

Discussion. The structure consists of $[\text{TeCl}_6]^{2-}$ octahedra and $[\text{NH}(\text{CH}_3)_3]^+$ groups. The six equivalent Te—Cl bonds have a length of 2.536 (1) Å without a libration correction and 2.546 (1) Å after a correction for librational motion has been made (Schomaker & Trueblood, 1968). They agree very well with the values of 2.541 (7) and 2.541 (5) Å respectively in $(\text{NH}_4)_2\text{TeCl}_6$ (Hazell, 1966) and Rb_2TeCl_6 (Webster & Collins, 1973). Each $[\text{TeCl}_6]^{2-}$ octahedron is connected by hydrogen bonding to two $[\text{NH}(\text{CH}_3)_3]^+$ groups. A stereoscopic view of an $[\text{NH}(\text{CH}_3)_3]_2[\text{TeCl}_6]$ unit is shown in Fig. 1.

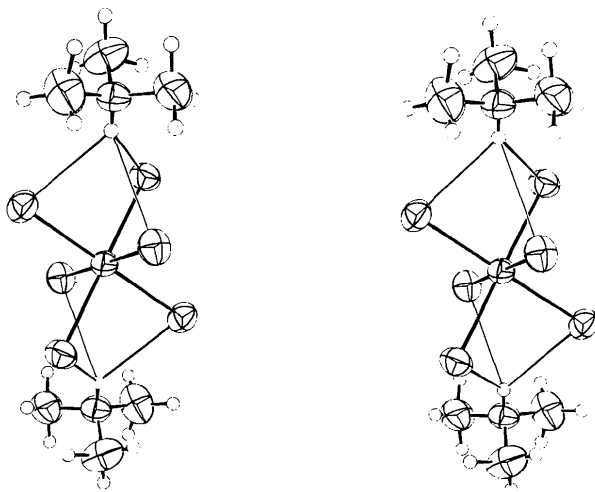


Fig. 1. A stereoscopic view of the structure. The thermal ellipsoids are the 50% probability surfaces; the H atoms are on an arbitrary scale.

The threefold symmetry of the structure would lead to a trifurcated hydrogen bond between N—H(1) and three related Cl atoms (Table 2). Such a feature is rather unusual in crystal structures. Moreover, the observed $\text{H}(1)\cdots\text{Cl}$ distance of 2.89 (2) Å corresponds to the sum of van der Waals radii of H and Cl, indicating that there is no significant hydrogen-bond interaction. However, the observed N—H(1) distance of 0.84 (2) Å is obviously too short. If the N—H(1) distance were assumed to be 1.03 Å, as commonly found in ammonium groups, the $\text{H}(1)\cdots\text{Cl}$ distance would be 2.76 Å. Consequently the hydrogen bond would be very weak.

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References

- BLESSING, R. H., COPPENS, P. & BECKER, P. (1974). *J. Appl. Cryst.* **7**, 488–492.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 HAZELL, A. C. (1966). *Acta Chem. Scand.* **20**, 165–169.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WEBSTER, M. & COLLINS, P. H. (1973). *J. Chem. Soc. Dalton Trans.* pp. 588–594.

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Structure of the Potassium Thiocyanate Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane-2,6-dione (2,6-Diketo-18-crown-6)

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Abstract. $\text{C}_{12}\text{H}_{20}\text{O}_8 \cdot \text{KSCN}$, monoclinic, $P2_1/c$, $M_r = 389.45$, $a = 12.517$ (5), $b = 10.943$ (3), $c = 15.145$ (2) Å, $\beta = 119.975$ (24)°, $V = 1796.7$ (11) Å³, $Z = 4$, $D_x = 1.44$ Mg m⁻³, colorless, m.p. 442–442.5 K. The cation is situated in the cavity of the polyether ring, coordinated to the six O atoms in the ring and to two anions. Resolution of the disorder in the anion and a

portion of the polyether gave $R = 0.046$ and $R_w = 0.016$ for 2675 reflections.

Introduction. The complex was synthesized by G. Maas (Maas, Bradshaw, Izatt & Christensen, 1977). Approximate cell parameters and the space group were determined from precession photographs. 2θ angles of

15 reflections for lattice-parameter determination ($6^\circ < 2\theta < 17^\circ$) and intensity data were measured on a Syntex P1 autodiffractometer utilizing graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and employing a $0.4 \times 0.4 \times 0.3 \text{ mm}$ crystal. The accurate lattice parameters (see *Abstract*) were determined by a least-squares treatment of the 15 2θ values. Intensities for 2843 independent reflections were measured at a scan speed of 2° min^{-1} for $2\theta \leq 47^\circ$ ($\sin \theta/\lambda = 0.561 \text{ \AA}^{-1}$). Of these, 168 were systematically extinct ($0k0$, k odd and $h0l$, l odd) and 581 had $l < 2\sigma(l)$ [$\sigma(l)$ computed according to Stout & Jensen (1968)]. Five check reflections, which were measured every 95 reflections, indicated no deterioration of the crystal. The data were corrected for Lorentz and polarization effects but not for absorption since $\mu = 0.447 \text{ mm}^{-1}$.

