Crystal Structures of Complexes between Alkali-metal Salts and Cyclic Polyethers. Part 10.[1] Complex formed between 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) and Two Molecules of Sodium Isothiocyanate

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

The crystal structure of the complex formed between two ion pairs of sodium isothiocyanate and one molecule of dibenzo-30-crown-10 has been determined from *X*-ray diffraction measurements. In a monoclinic unit cell, having a = 25.167(8), b = 8.921(3), c = 17.293(6) Å, β = 117.88(2)°, and space group $C2/c$, there are four neutral discrete molecules of complex and four of water of crystallisation. Full-matrix anisotropic refinement on 2 504 observed reflections was complete at R = 0.045. Each ligand complexes with two sodium cations, and each cation is also co-ordinated to one isothiocyanate anion through the nitrogen atom (Na–N 2.363 Å). The two halves of the complex are related by a crystallographic two-fold rotation axis which passes through two oxygen atoms, O(11) and O(28), of the ligand. These atoms bridge the cations (Na–O 2.531 and 2.585 Å respectively) which are 3.94 Å apart. The nitrogen atom and bridging atom O(28) form the apices of an approximately pentagonal-bipyramidal arrangement round the sodium ion (Na–O, unshared: 2.413, 2.493, 2.398, and 2.453 Å).

MACROCYCLIC polyethers, known as 'crown' compounds,[2] form complexes with salts of a variety of metals. The stoicheiometry of such compounds depends on the relative sizes of the cation and the cavity in the macrocycle, on the flexibility of the ether, and on the nature of the anion and the solvent.[3] The ratio of two metal cations to one crown ether has so far been found for dibenzo-24-crown-8 (1) and dibenzo-30-crown-10 (2) and then only for sodium and potassium salts.[4]

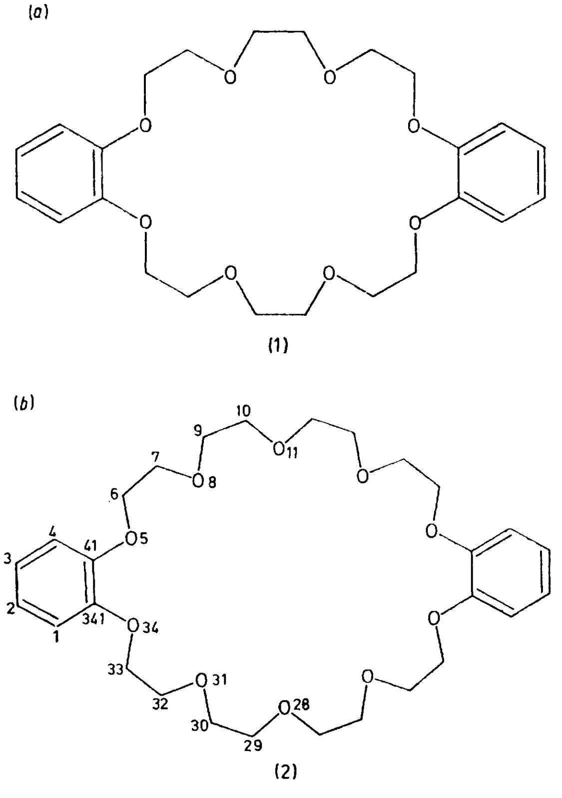


FIGURE 1 (*a*) Dibenzo-24-crown-8 (1), (*b*) dibenzo-30-crown-10 (2) showing the numbering scheme for the non-hydrogen atoms of the asymmetric unit

Crystal-structure analyses have established that there are two cations per ligand in the 2 : 1 complexes of (1) [1,5] and for this molecule the structures of 1 : 1 complexes (with barium) [6,7] and of the uncomplexed molecule [8] have also been determined. In the crystal (2) has an extended conformation [9] and in the 1 : 1 complex with potassium iodide the ligand is wrapped round the cation to the exclusion of solvent and anion,[9] while in the 1 : 1 complex with rubidium thiocyanate the same conformation of the molecule does not completely enclose the cation, to which one molecule of water is also co-ordinated.[10] The 2 : 1 complexes between sodium salts and (2) appeared from preliminary investigation[4] to be analogous to the 2 : 1 complex with (1) in having an extended conformation to the ether and crystallographic symmetry between the two cations. To determine the conformation of the ligand and the environment of the cation, we have analysed the crystal structure of 2Na[NCS]·(2) as described below and, contrary to the previous report,[4] have shown the presence of a solvent molecule, probably water, disordered to some extent in the crystal lattice.

