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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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, $V = 1895.0$ Å^3, $Z = 4$, $D_x = 1.49$ 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 ($h00$, $h = 2n + 1$; $0k0$, $k = 2n +$

1; and $00l$, $l = 2n + 1$) indicated the unambiguous space group $P2_12_12_1$. This choice of space group was substantiated during the data collection process and also by the location of Rb vectors in the Patterson map. Intensity data were collected using a Picker full-circle diffractometer (automated by L. Finger) employing graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Accurate lattice parameters were determined by a least-squares refinement of 20 2θ measurements at eight equivalent positions, $20° < 2\theta < 45°$. Three-dimensional diffraction data to a maximum 2θ of $130°$ ($\sin \theta/\lambda = 0.59$ Å^{-1}) were recorded for 1883 unique reflections using the $\omega/2\theta$ scan mode, of which 23 were systematically extinct and 147 were considered unobserved as $I < 2\sigma(I)$. 265 Friedel pairs were also measured to be used in the determination of the absolute configuration. The scan rate for intensity measurements was 1° min^{-1}, and the scan width was 1°. Background was measured 30 s on each side of the scan. Four standards measured every 4 h showed no significant change. No absorption corrections were made due to the small size of the crystal. The structure was solved using a combination of heavy-atom and direct methods. A Patterson synthesis clearly showed peaks on the Harker sections due to vectors between symmetry-related Rb atoms. Normalized structure factors were calculated and the 400 reflections with $|E(hkl)| > 1.24$ were used in the phasing program MULTAN (Germain, Main & Woolfson, 1971). An E map was calculated from the most consistent set of phases from which the Rb atom position was verified and the S atom of the macrocycle, the S atom of the more populated SCN group and an O atom were located. A difference Fourier map yielded the remainder of the non-H atoms. The positional parameters and isotropic thermal parameters of these atoms were then refined. The large deviation of the C(17)—C(18) bond length of 1.25 Å from the accepted value of 1.5 Å for cyclic polyethers (Dalley, 1978) indicated that part of the ligand was disordered. Disordered structures for cyclic polyethers are common (Groth, 1971; Dunitz & Seiler, 1974; Feneau-Dupont, Arte, Declercq, Germain & Van Meerssche, 1979; Campbell & Dalley, 1981). It was possible to obtain positions for the resolved disordered atoms C(17) and C(18) from a difference map. The peak heights suggested that the occupancies for the partial atoms C(17A), C(18A), C(17B) and C(18B) were about 0.5. A later difference map indicated that the SCN group was also disordered with the atoms of the more populated SCN(A) having an occupancy of about 0.8 and the occupancy of the less populated SCN(B) having a value of about 0.2. The structure was refined using a full-matrix least-squares procedure (Busing, Martin & Levy, 1962). Positional and anisotropic thermal parameters of SCN(A) and the non-H atoms of the polyether ligand, with the exception of C(17A), C(18A), C(17B) and C(18B), were refined.

Positional and isotropic thermal parameters of the disordered C atoms of the ligand were also refined. The positional parameters for SCN(B) and for the H atoms which were calculated from geometric considerations were not refined. The thermal parameters for the atoms of SCN(B) and the H atoms were set at a B value of 4.5 Å^2, the overall temperature factor obtained from a Wilson plot, and were not refined. The occupancy values assigned to the disordered atoms were held constant during the refinement; their approximate values were substantiated in subsequent difference maps. The positional parameters and isotropic temperature factors of the non-H atoms are listed in Table 1.* The final R was 0.048, while the weighted R using unit weights was 0.052. The 'goodness of fit', $[\sum w(\Delta F)^2/(n - m)]^{1/2}$, was 3.5 with $n = 1860$ and $m = 197$. Atomic-scattering-factor tables were taken from

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* Lists of structure factors, anisotropic thermal parameters and fractional coordinates of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35982 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *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. It is given for all atoms except S(B), C(B) and N(B) which were not refined and C(17A), C(18A), C(17B) and C(18B) which were refined isotropically.

