, O(6), making the Na–O(6) distance of 2·29(1) Å the shortest one. The Na–O(6) vector makes an angle of 9·7° with the normal to the mean plane through the

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

[4] For example, C. Romers, C. J. M. Rooymans, and R. A. G. de Graaf, *Acta Cryst.*, 1967, **22**, 766.

[5] M. A. Bush and M. R. Truter, *Chem. Comm.*, 1970, 1439.

[6] C. J. Pedersen, 1969, personal communication.

ether oxygen atoms. If it coincided with the normal, the complex cation would have an approximate plane of symmetry passing through O(7) and the mid-points of C(14)–C(19), and C(16)–C(17); this effect is shown by

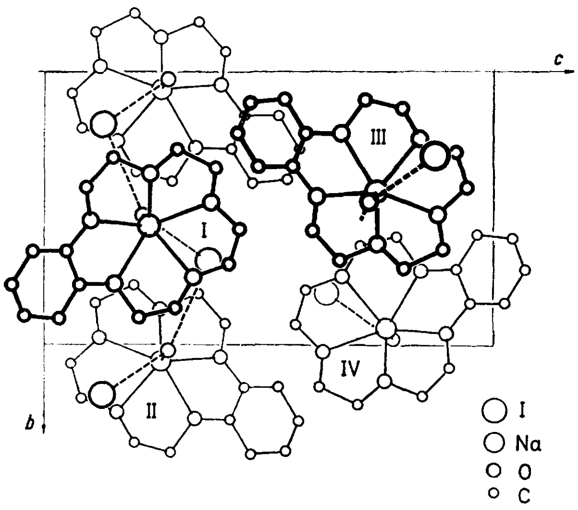

FIGURE 2 The structure projected down the *a*-axis. The molecule closest to the origin is the crystal chemical unit with the co-ordinates of Table 1, other molecules are related to this by:

I $-x, \frac{1}{2}+y, \frac{1}{2}-z$    III $\frac{1}{2}+x, \frac{1}{2}-y, 1+z$
II $x, 1+y, z$    IV $-\frac{1}{2}-x, 1-y, \frac{1}{2}+z$

Broken lines indicate the chain of interactions tentatively assigned to I · · · O(6) hydrogen bonds. Distances are O(6) · · · I, 3·51 and I · · · $O(6^{\mathrm{I}})$, 3·47 Å

the torsion angles (Table 2) and the Na–O(ether) distances (Table 3).

The bond lengths and angles of the cyclic ether are similar to those observed in other such complexes. The aliphatic C–C bonds (mean 1·47 Å) show the usual[1,3,7] apparent shortness, probably due to the neglect of the vibration parameters in the bond length evaluation; this systematic error may also account for the fact that the standard deviation in a C–C bond length in the benzenoid ring, calculated from the spread about the mean, is 0·04 Å whereas the value calculated[8] from the variance–covariance matrix obtained in least-squares refinement is 0·02 Å. The torsion angles show the same trends as those observed in the complexes of dibenzo-18-crown-6,[1,6] *i.e.* that the angles about the aliphatic C–C bonds are all gauche at *ca.* 60°, corresponding to staggered hydrogen and oxygen atom substituents, and that the torsion angles of the type C–O–C–C are commonly close to 180°.

TABLE 2

(*a*) Bond angles (°) in the ligand

| | | | |
|---|---|---|---|
| C(3)–O(4)–C(5) | 114(1) | C(11)–C(12)–O(13) | 108(1) |
| C(6)–O(7)–C(8) | 115(1) | O(1)–C(19)–C(18) | 125(1) |
| C(9)–O(10)–C(11) | 116(1) | O(13)–C(14)–C(15) | 122(1) |
| C(2)–O(1)–C(19) | 118(1) | O(1)–C(19)–C(14) | 114(1) |
| C(12)–O(13)–C(14) | 119(1) | O(13)–C(14)–C(19) | 118(2) |
| O(1)–C(2)–C(3) | 107(1) | C(14)–C(15)–C(16) | 116(2) |
| C(2)–C(3)–O(4) | 109(1) | C(15)–C(16)–C(17) | 124(2) |
| O(4)–C(5)–C(6) | 110(1) | C(16)–C(17)–C(18) | 120(2) |
| C(5)–C(6)–O(7) | 107(1) | C(17)–C(18)–C(19) | 119(2) |
| O(7)–C(8)–C(9) | 108(1) | C(18)–C(19)–C(14) | 122(2) |
| C(8)–C(9)–O(10) | 110(1) | C(19)–C(14)–C(15) | 119(1) |
| O(10)–C(11)–C(12) | 110(1) | | |

