

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, $V = 1849.3$ Å³, $Z = 4$, $D_x = 1.36$, $D_m = 1.35$ 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, $5^\circ < 2\theta$

* Contribution No. 210.

$< 21^\circ$. Intensity data were recorded as with the Na^+ complex (Campbell, Larson & Dalley, 1981). A total of 2466 independent reflections were measured to a 2θ limit of 55° ($\sin \theta/\lambda = 0.650 \text{ \AA}^{-1}$). These included 25

Table 1. Fractional coordinates ($\times 10^4$) and isotropic U values ($\times 10^3$) 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	$\bar{U} (\text{\AA}^2)$
K ⁺	1976 (2)	2396 (1)	2411 (1)	51 (1)
S	5940 (3)	2239 (2)	3106 (2)	91 (2)
C	7459 (13)	2414 (6)	2374 (6)	91 (6)
N	8324 (7)	2484 (5)	1881 (3)	59 (3)
S(1)	2342 (2)	718 (1)	1043 (1)	49 (1)
C(2)	4431 (8)	1163 (5)	886 (4)	54 (4)
C(3)	4416 (5)	2027 (4)	388 (15)	65 (4)
O(4)	3454 (5)	2688 (3)	829 (3)	53 (2)
C(5)	3884 (10)	3592 (5)	601 (5)	64 (4)
C(6)	2705 (11)	4230 (5)	1018 (5)	70 (4)
O(7)	2863 (5)	4166 (3)	1912 (3)	52 (2)
C(8)	1878 (9)	4830 (4)	2340 (5)	64 (4)
C(9)	1989 (10)	4679 (5)	3274 (5)	65 (4)
O(10)	1190 (5)	3840 (3)	3471 (3)	51 (2)
C(11)	1147 (11)	3653 (5)	4355 (5)	69 (4)
C(12)	393 (10)	2731 (5)	4493 (4)	67 (4)
O(13)	1503 (6)	2084 (3)	4132 (3)	58 (3)
C(14)	1032 (12)	1174 (5)	4308 (4)	72 (5)
C(15)	2290 (11)	540 (5)	3913 (4)	67 (4)
O(16)	2084 (5)	553 (3)	3027 (2)	47 (2)
C(17)	3312 (8)	-9 (4)	2621 (4)	50 (3)
C(18)	2741 (9)	-243 (4)	1732 (4)	52 (4)

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

	x	y	z	$U (\text{\AA}^2)$
H(2a)	515 (8)	128 (4)	146 (4)	22 (17)
H(2b)	502 (8)	74 (4)	66 (4)	12 (15)
H(3a)	559 (9)	228 (5)	27 (4)	39 (21)
H(3b)	396 (10)	201 (5)	-18 (5)	39 (22)
H(5a)	411 (13)	361 (6)	1 (6)	70 (32)
H(5b)	508 (13)	356 (6)	76 (6)	68 (32)
H(6a)	298 (9)	476 (5)	89 (4)	22 (17)
H(6b)	142 (12)	409 (6)	84 (6)	64 (30)
H(8a)	220 (9)	543 (5)	217 (4)	27 (19)
H(8b)	67 (8)	476 (4)	218 (4)	16 (17)
H(9a)	318 (13)	453 (7)	344 (6)	71 (32)
H(9b)	142 (10)	516 (5)	363 (5)	41 (23)
H(11a)	215 (12)	364 (6)	457 (6)	61 (30)
H(11b)	26 (10)	406 (5)	463 (5)	41 (22)
H(12a)	17 (9)	257 (6)	511 (5)	37 (19)
H(12b)	-79 (8)	267 (5)	422 (4)	23 (18)
H(14a)	85 (11)	107 (5)	484 (5)	40 (22)
H(14b)	-29 (12)	111 (6)	405 (6)	73 (32)
H(15a)	363 (11)	76 (6)	409 (5)	54 (25)
H(15b)	239 (11)	0 (6)	418 (5)	38 (22)
H(17a)	447 (6)	36 (3)	266 (3)	0 (12)
H(17b)	332 (10)	-65 (5)	295 (4)	38 (22)
H(18a)	347 (8)	-59 (4)	145 (4)	15 (15)
H(18b)	151 (9)	-56 (5)	172 (4)	26 (19)

reflections which were systematically extinct ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$) and 431 reflections which were considered unobserved as $I < 2\sigma(I)$, $\sigma(I)$ calculated considering only counting statistics. No absorption corrections were made as $\mu(\text{Mo}) = 0.521 \text{ mm}^{-1}$. The trial structure was obtained using direct methods. An E map calculated from the most consistent set of phases from *MULTAN* (Germain, Main & Woolfson, 1971) gave positions for the non-H atoms. The model was refined using a full-matrix least-squares procedure (Busing, Martin & Levy, 1962). Positions for the H atoms were obtained from a ΔF map. 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 unit weights. The positional parameters and isotropic temperature factors for the atoms are listed in Tables 1 and 2.* The final discrepancy index was $R = 0.074$ ($R_w = 0.062$) for all the data, while the final value of the 'goodness of fit', $[\sum w(\Delta F)^2/(n - m)]^{1/2}$, was 1.9 for $n = 2441$ and $m = 295$. A final difference Fourier map showed no significant features. Atomic-scattering-factor tables were taken from the same sources as for the Na^+ complex (Campbell *et al.*, 1981).

