Table 3. *Bond distances (Å) and bond and torsion angles (°)*

1	2	3	4	1–2	1–2–3	1–2–3–4
C(9')	S(1)	C(2)	C(3)	1·687 (7)	102·5 (3)	−81·3 (6)
S(1)	C(2)	C(3)	O(4)	1·641 (7)	115·5 (5)	78·3 (6)
C(2)	C(3)	O(4)	C(5)	1·498 (10)	109·5 (5)	−154·8 (5)
C(3)	O(4)	C(5)	C(6)	1·427 (7)	111·8 (5)	170·0 (5)
O(4)	C(5)	C(6)	O(7)	1·427 (8)	107·8 (5)	−65·8 (6)
C(5)	C(6)	O(7)	C(8)	1·491 (8)	110·0 (4)	173·4 (5)
C(6)	O(7)	C(8)	C(9)	1·402 (7)	112·9 (4)	176·9 (5)
O(7)	C(8)	C(9)	S(1')	1·430 (7)	106·4 (4)	176·4 (4)
C(8)	C(9)	S(1')	C(2')	1·490 (8)	107·5 (4)	165·7 (5)

molecule an elliptical shape (Dalley, Smith, Larson, Matheson, Christensen & Izatt, 1975).

The title compound is isomorphous with the hexaether 1,4,7,10,13,16-hexaoxacyclooctadecane (Dunitz & Seiler, 1974). The unit-cell origin and atomic labels for this structure were chosen to correspond to the hexaether structure solved by Dunitz & Seiler. It is interesting that replacement of an O by an S atom essentially leaves the packing arrangement and conformation unchanged. The longer C–S bond lengths, smaller C–S–C bond angles, and the larger size of the S atom evidently offset each other to yield virtually the same conformation as the hexaether.

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Sodium Thiocyanate Complex of 1,4,7,10,13-Pentaoxa-16-thiacyclooctadecane

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Abstract. $C_{12}H_{24}O_5S \cdot NaSCN$, $M_r = 361·458$, monoclinic, $P2_1/c$, $a = 17·289$ (8), $b = 13·7203$ (14), $c = 7·7412$ (9) Å, $\beta = 104·967$ (15)°, $V = 1773·9$ Å³, $Z = 4$, $D_x = 1·35$, $D_m = 1·35$ Mg m⁻³ (flotation in CCl_4 and heptane), $F(000) = 768$, colorless crystals, m.p. 383 K. The structure was solved by direct methods and refined to $R = 0·048$ ($R_w = 0·023$) for a total of 2961 unique reflections. The Na⁺ ion sits in a cavity formed by the five atoms to which it is coordinated. There is no interaction between the S atom of the polyether and the Na⁺ ion. The N of the thiocyanate ion completes the sixfold coordination to the Na⁺ ion.

Introduction. The complex was prepared by allowing the solvent to evaporate from an equimolar salt–ligand

mixture dissolved in methanol. A crystal was shaped to a suitable size (0·33 × 0·40 × 0·43 mm) for X-ray intensity measurements. Preliminary data obtained on a General Electric XRD-5 diffractometer were used to determine the space group. Systematic absences (0k0, $k = 2n + 1$, and h0l, $l = 2n + 1$) indicated the unambiguous space group $P2_1/c$. Intensity data were collected using a Syntex PĪ automated diffractometer employing graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å). Accurate lattice parameters were determined by a least-squares refinement of 15 2θ measurements, 25° < 2θ < 34°. Integrated intensities were measured by a $\theta/2\theta$ scan. The scan rate was 2° min⁻¹ over the peak width with a 2θ range from 1° below $K\alpha_1$ to 1° above $K\alpha_2$. Background counts at extremes of scan were taken with the total background time equalling the scan time. A total of 3109 unique

* Contribution No. 209.