(*b*) Torsion angles (°) in the cyclic ether ring

| | | | |
|---|---|---|---|
| O(1)–C(2)–C(3)–O(4) | −56 | C(9)–O(10)–C(11)–C(12) | −177 |
| C(2)–C(3)–O(4)–C(5) | 173 | O(10)–C(11)–C(12)–O(13) | 58 |
| C(3)–O(4)–C(5)–C(6) | −178 | C(11)–C(12)–O(13)–C(14) | −174 |
| O(4)–C(5)–C(6)–O(7) | 58 | C(12)–O(13)–C(14)–C(19) | 147 |
| C(5)–C(6)–O(7)–C(8) | −160 | O(13)–C(14)–C(19)–O(1) | 3 |
| C(6)–O(7)–C(8)–C(9) | 173 | C(14)–C(19)–O(1)–C(2) | −161 |
| O(7)–C(8)–C(9)–O(10) | −62 | C(19)–O(1)–C(2)–C(3) | −177 |
| C(8)–C(9)–O(10)–C(11) | 172 | | |

TABLE 3

Environment of the sodium ion

(*a*) Distances (Å)

| | | | |
|---|---|---|---|
| O(6)–Na | 2·285(14) | O(7)–Na | 2·354(11) |
| O(1)–Na | 2·372(11) | O(10)–Na | 2·416(12) |
| O(4)–Na | 2·427(12) | O(13)–Na | 2·369(12) |

Angles (°)

| | | | |
|---|---|---|---|
| O(6)–Na–O(1) | 114·6(4) | O(1)–Na–O(4) | 68·0(4) |
| O(6)–Na–O(4) | 122·0(5) | O(4)–Na–(O7) | 69·1(4) |
| O(6)–Na–O(7) | 97·6(4) | O(7)–Na–O(10) | 70·2(4) |
| O(6)–Na–O(10) | 107·3(5) | O(10)–Na–O(13) | 69·7(4) |
| O(6)–Na–O(13) | 99·5(4) | O(13)–Na–O(1) | 66·5(4) |

TABLE 4

Planes through various groups of atoms. Atoms used to define the plane are italicised. Deviations (Å) of atoms from the planes are given in square brackets

Plane (A): $-0{\cdot}940x + 0{\cdot}293y - 0{\cdot}175z - 3{\cdot}371 = 0$

[*O(1) −0·02, O(4) +0·23, O(7) −0·35, O(10) +0·35, O(13) −0·20, Na −0·75, O(6) −3·00*]

Plane (B): $-0{\cdot}844x + 0{\cdot}228y - 0{\cdot}486z - 0{\cdot}958 = 0$

[*C(14) −0·01, C(15) +0·02, C(16) −0·03, C(17) +0·02, C(18) −0·01, C(19) 0·00*]

Angle between normals to planes (A) and (B): 19°.

The only interactions <3·6 Å between non-hydrogen atoms are two involving the iodide ions and water molecules. These are shown by broken lines in Figure 2. We consider these may be hydrogen bonds because they are less than the sum of the van der Waals' radii (3·55 Å), and the angles subtended at oxygen by adjoining iodide ions (131°), and at iodine by adjoining oxygen atoms (100°) are consistent with this postulate. The existence of hydrogen bonding could not be proved because hydrogen atom positions were not observed in electron-density syntheses. However, the chain of interactions along the *b* axis is similar to that in unequivocally hydrogen-bonded structures, including NaBr(dibenzo-18-crown-6),$2H_2O$.[1]

## EXPERIMENTAL

Crystals of aquo(benzo-15-crown-5)-sodium iodide were obtained by slow evaporation of a methanol solution[6] (Found: C, 39·2; H, 5·2. Calc. for $C_{14}H_{22}INaO_6$: C, 38·6; H, 5·0%).

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[7] M. A. Bush and M. R. Truter, following paper, Part IV.

[8] Programmes from the Northwestern University adapted by D. Bright for the London University CDC 6600 computer.

Preliminary $X$-ray photographs showed that the crystal system was orthorhombic and the systematic absences ($h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$) uniquely determined the space group, $P2_12_12_1$ ($D_2^4$, No. 19).

The crystal used for the intensity determinations was cut from a much larger one and had dimensions $0{\cdot}18 \times 0{\cdot}18 \times 0{\cdot}14$ mm. It was set up on a Picker four-circle diffractometer * using the accurately centred positions of 14 reflections having a mean $2\theta$ value of 22°. These were used to refine the cell constants and the orientation angles.[8] Intensities were measured by the $2\theta$—$\theta$ scan procedure at a scan rate of 0·5° min$^{-1}$ from $2\theta_{\text{calc}}$ ($K_{\alpha.1}$) $-0{\cdot}5°$ to $2\theta$ calc ($K_{\alpha.2}$) $+0{\cdot}5°$. Stationary background counts for 25 s each were made at the ends of each scan. Zirconium-filtered molybdenum radiation was used throughout and the intensities were monitored using a scintillation counter with pulse-height discrimination. Reflections of the type $hkl$ only were measured out to a $2\theta$ value of 53·0° and the intensities of three standard reflections (6,0,0, 0,2,0, 0,2,4) were measured every 50 reflections and used to put the observations on a common scale. The intensities were corrected for Lorentz and polarisation effects and the standard deviations calculated as in ref. 3; reflections for which $I \leqslant 3\sigma_I$ were removed from the data set to produce 887 independent structure amplitudes.

