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

By **John D. Owen**, Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts., AL5 2JQ

The crystal structures of the three title compounds of 'benzo-15-crown-5' with Na[ClO$_4$] in 1 : 1 and 2 : 1 ratio and with Na[BPh$_4$] in 2 : 1 ratio have been determined from diffractometer data collected with molybdenum radiation. The 1 : 1 complex with Na[ClO$_4$] crystallises in the monoclinic space group $P2_1/c$ with cell dimensions a = 8.806(3), b = 8.310(10), c = 24.148(7) Å, β = 99.16(1)°, and Z = 4. The final R factor is 0.075 for 1 737 observations. The cation is irregularly co-ordinated to five oxygen atoms from the crown ligand and two from the anion. The conformation of the ether is similar to that found in the NaI·H$_2$O complex. The 2 : 1 complex with Na[ClO$_4$] forms crystals with the tetragonal space group $P4/n$, which are isomorphous with the KI complex, with a = 17.786(7), c = 9.869(5) Å, and Z = 4. The structure has been refined to R = 0.121 for 1 053 observations, due to disorder problems in the atomic positions. The complex has a centrosymmetric sandwich structure and two conformers are present in proportion 0.523 : 0.477, the first being similar to that found in the free ligand, the second, new. The co-ordination number of the cation is not clear, due to a wide spread in the range of Na–O distances. The 2 : 1 complex with Na[BPh$_4$] is monoclinic, space group $P2_1/c$ with a = 12.497(3), b = 19.450(3), c = 19.896(4) Å, β = 94.76(2)°, and Z = 4. The final R factor was 0.080 for 1 258 observations. A different sandwich structure is present in these crystals, with no symmetry, and again the co-ordination number of the cation is not clear. The conformations of the two independent ether molecules are similar to each other and to that found in the free-ligand crystals.

BENZO-15-CROWN-5 forms crystalline complexes with salts of metals in Groups 1A and 2A, with crown : metal ratios of 1 : 1 for a small cation and 2 : 1 for larger ones.[2-5] Thus, magnesium forms only a 1 : 1 complex,[5] whereas only 2 : 1 complexes are isolated for K$^+$, Cs$^+$, Sr^{2+}, and Ba^{2+}. Sodium and calcium have similar ionic radii and are exceptional in that they can form either 1 : 1 or 2 : 1 complexes depending on the reaction conditions.

Calcium [5] forms 1 : 1 complexes when the anion can act as a co-ordinating ligand (*e.g.* isothiocyanate [6] and 3,5-dinitrobenzoate [7]), but if tetraphenylborate is used, a 2 : 1 complex is formed. Calcium perchlorate forms complexes which have not yet been well characterised, but seem to be 2 : 1 complexes with various amounts of hydration.[5]

Sodium [2-4] usually forms 1 : 1 complexes with solvent co-ordinated to the cation, as was found typically in the NaI·H$_2$O complex.[8] The crystalline product with sodium perchlorate is usually an unsolvated 1 : 1 complex (1). However, from very concentrated solutions, an unsolvated 2 : 1 complex (2) can be isolated.[4] With sodium tetraphenylborate, the normal product is a solvated 1 : 1 complex when the reactants are present in this ratio. Using the required 2 : 1 ratio leads to the precipitation of an unsolvated 2 : 1 complex (3).[3]

Spectroscopic techniques indicated that the structure of (1) was similar to that of the NaI·H$_2$O complex, with the anion co-ordinating with the cation, displacing the solvent, and with a similar conformation of the ether. Both the complexes (2) and (3) were expected to be similar to the KI complex,[9] with the same conformation of the ether, a sandwich structure for the complex cations, and with discrete non-co-ordinating anions.

In order to identify the structures present in these complexes, the crystals of the title compounds were investigated by X-ray diffraction techniques and the results are reported here.

Intensity data were collected on two four-circle diffractometers and the structures of (1) and (3) solved by direct methods, and that of (2) by analogy with the isomorphous KI complex.[9] Parameters were refined by the usual least-squares methods and the final values are given in Tables 1—3. Bond lengths and selected bond angles are given in Tables 4 and 5. The atom-numbering scheme for the ether rings is shown in Figure 1. The hydrogen atoms are numbered according to the carbon atom to which they are attached, thus H(161) and

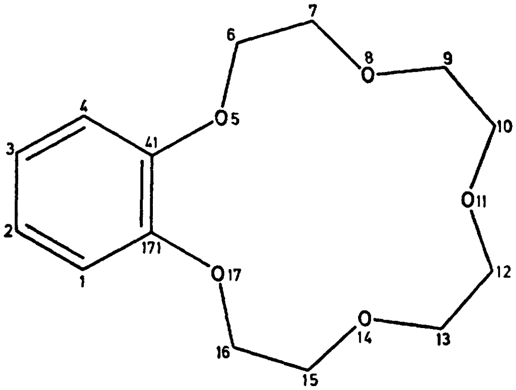

FIGURE 1 Numbering scheme for the ether atoms

H(162) are bonded to atom C(16). Mean planes and torsion angles within the macrocycles are given in Tables 6 and 7.

RESULTS AND DISCUSSION

The sodium cation in (1) is irregularly co-ordinated to seven oxygen atoms, five on the ether, and two on the perchlorate anion (see Figure 2). The splitting of the asymmetric ClO_4^- bending frequency and the unsolvated nature of the complex [4] were both given as evidence for the co-ordination of the anion, and this is confirmed by the structure determination. The Na–O (perchlorate) distances [2.426(7) and 2.634(6) Å] show the unsymmetrical nature of the co-ordination between cation and anion. The oxygen atoms appear to undergo quite large anisotropic thermal motion, with the smallest movement along the Cl–O bonds as might be expected. The Cl–O distances are not significantly different from

TABLE 1

Fractional atomic co-ordinates ($\times 10^3$ for H, $\times 10^4$ for others) for (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) Non-hydrogen atoms			
Na	1 391(3)	2 227(3)	1 266(1)
Cl	−1 858(2)	3 623(2)	871(1)
O(18)	−2 524(8)	5 028(9)	1 045(3)
O(19)	−598(6)	4 005(8)	599(2)
O(20)	−1 295(7)	2 660(10)	1 338(3)
O(21)	−2 998(7)	2 846(10)	495(3)
C(1)	3 090(7)	3 122(8)	3 161(3)
C(2)	3 861(9)	4 420(10)	3 439(3)
C(3)	4 246(9)	5 698(10)	3 162(3)
C(4)	3 907(8)	5 797(10)	2 583(3)
C(41)	3 145(7)	4 525(8)	2 290(3)
O(5)	2 737(5)	4 512(5)	1 717(2)
C(6)	3 803(8)	5 235(9)	1 398(3)
C(7)	3 338(8)	4 834(9)	797(3)
O(8)	3 294(5)	3 130(5)	743(2)
C(9)	2 905(8)	2 592(9)	182(3)
C(10)	2 737(8)	813(9)	192(3)
O(11)	1 576(5)	432(6)	512(2)
C(12)	1 481(8)	−1 239(10)	643(3)
C(13)	650(8)	−1 416(9)	1 121(3)
O(14)	1 517(5)	−591(5)	1 587(2)
C(15)	811(8)	−528(9)	2 071(3)
C(16)	1 751(8)	472(9)	2 501(3)
O(17)	1 917(5)	2 030(5)	2 258(2)
C(171)	2 735(7)	3 211(8)	2 580(2)
(*b*) Hydrogen atoms			
H(1)	280	221	337
H(2)	412	439	384
H(3)	477	658	337
H(4)	421	673	239
H(61)	482	484	153
H(62)	380	638	145
H(71)	407	527	58
H(72)	234	527	66
H(91)	370	288	−3
H(92)	196	307	1
H(101)	369	33	36
H(102)	246	41	−18
H(121)	249	−168	73
H(122)	94	−180	32
H(131)	57	−254	121
H(132)	−36	−97	103
H(151)	72	−159	222
H(152)	−20	−7	198
H(161)	274	0	261
H(162)	125	58	282

