Crystal Structures of Complexes between Alkali-metal Salts and Cyclic Polyethers. Part IX.† Complex formed between Dibenzo-24-crown-8 (6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,-16,19,22]octaoxacyclotetracosin) and two molecules of Sodium *o*-Nitrophenolate

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The crystal structure of the title complex has been determined by direct methods from *X*-ray diffractometer data. Crystals are monoclinic, space group $C2/c$, $a = 19.629(11)$, $b = 10.755(6)$, $c = 17.425(31)$ Å, $\beta = 90.21(6)°$, $Z = 4$. Refinement of atomic parameters by full-matrix least-squares methods gave R 0.084 for 1 894 reflections.

The two halves of the complex are related by a two-fold symmetry axis which passes through a pair of aliphatic C–C bonds on opposite sides of the crown ring. The polyether ring folds around the pair of sodium ions. Each cation interacts with three oxygen atoms of the ligand; each of the fourth pair of oxygen atoms is 2.965 Å from a cation, not directed towards the cation, and not involved in co-ordination. Torsion angles in the crown ring differ considerably from normal; about the two-fold axis, the torsion angle of one C–C bond (where there is slight site disorder) is 117°, an eclipsed arrangement, and of the other bond is 139°.

An *o*-nitrophenolate anion on each side of the crown ring completes the six-fold co-ordination of the cations. Each anion chelates a cation and the phenolate oxygen (carrying most of the anionic charge) bridges the pair of cations. Molecular dimensions are as expected. Packing in the crystal is by van der Waals' interactions, including the parallel arrangement of benzene rings of crown ligands about a centre of symmetry.

THE synthesis of macrocyclic polyether, 'crown', compounds and their reactions with alkali-metal salts to form crystalline complexes of various cation-to-ligand ratios [1] has enabled us to examine the environments and co-ordination requirements of each of the alkali-metal cations in several of their complexes.[2-8] Poonia and Truter [9] have described the preparation of complexes having the ratio 2 : 1 of metal salt–ether, and Mercer and Truter [8] completed the crystal structure analysis of the bis(potassium thiocyanate) complex with dibenzo-24-crown-8. This same ligand was found to co-ordinate with two smaller sodium ions in the presence of thiocyanate or chelating anions. The crystal-structure analysis of the complex dibenzo-24-crown-8–bis(sodium *o*-nitrophenolate) was undertaken to examine the effects of the chelating anion and for comparison of the conformations of the macrocyclic ring when this is co-ordinated to sodium or potassium cations.

EXPERIMENTAL

After slow room-temperature evaporation of solvent from a mixture of ethanolic solutions of sodium *o*-nitrophenolate and dibenzo-24-crown-8, two types of crystal were obtained: colourless crystals of the pure ligand, and orange lozenge-shaped crystals of the complex. Samples of the latter were separated from the mixture under a microscope and one crystal suitable for *X*-ray analysis was found.

After preliminary determination of space group and cell dimensions from oscillation, Weissenberg, and precession photographs, the crystal was mounted on a diffractometer, and improved cell dimensions were derived from the least-squares refinement of 2θ setting of 15 reflections.

Crystal Data. $C_{36}H_{40}N_2Na_2O_{14}$, $M = 770.7$, Monoclinic, $a = 19.629(11)$, $b = 10.755(6)$, $c = 17.425(31)$, $\beta = 90.21(6)°$, $U = 3\,678.6$ Å^3, $D_c = 1.391$ g cm^{-3}, $Z = 4$, $D_m = 1.40$ g cm^{-3} (by flotation), $F(000) = 1\,616$. $\mu(\text{Mo-}K_{\bar{\alpha}}) = 1.19$ cm^{-1}, $\lambda(\text{Mo-}K_{\bar{\alpha}}) = 0.710\,69$ Å (1 Å = 10^{-8} cm). Space group $C2/c$. Molecular symmetry 2 (from structure analysis).