The structure of the title compound was solved by direct methods from intensity data collected on a four-circle diffractometer. Refinement was done by the usual full-matrix least-squares techniques and the final parameters are listed in Table 1. The numbering scheme for the atoms of the macrocycle are shown in Figure 1. The hydrogen atoms are numbered according to the carbons to which they are attached. Thus H(321) and H(322) are bonded to C(32). The solvent atom is labelled 'wat,' and the scattering factor curve for oxygen was used for it. Bond lengths and angles are shown in Table 2(*a*) and (*b*), torsion angles in Table 3, and mean planes in Table 4.

RESULTS AND DISCUSSION

The structure of one discrete neutral molecule of the complex is shown in Figure 2. Each ligand complexes

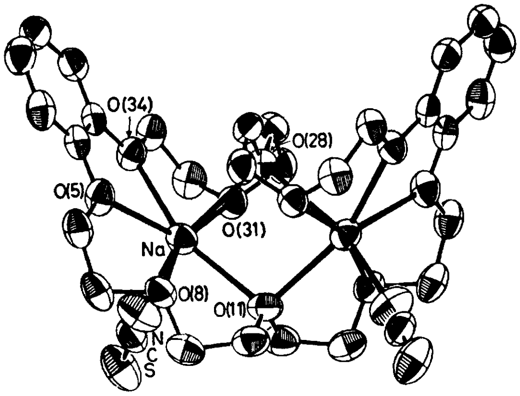


FIGURE 2 Molecule of the complex showing the 50% thermal ellipsoids. The crystallographic two-fold axis lies in the plane of the paper and runs through atoms O(11) and O(28)

with two sodium cations, and each cation is also co-ordinated to one isothiocyanate anion through the nitrogen atom. The two halves of the complex are related by a crystallographic two-fold rotation axis which passes through the O(11) and O(28) atoms of the ligand. The macrocycle is in an extended conformation, twisted so that, viewed down the two-fold axis, the molecule assumes a figure-of-eight shape, with the cations at the centres of the two loops. The cations are bridged by the two oxygens on the rotation axis and are 3.940 Å apart, a distance which is long compared with the Na–Na distance [1] of 3.38 Å and the K–K distance [5] of

TABLE 1

Fractional co-ordinates (with estimated standard deviations in parentheses)

Atom	x	y	z
(a) $\times 10^5$ for non-hydrogen atoms			
Wat	0	50 000	0
Na	8 256(4)	−3 710(9)	34 743(6)
S	14 383(4)	−36 004(10)	61 193(5)
C(35)	13 331(11)	−27 875(30)	52 151(18)
N	12 594(13)	−22 118(29)	45 783(19)
C(1)	18 757(10)	41 338(26)	45 914(15)
C(2)	22 615(11)	49 534(29)	43 728(17)
C(3)	24 299(11)	43 906(32)	37 903(17)
C(4)	22 337(10)	29 936(31)	34 184(15)
C(41)	18 655(9)	21 571(26)	36 442(13)
O(5)	16 533(7)	7 404(19)	33 414(10)
C(6)	18 952(11)	−472(29)	28 553(16)
C(7)	17 135(11)	−16 420(30)	28 226(17)
O(8)	10 722(7)	−17 072(17)	24 163(10)
C(9)	8 355(12)	−31 794(27)	23 461(18)
C(10)	1 619(12)	−30 122(27)	19 425(17)
O(11)	0	−21 517(23)	25 000
O(28)	0	15 052(22)	25 000
C(29)	−1 410(11)	24 053(26)	30 615(17)
C(30)	−2 276(11)	14 208(29)	36 965(17)
O(31)	2 828(7)	5 205(17)	42 116(10)
C(32)	7 058(11)	11 196(29)	50 390(15)
C(33)	10 873(10)	23 615(27)	49 662(15)
O(34)	13 044(6)	18 250(17)	43 915(9)
C(341)	16 811(9)	27 417(25)	42 273(13)
(b) $\times 10^4$ for hydrogen atoms			
H(1)	1 748	4 540	4 992
H(2)	2 408	5 914	4 637
H(3)	2 687	4 970	3 634
H(4)	2 352	2 606	3 004
H(61)	1 733	352	2 273
H(62)	2 325	39	3 141
H(71)	1 880	−2 037	3 406
H(72)	1 857	−2 219	2 489
H(91)	941	−3 790	1 982
H(92)	990	−3 628	2 915
H(101)	−19	−3 987	1 855
H(102)	18	−2 513	1 389
H(291)	182	3 094	3 377
H(292)	−504	2 955	2 716
H(301)	−565	774	3 374
H(302)	−309	2 045	4 081
H(321)	489	1 503	5 329
H(322)	967	325	5 382
H(331)	1 417	2 584	5 530
H(332)	849	3 247	4 729