	x	y	z	$U/\bar{U}$ (Å^2)
Rb$^+$	340 (1)	952 (1)	812 (0)	54 (1)
S(A)	3036 (5)	753 (4)	2264 (2)	86 (2)
C(A)	2947 (14)	−324 (13)	1697 (6)	64 (8)
N(A)	2754 (12)	−1063 (11)	1287 (6)	72 (7)
S(B)	3167 (30)	−958 (30)	1417 (15)	57
C(B)	3042 (30)	125 (30)	1979 (15)	57
N(B)	2900 (30)	870 (30)	2370 (15)	57
S(1)	−1187 (3)	2614 (3)	−440 (1)	70 (2)
C(2)	240 (14)	3792 (13)	−364 (6)	99 (8)
C(3)	−130 (18)	4526 (8)	245 (6)	96 (8)
O(4)	75 (8)	3743 (5)	813 (3)	70 (4)
C(5)	−430 (15)	4295 (8)	1409 (5)	76 (6)
C(6)	−338 (13)	3365 (9)	1952 (4)	69 (6)
O(7)	−1388 (8)	2381 (6)	1807 (3)	59 (4)
C(8)	−1532 (14)	1595 (10)	2364 (5)	75 (7)
C(9)	−2543 (13)	507 (12)	2170 (5)	82 (8)
O(10)	−1718 (8)	−227 (6)	1721 (3)	64 (4)
C(11)	−2525 (13)	−1320 (10)	1525 (5)	76 (7)
C(12)	−1583 (14)	−2000 (8)	1039 (6)	81 (7)
O(13)	−1542 (9)	−1316 (5)	437 (3)	68 (4)
C(14)	−665 (16)	−1893 (8)	−54 (6)	86 (8)
C(15)	−707 (15)	−1148 (10)	−677 (5)	89 (8)
O(16)	146 (12)	−34 (6)	−583 (3)	90 (6)
C(17A)	520 (24)	806 (20)	−1096 (9)	65 (5)
C(18A)	−948 (25)	1574 (19)	−1183 (10)	61 (5)
C(17B)	−452 (27)	679 (20)	−1180 (10)	69 (5)
C(18B)	4 (25)	1916 (19)	−1107 (20)	68 (5)

the same sources as for the Na^+ complex (Campbell, Larson & Dalley, 1981). Anomalous-dispersion corrections for Rb and S were taken from Cromer & Liberman (1970).

Discussion. The conformation of the complex and the atom labels are shown in Fig. 1. Bond lengths, angles, and torsion angles are shown in Table 2. Table 3 lists the Rb^+-ion coordination contact distances in the complex. The Rb^+–polyether donor-atom contact distances are slightly longer than the sum of the corresponding ionic and van der Waals radii (Pauling, 1960). The Rb^+ ion further coordinates to the thiocyanate anion and shows a preference (ca 80%) for coordination through N. This preference for coordination to N over S is also seen in the Rb^+ complex of
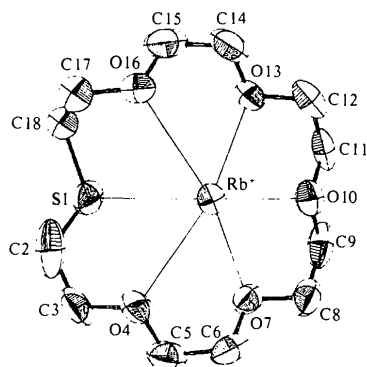
1,4,7,10,13,16-hexaoxacyclooctadecane (Dobler & Phizackerley, 1974). The $Rb-C(A)$ interatomic distance of 3·20 (1) Å is rather short and may indicate some interaction between these two atoms. However, the difficulty in resolving and refining the positional parameters of the C atoms of the disordered SCN perhaps makes this distance artificially short. The Rb^+ cation also appears to be in contact with an S atom $(Rb-S$ distance, 3·47 Å) of an adjacent ligand related by the screw axis running parallel to the a axis (see Fig. 2). It appears that the S–Rb interaction from the adjacent ligand plays a major role in the crystal packing.

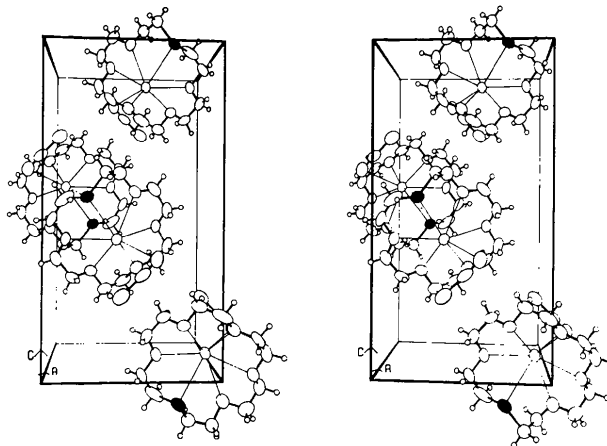Equations for least-squares planes along with deviations from these planes are shown in Table 4.