Intensity data for 2 351 independent reflections, with $2\theta \leqslant 45°$, were measured on a card-automated Picker four-circle diffractometer with scintillation counter, filtered Mo-$K_{\bar{\alpha}}$ radiation, and a θ—2θ scan. Owing to instrumental problems, some data in the 2θ range 35—45° were later considered unreliable and the data set was reduced to 1 894 independent reflections.

389 reflections, *i.e.* 21%, were considered unobserved, having $I < 2\sigma_I$, with $\sigma_I^2 = T + (b_1 + b_2)(t_s/50)^2$, where T is the scan count, b_1 and b_2 background counts each for 25 s, and t_s the time of the scan; the scan speed was 0.5° min^{-1}.

Lorentz and polarisation factors were applied to the intensity data, but no absorption corrections were made. Structure amplitudes were then computed.

Structure Analysis.—The structure of the title complex was determined by direct methods, in the sequence of programs described in ref. 10. The E statistics confirmed the centrosymmetric space group $C2/c$. For the multisolution sign-determining program, MULSA, two origin-determining reflections (indices $\bar{7}34$ and 023) were input, and five further reflections for the starting set were selected by the program. An E map from the best-looking set of signs for 150 reflections with $|E| \geqslant 1.80$ showed all non-hydrogen atom positions clearly.

The two halves of the complex were shown to be related by a two-fold symmetry axis which passes through the C(9)–C(9$^{\text{I}}$) and C(24)–C(24$^{\text{I}}$) bonds of the crown ligand (see Figure 1).

Refinement of the structure was by full-matrix least-squares methods. Initially, reflections were assigned weights derived from their intensity data: $w = \sigma_c^{-2}$, where $\sigma_c^2 = \sigma_I^2/(4.I.Lp)$ and Lp is the Lorentz-polarisation

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† Part VIII, P. R. Mallinson, *J.C.S. Perkin II*, 1975, 261.

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

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

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

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

[5] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 345.

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

[7] M. Mercer and M. R. Truter, *J.C.S. Dalton*, 1973, 2215.

[8] M. Mercer and M. R. Truter, *J.C.S. Dalton*, 1973, 2469.

[9] N. S. Poonia and M. R. Truter, *J.C.S. Dalton*, 1973, 2062.

[10] D. L. Hughes, *J.C.S. Dalton*, 1973, 2347.

factor. Scattering factors for the Na^+, O, O^- (phenolate), N, and C atoms were taken from ref. 11. Most of the hydrogen atom positions were apparent in a difference-Fourier synthesis; their co-ordinates were also calculated from tetrahedral or trigonal arrangements about their neighbouring carbon atoms, and they were assigned temperature factors equal to those of their carbon atoms. Scattering factors for the hydrogen atoms were taken from ref. 12, and all the hydrogen atom parameters were then included in the refinement process. Atomic designations are shown in Figures 1 and 2.

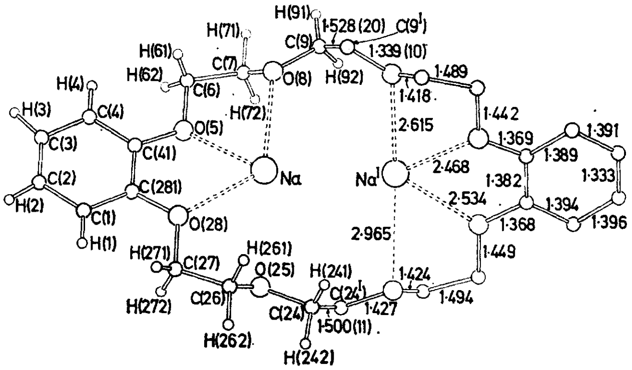

FIGURE 1 Projection of the crown ligand and sodium ions on the mean plane of the eight ether oxygen atoms. A two-fold symmetry axis, in the plane of the diagram, passes through the bonds (C9)–C(9^{I}) and C(24)–C(24^{I}). (Atom numbers with superscripts I have co-ordinates $1 - x, y, \frac{1}{2} - z$.) The atomic numbering, shown on the left-hand side, is related to one of the numbering schemes used in the systematic nomenclature of the ligand. Bond lengths (Å) between non-hydrogen atoms and Na · · · O distances are on the right. Mean standard deviations, except those shown in parentheses are: C–C 0.007, C–O 0.006, Na · · · O 0.004 Å