reflections were collected to a 2θ limit of 49° (sin $\theta/\lambda =$ 0·583 Å^{-1}), of which 146 were systematically extinct and 485 were considered unobserved as $I < 2\sigma(I)$; $\sigma(I)$ being based only on counting statistics. Five check reflections measured every 95 reflections showed no significant change. The data were corrected for Lorentz and polarization effects; however, no absorption corrections were calculated as μ(Mo) = 0·341 mm^{-1}. The structure was solved by direct methods. Normalized structure factors were calculated, and the 400 reflections with $|E(hkl)| > 1·50$ were used in the phasing program *MULTAN* (Germain, Main & Woolfson, 1971). An E map was calculated from which the 22 non-H atoms were located. The structure was refined by full-matrix least-squares methods (Busing, Martin & Levy, 1962). Positions of the H atoms were calculated from stereochemical considerations. The positional parameters of all the atoms and the anisotropic thermal parameters of the non-H atoms and isotropic ones of the H atoms were refined using experimental weights (Stout & Jensen, 1968). Two reflections, the 002 due to extinction and the 100 due to interference of the scintillation counter by the beam stop, were not included in the refinement. A final difference Fourier map showed no significant features. The positional parameters and isotropic temperature factors of the atoms are listed in Tables 1 and 2.* The final R was 0·048, while the weighted R was 0·023. The 'goodness of fit', $[\sum w(\Delta F)^2/(n - m)]^{1/2}$, was 1·8 with $n = 2963$ and $m = 295$. Atomic-scattering-factor tables for the non-H atoms were obtained from Cromer & Waber (1965). The 3s electron of the Na atom was distributed equally on the S and N atoms of the thiocyanate; *i.e.*, the scattering-factor tables for the S and the N of the thiocyanate were interpolations of the S and S$^-$ and the N and N$^-$ tables. Anomalous-dispersion corrections for Na and S along with the scattering-factor tables for S$^-$, N$^-$ and H were taken from *International Tables for X-ray Crystallography* (1968).

Discussion. Fig. 1 shows the ring conformation and coordination of the complex. Bond lengths, angles and torsion angles are shown in Table 3. As in other structures in this series, the C—C bonds appear to be abnormally short [mean 1·495 (6) Å] while the C—O bonds are normal [mean 1·422 (7) Å]. All torsion angles about C—C bonds are close to 60°, the two C—S bonds have torsion angles of about 80°, while those about C—O bonds [with the exception of O(4)—C(5)] are close to 180°. Torsion angles about C—O bonds of 180° are typical of 18-crown-6

* Lists of structure factors, anisotropic thermal parameters, C—H bond distances and bond angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35980 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^5$) *and isotropic* U *values* ($\times 10^4$) *for the non-*H *atoms with e.s.d.'s in parentheses*

$\bar{U}$ is the average of the three eigenvalues of each anisotropic vibration tensor.

	x	y	z	$\bar{U}$ (Å^2)
Na$^+$	25930 (4)	−1109 (5)	69794 (10)	432 (5)
S	32853 (4)	900 (5)	12267 (8)	577 (4)
C	27704 (13)	392 (14)	27374 (27)	458 (14)
N	24111 (12)	59 (14)	38114 (24)	637 (14)
S(1)	1923 (3)	−8819 (4)	78062 (8)	532 (4)
C(2)	10169 (12)	−3026 (14)	93634 (26)	472 (13)
C(3)	11332 (13)	7615 (14)	90428 (26)	483 (12)
O(4)	13998 (7)	8646 (9)	74493 (16)	452 (8)
C(5)	15156 (13)	18596 (14)	70188 (29)	517 (14)
C(6)	23448 (13)	22081 (14)	78796 (28)	523 (13)
O(7)	28694 (8)	16640 (9)	71091 (17)	479 (9)
C(8)	36832 (13)	19315 (15)	77466 (30)	557 (14)
C(9)	41597 (13)	12487 (15)	69319 (32)	591 (14)
O(10)	40555 (8)	3057 (10)	75795 (18)	548 (10)
C(11)	44596 (12)	−4387 (16)	68770 (33)	607 (15)
C(12)	43026 (12)	−13642 (17)	77485 (35)	643 (16)
O(13)	34744 (8)	−15676 (9)	71769 (17)	469 (9)
C(14)	32290 (13)	−23004 (15)	82161 (29)	565 (14)
C(15)	23903 (13)	−25796 (14)	73295 (29)	553 (14)
O(16)	18820 (8)	−17444 (9)	71507 (17)	449 (8)
C(17)	11148 (12)	−19654 (16)	60118 (28)	536 (13)
C(18)	5663 (12)	−11063 (17)	58745 (26)	510 (13)