TABLE 2

Fractional atomic co-ordinates ($\times 10^3$ for H, $\times 10^4$ for others) for (2)

Atom	*x*	*y*	*z*
(*a*) Non-hydrogen atoms			
Na	5 000	5 000	5 000
C(1)	7 001(8)	4 519(8)	1 993(13)
C(2)	7 224(8)	4 947(8)	947(15)
C(3)	7 071(8)	5 684(8)	783(16)
C(4)	6 651(7)	6 046(8)	1 766(13)
C(41)	6 417(7)	5 642(6)	2 896(13)
O(5)	6 013(5)	5 921(5)	3 960(9)
C(6)	5 897(8)	6 717(7)	4 104(15)
C(7)	5 744(8)	6 884(8)	5 492(15)
O(8)	5 110(5)	6 493(4)	5 961(9)
C(9)	5 020(9)	6 503(9)	7 373(16)
C(10)	5 484(10)	5 962(9)	8 147(17)
O(11)	5 282(6)	5 240(6)	7 773(11)
C(12)A	5 844(13)	4 832(11)	8 533(24)
C(12)B	5 451(15)	4 529(12)	8 422(29)
C(13)A	5 673(16)	4 052(13)	8 035(16)
C(13)B	6 194(13)	4 227(16)	7 947(19)
O(14)	5 914(6)	3 972(6)	6 643(11)
C(15)	6 647(9)	3 882(9)	6 108(16)
C(16)	6 684(8)	3 877(8)	4 668(14)
O(17)	6 333(5)	4 561(5)	4 155(9)
C(171)	6 607(7)	4 866(7)	3 008(12)
Cl(21)	7 500	2 500	0
O(22)	6 869(12)	2 700(11)	646(26)
Cl(31)	2 500	2 500	2 251(10)
O(32)	2 500	2 500	3 674(10)
O(33)	2 684	3 221	1 777(10)
O(34)	1 783	2 299	1 777(10)
O(35)	3 032	1 980	1 777(10)
(*b*) Hydrogen atoms			
H(1)	712	398	204
H(2)	752	470	24
H(3)	725	596	−2
H(4)	652	658	167
H(61)	547	687	354
H(62)	635	699	381
H(71)	565	743	558
H(72)	618	674	604
H(91)	514	701	769
H(92)	449	639	757
H(101)	540	603	912
H(102)	602	604	794
H(151)	696	430	644
H(152)	685	340	644
H(161)	721	386	438
H(162)	642	344	432

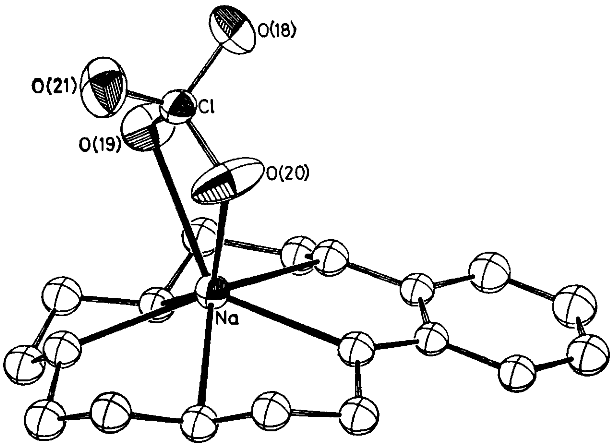

FIGURE 2 Molecule of (1), showing the 30% thermal ellipsoids

each other to the accuracy of this structure determination.

The sodium–ether co-ordination is very similar to that found[8] in the NaI·H_2O complex with benzo-15-crown-5 in all aspects (see Tables 4—7). The bond lengths and angles are similar to those found in other crown ethers and their complexes, and there are no short contacts between the molecules in this crystal.

TABLE 3

Fractional atomic co-ordinates (× 10^3 for H, × 10^4 for others) for (3)