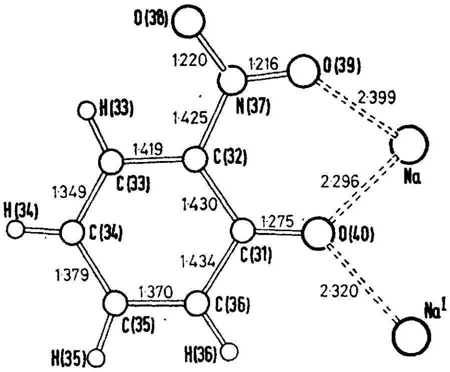

FIGURE 2 Projection of the *o*-nitrophenolate ion on the mean plane of the six ring-carbon atoms. The atomic numbering scheme, bond lengths, and Na · · · O distances (Å) are shown. Mean standard deviations for the bond lengths are: C–C 0.007, Na · · · O 0.004, all others 0.006 Å

The temperature factors of C(9) and, to a lesser extent, of O(8) were found to be larger than those of similar atoms. There appears to be site disorder of the C(9) atoms and possibly of the neighbouring oxygen atoms. However, the separate sites could not be located and the separation of electron density seemed to be accommodated satisfactorily by the anisotropic temperature factors of these atoms. The bond lengths and angles in this region cannot therefore be taken as strictly accurate. Similar examples of disorder have been observed in dibenzo-18-crown-6 [2] and benzo-15-crown-5 [6] complexes.

TABLE 1

Final atomic co-ordinates (fractional $\times 10^4$) and thermal parameters (B/Å^2, U/Å^2 $\times 10^4$), with standard deviations in parentheses

	x	y	z	B
Na	4 187(1)	2 935(2)	2 175(1)	*
C(1)	1 950(3)	1 850(6)	1 301(3)	3.72(12)
C(2)	1 496(3)	2 495(6)	828(3)	4.12(13)
C(3)	1 671(3)	3 560(6)	490(3)	4.41(13)
C(4)	2 321(3)	4 052(6)	589(3)	4.11(13)
C(41)	2 788(2)	3 425(5)	1 047(3)	3.11(11)
O(5)	3 446(2)	3 806(3)	1 163(2)	3.61(8)
C(6)	3 635(3)	4 979(6)	824(4)	3.99(12)
C(7)	4 365(3)	5 196(6)	1 018(4)	4.15(13)
O(8)	4 434(2)	5 256(4)	1 827(2)	*
C(9)	4 990(8)	5 870(11)	2 062(6)	*
C(24)	4 680(3)	−262(6)	2 733(3)	3.79(12)
O(25)	4 141(2)	182(3)	2 254(2)	3.71(8)
C(26)	3 512(3)	175(6)	2 659(3)	3.78(12)
C(27)	2 948(3)	548(5)	2 130(3)	3.71(12)
O(28)	3 096(2)	1 787(3)	1 850(2)	3.61(8)
C(281)	2 603(2)	2 330(5)	1 405(3)	3.10(10)
H(1)	1 840(24)	1 099(51)	1 524(29)	5.6(14)
H(2)	1 059(24)	2 080(45)	818(27)	5.1(13)
H(3)	1 425(28)	4 118(53)	119(32)	7.6(16)
H(4)	2 462(21)	4 797(45)	325(24)	4.1(12)
H(61)	3 354(21)	5 601(43)	1 119(24)	3.9(11)
H(62)	3 595(21)	4 815(42)	215(27)	4.6(12)
H(71)	4 513(24)	6 106(51)	752(29)	6.4(14)
H(72)	4 641(19)	4 582(37)	813(21)	2.4(9)
H(91)	5 028(31)	6 598(60)	1 845(36)	7.3(19)
H(92)	5 334(52)	5 482(100)	1 917(62)	18.7(55)
H(241)	4 651(19)	264(39)	3 184(24)	3.1(10)
H(242)	4 522(23)	−1 116(51)	2 902(28)	6.0(14)
H(261)	3 491(22)	794(46)	3 126(27)	4.8(12)
H(262)	3 420(22)	−731(47)	2 838(26)	4.6(12)
H(271)	2 501(26)	587(48)	2 498(29)	6.2(14)
H(272)	2 965(20)	−4(40)	1 653(25)	3.8(11)
C(31)	4 506(2)	2 441(4)	3 998(3)	2.69(10)
C(32)	3 825(2)	2 592(4)	4 270(3)	2.82(10)
C(33)	3 613(3)	2 131(5)	4 994(3)	3.66(12)
C(34)	4 058(3)	1 558(5)	5 467(3)	3.96(12)
C(35)	4 728(3)	1 443(5)	5 243(3)	4.08(13)
C(36)	4 954(3)	1 876(5)	4 549(3)	3.66(12)
N(37)	3 326(2)	3 214(4)	3 815(3)	4.14(10)
O(38)	2 764(2)	3 383(6)	4 092(3)	*
O(39)	3 450(2)	3 634(4)	3 182(2)	*
O(40)	4 729(2)	2 755(3)	3 340(2)	*
H(33)	3 140(22)	2 202(40)	5 079(23)	3.5(11)
H(34)	3 871(31)	1 222(61)	5 935(37)	10.8(20)
H(35)	5 093(25)	987(47)	5 505(28)	5.4(14)
H(36)	5 411(25)	1 744(46)	4 363(28)	5.5(13)