Discussion. Fig. 1 shows the ring conformation and the coordination of K^+ by the macrocycle. Bond lengths, angles, and torsion angles are shown in Table 3. Bond lengths and angles are typical of those seen in other polyether macrocycles (Dalley, 1978). All torsion-angle magnitudes about C-C bonds are close to 60° , those

* 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 35981 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

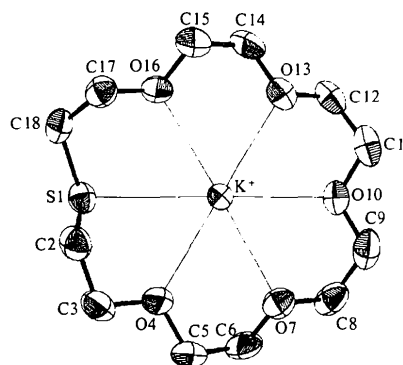


Fig. 1. ORTEP (Johnson, 1965) drawing of the macrocyclic ligand and metal ion, showing atom numbering. The H atoms and the thiocyanate anion are omitted for clarity. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

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)	1.813 (7)	111.8 (4)	59.7 (10)
C(2)	C(3)	O(4)	C(5)	1.489 (15)	109.2 (13)	156.8 (6)
C(3)	O(4)	C(5)	C(6)	1.420 (13)	112.5 (6)	174.0 (9)
O(4)	C(5)	C(6)	O(7)	1.415 (8)	108.8 (6)	63.1 (8)
C(5)	C(6)	O(7)	C(8)	1.483 (11)	110.0 (6)	174.1 (6)
C(6)	O(7)	C(8)	C(9)	1.416 (9)	112.1 (5)	175.4 (6)
O(7)	C(8)	C(9)	O(10)	1.423 (8)	109.4 (6)	-67.3 (7)
C(8)	C(9)	O(10)	C(11)	1.489 (12)	108.5 (6)	-176.8 (6)
C(9)	O(10)	C(11)	C(12)	1.420 (8)	113.1 (5)	-176.1 (6)
O(10)	C(11)	C(12)	O(13)	1.420 (9)	109.1 (6)	65.5 (7)
C(11)	C(12)	O(13)	C(14)	1.498 (11)	107.0 (6)	173.0 (6)
C(12)	O(13)	C(14)	C(15)	1.419 (9)	112.6 (6)	-179.2 (5)
O(13)	C(14)	C(15)	O(16)	1.414 (9)	108.9 (7)	-71.8 (7)
C(14)	C(15)	O(16)	C(17)	1.505 (12)	108.9 (6)	177.2 (6)
C(15)	O(16)	C(17)	C(18)	1.404 (8)	110.8 (5)	161.0 (5)
O(16)	C(17)	C(18)	S(1)	1.433 (7)	109.6 (5)	58.2 (6)
C(17)	C(18)	S(1)	C(2)	1.512 (9)	115.6 (4)	68.7 (5)
C(18)	S(1)	C(2)	C(3)	1.806 (6)	101.5 (3)	-174.9 (9)
S	C	N		1.695 (10)	174.3 (9)	
C	N			1.045 (11)		

Table 4. K⁺-ion contact distances (Å)

K ⁺ ...S(1)	3.284 (2)	K ⁺ ...O(13)	2.775 (4)
K ⁺ ...O(4)	2.791 (4)	K ⁺ ...O(16)	2.874 (4)
K ⁺ ...O(7)	2.803 (4)	K ⁺ ...S	3.366 (3)
K ⁺ ...O(10)	2.768 (4)	K ⁺ ...N'	3.043 (6)

about C—O bonds are close to 180°, while the two C—S bonds have torsion angles of 69 and -175°.

Table 4 shows the K⁺-ion coordination contact distances in the metal-ion-polyether complex. The K—O distances [mean, 2.80 (4) Å] and K—S distance [3.284 (2) Å] are slightly longer than the sum of the corresponding ionic and van der Waals radii (2.73 Å for K—O, 3.18 Å for K—S) as given by Pauling (1960). The K—O ion-dipole interaction is undoubtedly the main factor in the stability of the complex; however, the K—S contact distance indicates the K—S interaction contributes further stability. Stereochemical calculations indicate that all six heteroatoms have a pair of non-bonding electrons directed toward the K⁺ ion.

Table 5 gives the equations of and the atomic deviations from selected least-squares planes. The S(1) and O(10) atoms are below the least-squares plane (B), while the O(4), O(7), O(13), and O(16) atoms are above the plane. Thus, the hexagon formed by the six heteroatoms takes on a boat conformation. In the KSCN complex of 1,4,7,10,13,16-hexaoxacyclooctadecane, the six O atoms are alternately above and below their mean plane in a chair form (Seiler, Dobler & Dunitz, 1974). The interatomic O—O distances between adjacent O atoms [mean, 2.83 (4) Å] are approximately equal to the sum of the van der Waals radii (2.80 Å), and the adjacent S—O distances [3.043 (4) and 3.139 (4) Å] are shorter than the sum of the van der Waals radii (3.25 Å). Thus, neighboring heteroatoms are in contact with one another.