Fig. 1. *ORTEP* (Johnson, 1965) drawing of $C_{12}H_{24}O_5S$. RbSCN with 50% probability thermal ellipsoids for atoms. The H atoms and thiocyanate anion are omitted for clarity.

Fig. 2. Molecular packing. Stereoscopic view of four equivalent molecules viewed along the a axis. The intermolecular $Rb^+\cdots S$ interaction is shown (two center molecules) by a dashed line. The disorder in the C(17) and C(18) atoms is shown in the bottom-right molecule.

Table 2. *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)	1·784 (13)	107·5 (9)	66·4 (12)
C(2)	C(3)	O(4)	C(5)	1·499 (17)	108·5 (8)	–172·5 (10)
C(3)	O(4)	C(5)	C(6)	1·437 (12)	113·1 (7)	173·6 (10)
O(4)	C(5)	C(6)	O(7)	1·413 (12)	109·0 (7)	–63·9 (11)
C(5)	C(6)	O(7)	C(8)	1·492 (13)	108·5 (8)	–169·8 (8)
C(6)	O(7)	C(8)	C(9)	1·431 (12)	109·9 (7)	–175·2 (8)
O(7)	C(8)	C(9)	O(10)	1·415 (12)	108·2 (8)	69·5 (11)
C(8)	C(9)	O(10)	C(11)	1·519 (17)	108·2 (9)	177·1 (8)
C(9)	O(10)	C(11)	C(12)	1·402 (13)	113·4 (8)	178·4 (9)
O(10)	C(11)	C(12)	O(13)	1·429 (13)	109·2 (9)	–69·5 (11)
C(11)	C(12)	O(13)	C(14)	1·479 (16)	108·4 (8)	179·7 (9)
C(12)	O(13)	C(14)	C(15)	1·428 (13)	112·6 (7)	178·2 (9)
O(13)	C(14)	C(15)	O(16)	1·398 (14)	110·1 (8)	70·0 (12)
C(14)	C(15)	O(16)	C(17A)	1·494 (15)	109·3 (9)	171·1 (13)
C(15)	O(16)	C(17A)	C(18A)	1·426 (14)	124·3 (10)	81·1 (17)
O(16)	C(17A)	C(18A)	S(1)	1·416 (21)	104·0 (15)	70·7 (16)
C(17A)	C(18A)	S(1)	C(2)	1·530 (30)	108·9 (13)	67·1 (15)
C(18A)	S(1)	C(2)	C(3)	1·886 (20)	114·7 (8)	179·8 (10)
C(14)	C(15)	O(16)	C(17B)	1·494 (15)	109·3 (9)	164·6 (12)
C(15)	O(16)	C(17B)	C(18B)	1·426 (14)	98·4 (11)	–167·9 (17)
O(16)	C(17B)	C(18B)	S(1)	1·524 (22)	107·6 (20)	–72·5 (20)
C(17B)	C(18B)	S(1)	C(2)	1·403 (30)	107·9 (19)	160·5 (20)
C(18B)	S(1)	C(2)	C(3)	1·859 (32)	88·1 (8)	–170·2 (13)
S(A)	C(A)	N(A)		1·636 (14)	174·2 (12)	
C(A)	N(A)			1·164 (18)		
S(B)	C(B)	N(B)		1·636 (44)	177·6 (28)	
C(B)	N(B)			1·135 (44)		

Table 3. Rb^+-*ion contact distances (Å)*

$Rb^+\cdots S(1)$	3·374 (3)	$Rb^+\cdots O(16)$	3·017 (6)
$Rb^+\cdots O(4)$	3·028 (5)	$Rb^+\cdots N(A)$	3·171 (11)
$Rb^+\cdots O(7)$	2·946 (6)	$Rb^+\cdots S(B)$	3·431 (29)
$Rb^+\cdots O(10)$	2·860 (7)	$Rb^+\cdots S(1')$	3·470 (3)
$Rb^+\cdots O(13)$	3·043 (6)		