* Anisotropic thermal parameters in the form: $\exp[-2\pi^2 \cdot 10^{-4}(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	341(12)	723(16)	404(13)	22(11)	7(10)	109(11)
O(8)	701(28)	721(31)	558(28)	−241(25)	−74(22)	−18(23
C(9)	1 583(115)	801(69)	833(62)	−475(85)	−610(76)	333(60)
O(38)	469(28)	2 597(76)	1 436(50)	661(38)	544(30)	1 291(51)
O(39)	525(25)	871(33)	447(25)	260(23)	33(19)	170(23)
O(40)	329(20)	584(25)	379(22)	61(18)	29(16)	−2(19)

In the later stages of the refinement, the sodium ion, O(8), C(9), and all the oxygen atoms of the *o*-nitrophenolate anion were refined anisotropically and the remainder of the atoms isotropically. The final weighting scheme, adjusted so that the mean value of $w(|F_o| - |F_c|)^2$ over several ranges of $|F_o|$ values remained fairly constant, was $w = \sigma_c^{-2}(-2.97 + 0.865|F_o|)^{-1}$ for reflections with $|F_o| > 4.0$, and

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[11] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

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

$w = \sigma_c^{-2}$ for those with $|F_o| < 4.0$. The refinement was concluded with R 0.084 and R' 0.077, for the 1 894 reflections.

Final atomic parameters are in Table 1. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21483 (12 pp., 1 microfiche).*

Computing.—The programs of the *X*-RAY ARC library for the IBM 1130 computer of this laboratory, and the programs NUCLS and ORFFE for the IBM 360/651 computer of University College, London, are described in refs. 10 and 13. In the program ORFFE, calculation of the estimated standard deviations in bond lengths and angles was from the least-squares variance–covariance matrix, with allowance for errors in unit-cell dimensions.