Table 2. *Fractional coordinates* ($\times 10^4$) *and isotropic* U *values* ($\times 10^3$) *for the* H *atoms with e.s.d.'s in parentheses*

	x	y	z	U (Å^2)
H(2a)	1517 (10)	−680 (11)	9424 (20)	11 (5)
H(2b)	900 (10)	−374 (12)	10447 (22)	12 (5)
H(3a)	1541 (10)	1046 (12)	10055 (22)	15 (5)
H(3b)	622 (10)	1130 (12)	8882 (22)	21 (5)
H(5a)	1103 (11)	2283 (13)	7356 (24)	36 (6)
H(5b)	1428 (10)	1856 (12)	5700 (23)	21 (5)
H(6a)	2490 (10)	2115 (12)	9209 (22)	17 (5)
H(6b)	2404 (10)	2884 (14)	7631 (20)	19 (5)
H(8a)	3871 (10)	1859 (12)	9115 (23)	21 (5)
H(8b)	3746 (10)	2580 (12)	7456 (22)	18 (5)
H(9a)	4749 (11)	1421 (14)	7299 (24)	40 (6)
H(9b)	3983 (11)	1256 (13)	5608 (24)	27 (6)
H(11a)	5018 (12)	−268 (14)	7300 (24)	37 (6)
H(11b)	4236 (11)	−496 (13)	5500 (25)	34 (6)
H(12a)	4448 (11)	−1278 (13)	9087 (25)	29 (6)
H(12b)	4592 (11)	−1893 (15)	7380 (24)	43 (7)
H(14a)	3295 (10)	−2019 (12)	9442 (22)	19 (5)
H(14b)	3578 (11)	−2832 (13)	8316 (23)	29 (6)
H(15a)	2199 (10)	−3064 (13)	8047 (22)	19 (5)
H(15b)	2340 (10)	−2836 (12)	6063 (23)	19 (5)
H(17a)	903 (10)	−2532 (12)	6454 (22)	21 (6)
H(17b)	1183 (10)	−2119 (13)	4786 (23)	28 (6)
H(18a)	116 (11)	−1250 (13)	4990 (23)	24 (6)
H(18b)	795 (10)	−523 (13)	5558 (22)	16 (5)

complexes where all six heteroatoms coordinate in a planar configuration about the cation (Seiler, Dobler & Dunitz, 1974; Bush & Truter, 1971). However, when a non-planar configuration is formed or when less than
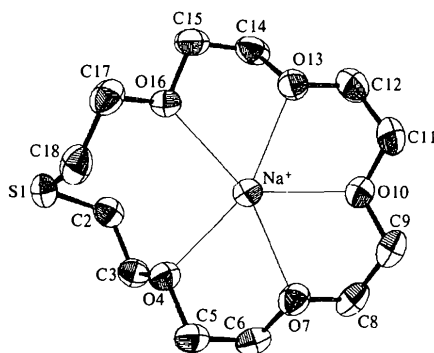
Fig. 1. *ORTEP* (Johnson, 1965) drawing of the complex viewed in a direction normal to the least-squares plane of the O atoms, showing atom numbering. The H atoms and the thiocyanate anion are omitted for clarity. The vibration ellipsoids are drawn at the 50% probability level.