Atom	*x*	*y*	*z*
(*a*) Non-hydrogen atoms			
Na	2 280(9)	1 973(4)	115(5)
C(101)	3 150(16)	1 451(10)	2 473(10)
C(102)	2 338(18)	1 157(11)	2 853(10)
C(103)	1 314(17)	1 324(10)	2 717(10)
C(104)	966(15)	1 754(10)	2 188(9)
C(141)	1 770(16)	2 003(10)	1 797(10)
O(105)	1 525(11)	2 424(7)	1 244(7)
C(106)	553(17)	2 792(11)	1 126(10)
C(107)	667(16)	3 302(10)	613(9)
O(108)	1 056(10)	2 986(6)	55(6)
C(109)	1 426(18)	3 460(12)	−427(11)
C(110)	2 520(18)	3 647(11)	−240(11)
O(111)	3 180(12)	3 055(7)	−295(7)
C(112)	4 279(20)	3 256(13)	−146(13)
C(113)	4 950(18)	2 653(11)	−95(11)
O(114)	4 739(10)	2 198(7)	446(7)
C(115)	5 138(15)	2 437(10)	1 089(9)
C(116)	4 628(15)	2 017(10)	1 605(9)
O(117)	3 485(10)	2 177(6)	1 513(6)
C(171)	2 828(15)	1 881(10)	1 945(10)
C(201)	−1 884(19)	1 650(11)	−115(11)
C(202)	−2 464(19)	1 471(11)	429(12)
C(203)	−2 035(19)	1 103(11)	960(11)
C(204)	−959(18)	867(10)	1 015(11)
C(241)	−374(18)	1 028(11)	462(11)
O(205)	661(13)	823(7)	439(7)
C(206)	1 186(16)	380(10)	934(10)
C(207)	2 214(18)	175(11)	672(11)
O(208)	2 868(11)	758(7)	602(7)
C(209)	3 797(19)	606(12)	234(11)
C(210)	3 507(18)	596(11)	−480(11)
O(211)	3 172(12)	1 253(8)	−705(8)
C(212)	2 833(24)	1 198(16)	−1 406(15)
C(213)	2 387(23)	1 823(15)	−1 607(14)
O(214)	1 446(15)	2 035(9)	−1 281(8)
C(215)	477(19)	1 830(12)	−1 579(12)
C(216)	−384(18)	1 947(12)	−1 126(11)
O(217)	−118(13)	1 507(8)	−553(8)
C(271)	−846(19)	1 419(11)	−70(11)
B	2 569(16)	−4 303(10)	1 467(10)
CA(1)	3 396(8)	−3 071(6)	1 602(5)
CA(2)	3 513(8)	−2 420(6)	1 892(5)
CA(3)	2 842(8)	−2 215(6)	2 381(5)
CA(4)	2 053(8)	−2 661(6)	2 580(5)
CA(5)	1 935(8)	−3 312(6)	2 289(5)
CA(6)	2 607(8)	−3 517(6)	1 800(5)
CB(1)	1 139(8)	−4 931(6)	2 172(5)
CB(2)	171(8)	−5 260(6)	2 263(5)
CB(3)	−598(8)	−5 342(6)	1 720(5)
CB(4)	−398(8)	−5 093(6)	1 084(5)
CB(5)	571(8)	−4 764(6)	993(5)
CB(6)	1 339(8)	−4 682(6)	1 536(5)
CC(1)	4 272(11)	−4 549(5)	2 299(7)
CC(2)	5 047(11)	−4 984(5)	2 615(7)
CC(3)	5 012(11)	−5 688(5)	2 482(7)
CC(4)	4 202(11)	−5 957(5)	2 034(7)
CC(5)	3 427(11)	−5 523(5)	1 719(7)
CC(6)	3 462(11)	−4 819(5)	1 851(7)
CD(1)	3 474(9)	−4 636(5)	328(6)
CD(2)	3 648(9)	−4 545(5)	−350(6)
CD(3)	3 102(9)	−4 030(5)	−726(6)
CD(4)	2 381(9)	−3 605(5)	−424(6)
CD(5)	2 206(9)	−3 695(5)	254(6)
CD(6)	2 752(9)	−4 211(5)	603(6)
(*b*) Hydrogen atoms			
H(101)	390	135	258
H(102)	254	84	321
H(103)	79	114	300
H(104)	22	187	210
H(1061)	−1	248	98
H(1062)	38	301	153
H(1071)	116	365	78
H(1072)	−2	351	49
H(1091)	99	387	−44
H(1092)	137	325	−87
H(1101)	259	381	22
H(1102)	274	400	−54
H(1121)	450	354	−50
H(1122)	435	350	27
H(1131)	568	280	−3
H(1132)	485	240	−51
H(1151)	590	238	114
H(1152)	496	291	114
H(1161)	491	214	205
H(1162)	474	154	153
H(201)	−219	191	−49
H(202)	−320	162	43
H(203)	−248	100	132
H(204)	−65	62	140
H(2061)	132	62	136
H(2062)	75	−2	100
H(2071)	207	−4	24
H(2072)	258	−14	98
H(2091)	408	16	37
H(2092)	433	95	33
H(2101)	293	27	−58
H(2102)	412	46	−71
H(2121)	231	84	−148
H(2122)	344	110	−166
H(2131)	293	217	−152
H(2132)	219	180	−208
H(2151)	32	209	−199
H(2152)	51	135	−168
H(2161)	−107	182	−135
H(2162)	−40	242	−99
HA(1)	386	−321	127
HA(2)	406	−211	176
HA(3)	292	−177	258
HA(4)	159	−252	292
HA(5)	139	−362	243
HB(1)	167	−487	255
HB(2)	3	−543	270
HB(3)	−126	−557	178
HB(4)	−93	−515	71
HB(5)	71	−459	56
HC(1)	430	−406	239
HC(2)	560	−480	292
HC(3)	555	−599	270
HC(4)	418	−644	194
HC(5)	287	−571	141
HD(1)	385	−499	59
HD(2)	414	−484	−56
HD(3)	322	−397	−119
HD(4)	200	−325	−68
HD(5)	171	−340	46

Complex (2) is isomorphous with that of the KI·2(benzo-15-crown-5) complex reported a few years ago.[9] The cell dimensions and diffraction pattern are so similar that it was possible to refine successfully this structure starting with the co-ordinates of the KI complex. The presence of perchlorate anions instead of iodide has introduced further disorder problems, but they occupy the same sites in the crystal as the iodide anions do, and form no strong interactions with the surrounding complex ions. The perchlorate anions are larger than the iodide ions (though non-spherical). This implies that the packing is better, since the cell volumes are almost identical in the two crystals [3 102 Å^3 in the KI complex and 3 122 Å^3 in (2)]. One perchlorate ion, with $\bar{4}$ symmetry, seems to be statistically ordered, but undergoes large thermal motion. The other is statistically disordered about the crystallographic four-fold rotation axis which is parallel to one Cl–O bond. The model used in this refinement has the chlorine and one oxygen on the four-fold axis and the other three oxygens disordered about 12 positions retaining idealised tetrahedral symmetry for the ion. This is probably inadequate in two respects. Fourier maps indicate that the disorder of the three oxygens is over more than 12 positions, and there is also further electron density near the chlorine which is not accounted for in this model. However, it is clear that there are no strong intermolecular interactions in this crystal. This was expected in view of the single asymmetric ClO_4^- bending frequency observed in the i.r. spectrum.

There is also disorder in the positions of two of the carbon atoms in the polyether, C(12) and C(13). This was handled by constraining the refinement so that the C–C and C–O bonded distances involving these two atoms took reasonable values. This resulted in two conformations, A and B, with torsion angles 72 and −76° about the C(12)–C(13) bonds which are present in almost equal proportions (0.523 and 0.477). A similar treatment of the KI complex using the original data[9] gave the same two conformers, with torsion angles 73° and −71°, and occupancies 0.60 and 0.40. Conformer A has very similar torsion angles to that found in the crystal structure of the uncomplexed polyether,[10] and shows an approximate mirror plane of symmetry through O(11) and the centre of the benzene ring and perpendicular to it. Conformer B is new and has no mirror symmetry. It differs only in having the other *gauche* conformation about the C(12)–C(13) bond and correspondingly changed torsion angles in the nearest two bonds on either side. There is also some evidence for partial disorder of the neighbouring oxygen atoms in their large temperature factors, but this has not been resolvable using the present data.

The presence of such large disorder cast doubt on the assignment of the space group as $P4/n$. This space group is uniquely defined by the condition $hk0: h + k = 2n$, and long-exposure diffraction photographs showed no evidence for contravening this. This crystal seems to be an unfortunate example of genuine statistical disorder in several atoms, and accounts for the poor agreement indices found and the inaccurate bond lengths and angles.