TABLE 2

Lengths (Å) of bonds involving hydrogen atoms, with standard deviations in parentheses

C(1)–H(1)	0.92(5)	C(24)–H(241)	0.97(4)
C(2)–H(2)	0.97(5)	C(24)–H(242)	1.01(5)
C(3)–H(3)	1.00(6)	C(26)–H(261)	1.05(5)
C(4)–H(4)	0.97(5)	C(26)–H(262)	1.04(5)
C(6)–H(61)	1.01(4)	C(27)–H(271)	1.09(5)
C(6)–H(62)	1.08(4)	C(27)–H(272)	1.02(4)
C(7)–H(71)	1.12(5)	C(33)–H(33)	0.94(4)
C(7)–H(72)	0.93(4)	C(34)–H(34)	0.97(6)
C(9)–H(91)	0.87(6)	C(35)–H(35)	0.98(5)
C(9)–H(92)	0.83(11)	C(36)–H(36)	0.97(5)

TABLE 3

Valence angles (°) between non-hydrogen atoms, with standard deviations in parentheses

(*a*) The crown ligand

C(281)–C(1)–C(2)	118.5(6)	C(7)–O(8)–C(9)	113.6(6)
C(1)–C(2)–C(3)	121.6(6)	O(8)–C(9)–C(9^{I})	108.8(14)
C(2)–C(3)–C(4)	120.6(6)	C(24^{I})–C(24)–O(25)	107.8(6)
C(3)–C(4)–C(41)	119.4(6)	C(24)–O(25)–C(26)	110.5(4)
C(4)–C(41)–C(281)	119.9(5)	O(25)–C(26)–C(27)	109.6(5)
C(4)–C(41)–O(5)	124.1(5)	C(26)–C(27)–O(28)	107.8(4)
C(281)–C(41)–O(5)	116.0(4)	C(27)–O(28)–C(281)	116.1(4)
C(41)–O(5)–C(6)	116.5(4)	O(28)–C(281)–C(41)	115.6(4)
O(5)–C(6)–C(7)	107.1(5)	O(28)–C(281)–C(1)	124.3(5)
C(6)–C(7)–O(8)	108.7(5)	C(41)–C(281)–C(1)	120.0(5)

(*b*) The *o*-nitrophenolate anion

C(36)–C(31)–C(32)	113.4(5)	C(36)–C(31)–O(40)	120.3(4)
C(31)–C(32)–C(33)	122.1(5)	C(31)–C(32)–N(37)	120.8(5)
C(32)–C(33)–C(34)	120.8(5)	C(33)–C(32)–N(37)	117.1(4)
C(33)–C(34)–C(35)	118.9(6)	C(32)–N(37)–O(38)	118.1(5)
C(34)–C(35)–C(36)	122.1(6)	C(32)–N(37)–O(39)	122.6(5)
C(35)–C(36)–C(31)	122.4(5)	O(38)–N(37)–O(39)	119.2(5)
C(32)–C(31)–O(40)	126.3(4)		

(*c*) Angles (°) subtended at the sodium ion by co-ordinating oxygen atoms, $O_i \cdots Na \cdots O_j$, with standard deviations in parentheses

O_i \ O_j	O(5)	O(8)	O(28)	O(39)	O(40)
O(8)	65.2(1)				
O(28)	61.9(1)	124.8(1)			
O(39)	92.8(2)	89.0(2)	78.8(1)		
O(40)	159.1(2)	101.5(1)	123.1(1)	70.1(1)	
O(40^{I})	107.1(2)	79.6(1)	130.4(1)	149.9(2)	84.9(2)

DISCUSSION

In this crystal, a two-fold symmetry axis relates the two halves of the complex. The crown ligand and the sodium ions are shown in Figure 1, and one of the *o*-nitrophenolate anions in Figure 2. Bond distances involving the hydrogen atoms are in Table 2, valence angles and O $\cdots$ Na $\cdots$ O angles in Table 3.