*Crystal Data*.—$C_{14}H_{22}O_6NaI$, $M = 436{\cdot}3$, m.p. 150°, Orthorhombic, $a = 12{\cdot}271(4)$, $b = 9{\cdot}550(4)$, $c = 15{\cdot}719(5)$ Å, $U = 1842{\cdot}1$ Å$^3$, $F(000) = 872$. $D_m = 1{\cdot}58$ g cm$^{-3}$, $Z = 4$, $D_c = 1{\cdot}57$ g cm$^{-3}$. Space group $P2_12_12_1$ ($D_2^4$, No. 19). Mo-$K_\alpha$ radiation, $\lambda(K_{\alpha.1})$ 0·7093 Å, $\lambda(K_{\alpha.2})$ 0·7135 Å (1 Å $\equiv$ $10^{-10}$ m); $\mu$(Mo-$K_\alpha$) = 18·1 cm$^{-1}$.

The position of the iodide ion was readily obtained from a three-dimensional Patterson synthesis and the co-ordinates of the remaining 21 light atoms were obtained from subsequent electron density syntheses. The atomic co-ordinates, isotropic vibration parameters, and an overall scale-factor were then refined using full-matrix least-squares [8] with unit weights and scattering factors for $I^-$, $Na^+$, C, and O from ref. 9. Four cycles gave convergence at $R$ 0·072 and $R'$ $[(\Sigma w(\Delta)^2/\Sigma(wF_o)^2)^{\frac{1}{2}}]$ suggested that the iodide ion should be allowed anisotropic vibration parameters; two further cycles then produced $R$ 0·060 and $R'$ 0·063. The positions of the 20 hydrogen atoms of the ether were computed [10] assuming C–H 0·95 Å; these were included in subsequent structure-factor calculations but were not refined. Scattering factors for hydrogen were taken from ref. 11 and an isotropic temperature factor, $B$ 5·5 Å$^2$, was assigned to all. The iodide scattering curve was corrected for the effects of anomalous dispersion [12] and the weighting scheme adjusted to the form $\sigma_{F_o} = \sigma(F_o$ from counting statistics$) + A|F_o|^2$ with the coefficient $A$ chosen to produce satisfactory consistency of $\Sigma w\Delta^2$ when systematically analysed in terms of $|F_o|$ and $\sin\theta$. Two further cycles of refinement resulted in $R$ 0·048 and $R'$ 0·055.

Because the space group is non-centrosymmetric, the presence of an anomalous scatter should allow the absolute configuration of the molecule to be determined.[13] The last two cycles of refinement were, therefore, recomputed with the $h$ indices changed from positive to negative. The normal and weighted $R$ values obtained were 0·052 and 0·062, respectively; these quantities were also greater than the previous corresponding values in all $|F_o|$ and $\sin\theta$ ranges of the data. This strongly suggests [14] that the previous configuration was indeed correct.

A final electron-density difference map showed only random maxima between $+0{\cdot}3$ and $-0{\cdot}3$ eÅ$^{-3}$, except for peaks of 0·5 eÅ$^{-3}$ near the iodide position. No significant evidence of anisotropic thermal motion of the light atoms could be found, neither could the positions of the hydrogen atoms of the water molecule be unequivocally determined, even when the reflection data were limited to a maximum $\sin\theta/\lambda$ of 0·35 Å$^{-1}$. The refinement was, therefore, concluded.

Calculated and observed structure amplitudes are listed in Supplementary Publication No. SUP 20283 (8 pp., 1 microfiche).†

Planes through groups of atoms, torsion angles, and intermolecular distances were calculated [10] on the IBM 1130 computer.

Bond lengths and angles were computed using ORFFE which uses the complete variance–covariance matrix in its evaluation of the errors. This programme, like the full-matrix least-squares refinement, was run on the CDC 6600 computer.[8]

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

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

[10] Programmes written by B. L. Vickery for IBM 1130 computer.

[11] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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

[13] J. M. Bijvoet, A. F. Peerdeman, and A. J. Van Bommel, *Nature*, 1951, **168**, 271.

[14] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.