TABLE 2

Bond lengths (Å) and angles (°)

(a) Lengths

Na–N	2.363(3)	Na–O(28)	2.585(2)
Na–O(5)	2.413(2)	Na–O(31)	2.398(2)
Na–O(8)	2.493(2)	Na–O(34)	2.453(2)
Na–O(11)	2.531(2)		
S–C(35)	1.629(3)	C(35)–N	1.149(3)
C(1)–C(2)	1.401(3)	O(8)–C(9)	1.424(3)
C(1)–C(341)	1.375(3)	C(9)–C(10)	1.509(4)
C(2)–C(3)	1.359(4)	C(10)–O(11)	1.433(2)
C(3)–C(4)	1.383(4)	O(28)–C(29)	1.427(3)
C(4)–C(41)	1.381(3)	C(29)–C(30)	1.499(3)
C(41)–O(5)	1.377(3)	C(30)–O(31)	1.421(3)
C(41)–C(341)	1.393(3)	O(31)–C(32)	1.429(3)
O(5)–C(6)	1.432(2)	C(32)–C(33)	1.509(3)
C(6)–C(7)	1.487(4)	C(33)–O(34)	1.422(2)
C(7)–O(8)	1.429(3)	O(34)–C(341)	1.379(2)

(b) Angles subtended at sodium, e.s.d. 0.1°

	N	O(5)	O(8)	O(11)	O(31)	O(34)
O(5)	105.6					
O(8)	94.7	66.7				
O(11)	91.5	132.1	67.7			
O(31)	87.9	130.2	169.4	93.9		
O(34)	97.5	63.2	129.8	159.0	67.7	
O(28)	154.6	98.0	103.4	79.2	69.4	84.6

(c) Other bond angles, e.s.d. 0.2°

Na–N–C(35)	153.1	Na–O(11)–C(10)	112.4
N–C(35)–S	179.9	Na–O(11)–C(10$^{\mathrm{I}}$)	107.0
Na–O(11)–Na$^{\mathrm{I}}$	102.2	Na–O(28)–C(29)	107.5
Na–O(28)–Na$^{\mathrm{I}}$	99.3	Na–O(28)–C(29$^{\mathrm{I}}$)	115.3
C(341)–C(1)–C(2)	119.4	C(9)–C(10)–O(11)	110.7
C(1)–C(2)–C(3)	120.2	C(10)–O(11)–C(10$^{\mathrm{I}}$)	115.2
C(2)–C(3)–C(4)	120.7	C(29$^{\mathrm{I}}$)–O(28)–C(29)	111.5
C(3)–C(4)–C(41)	119.8	O(28)–C(29)–C(30)	109.7
C(4)–C(41)–C(341)	119.8	C(29)–C(30)–O(31)	113.1
C(4)–C(41)–O(5)	125.5	C(30)–O(31)–C(32)	116.6
C(341)–C(41)–O(5)	114.7	O(31)–C(32)–C(33)	113.3
C(41)–O(5)–C(6)	118.5	C(32)–C(33)–O(34)	106.2
O(5)–C(6)–C(7)	106.5	C(33)–O(34)–C(341)	118.1
C(6)–C(7)–O(8)	108.3	O(34)–C(341)–C(1)	125.0
C(7)–O(8)–C(9)	114.3	O(34)–C(341)–C(41)	114.9
O(8)–C(9)–C(10)	106.4	C(1)–C(341)–C(41)	120.1