TABLE 4

Bond lengths (Å) for (1)—(3) with estimated standard deviations in parentheses

(*a*) Complex cations

			(3)	
	(1)	(2)	Molecule 1	Molecule 2
Na–O(5)	2.405(5)	2.642(9)	2.658(15)	3.119(17)
Na–O(8)	2.375(5)	2.827(8)	2.492(15)	2.636(16)
Na–O(11)	2.378(5)	2.815(11)	2.553(17)	2.482(17)
Na–O(14)	2.464(5)	2.935(10)	3.120(17)	2.887(19)
Na–O(17)	2.373(5)	2.631(8)	3.077(16)	3.304(18)
Na–O(19)	2.634(6)			
Na–O(20)	2.426(7)			
C(1)–C(2)	1.389(10)	1.346(17)	1.434(23)	1.396(25)
C(2)–C(3)	1.328(11)	1.349(17)	1.326(24)	1.350(25)
C(3)–C(4)	1.386(11)	1.384(18)	1.385(22)	1.417(25)
C(4)–C(41)	1.385(10)	1.390(16)	1.408(22)	1.405(24)
C(41)–C(171)	1.377(9)	1.426(15)	1.352(21)	1.394(24)
C(171)–C(1)	1.391(9)	1.366(16)	1.375(22)	1.369(25)
C(41)–O(5)	1.373(7)	1.366(14)	1.385(20)	1.359(22)
O(5)–C(6)	1.437(8)	1.438(14)	1.413(20)	1.426(20)
C(6)–C(7)	1.480(10)	1.428(18)	1.439(22)	1.481(23)
C(7)–O(8)	1.422(9)	1.403(15)	1.392(18)	1.413(21)
O(8)–C(9)	1.415(8)	1.403(17)	1.435(21)	1.453(22)
C(9)–C(10)	1.487(11)	1.479(19)	1.434(25)	1.437(24)
C(10)–O(11)	1.414(8)	1.383(17)	1.424(22)	1.406(21)
O(11)–C(12)	1.429(9)	1.45(1) *	1.435(23)	1.428(27)
C(12)–C(13)	1.470(10)	1.50(1) *	1.440(26)	1.383(32)
C(13)–O(14)	1.430(9)	1.45(1) *	1.435(20)	1.448(25)
O(14)–C(15)	1.408(8)	1.416(17)	1.413(19)	1.363(22)
C(15)–C(16)	1.478(10)	1.422(19)	1.495(21)	1.477(25)
C(16)–O(17)	1.438(8)	1.459(15)	1.459(18)	1.444(22)
O(17)–C(171)	1.381(7)	1.347(13)	1.365(18)	1.387(21)

(*b*) Anions

(1)		(2)		(3)	
Cl–O(18)	1.400(8)	Cl(21)–O(22)	1.339(16)	B–CA(6)	1.665(22)
Cl–O(19)	1.412(6)			B–CB(6)	1.722(23)
Cl–O(20)	1.407(8)			B–CC(6)	1.642(24)
Cl–O(21)	1.400(7)			B–CD(6)	1.710(22)

* Constrained, see text.

TABLE 5

Selected bond angles (°) for (1)—(3) *

(*a*) Within the macrocycles and anions

	(1)	(2)	(3) Molecule 1	(3) Molecule 2
C(1)–C(2)–C(3)	121.5	125.6	120.5	122.8
C(2)–C(3)–C(4)	121.6	118.5	122.6	123.0
C(3)–C(4)–C(41)	118.7	118.9	115.8	114.8
C(4)–C(41)–C(171)	119.4	119.5	123.3	120.1
C(41)–C(171)–C(1)	121.4	120.1	119.5	124.5
C(171)–C(1)–C(2)	117.4	117.3	118.1	114.7
C(4)–C(41)–O(5)	123.3	125.9	121.5	121.3
C(171)–C(41)–O(5)	117.3	114.6	115.2	118.6
C(1)–C(171)–O(17)	122.9	128.1	125.8	126.0
C(41)–C(171)–O(17)	115.7	111.7	114.6	109.5
C(41)–O(5)–C(6)	116.6	120.5	124.2	122.6
O(5)–C(6)–C(7)	109.2	109.1	109.5	106.4
C(6)–C(7)–O(8)	108.3	111.6	108.8	110.1
C(7)–O(8)–C(9)	113.7	114.5	113.7	112.3
O(8)–C(9)–C(10)	108.0	116.1	110.0	110.7
C(9)–C(10)–O(11)	108.3	108.7	108.8	110.3
C(10)–O(11)–C(12)	114.3	98.5, 129.7	108.4	107.4
O(11)–C(12)–C(13)	108.9	98.9, 110.9	109.6	107.2
C(12)–C(13)–O(14)	107.4	110.0, 94.9	114.4	116.4
C(13)–O(14)–C(15)	114.8	129.6, 92.8	113.8	116.6
O(14)–C(15)–C(16)	109.4	114.6	107.7	110.9
C(15)–C(16)–O(17)	107.5	108.7	105.4	105.0
C(16)–O(17)–C(171)	119.2	118.2	117.6	119.9
Mean e.s.d.	0.6	1.3	1.8	2.1

O(18)–Cl–O(19)	110.5
O(18)–Cl–O(20)	110.2
O(18)–Cl–O(21)	106.7
O(19)–Cl–O(20)	107.3
O(19)–Cl–O(21)	109.6
O(20)–Cl–O(21)	112.5
Na–O(19)–Cl	94.9
Na–O(20)–Cl	104.4
Mean e.s.d.	0.4

O(22)–Cl(21)–O(22)	123.1
O(22)–Cl(21)–O(22)	103.1

CA(6)–B–CB(6)	110.0
CA(6)–B–CC(6)	112.3
CA(6)–B–CD(6)	106.9
CB(6)–B–CC(6)	106.1
CB(6)–B–CD(6)	108.4
CC(6)–B–CD(6)	112.2
Mean e.s.d.	1.2

(*b*) Around the cations

(i) Complex (1)

	O(8)	O(11)	O(14)	O(17)	O(19)	O(20)
O(5)	69.7	138.8	127.8	66.1	93.8	105.4
O(8)		69.6	117.9	121.2	87.4	140.4
O(11)			68.9	134.7	90.3	109.6
O(14)				67.9	135.9	96.5
O(17)					131.3	88.4
O(19)						53.2

Mean e.s.d. 0.2

(ii) Complex (2)

	O(8)	O(11)	O(14)	O(17)
O(5)	60.0	99.3	102.9	56.4
O(8)		61.2	111.2	108.8
O(11)			57.2	101.1
O(14)				59.4

Mean e.s.d. 0.3

(iii) Complex (3)

	O(108)	O(111)	O(114)	O(117)	O(205)	O(208)	O(211)	O(214)	O(217)
O(105)	61.3	101.2	100.8	51.3	77.3	95.3	162.2	132.4	93.3
O(108)		67.5	119.3	101.1	99.8	151.4	136.2	75 5	70.4
O(111)			60.0	89.2	165.5	137.8	91.3	78.0	120.5
O(114)				52.5	134.5	79.0	74.3	117.9	165.6
O(117)					100.5	71.5	117.0	167.1	139.4
O(205)						56.4	93.8	92.3	45.9
O(208)							67.0	117.3	96.8
O(211)								62.5	91.3
O(214)									51.8

Mean e.s.d. 0.5

* e.s.d. = Estimated standard deviation.