In the crystal structure analysis of the dibenzo-24-crown-8–bis(potassium thiocyanate) complex[8] it was found that: (i) the complex has a centre of symmetry and therefore the crown ring is generally planar around the pair of potassium ions, (ii) all the ether oxygen atoms interact with the cations, and one pair of oxygen atoms of the ring bridges the pair of cations, and (iii) the co-ordination sphere of each potassium ion comprises five oxygen atoms of the crown ring, the nitrogen atoms of both thiocyanate anions, and the π-electrons of a neighbouring benzene ring.

In contrast, we find in the sodium complex, that to accommodate the smaller cations, the crown ring folds around the two sodium ions. Each cation co-ordinates three ring oxygen atoms; a pair of oxygen atoms O(25) and O(25^{I}) do not appear to be involved in co-ordination; this is the first example of a cyclic polyether–alkali-metal complex in which not all the oxygen atoms of the ring are co-ordinated to the cation.

The two *o*-nitrophenolate anions interact with the cations from either side of the crown ring (Figure 3). The co-ordination sphere of the sodium ion comprises six oxygen atoms, from the crown ring and surrounding anions.

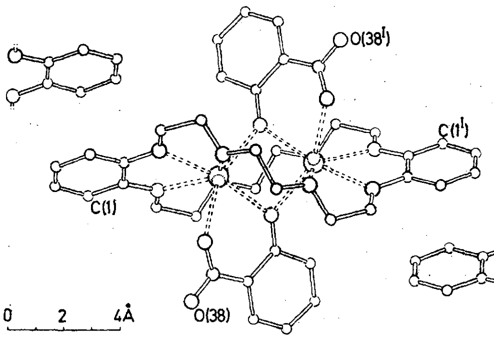

FIGURE 3 View of the complex down the two-fold symmetry axis. Benzene rings of neighbouring crown ligands are also shown. The non-co-ordinated oxygen atom, O(25), is eclipsed by the cation

Sodium Co-ordination.—There are six Na $\cdots$ O distances in the range 2.296—2.615 Å arranged irregularly about the cation. Three crown ring oxygen atoms are 2.468, 2.615, and 2.534 Å from a sodium ion. The *o*-nitrophenolate ion chelates a sodium ion through O(39) on the nitro-group and the phenolate oxygen O(40) at distances 2.399 and 2.296 Å. O(40), from the second anion, completes the co-ordination sphere, 2.320 Å from the cation; each anion thus bridges the pair of cations.

The Na $\cdots$ Na distance (3.383 Å) is similar to that found in other bridging systems, *e.g.* 3.23, 3.51, and 3.51 in $Na_3Fe_5O_9$,[14] 3.76 and 3.77 in sodium hydrogenoxydiacetate,[15] and 3.55 in washing soda, $Na_2CO_3 \cdot 10H_2O$.[16]

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

[13] D. L. Hughes and M. R. Truter, *J.C.S. Dalton*, 1972, 2214.

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

[15] J. Albertsson, I. Grenthe, and H. Herbertsson, *Acta Cryst.*, 1973, **B29**, 1855.

[16] T. Taga, *Acta Cryst.*, 1969, **B25**, 2656.

The two non-co-ordinated oxygen atoms, O(25) and the related O(25^{I}), are each 2.965 Å from a cation. The sodium ion is 2.74 Å out of the plane of O(25) and its two carbon neighbours, a distance very much larger than the corresponding displacements of the cation from C–O–C planes involving O(5), O(8), and O(28), *viz.* 0.62, 1.87, and 0.05 Å. In terms of oxygen lone-pair electron arrangements (Table 4 and ref. 7) the catechol oxygen atoms show interaction with the cation such that the Na · · · O lines are close to the direction of the idealised trigonal arrangement for the lone-pair of electrons; the Na · · · O(8) line is close to one of the directions for tetrahedral arrangement. In contrast, the lone-pairs of electrons of O(25) are directed away from the cation, an ' outside tetrahedral ' arrangement. It is thus concluded that there is no co-ordination of O(25) with the cation.