(d) Selected intermolecular distances

Na · · · Na$^{\mathrm{I}}$	3.94	H(4) · · · H(72$^{\mathrm{II}}$)	2.51
Wat · · · S$^{\mathrm{III}}$	3.44	Wat · · · H(302$^{\mathrm{V}}$)	2.99
Wat · · · S$^{\mathrm{IV}}$	3.44	Wat · · · H(332$^{\mathrm{I}}$)	2.86
Wat · · · H(302$^{\mathrm{I}}$)	2.99	Wat · · · H(332$^{\mathrm{V}}$)	2.86
S · · · H(1$^{\mathrm{VI}}$)	2.93	S · · · H(302$^{\mathrm{VIII}}$)	3.03
S · · · H(62$^{\mathrm{VII}}$)	3.04		
C(35) · · · H(1$^{\mathrm{VI}}$)	2.70		
C(341) · · · C(1$^{\mathrm{IX}}$)	3.64	C(341) · · · C(41$^{\mathrm{IX}}$)	3.79
C(341) · · · C(2$^{\mathrm{IX}}$)	3.56	C(341) · · · C(341$^{\mathrm{IX}}$)	3.74
C(341) · · · C(3$^{\mathrm{IX}}$)	3.63	C(1) · · · C(41$^{\mathrm{IX}}$)	3.41
C(341) · · · C(4$^{\mathrm{IX}}$)	3.75	C(3) · · · O(34$^{\mathrm{IX}}$)	3.44

Roman numeral superscripts denote the following equivalent positions relative to the asymmetric unit at x, y, z:

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

TABLE 3

Torsion angles (°)

O(34)–C(341)–C(41)–O(5)	−1.5(3)
C(341)–C(41)–O(5)–C(6)	−170.0(2)
C(41)–O(5)–C(6)–C(7)	165.3(2)
O(5)–C(6)–C(7)–O(8)	58.7(3)
C(6)–C(7)–O(8)–C(9)	−179.7(2)
C(7)–O(8)–C(9)–C(10)	177.5(2)
O(8)–C(9)–C(10)–O(11)	−62.6(3)
C(9)–C(10)–O(11)–C(10$^{\mathrm{I}}$)	−96.6(2)
C(29$^{\mathrm{I}}$)–O(28)–C(29)–C(30)	−174.6(2)
O(28)–C(29)–C(30)–O(31)	57.7(3)
C(29)–C(30)–O(31)–C(32)	93.0(2)
C(30)–O(31)–C(32)–C(33)	−74.4(3)
O(31)–C(32)–C(33)–O(34)	−48.3(3)
C(32)–C(33)–O(34)–C(341)	−178.5(2)
C(33)–O(34)–C(341)–C(41)	−178.7(2)

3.42 Å in the anion-bridged 2 : 1 complexes of dimeric ion pairs with (1).