Table 4. Na^+-*ion contact distances* (Å)

$Na^+\cdots S(1)$	4·486 (2)	$Na^+\cdots O(13)$	2·494 (2)
$Na^+\cdots O(4)$	2·563 (2)	$Na^+\cdots O(16)$	2·576 (2)
$Na^+\cdots O(7)$	2·479 (1)	$Na^+\cdots N$	2·396 (2)
$Na^+\cdots O(10)$	2·516 (2)	$Na^+\cdots S'$	3·207 (1)

Fig. 2. Molecular packing. Stereoscopic view of four equivalent molecules viewed along the c axis.

Table 3. *Bond distances* (Å) *and bond and torsion angles* (°)

1	2	3	4	1–2	1–2–3	1–2–3–4
S(1)	C(2)	C(3)	O(4)	1·797 (2)	115·82 (13)	−69·38 (20)
C(2)	C(3)	O(4)	C(5)	1·503 (3)	108·96 (16)	179·10 (15)
C(3)	O(4)	C(5)	C(6)	1·431 (3)	112·98 (15)	89·02 (21)
O(4)	C(5)	C(6)	O(7)	1·432 (2)	112·14 (15)	65·41 (22)
C(5)	C(6)	O(7)	C(8)	1·495 (3)	106·73 (16)	178·06 (16)
C(6)	O(7)	C(8)	C(9)	1·420 (3)	113·77 (15)	175·54 (16)
O(7)	C(8)	C(9)	O(10)	1·414 (3)	107·34 (16)	−63·61 (20)
C(8)	C(9)	O(10)	C(11)	1·491 (3)	105·85 (20)	178·34 (15)
C(9)	O(10)	C(11)	C(12)	1·416 (3)	113·63 (18)	178·26 (15)
O(10)	C(11)	C(12)	O(13)	1·422 (3)	106·84 (20)	65·27 (22)
C(11)	C(12)	O(13)	C(14)	1·495 (3)	108·28 (16)	−166·62 (19)
C(12)	O(13)	C(14)	C(15)	1·413 (2)	112·92 (15)	−170·38 (18)
O(13)	C(14)	C(15)	O(16)	1·419 (3)	108·66 (16)	−58·50 (23)
C(14)	C(15)	O(16)	C(17)	1·485 (3)	109·91 (16)	169·02 (18)
C(15)	O(16)	C(17)	C(18)	1·429 (2)	109·92 (14)	177·71 (18)
O(16)	C(17)	C(18)	S(1)	1·423 (2)	110·34 (17)	−74·67 (21)
C(17)	C(18)	S(1)	C(2)	1·499 (3)	115·55 (15)	78·09 (17)
C(18)	S(1)	C(2)	C(3)	1·802 (2)	103·87 (10)	78·95 (19)
S	C	N		1·644 (3)	179·56 (18)	
C	N			1·160 (3)		

the optimum of six heteroatoms takes part in the coordination, deviations from the 180° torsion angles are found (Dobler, Dunitz & Seiler, 1974; Herceg & Weiss, 1973). The O(4)–C(5) torsion angle of 89° found in this complex is necessary in order for the S atom to point out of the ring.

The complex can be divided into two parts, the roughly planar complexing unit [containing the O(4) through O(16) atoms] and the S-containing unit [containing the C(17), C(18), S(1), C(2), and C(3) atoms]. In the complexing unit, coordination of the Na⁺ to the ligand is directed to the five O atoms, which form a fairly planar pentagon with the O(7), O(13), and O(16) atoms 0·19, 0·06, 0·04 Å below and the O(4) and O(10) atoms 0·12 and 0·17 Å above their least-squares plane respectively. The Na⁺ cation deviates 0·23 Å from the mean plane of the O atoms toward the N of the thiocyanate. The adjacent O—O distances, which range from 2·725 (2) to 2·841 (2) Å, are

approximately equal to the sum of the van der Waals radii of 2·80 Å (Pauling, 1960).