The phases for 386 reflections ($|E| > 1.45$) were determined by *MULTAN* (Germain, Main & Woolfson, 1971); an *E* map, generated with these phases, provided positions for all non-hydrogen atoms in the molecule. The model was refined by a full-matrix least-squares procedure (Busing, Martin & Levy, 1962) to an *R* of 0.094 with the refinement based on *F*. H positions, calculated from stereochemical considerations, were added to the model at this point. The positions and anisotropic thermal parameters of all non-hydrogen atoms were refined. The positions [except for H(81), H(82), H(91) and H(92)] and isotropic thermal parameters of the H atoms were refined. The scattering-factor tables for C and O were taken from Cromer & Waber (1965); the tables for K^+ , H, N, N^{1-} , S and S^{1-} were taken from *International Tables for X-ray Crystallography* (1968). No anomalous-dispersion corrections were applied. The 3s electron of the K atom was distributed equally between the N and S of the SCN^- group by averaging the N and N^{1-} tables for N and S and S^{1-} tables for S. The final residuals were $R = 0.068$ and $R_w = 0.018$. The 'goodness of fit' was 1.02 with $m = 2675$ and $n = 285$. The weighting scheme which was applied during the last cycles of refinement was $w = 1/(\sigma_p + |\Delta F|/2.25)^2$. The *U* values of the anion and of atoms O(7), C(8), C(9) and O(10) in the ligand indicated disorder in the structure. Resolution of the atoms and further refinement is described below.

Discussion. In both the ligand, where it was possible to resolve atoms O(7), C(8), C(9) and O(10), and the anion there were a set of positions with population factors of about 0.75 (labeled *A*) and another set with populations of about 0.25 (labeled *B*). Atomic positions for the '*A*' atoms were obtained from difference maps as were the positions of the '*B*' atoms of the polyether ligand. Positions for the '*B*' atoms of the SCN^- were estimated from the geometry reported for other disordered thiocyanates (Dobler & Phizackerley, 1974; Campbell, Dalley & Simonsen,

1981) and were confirmed by a difference map. Positional parameters for all the atoms including the resolved atoms are listed in Table 1.* Population ratios were determined by refinement at various fixed ratios (range 80:20 to 75:25 for SCN and 80:20 to 72:28 for C—C bridge). The population parameters which resulted in the most consistent bond lengths and angles were 80:20 for $SCN(A):SCN(B)$ and 75:25 (*A*:*B*) for the C—C bridge. Figs. 1 and 2 illustrate the labeling for the atoms and the average conformation while Figs. 3 and 4 show the two conformations. Refinement of all parameters except the positions of the H atoms on the disordered carbon pairs, C(8) and C(9), resulted in $R = 0.046$, $R_w = 0.016$ and a goodness of fit of 0.99 with $m = 2675$ and $n = 317$. The final difference map contained no spurious peaks.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36580 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^5$, for '*B*' atoms $\times 10^4$) and *equivalent isotropic thermal parameters* ($\times 10^4$, for '*B*' atoms $\times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (\AA^2)
K ⁺	27418 (3)	18050 (3)	74342 (3)	508 (2)
S	18402 (7)	32882 (10)	41800 (6)	765 (4)
C	26891 (24)	23627 (28)	51327 (23)	646 (18)
N	33108 (35)	17474 (51)	58169 (28)	946 (24)
O(1)	51985 (8)	25447 (9)	88000 (7)	489 (5)
C(2)	60820 (13)	18344 (14)	88326 (10)	488 (7)
C(3)	58752 (13)	4928 (15)	88966 (13)	515 (8)
O(4)	46295 (8)	2236 (8)	85904 (7)	521 (5)
C(5)	44744 (15)	-10079 (14)	87978 (14)	528 (9)
C(6)	31452 (15)	-13671 (14)	82997 (13)	558 (9)
O(7A)	24614 (25)	-7342 (25)	74190 (21)	549 (11)
C(8A)	12123 (20)	-11553 (20)	67373 (23)	647 (13)
C(9A)	2735 (20)	-2752 (21)	66839 (23)	585 (13)
O(10A)	4106 (64)	8606 (77)	62730 (50)	715 (18)
C(11)	-5161 (14)	17001 (16)	61302 (15)	637 (9)
C(12)	-2474 (15)	29198 (17)	58422 (14)	678 (9)
O(13)	8234 (8)	34019 (9)	66921 (7)	541 (5)
C(14)	11765 (14)	45685 (15)	65164 (13)	567 (8)
C(15)	22515 (14)	50012 (15)	75009 (13)	578 (9)
O(16)	33005 (8)	42537 (8)	77303 (7)	473 (5)
C(17)	43100 (14)	45003 (15)	87215 (12)	557 (9)
C(18)	54292 (15)	38623 (15)	88437 (14)	567 (9)
O(19)	69876 (9)	22113 (10)	88432 (8)	731 (7)
O(20)	28025 (11)	-22001 (11)	86070 (9)	893 (7)
S(<i>B</i>)	2944 (5)	1606 (8)	5465 (5)	77 (1)
C(<i>B</i>)	2370 (11)	2713 (11)	4623 (9)	43 (3)
N(<i>B</i>)	2289 (15)	3523 (16)	4145 (13)	180 (10)
O(7B)	2332 (9)	-636 (9)	7637 (7)	49 (3)
C(8B)	999 (8)	-927 (8)	7185 (6)	62 (2)
C(9B)	348 (8)	-346 (8)	6154 (6)	69 (3)
O(10B)	473 (19)	916 (22)	6295 (13)	55 (5)