The Crown Ligand.—The molecular dimensions of the dibenzo-24-crown-8 ligand are very similar to those expected. The bond lengths about the catechol oxygen atoms are *ca.* 1.37 and 1.44 Å, and about the other oxygen atoms the C–O distances are *ca.* 1.42 Å. The aliphatic CH_2–CH_2 bonds are short, 1.49—1.50 Å, but appear to be normal for this type of ligand; to account for this shortening of C–C bonds and, to a lesser extent, of the C–O bonds, Bush and Truter[3,4] suggested inadequate treatment of thermal parameters, and Dunitz *et al.*[17] have suggested a theory of curvilinear motion of these groups of atoms.

Table 4

Deviations (°) of Na · · · O directions from the calculated (ref. 7) idealised directions of lone-pairs of electrons of the oxygen atoms

	Tetrahedral		
	(1)	(2)	Trigonal
O(5)	69.1	40.0	14.8
O(8)	14.9	101.6	48.8
O(25)	123.4	17.9	69.8
O(28)	55.6	53.4	1.4

In the benzene ring, most of the dimensions are normal, but the outermost C–C distance is 1.33 Å, again similar to results of previous analyses of crown complexes.

The torsion angles of the crown ring are listed in Table 5. The notable exception to the general rule for torsion angles in crown ligands (*trans* arrangements angles *ca.* 180°, or *gauche ca.* 60°, for C–O bonds, and *gauche* for aliphatic C–C bonds) is the apparently eclipsed arrangement, angle of 117°, about C(9)–C(9^{I}); however, as these atoms are probably disordered, the exact arrangement is difficult to determine. On the other side of the ring, at C(24)–C(24^{I}), the angle is 139, and at C(7)–O(8), 157°; these values, too, differ from normal. The ring in the dibenzo-24-crown-8–bis(potassium thiocyanate) complex[8] also shows considerable deviations from the general rule.

The atoms of the benzene ring form a good plane (Table 6). A centre of symmetry relates this plane to the neighbouring ring (Figure 3) at the van der Waals distance of 3.57 Å. This interaction is probably a principal factor in the packing of units in the crystal.

The o-*Nitrophenolate Ion.*—The dimensions of the anion (Figure 2 and Table 3) are similar to those reported for related anions.[10,18] The present rotation of the nitro-group about C(32)—N(37) is 2.6° and the distance O(39) · · · O(40) (2.70 Å) is remarkably similar to those of ref. 10.

Table 5

Torsion angles (°) in the crown ligand

C(281)–C(1)–C(2)–C(3)	−1
C(1)–C(2)–C(3)–C(4)	1
C(2)–C(3)–C(4)–C(41)	0
C(3)–C(4)–C(41)–C(281)	−1
C(4)–C(41)–C(281)–C(1)	0
C(41)–C(281)–C(1)–C(2)	0
O(28)–C(281)–C(41)–O(5)	2
C(281)–C(41)–O(5)–C(6)	−177
C(41)–O(5)–C(6)–C(7)	180
O(5)–C(6)–C(7)–O(8)	−61
C(6)–C(7)–O(8)–C(9)	−157
C(7)–O(8)–C(9)–C(9^{I})	180
O(8)–C(9)–C(9^{I})–O(8^{I})	117
O(25^{I})–C(24^{I})–C(24)–O(25)	139
C(24^{I})–C(24)–O(25)–C(26)	179
C(24)–O(25)–C(26)–C(27)	−176
O(25)–C(26)–C(27)–O(28)	−60
C(26)–C(27)–O(28)–C(281)	−175
C(27)–O(28)–C(281)–C(41)	−171

Table 6

Deviations (Å) of atoms from mean planes through groups of atoms; values marked with an asterisk indicate atoms included in the calculation of the mean plane