Table 4 shows the Na⁺-ion coordination contact distances in the complex. The Na—O distances (2·48 to 2·58 Å) are slightly longer than the sum of the corresponding ionic and van der Waals radii of 2·35 Å. The Na—N contact distance of 2·396 (2) Å indicates that the N of the thiocyanate interacts strongly with the Na⁺ ion. The S of the SCN⁻ unit translated one unit cell in the c direction [Na—S' distance 3·207 (1) Å] interacts weakly with the Na⁺. The result is a SCN⁻ complex cation chain parallel to the c axis.

The S-containing unit of the ligand does not take part directly in complex formation. The S atom is directed away from the cavity and gives the ligand an elliptical shape. Structures of uncomplexed S-containing macrocycles also show this feature (Dalley, Smith, Larson, Matheson, Christensen & Izatt, 1975).

The planar conformation of this complex is in marked contrast to the Na⁺ complex of 1,4,7,10,13,16-hexaoxacyclooctadecane in which all six O atoms of the ligand take part in coordination. In the ligand containing six O atoms, one of them is positioned 1·95 Å above the mean plane of the other five to give a somewhat irregular pentagonal pyramidal coordination of the Na⁺ ion (Dobler *et al.*, 1974). The irregular conformation of the ring is undoubtedly strained; however, the conformational strain is evidently compensated by better coordination with the cation. In the S-containing ligand, the possible stabilizing effect due to an interaction of the S atom with the Na⁺ ion must be outweighed by the destabilizing conformational strain associated with a S—Na coordination geometry.

Fig. 2 is a stereoscopic view of the unit cell. The Na⁺–polyether cations related by a unit translation

along the c axis are linked together by the thiocyanate anions. There are two short intermolecular contacts in the structure; the distance between the H(14a) and H(15b) atoms of adjacent molecules is 2·16 Å, while the distance between the thiocyanate S to the H(11a) atom is 2·76 Å.* The remainder of the packing appears to be determined by weak van der Waals contacts. Intermolecular van der Waals interactions include a S(1)···H(2b) distance of 3·04 Å, a N···H(15a) distance of 2·64 Å, and several H···H contacts of about 2·4 Å.

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* H positions used for calculating crystal packing were calculated assuming a tetrahedral configuration about the C atom with a C–H distance of 1·08 Å.

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Structure and Absolute Configuration of the Potassium Thiocyanate Complex of 1,4,7,10,13-Pentaoxa-16-thiacyclooctadecane

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Abstract. $C_{12}H_{24}O_5S$.KSCN, $M_r = 377·57$, orthorhombic, $P2_12_12_1$, $a = 8·0083$ (11), $b = 14·6663$ (23), $c = 15·7459$ (34) Å, $V = 1849·3$ Å^3, $Z = 4$, $D_x = 1·36$, $D_m = 1·35$ Mg m^{-3}, $F(000) = 800$, colorless crystals, m.p. 415 K. The structure was solved by direct methods and refined to $R = 0·074$ ($R_w = 0·062$) for a total of 2441 independent reflections. The K$^+$ ion sits in a cavity formed by the six heteroatoms arranged in a hexagon. Coordination is to all six heteroatoms in the ring. The thiocyanate ions interact only weakly with the K$^+$ and link adjacent molecules along the a axis.

Introduction. The complex was prepared by allowing a mixture of the salt (large excess) and ligand dissolved in water to stand for one week. The crystals which had formed were filtered, and a crystal was shaped to a suitable size (roughly spherical, $d = 0·35$ mm) for X-ray intensity measurements. The space group and approximate lattice parameters were obtained from precession-camera photographs. Cell parameters and intensity data were measured on a Syntex P$\bar{1}$ autodiffractometer using Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å) with a graphite monochromator. Accurate lattice parameters were determined by a least-squares refinement of the 2θ measurements of 15 reflections, $5° < 2\theta$

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* Contribution No. 210.