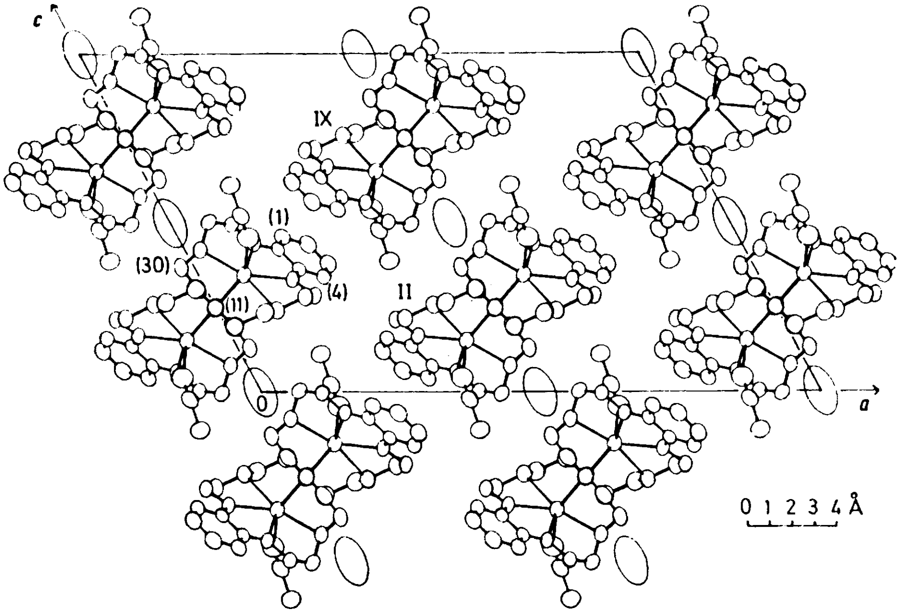


FIGURE 3 The unit cell viewed down the crystallographic *b* axis, negative *y* towards the reader. Atoms are depicted as the outlines of ellipsoids of vibration at the 50% confidence level so that the solvent molecules appear as large ovals

The crystal structure (Figure 3) consists of the packing of discrete molecules of the complex with disordered molecules of solvent, probably water. The benzene rings of asymmetric units at *x*, *y*, *z* and $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$ are stacked parallel and 3.40 Å apart, with C(341) almost directly over the centre of the other ring. The solvent molecules occupy centres of symmetry at 0, $\frac{1}{2}$, 0, *etc.* The anisotropic vibration parameters for oxygen atoms at 0, $\frac{1}{2}$, 0 were very much higher than those for the other atoms, and the root-mean-square deviations were up to 0.76 Å. However, only one site was indicated by the difference maps, and although it is not possible to discount entirely a disordered methanol molecule, the solvent is probably water, disordered statistically or by large thermal motion. The sulphur atoms are 3.44 Å from 0, $\frac{1}{2}$, 0, probably too long a distance to be considered as an O–H · · · S interaction, unless the solvent atoms are statistically disordered about two sites, one closer to sulphur than the mean. This is not confirmed by the orientation of the ellipsoid, the root-mean-square (r.m.s.) deviation along the wat · · · S direction being the smallest of the three, 0.42 Å. There are no wat · · · O contacts less than 3.0 Å; the nearest atoms are H(302) and H(332), Table 2(*c*). Thus there seems to be no strong interaction with the solvent, and this may be the cause of the apparent disorder. One definite conclusion which can be drawn from the closest distance, Na · · · wat 5.78 Å, is that the solvent is not co-ordinated to the cation. This is indicated by the i.r. spectrum, which has a broad weak band at 3 420 cm^{-1}, typical of non-co-ordinated water.

TABLE 4

Deviations (Å) from the mean planes through (*a*) the benzene carbon atoms, and (*b*) the atoms forming the equatorial plane of the pentagonal bipyramid around the sodium cation

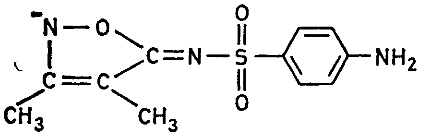
(*a*) C(1) 0.006(2), C(2) −0.010(3), C(3) 0.003(3), C(4) 0.007(3), C(41) −0.011(2), C(341) 0.004(2), O(5) −0.046(2), O(34) 0.013(1), Na 0.484

(*b*) Na −0.167 (1), O(5) 0.142(2), O(8) −0.118(2), O(11) 0.148(1) O(31) −0.015(2), O(34) 0.010(1)

The co-ordination polyhedron around the cation is a distorted pentagonal bipyramid, the two apical atoms being the nitrogen of the anion and O(28). The angles [Table 2(*b*)] subtended at sodium by O–C–C–O entities in the equatorial plane are all less than 72°; the O(11)–Na–O(31) angle is much larger and provides the main deviation from a regular pentagon. As shown in Table 4 the oxygen atoms forming the equatorial plane are reasonably coplanar with the sodium ion which is displaced by 0.2 Å towards the N atom. The two equatorial planes in the complex are inclined at 82° to each other, and each is at 72° to the plane of the sodium–oxygen bridge, and at 21° to the corresponding benzene plane.