Table 5. Least-squares planes

(a) Equations of least-squares planes	Atoms used to determine plane
(A) $7.507x + 1.004y + 5.377z = 3.382 \text{ \AA}$	ligand atoms
(B) $7.705x - 0.498y + 4.256z = 2.631 \text{ \AA}$	S(1), O(4), O(7), O(10), O(13) & O(16)
(C) $7.518x + 0.745y + 5.367z = 3.302 \text{ \AA}$	O(4), O(7), O(10), O(13) & O(16)
(b) Deviations (Å × 10 ³) from the least-squares planes [e.s.d.'s range from 0.002 Å, for K ⁺ and S(1), to 0.005 Å, for O(13)]	
	K ⁺ S(1) O(4) O(7) O(10) O(13) O(16)
(A)	-361 -991 -74 +214 -237 +178 -134
(B)	-202 -419 +249 +181 -428 +182 +235
(C)	-344 -928 -61 +187 -258 +201 -69

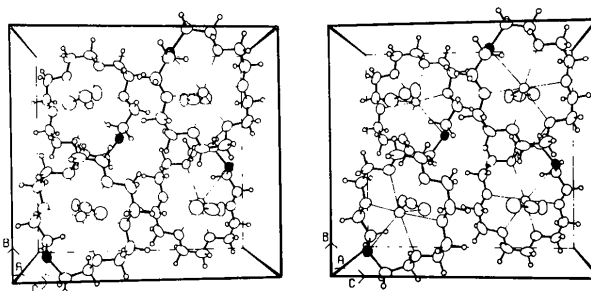


Fig. 2. Stereoscopic view of the crystal structure looking along the *a* axis. The C—H...O interactions between the two molecules to the right are shown by lines connecting the H and O atoms.

A view of the crystal structure down the *a* axis (Fig. 2) shows features of interest regarding the packing. The K⁺-polyether cations related by a unit translation along the *a* axis are linked together by the thiocyanate anions. The K—N' [3.043 (6) Å], N' being translated one unit cell in the *a* direction from N, and K—S [3.366 (3) Å] distances indicate the thiocyanate interactions with the cations are weak. The observed packing arrangement appears to be stabilized by a two-dimensional network of C—H...O interactions.* Molecular units related by a screw axis parallel to the *b* axis are connected *via* possible C—H...O interactions to form a zig-zag chain. Each polyether molecule participates in four such interactions [*via* atoms C(18), H(18*b*), O(10) and C(8), H(8*b*), O(16)]. The H...O distances (2.399 and 2.445 Å) are 0.15–0.2 Å shorter than the sum of the appropriate van der Waals radii. The corresponding angles C(18)—H(18*b*)—O(10) and C(8)—H(8*b*)—O(16) are 161 and 152°, respectively. The geometry of both C—H...O contacts is consistent with the expected spatial arrangement for a 'normal' hydrogen bond

* 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.

between a H atom and an orbital containing non-bonded electrons on O (Hamilton & Ibers, 1968). The same type of interaction involving a polyether, along with its implications, has been discussed previously (Goldberg, 1975). The distance from the S atom of the thiocyanate to the H(12a) atom of 2.788 Å is the only other short intermolecular contact. The remainder of the packing appears to be determined by van der Waals contacts of 2.4 Å between H atoms of adjacent molecules.

Since the complex crystallizes in a non-centrosymmetric space group, the possibility of determining the absolute configuration was investigated. The reported configuration and its enantiomorph (obtained by changing the sign of x) were refined to $R = 0.0736$ and 0.0741 respectively. Hamilton's R -factor ratio indicates that we may reject at the 0.005 level the hypothesis that the absolute configuration is the second of the two (Hamilton, 1965).

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diffractometer. The work was supported in part by the US Public Health Service NIH Grant 18811.

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

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Abstract. $C_{12}H_{24}O_5S.RbSCN$, $M_r = 423.94$, orthorhombic, $P2_12_12_1$, $a = 8.6724$ (6), $b = 10.818$ (1), $c = 20.199$ (2) Å, $V = 1895.0$ Å³, $Z = 4$, $D_x = 1.49$ Mg m⁻³, $F(000) = 872$, $\mu(Cu K\alpha) = 6.098$ mm⁻¹, colorless crystals, m.p. 380 K. The structure was solved by a combination of heavy-atom and direct methods and refined to $R = 0.048$ ($R_w = 0.052$) for a total of 1860 independent reflections. The Rb⁺ cation is located about 1.2 Å above the mean plane of the ligand and coordinates to all six heteroatoms of the ligand. The

Rb⁺ ion further coordinates to the thiocyanate anion and an S atom from an adjacent ligand.

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 (prolate shaped, maximum dimension 0.15 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 ($h00$, $h = 2n + 1$; $0k0$, $k = 2n +$

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