The structure is sufficiently well defined to show that the cation is close to ten oxygen atoms in a sandwich structure (see Figure 3). The formal co-ordination number of the sodium is not clear, due to the wide range of the Na–O distances [2.631(8)—2.935(10) Å]. The distances are all longer than those found in (1), indicating the cation–ligand bonding is fairly weak. This may explain the preferred formation of the 1 : 1 complex, except under exceptional conditions. The cation sits on the centre of symmetry which relates the two rings in the sandwich. The cation–mean oxygen plane distance, 1.53 Å, is much larger than that in (1) where steric interactions are much less between the ligands and the cation.

TABLE 6

Deviations (Å) from the mean planes

(*a*) Through the ether oxygen atoms

Compound	O(5)	O(8)	O(11)	O(14)	O(17)	Na+
(1)	−0.204	0.346	−0.337	0.207	−0.012	−0.769
(2)	0.134	−0.149	0.126	−0.054	−0.056	−1.526
(3) molecule 1	−0.064	−0.133	0.251	−0.266	0.212	−1.532
(3) molecule 2	0.088	−0.221	0.278	−0.220	0.075	−1.650

(*b*) Through the benzene carbon atoms

	C(1)	C(2)	C(3)	C(4)	C(41)	C(171)
(1)	−0.005	0.001	0.002	−0.003	−0.001	0.004
(2)	−0.015	0.006	0.007	−0.010	0.000	0.012
(3) molecule 1	0.012	−0.026	0.013	0.015	−0.030	0.016
(3) molecule 2	−0.003	0.005	0.003	−0.012	0.014	−0.007

	(1)	(2)	(3) Molecule 1	(3) Molecule 2
Interplanar angle (°)	20	6	16	11

Angle between planes (*a*) for the two molecules of (3) = 10°

TABLE 7

Torsion angles (°) for (1)—(3)

	(1)	(2)	(3) Molecule 1	(3) Molecule 2
C(171)–C(41)–O(5)–C(6)	−144	169	−159	−175
C(41)–O(5)–C(6)–C(7)	169	−157	166	170
O(5)–C(6)–C(7)–O(8)	−58	−58	52	63
C(6)–C(7)–O(8)–C(9)	−178	167	−167	−169
C(7)–O(8)–C(9)–C(10)	−174	−80	85	80
O(8)–C(9)–C(10)–O(11)	59	−63	66	65
C(9)–C(10)–O(11)–C(12)	−169	175, −166	177	−176
C(10)–O(11)–C(12)–C(13)	161	−175, −87	171	173
O(11)–C(12)–C(13)–O(14)	−61	72, −77	−63	−62
C(12)–C(13)–O(14)–C(15)	175	76, 165	−75	−89
C(13)–O(14)–C(15)–C(16)	−175	−175, −159	166	168
O(14)–C(15)–C(16)–O(17)	57	55	−65	−64
C(15)–C(16)–O(17)–C(171)	179	147	−177	−171
C(16)–O(17)–C(171)–C(41)	166	−158	−175	−174
O(17)–C(171)–C(41)–O(5)	−1	1	−2	2
Mean e.s.d.s	1	2	2	2

Complex (3) also has two benzo-15-crown-5 molecules surrounding a sodium cation in a sandwich structure (see Figure 4), but the two rings are not related by symmetry. The cation co-ordination is again irregular but different from that in (2). Again there is a range of Na–O distances [2.482(17)—3.304(18) Å], wider than that in (2). All the atoms have large thermal motion parameters which give rise to several short bond lengths but there is no evidence for statistical disorder in this crystal. The large anisotropic thermal motion parameters of the sodium and the long Na–O distances again indicate weak co-ordination between the cation and the ligands. The cation–mean oxygen plane distances are similar to that in (2), and the two planes subtend at an angle of 10°. The conformations of the two macrocycles are very similar to each other and to that found in the crystal structure of the free ligand [10] and the conformer A in (2).

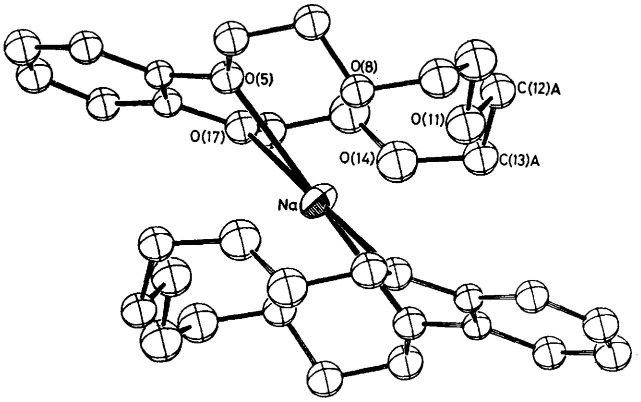

FIGURE 3 Molecule of (2) conformer A, showing the 25% thermal ellipsoids and Na–O distances <2.7 Å

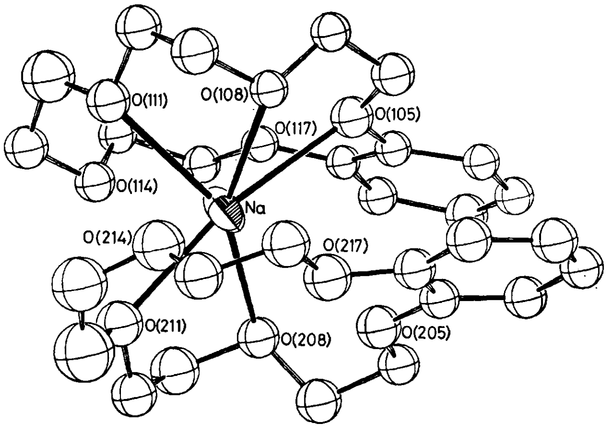

FIGURE 4 Molecule of (3), showing the 25% thermal ellipsoids and Na–O distances <2.7 Å

The tetraphenylborate anion has unremarkable geometry; a similar set of torsion angles around the B–C bonds has been observed previously.[11]

There are no strong intermolecular interactions, in particular no ‘ stacking ’ of parallel benzene rings, to be found anywhere in these crystals.