Table 4. *Least-squares planes*

(a) Equations of least-squares planes	Atoms used to determine planes
(A) $8\cdot366x - 1\cdot889y + 3\cdot984z = -0\cdot749$ Å	ligand atoms
(B) $8\cdot423x - 1\cdot520y + 3\cdot886z = -0\cdot726$ Å	S(1), O(4), O(7), O(10), O(13) & O(16)
(C) $7\cdot911x - 2\cdot580y + 6\cdot731z = -0\cdot370$ Å	O(4), O(7), O(10), O(13) & O(16)

(b) Deviations (Å $\times 10^3$) from the least-squares planes [e.s.d.'s range from 0·001 Å, for Rb^+, to 0·010 Å, for O(16)]

	Rb^+	S(1)	O(4)	O(7)	O(10)	O(13)	O(16)
(A)	+1177	–914	+429	–142	+40	–118	+645
(B)	+1183	–842	+537	–102	–18	–202	+628
(C)	+940	–1540	+11	–125	+228	–216	+102

Table 5. *Measured and calculated Bijvoet ratios*

hkl	$100\dfrac{\Delta F}{F_{calc}}$	$100\dfrac{\Delta F}{F_{obs}}$	$\dfrac{\Delta F_{obs}}{\sigma(\Delta F)}$
1 2 2	+28	+21	6·7
1 2 8	+11	+16	5·4
1 3 6	+14	+33	4·7
1 3 7	+23	+22	6·3
1 3 9	+5	+12	4·0
2 2 8	+14	+17	4·8
2 2 10	+10	+19	5·3
2 3 7	+23	+30	7·4
3 3 7	+8	+12	3·9

Least-squares plane (C) indicates the five O atoms are fairly planar. The Rb^+ cation is displaced 0·94 Å above the plane (C) due to the inability of the ligand to enlarge its cavity enough to fit the cation. The S atom is situated 1·54 Å below the mean plane (C) toward the Rb^+ cation of an adjacent ligand.

The absolute configuration was determined by the Bijvoet ratios, $\Delta F/F = (F_{hkl} - F_{\bar{h}\bar{k}\bar{l}})/0.5(F_{hkl} + F_{\bar{h}\bar{k}\bar{l}})$. Nine Friedel pairs were chosen from the 265 measured because they were regarded as statistically significant, where $\Delta F > 3.8\sigma(\Delta F)$. The term $3.8\sigma(\Delta F)$ was chosen from consideration of 105 equivalent (calculated F's are equal) Friedel pairs; none of the 105 showed a ΔF greater than $3.8\sigma(\Delta F)$. Table 5 compares the measured and calculated Bijvoet ratios. Comparison of the signs shows the absolute configuration to be that reported in Table 1.

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Hydrated Silver Nitrate Complex of 1,4,7,10,13-Pentaoxa-16-thiacyclooctadecane

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Abstract. $C_{12}H_{24}O_5S.AgNO_3.H_2O$, $M_r = 468.28$, monoclinic, $P2_1/c$, $a = 9.856$ (4), $b = 19.923$ (6), $c = 9.310$ (2) Å, $\beta = 92.11$ (3)°, $V = 1826.9$ Å^3, $Z = 4$, $D_x = 1.70$, $D_m = 1.71$ Mg m^{-3} (flotation in CCl_4 and $CHBr_3$), $F(000) = 960$, colorless crystals, m.p. 360 K. The structure was solved by the heavy-atom method and refined to $R = 0.078$ ($R_w = 0.070$) for a total of 3203 independent reflections. The Ag^+ cation sits in the cavity of the ligand and coordinates to the five O atoms and the S atom. It also coordinates to an S atom from an adjacent ligand. The Ag–S contact distances indicate covalent character in the Ag–S interaction. Each nitrate anion hydrogen bonds to two water molecules and does not interact with an Ag^+ cation.

Introduction. The complex was prepared by allowing the solvent to evaporate from an equimolar salt–ligand mixture dissolved in aqueous methanol. The crystal was shaped to a sphere ($d = 0.25$ mm) with a Nonius crystal spherizer. Preliminary crystallographic 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 $P2_1/c$. The

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