The isothiocyanate ligand is linear with the Na–N–C angle of 153.1°. The observed splitting of ν(C–N) in the i.r. spectrum [4] may result from the non-parallel disposition of the two anions. A similar splitting was found [11] for the calcium isothiocyanate complexes of benzo-15-crown-5 in which both isothiocyanate ions are co-ordinated to the same cation.

The Na–O distances are in the range 2.399—2.585 Å, those to the two bridging oxygens being longest, and the Na–N distance is 2.363 Å. Four exactly comparable environments, *i.e.* six oxygens and one nitrogen round sodium, have been reported. Of these, two are sodium isothiocyanate complexes of open-chain polyethers having pentagonal-bipyramidal dispositions of ligands with the co-ordinated nitrogen atom axial. In one the molecule of the polyether, $o\text{-MeOC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{OMe-}o$,[12] provides the five equatorial oxygen atoms (Na–O 2.354—2.536 Å) and the axial oxygen atom (Na–O 2.490 Å); the Na–N distance in the discrete complex is 2.332 Å. The other, with the polyether diol $\text{HOCH}_2\text{CH}_2\text{O}(o\text{-C}_6\text{H}_4)\text{OCH}_2\text{CH}_2\text{O}(o\text{-C}_6\text{H}_4)\text{OCH}_2\text{CH}_2\text{OH}$, is polymeric;[13] the ligand provides five equatorial oxygen atoms (Na–O 2.421—2.558 Å) to one sodium ion and the axial oxygen to another sodium ion (Na–OH 2.424 Å) and the Na–N distance is 2.415 Å. A second independent polymeric complex has $\text{Na–O}_{\text{eq.}}$ 2.453—2.537, $\text{Na–O}_{\text{ax.}}$ 2.408, and Na–N 2.407 Å. The other two compounds are the sodium salt of sulphisooxazolohexahydrate [14] [see structure (3)] with Na–N 2.564, and Na–O from 2.408 to 3.297 Å, and the two independent sodium ions in the β-cytidine 2′,3′-cyclic phosphate dihydrate,[15] with Na–N 3.443, Na–O 2.345—2.560 and with Na–N 2.820 Å, Na–O 2.293—3.153 Å.



(3)

Sulphisoxazole (3,4-dimethyl-5-sulphanilylimino-isoxazoline) anion

The bond lengths and angles within the ether are similar to those found in other crown ethers and their complexes. The ether takes up an extended conformation twisted about the Na···Na^{I} direction and folds around the cations to exclude co-ordination by the solvent but not the anions. Bond angles at the bridging oxygen atoms are fairly close to tetrahedral [Table 2(*b*)]. The torsion angles (Table 3) show some values which differ from the usual ±*gauche* for C–C bonds and *trans* for C–O: in particular, the torsion angles C(9)–C(10)–O(11)–C(10$^{\text{I}}$), −97°, about the bridging oxygen atom in the equatorial plane and about C(30)–O(31), 93°; while the angle about O(31)–C(32) at −74° is close to a *gauche* conformation.

This ligand shows considerable discrimination between sodium and potassium, both in solution and in the stoicheiometry of the complexes isolated. Frensdorff [16] and Chock,[17] who used different experimental techniques, both agreed that the formation constants in solution for 1 : 1 complexes were 100 times greater for potassium than for sodium and neither detected any evidence for a 2 : 1 sodium-crown complex in solution, a result confirmed in this laboratory.[18] Frensdorff suggested that the additional stability of the potassium complex might be due to the ligand being wrapped round the cation as was subsequently found in the crystalline form.[9] The remarkable effect is that, while there seems plenty of room for two potassium ions to be accommodated in the ligand, no 2 : 1 complexes have been isolated for (2), whereas that is the normal stoicheiometry for sodium complexes in the presence of small anions or water; even the tetraphenylborate requires anhydrous conditions to give a 1 : 1 complex.[19] The difference does not lie in the non-bonded interaction of the macrocyclic ether. Although this sodium complex and the potassium one have such different conformations, they have conformational energy terms (computed from the Lennard-Jones 6—12 potential with Hopfinger's parameters [20]) which are essentially identical, −43 and −44 units, and both are more favourable than that for the uncomplexed ether, −36 units. The formation-constant measurements do not reveal the degree of solvation of the ions.