Comparison of the 2 : 1 *‘ Sandwich ’ Complexes of Benzo*-15-*crown*-5.—Three complexes with ‘ sandwich ’ structures have so far been reported. The structure of the first, the KI complex,[9] was considered to have been decided by the intermolecular contacts between the two crown rings, with the potassium cation occupying the central cavity, and no covalent character in its bonding. This structure may be directly compared with (2), which forms isomorphous crystals. In both cases, the centre of gravity of the oxygen atoms of the ring is the same distance from the cation as is the mean plane of the oxygen atoms. However, for the KI complex, this distance is **3.34** Å compared with **3.06** Å in (2). This means the two rings in (2) have moved closer together by 0.28 Å with no sideways slippage of the sandwich. The inter-ring contacts are generally shorter in (2) for all atoms (see Table 8), though still longer than the sum of the relevant van der Waals radii. The cation in (2) is also 0.14 Å closer to the mean plane than in the KI complex, as a result of this movement. For (2), the

TABLE 8

(a) Shortest contacts (Å) between the two macrocycles in the 2: 1 complexes

	KI complex		(2)		(3)	
CH ··· CH	>4		>4		C(104) ··· C(204)	3.65
CH ··· CH$_2$	>4		C(4) ··· C(12)B$^{\mathrm{I}}$	3.88	C(104) ··· C(206)	3.68
					C(202) ··· C(115)	3.86
CH ··· O	>4		>4		C(101) ··· O(208)	3.95
					C(104) ··· O(205)	3.91
CH$_2$ ··· CH$_2$	C(6) ··· C(13)A$^{\mathrm{I}}$	3.99	C(6) ··· C(13)A$^{\mathrm{I}}$	3.76	C(109) ··· C(216)	3.90
	C(9) ··· C(16)$^{\mathrm{I}}$	3.98	C(9) ··· C(16)$^{\mathrm{I}}$	3.70	C(116) ··· C(209)	3.95
CH$_2$ ··· C	C(12)B ··· C(41)$^{\mathrm{I}}$	3.96	C(12)B ··· C(41)$^{\mathrm{I}}$	3.58	C(206) ··· C(141)	3.64
			C(9) ··· C(171)$^{\mathrm{I}}$	3.80	C(106) ··· C(241)	3.82
					C(106) ··· C(271)	3.89
CH$_2$ ··· O	C(16) ··· O(8)$^{\mathrm{I}}$	3.61	C(16) ··· O(8)$^{\mathrm{I}}$	3.32	C(109) ··· O(214)	3.25
	C(9) ··· O(17)$^{\mathrm{I}}$	3.76	C(9) ··· O(17)$^{\mathrm{I}}$	3.41	C(209) ··· O(114)	3.33
	C(6) ··· O(14)$^{\mathrm{I}}$	3.78	C(6) ··· O(14)$^{\mathrm{I}}$	3.52	C(216) ··· O(108)	3.49
C ··· O	C(171) ··· O(11)$^{\mathrm{I}}$	3.63	C(171) ··· O(11)$^{\mathrm{I}}$	3.45	C(171) ··· O(208)	3.45
	C(41) ··· O(11)$^{\mathrm{I}}$	3.69	C(41) ··· O(11)$^{\mathrm{I}}$	3.47		
O ··· O	O(8) ··· O(14)$^{\mathrm{I}}$	3.42	O(8) ··· O(14)$^{\mathrm{I}}$	3.26	O(108) ··· O(214)	3.31
	O(8) ··· O(17)$^{\mathrm{I}}$	3.50	O(8) ··· O(17)$^{\mathrm{I}}$	3.18	O(117) ··· O(208)	3.36
	O(11) ··· O(17)$^{\mathrm{I}}$	3.66	O(11) ··· O(17)$^{\mathrm{I}}$	3.46	O(108) ··· O(217)	3.41
					O(114) ··· O(211)	3.42
					O(111) ··· O(214)	3.43

The two rings in the KI complex and in complex (2) are related by a centre of symmetry at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.

(b) Selected intermolecular contacts (Å)

(1)	O(18) ··· H(61)$^{\mathrm{I}}$	2.78	H(2) ··· H(101)$^{\mathrm{IV}}$	2.62
	O(19) ··· H(122)$^{\mathrm{II}}$	2.86	H(3) ··· H(61)$^{\mathrm{IV}}$	2.74
	O(21) ··· H(102)$^{\mathrm{II}}$	2.87	H(122) ··· H(92)$^{\mathrm{II}}$	2.76
	O(8) ··· H(3)$^{\mathrm{III}}$	2.83	H(161) ··· H(61)$^{\mathrm{III}}$	2.74

Symmetry codes

I $-1 + x, y, z$

II $-x, -y, -z$

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

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

(2)	H(2) ··· H(91)$^{\mathrm{I}}$	2.76	H(91) ··· H(151)$^{\mathrm{III}}$	2.68
	H(3) ··· H(4)$^{\mathrm{II}}$	2.84	H(152) ··· H(161)$^{\mathrm{IV}}$	2.59
	H(71) ··· H(151)$^{\mathrm{III}}$	2.78	H(161) ··· H(162)$^{\mathrm{V}}$	2.58

Symmetry codes

I $\frac{3}{2} - y, x, -1 + z$

II $\frac{3}{2} - y, x, z$

III $y, \frac{3}{2} - x, z$

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

V $\frac{1}{2} + y, 1 - x, 1 - z$

(3)	H(101) ·· HC(1)$^{\mathrm{I}}$	2.40	H(1101) ··· HC(5)$^{\mathrm{IV}}$	2.55
	H(101) ··· HC(2)$^{\mathrm{I}}$	2.55	H(1151) ··· H(202)$^{\mathrm{VI}}$	2.40
	H(102) ··· H(1102)$^{\mathrm{II}}$	2.51	H(1152) ··· HC(4)$^{\mathrm{IV}}$	2.31
	H(103) ··· H(1092)$^{\mathrm{II}}$	2.61	H(1162) ··· HC(1)$^{\mathrm{I}}$	2.64
	H(104) ··· HA(4)$^{\mathrm{III}}$	2.55	H(2091) ·· H(2102)$^{\mathrm{VII}}$	2.60
	H(104) ··· HA(5)$^{\mathrm{III}}$	2.50	H(2152) ··· HB(2)$^{\mathrm{VIII}}$	2.22
	H(1071) ··· HC(5)$^{\mathrm{IV}}$	2.69	HA(2) ··· HC(3)$^{\mathrm{I}}$	2.48
	H(1072) ··· HD(4)$^{\mathrm{V}}$	2.59	HA(3) ··· HC(3)$^{\mathrm{I}}$	2.54
	H(1091) ··· HB(4)$^{\mathrm{V}}$	2.55	HB(4) ··· HB(5)$^{\mathrm{IX}}$	2.60
	H(1091) ··· HB(5)$^{\mathrm{V}}$	2.54	HD(1) ··· HD(2)$^{\mathrm{X}}$	2.53

Symmetry codes

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

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

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

IV $-x, 1 + y, z$

V $-x, -y, -z$

VI $1 + x, y, z$

VII $1 - x, -y, -z$

VIII $x, -\frac{1}{2} - y, -\frac{1}{2} + z$

IX $-x, -1 - y, -z$

X $1 - x, -1 - y, -z$

oxygen atoms attached to the benzene ring are much the closest to the sodium, and the spread of values of the cation–oxygen distances is much greater than in the KI complex. Both complexes have a crystallographic centre of symmetry at the cation in spite of the presumably bad fit of the latter into the cavity in complex (2).