Plane (*A*): benzene ring of crown ligand

C(1) −0.005*, C(2) 0.008*, C(3) −0.004*, C(4) −0.003*, C(41) 0.004*, C(281) −0.001*, O(5) 0.047, O(28) −0.007

Plane (*B*): benzene ring, except C(31), of anion

C(31) 0.057, C(32) 0.001*, C(33) −0.004*, C(34) 0.005*, C(35) −0.003*, C(36) 0.000*, N(37) −0.046, O(40) 0.148

Plane (*C*): phenolate substituent of anion

C(31), C(32), C(36), O(40) each 0.000 *

Plane (*D*): about C(32) of anion

C(31) 0.000*, C(32) −0.001*, C(33) 0.001*, N(37) 0.000*, O(38) −0.082, O(39) 0.013

Plane (*E*): nitro-group

C(32) −0.005*, N(37) 0.018*, O(38) −0.009*, O(39) −0.004*, C(31) −0.068, C(33) 0.041

The phenolate oxygen atom, O(40), was considered to be an O^- group, and the final refinement of atomic parameters supports this. This atom has strong interaction with the pair of sodium ions, bridging them with short distances of 2.296 and 2.320 Å.

Atom O(38), whose vibrations are not restricted by co-ordination, has temperature factors considerably larger than those of O(39) and O(40) (Table 1).

The benzene ring is not planar (Table 6); five carbon atoms form a very good plane but the sixth, C(31) is 0.06 Å displaced from that plane. Planes (*C*), (*D*), and (*E*) describe other planes in the anion; the groups of atoms form good planes in (*C*) and (*D*), but there is a

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[17] J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackerley, *Acta Cryst.*, 1974, **B30**, 2733.

[18] E. K. Andersen and I. G. K. Andersen, *Acta Cryst.*, 1975, **B31**, 391.

slight umbrella conformation about N(37) in the nitro-group, plane (*E*).

Packing Arrangements.—The van der Waals interactions between neighbouring benzene rings of the crown ligands have been described. These and other short intermolecular distances are listed in Table 7; all correspond to van der Waals interactions. Also, H(262) [$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$] points into the centre of the crown benzene ring, with the six H · · · C distances 3.01—3.20 Å; the hydrogen atom is 2.77 Å from the mean plane of the ring. Similarly H(71) [$x, 1 - y, z + \frac{1}{2}$], 2.61 Å from the mean plane of the anion ring, is directed at C(33), C(34), and C(35) with H · · · C distances 2.71—2.91 Å. The packing arrangement is shown in Figure 4.

TABLE 7

Intermolecular distances (Å) which are less than, or equal to, those of van der Waals interactions

C(2) · · · C(41^{II})	3.70	C(27) · · · O(38^{V})	3.45
C(3) · · · C(41^{II})	3.59	C(27) · · · O(39^{V})	3.47
C(3) · · · C(26^{III})	3.68	C(33) · · · O(38^{VI})	3.19
C(4) · · · C(26^{III})	3.67	C(35) · · · C(35^{VII})	3.39
C(6) · · · C(33^{IV})	3.43	H(272) · · · O(38^{V})	2.59
C(7) · · · C(33^{IV})	3.69	H(33) · · · O(38^{VI})	2.38
C(7) · · · C(34^{IV})	3.67		

Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at *x,y,z*

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

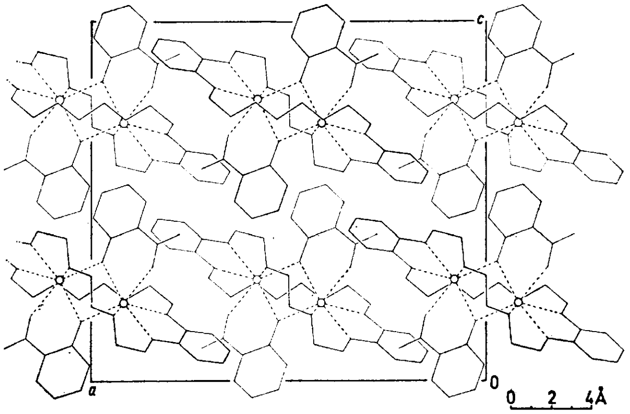

FIGURE 4 Packing arrangement of the complex, viewed down the *b* axis

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