If the sodium ion, co-ordinated only by the ligand, were to occupy the central cavity with the usual Na–O (polyether) distances, very unfavourable non-bonded interactions would be induced in the molecule; a more probable arrangement would be for the sodium to be off-centre, co-ordinated more strongly by some oxygen atoms than by others.

It seems possible that the key to the behaviour of the sodium lies in the stronger interactions it forms with anion and solvent, so that in solution only a few oxygen atoms of the ligand interact with one sodium, the remainder of the molecule being free to adopt a variety of conformations. While the equilibrium concentration of the 2 : 1 species in solution is low, it has a greatly reduced flexibility in the ligand so it is more readily crystallised. Similar arguments apply to the analogous sodium iodide complex $2\text{NaI}\cdot(2)\cdot\text{H}_2\text{O}$ although the i.r. spectrum [4] indicates a different conformation for the ligand and that the water is not co-ordinated. Stronger interactions with solvent and anions than with the oxygen atoms of polyethers containing O–C–C–O groups are also suggested by the relative distances, for example as in the Na–N distances in this and the other isothiocyanate complexes [12,13] and in Na–O(water) distances in 1 : 1 crown complexes.[21,22]

EXPERIMENTAL

Crystal Data.—$\text{C}_{30}\text{H}_{42}\text{Na}_2\text{N}_2\text{O}_{11}\text{S}_2$, $M = 716.8$, Monoclinic, colourless needles, $a = 25.167(8)$, $b = 8.921(3)$, $c = 17.293(6)$ Å, $\beta = 117.88(2)$°, $U = 3\,431.7$ Å^3, $D_m = 1.35$ g cm^{-3} (flotation), $Z = 4$, $D_c = 1.39$ g cm^{-3}, $F(000) = 1\,512$, space group $C2/c$ (C_{2h}^6, no. 15), molecular symmetry 2 (from structure analysis), Mo-K_α radiation, graphite monochromator, $\lambda = 0.710\ 7$ Å, $\mu = 2.29$ cm^{-1} (Found:[4] C, 51.3; H, 5.9; N, 4.1; Na, 6.4. Calc. for $C_{30}H_{42}Na_2N_2O_{11}S_2$: C, 50.3; H, 5.9; N, 3.9; Na, 6.4%).

Data Collection.—Crystals were obtained by methods which have been described[4] and a crystal of dimensions 0.79 × 0.29 × 0.19 mm was mounted on an Enraf–Nonius CAD-4 diffractometer and accurate unit-cell dimensions obtained from the settings of 18 reflections. Intensity data were collected using symmetric ω—2θ scans and the intensities of two standard reflections measured every 2 h of exposure time. No systematic variation of the intensities of these reflections was observed throughout the data collection. Intensities were measured for 6 032 planes with $k \geqslant 0$ up to a maximum $\theta = 25°$. An empirical absorption correction was carried out by measuring the intensities of eight reflections at various angles of rotation about the diffraction vector, and using these data to refine the crystal as an ellipsoid.[23] Equivalent reflections were then averaged to give 3 021 planes, of which 2 504 had $I > 2\sigma(I)$ and were classed as observed. The structure solution and initial refinement were carried out using the 1 450 observed planes with $\theta < 20°$.

Structure Determination.—The statistical distribution of the E values calculated using a K curve showed that the atomic arrangement was centrosymmetric. This indicated the space group was $C2/c$ (later confirmed by the structure analysis), and thus the asymmetric unit was Na[NCS] + half a molecule of dibenzo-30-crown-10. A multisolution direct-methods program[24] was used to solve the structure. The non-hydrogen atoms were later refined with anisotropic temperature factors and a difference map then showed the hydrogen atoms in their expected positions. These were included in positions calculated from the geometry of the rest of the molecule and with a C–H distance of 0.96 Å. A common isotropic temperature factor was used for the phenyl H atoms, and this refined to a value of $U = 0.068(4)$ Å^2. The other hydrogen atoms on the ether were treated in a similar way and the temperature factor refined to $U = 0.068(2)$ Å^2. A consistent feature of the difference maps at this stage was a large peak (1.75 e Å^{-3}) at 0, $\frac{1}{2}$, 0, and the weighting analysis showed poorest agreement between $|F_o|$ and $|F_c|$ when the l index was even. The inclusion of an oxygen atom at this position with anisotropic vibration parameters gave much better agreement for the l even planes, and the highest peak on the final difference map was 0.2 e Å^{-3}. The thermal parameters of this atom are very large and indicate site disorder, but a difference map in this region showed only one broad peak. For this and other reasons described above, the solvent in the crystals was represented by a single oxygen atom undergoing large thermal motion.