The two oxygen mean planes in (3) are not parallel, and the centre of gravity of the oxygen atoms in each ring is 3.35 Å from the other. This is comparable with that found in the KI complex, and there are several interatomic contacts between the ligands which are shorter than in either of the other two complexes (see Table 8). Again there are none shorter than the sum of the van der Waals radii, and there is no evidence for strong C–H $\cdots$ O interactions. The overall shape of complex (3) is different. In projection perpendicular to the mean plane of the oxygens of one of the rings, the centres of the two benzene rings make an angle of 63° at the cation, compared with 180° in the KI complex and (2).

The two different shapes which have been found for the sandwich complexes are probably not of very different energies since there are no very short interactions between the two rings, and the conformer A is present in both cases. The minor conformer B is expected to have similar energy to that of A, since it is present in an almost equal amount in the crystals of (2).

It is difficult to give a satisfactory explanation of why the 2 : 1 sandwich complex between benzo-15-crown-5 and sodium should crystallise in two different shapes depending on the anion. The ubiquitous (and undefined) ' packing forces ' may be called upon of course. Alternatively, it is possible that some complex cation–anion interactions may occur in methanol solution but do not survive to the solid state. Further solution studies may help to clarify this.

EXPERIMENTAL

Crystal Data.—(1) $C_{14}H_{20}ClNaO_9$, $M = 390.75$, Monoclinic, colourless needles, $a = 8.806(3)$, $b = 8.310(10)$, $c = 24.148(7)$ Å, $\beta = 99.16(1)°$, $U = 1\,745$ Å^3, $D_m = 1.47$ g cm^{-3} (flotation), $Z = 4$, $D_c = 1.48$ g cm^{-3}, $F(000) = 816$, space group $P2_1/c$ (C^5_{2h}, no. 14), no molecular symmetry required, Mo-K_α radiation, Zr filter, $\lambda = 0.710\,7$ Å, $\mu = 2.83$ cm^{-1}, no absorption correction applied.

(2) $C_{28}H_{40}ClNaO_{14}$, $M = 659.07$, Tetragonal, colourless needles, $a = b = 17.786(7)$, $c = 9.869(5)$ Å, $U = 3\,122$ Å^3, $D_m = 1.40$ g cm^{-3} (flotation), $Z = 4$, $D_c = 1.40$ g cm^{-3}, $F(000) = 1\,392$, space group $P4/n$ (C^3_{4h}, no. 85); symmetry required: $\bar{1}$ for complex cation, $\bar{4}$ for one perchlorate, 4 for the other; Mo-K_α radiation, Zr filter, $\lambda = 0.710\,7$ Å, $\mu = 1.98$ cm^{-1}, no absorption correction applied.

(3) $C_{52}H_{60}BNaO_{10}$, $M = 878.85$, Monoclinic, colourless needles, $a = 12.497(3)$, $b = 19.450(3)$, $c = 19.896(4)$ Å, $\beta = 94.76(2)°$, $U = 4\,819$ Å^3, $D_m = 1.21$ g cm^{-3} (flotation), $Z = 4$, $D_c = 1.21$ g cm^{-3}, $F(000) = 1\,872$, space group $P2_1/c$ (C^5_{2h}, no. 14), no molecular symmetry required, Mo-K_α radiation, graphite monochromator, $\lambda = 0.710\,7$ Å, $\mu = 0.843$ cm^{-1}, no absorption correction applied.

Data Collection.—Crystals of all three complexes were obtained by methods which have been described previously.[3,4]

A crystal of (1) of dimensions 0.14 × 0.19 × 0.71 mm was mounted on a Picker four-circle diffractometer and accurate cell dimensions were obtained from the settings of 25 reflections. Intensities were collected for all reflections with $k \geqslant 0$ to a maximum 2θ of 45°. The data were collected using ω—2θ scans at 0.5° min^{-1}, from $2\theta_{calc.}(K_{\alpha 1}) - 0.5°$ to $2\theta_{calc.}(K_{\alpha 2}) + 0.5$. Stationary-crystal-stationary counter background measurements were recorded for 25 s. Three references reflections were measured every 50 normal reflections and showed a systematic variation of up to 10% over the data collection. The data were scaled according to this variation and equivalent reflections were averaged to give 2 293 independent planes. A total of 1 737 reflections had $I > 2\sigma(I)$ and were classed as observed.

A crystal of (2) of dimensions 0.43 × 0.31 × 0.48 mm was mounted on the Picker diffractometer. Accurate unit-cell dimensions were obtained from the settings of 14 planes and intensities were then collected for reflections with $h, l \geqslant 0$ up to a maximum 2θ value of 20°. These crystals diffract X-rays relatively poorly, indicating large thermal motion of the atoms. The data were collected using the same techniques as for the crystal of (1). The intensities of the three reference reflections fell by an average of 37%. The data were scaled to this change and equivalent reflections averaged to give 1 480 planes, of which 1 053 were classed as observed.

An Enraf–Nonius CAD-4 diffractometer was used for data collection in the case of (3). The crystal size was 0.30 × 0.32 × 0.55 mm and the cell refined from the positions of 16 accurately centred reflections. The data were collected using symmetric ω—2θ scans, and the intensity of a reference reflection measured every 2 h of exposure time. No systematic variation of the intensity of this reflection was observed throughout the data collection. Intensities were measured for 3 260 planes with $k, l \geqslant 0$ up to a maximum $2\theta = 35°$. The data were processed to give 1 258 reflections with $I > 2\sigma(I)$ which were classed as observed.

Structure Determination.—The structure of (1) was solved using the automatic multisolution direct methods section of the SHELX suite of programs [12] and refined using the usual least-squares techniques,[13] to give final values of the conventional agreement indices $R = 0.075$ and $R' = 0.081$. The weights used in the refinement were derived from a two-degree polynomial, weight $= 4.194 - 0.139\,2\ F_o + 0.002\,63\ F_o^2$ and showed no systematic variation against ranges of $|F_o|$ or $(\sin\theta)/\lambda$. The largest value of shift-to-error on the final cycle was 0.02. The hydrogen atoms were included in positions calculated from the geometry of the rest of the molecule at a distance of 0.96 Å from the corresponding carbon atom and with a fixed isotropic temperature factor of $U_{iso.} = 0.051$ Å^2. The final ΔF map showed no unexpected features.