The scattering factors used throughout were calculated using the analytical approximation coefficients given in Table 2.2B of ref. 25. The final values of the conventional agreement indices were $R = 0.045$ and $R' = 0.047$. The weights used in the least-squares refinements were those derived from the counting statistics, and a weighting analysis showed no obvious trends against ranges of $(\sin\theta)/\lambda$ or $|F_o|$. The largest value of shift/e.s.d. on the final cycle was 0.04. Several correlation-matrix elements had values greater than 0.5 (maximum 0.67), due to the large β angle of the unit cell. The full-matrix least-squares refinement and the Fourier maps were done using SHEL-X;[24] the geometry calculations were carried out on an IBM 1130 computer[26] and the diagrams were drawn using ORTEP.[27] Observed and calculated structure factors and anisotropic temperature factors are listed in Supplementary Publication No. SUP 22585 (17 pp.).*

We thank the Royal Society for some apparatus.

[9/156 *Received*, 31*st January*, 1979]

REFERENCES

[1] Part 9, D. L. Hughes, *J.C.S. Dalton*, 1975, 2374.
[2] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.
[3] C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, 1972, **84**, 16 (*Internat. Edn.*, 1972, **11**, 16).
[4] N. S. Poonia and M. R. Truter, *J.C.S. Dalton*, 1973, 2062.
[5] M. Mercer and M. R. Truter, *J.C.S. Dalton*, 1973, 2469.
[6] D. L. Hughes and J. N. Wingfield, *J.C.S. Chem. Comm.*, 1977, 804.
[7] D. L. Hughes, C. L. Mortimer, and M. R. Truter, *Acta Cryst.*, 1978, **B34**, 800.
[8] I. R. Hanson, D. L. Hughes, and M. R. Truter, *J.C.S. Perkin II*, 1976, 972.
[9] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 345.
[10] J. Hasek, K. Huml, and D. Hlavata, personal communication.
[11] J. D. Owen, *J.C.S. Dalton*, 1978, 1418.
[12] I.-H. Suh, G. Weber, and W. Saenger, *Acta Cryst.*, 1978, **B34**, 2752.
[13] D. L. Hughes and J. N. Wingfield, *J.C.S. Chem. Comm.*, 1978, 1001, and personal communication.
[14] Y. J. Park and C. H. Koo, *J. Korean Chem. Soc.*, 1976, **20**, 19.
[15] C. L. Coulter, *J. Amer. Chem. Soc.*, 1973, **95**, 570.
[16] H. K. Frensdorff, *J. Amer. Chem. Soc.*, 1971, **93**, 600.
[17] P. B. Chock, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 1939.
[18] J. N. Wingfield, personal communication.
[19] D. G. Parsons, M. R. Truter, and J. N. Wingfield, *Inorg. Chim. Acta*, 1975, **14**, 45.
[20] A. J. Hopfinger, 'Conformational Properties of Macromolecules,' Academic Press, New York, 1973, p. 47.
[21] M. Dobler, J. D. Dunitz, and P. Seiler, *Acta Cryst.*, 1974, **B30**, 2741.
[22] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 341.
[23] G. M. Sheldrick, G. Orpen, B. E. Reichert, and P. R. Raithby, Fourth European Crystallographic Meeting, Oxford, 1977, abstract PI26.
[24] G. M. Sheldrick, SHEL–X, Programs for Crystal Structure Determination, University Chemical Laboratory, Cambridge.
[25] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 99.
[26] '*X*-RAY ARC,' Library of Programs for the IBM 1130 Computer (*J. Appl. Cryst.*, 1973, **6**, 309).
[27] ORTEP, Report No. ORNL–3794, C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.