A study of the cell, dimensions, space group, and diffraction pattern of (2) indicated that these crystals were isomorphous with the complex KI·2(benzo-15-crown-5) the structure of which was reported as Part 5 of this series.[9] There are two independent perchlorate ions in the crystals, one on a site of $\bar{4}$ symmetry, the other on a four-fold rotation axis. Thus the latter ion must be disordered to some extent, though the former need not be. The complexed cation contains a centre of symmetry at the sodium relating the two ether ligands. The co-ordinates from the KI complex were used as a starting point for refinement of the cation and chlorine atoms. The refinement [13] progressed smoothly though there were indications of statistical disorder in two of the ether carbon atoms [C(12) and C(13)]. The same two atoms were disordered in the KI complex structure. Fourier maps intended to locate the oxygen atoms on the perchlorate ions showed that the one with $\bar{4}$ symmetry seems to be undergoing large anisotropic thermal motion, and the other on the four-fold axis seems to be undergoing unhindered rotation about one Cl–O bond along the symmetry axis. This was modelled by setting up a rigid group of the five perchlorate atoms. One oxygen atom O(32) and the chlorine Cl(31) were located on the four-fold axis, and the remaining atoms set up as an idealised tetrahedron, with a short Cl–O distance, 1.40 Å, since the thermal motion was expected to be large. The occupancy factor was fixed at 0.25, and the z co-ordinate of the chlorine atom was allowed to refine, and the remaining atoms moved by the same amount in z.[12] This produces 12 sites, each of occupancy 0.25, separated by 30° rotation about the four-fold axis, representing the statistically disordered three oxygen atoms O(33)—O(35). The disordered oxygen atoms were given a common isotropic temperature factor [refined value 0.100(8) Å^2] and the other oxygen and the chlorine refined with anisotropic temperature factors.

The disorder in the ether ring was handled by assuming two sites for each carbon, of occupancy p and $1 - p$, and refining them with distances constrained to be 1.44(1) Å for C–O bonds and 1.50(1) Å for the C–C bonds. This led to poor values for the bond angles around these atoms, but attempts to improve these by similar constraints for the non-bonded C ··· O and C ··· C distances led to poor agreement in the structure amplitudes, and consequently large values for the estimated standard deviations of the positional parameters of all atoms. The refinement was considered more acceptable than one in which disorder was not allowed for, in spite of the poor bond angles, because the torsion angles in this region of the molecule are much more reasonable, *i.e.* closer to ±*gauche* about the C–C bonds.

The final values of the conventional agreement indices were $R = 0.121$ and $R' = 0.138$, and the weights were calculated using the expression weight $\propto[\sigma^2(F_o) + 0.001\,99F^2]$. An analysis of this weighting scheme showed no systematic variation against ranges of $|F_o|$ or $(\sin\theta)/\lambda$. The largest shift-to-error on the final cycle was 0.05. The hydrogen atoms were included in positions calculated from the geometry of the rest of the molecule, with a C–H distance of 0.98 Å. Those attached to the disordered carbon atoms were not included. A common isotropic temperature factor for the hydrogen atoms refined to $U = 0.103(12)$ Å. The refined values for the common isotropic temperature factor of the disordered atoms in the ligand and of the occupancy factor were $U = 0.073(4)$ Å^2 and $p = 0.523(16)$ respectively.

The structure of (3) was solved using the MULTAN 76 suite of programs.[14] Normalised structure amplitudes were calculated assuming the presence of two rigid groups in random orientation and position in the cell. One group was assumed to have the same structure as the complexed cation in the KI·2(benzo-15-crown-5) structure [9] and the other to be a tetraphenylborate anion taken at random from the literature.[15] The calculated Debye curve was not a straight line, but was closer to one than the observed Wilson plot. The data were then renormalised by parity group, and the 499 planes with the highest E values used. The 4 000 strongest relations were used with a starting set consisting of three origin defining planes (2, 9, −12), (5, 8, −3), and (1, 9, 4), and seven others. A total of 2^7 permutations were carried out and the set of phases with an outstandingly high combined figure of merit used to calculate a Fourier map. This showed the positions of 57 of the 64 non-hydrogen atoms as recognisable fragments, the remaining seven atoms appeared on the subsequent Fourier map. Refinement [12] then proceeded smoothly with the phenyl groups on the anion treated as rigid regular hexagons with the C–C distance of 1.395 Å and C–H 0.98 Å. The hydrogen atoms in the ligands were included in geometrically expected positions, with the same C–H distance. The hydrogen atoms were refined with common isotropic temperature factors (U/Å^2) depending on their type: ligand (aromatic) 0.22(4); ligand (aliphatic) 0.15(2); anion (*ortho*) 0.11(2); anion (*meta*) 0.14(3); and anion (*para*) 0.18(4).

Individual isotropic temperature factors were used for all the non-hydrogen atoms except sodium, which was allowed to refine anisotropically. Unit weights were used, since they gave the best weighting analysis results. The largest shift-to-error value on the final cycle was 0.16 and the value of the conventional agreement index was $R = 0.080$.

The largest peaks on the final difference map were $< 0{\cdot}3$ e Å^{-3} and appeared close to atoms which are undergoing large thermal motion, but no attempt was made to cater for these utilising statistical disorder.

Scattering factors were calculated using the analytical approximation coefficients given in Table 2.2B of ref. 16. Geometry calculations were carried out on an IBM 1130 computer [13] and the figures drawn using ORTEP.[17] Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22737 (31 pp.).*

I thank Dr. J. N. Wingfield for supplying the crystals, Dr. M. R. Truter for valuable discussions, and the Royal Society for some apparatus.

[9/1541 *Received, 26th September,* 1979]

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

REFERENCES

[1] Part 10, J. D. Owen and M. R. Truter, *J.C.S. Dalton*, 1979, 1831.

[2] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017; 1970, **92**, 386.

[3] D. G. Parsons, M. R. Truter, and J. N. Wingfield, *Inorg. Chim. Acta*, 1975, **14**, 45.

[4] D. G. Parsons and J. N. Wingfield, *Inorg. Chim. Acta*, 1976, **17**, L25.

[5] D. G. Parsons and J. N. Wingfield, *Inorg. Chim. Acta*, 1976, **18**, 263.

[6] J. D. Owen, *J.C.S. Dalton*, 1978, 1418.

[7] P. D. Cradwick and N. S. Poonia, *Acta Cryst.*, 1977, **B33**, 197.

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

[9] P. R. Mallinson and M. R. Truter, *J.C.S. Perkin II*, 1972, 1818.

[10] I. R. Hanson, *Acta Cryst.*, 1978, **B34**, 1026.

[11] C. G. Pierpont, L. C. Francesconi, and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 2367.

[12] G. M. Sheldrick, SHELX, Programs for Crystal Structure Determination, University Chemical Laboratory, Cambridge.

[13] '*X*-RAY ARC,' Library of Programs for the IBM 1130 Computer, *J. Appl. Cryst.*, 1973, **6**, 309.

[14] P. Main, M. M. Woolfson, and G. Germain, 'MULTAN 76,' A

Computer Program for the Automatic Solution of Crystal Structures, University of York, 1976.

[15] T. R. Felthouse, E. J. Laskowski, and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 1077.

[16] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 99.

[17] ORTEP, Report No. ORNL-3794, C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.