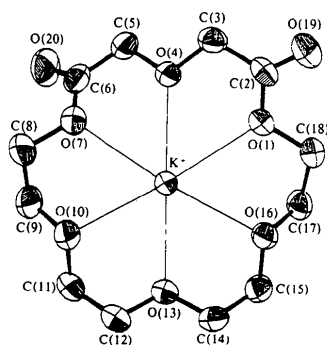


Fig. 1. ORTEP (Johnson, 1965) drawing of the K-polyether complex viewed from a direction normal to the plane of the coordinating atoms. The SCN⁻ and H atoms are omitted for clarity.

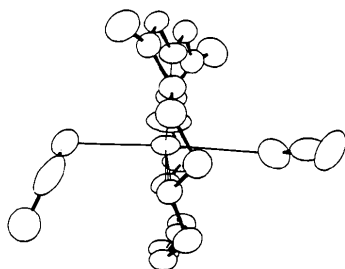


Fig. 2. ORTEP (Johnson, 1965) drawing of the KSCN-polyether complex rotated 90° from the view of Fig. 1. The SCN⁻ is included.

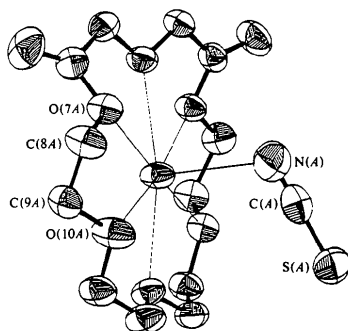


Fig. 3. ORTEP (Johnson, 1965) drawing illustrating the conformation of *A* atoms.

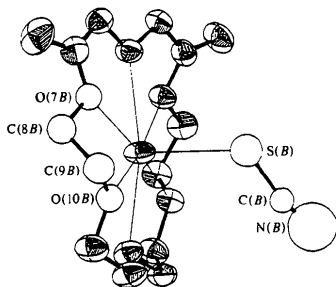


Fig. 4. ORTEP (Johnson, 1965) drawing illustrating the conformation of *B* atoms.

Table 2. Bond distances (Å), bond angles (°) and torsion angles (°)

1	2	3	4	1-2	1-2-3	1-2-3-4
Involving the polyether ring						
O(1)	C(2)	C(3)	O(4)	1.332 (2)	113.94 (15)	18.7 (2)
C(2)	C(3)	O(4)	C(5)	1.502 (2)	112.26 (12)	-171.02 (15)
C(3)	O(4)	C(5)	C(6)	1.418 (2)	112.00 (11)	-168.86 (16)
O(4)	C(5)	C(6)	O(7A)	1.419 (2)	112.25 (12)	30.2 (3)
C(5)	C(6)	O(7A)	C(8A)	1.496 (2)	110.9 (2)	167.2 (3)
C(6)	O(7A)	C(8A)	C(9A)	1.360 (3)	117.5 (3)	111.6 (3)
O(7A)	C(8A)	C(9A)	O(10A)	1.452 (3)	111.9 (2)	62.6 (4)
C(8A)	C(9A)	O(10A)	C(11)	1.490 (4)	108.7 (4)	175.4 (3)
C(9A)	O(10A)	C(11)	C(12)	1.438 (9)	111.3 (6)	172.2 (3)
O(10A)	C(11)	C(12)	O(13)	1.409 (9)	109.8 (4)	67.9 (4)
C(11)	C(12)	O(13)	C(14)	1.494 (3)	108.44 (13)	-179.8 (5)
C(12)	O(13)	C(14)	C(15)	1.417 (2)	113.99 (12)	175.42 (17)
O(13)	C(14)	C(15)	O(16)	1.419 (2)	107.83 (13)	69.1 (2)
C(14)	C(15)	O(16)	C(17)	1.501 (2)	108.57 (15)	171.98 (15)
C(15)	O(16)	C(17)	C(18)	1.435 (2)	111.72 (13)	-170.21 (15)
O(16)	C(17)	C(18)	O(1)	1.424 (2)	109.02 (15)	64.78 (18)
C(17)	C(18)	O(1)	C(2)	1.492 (3)	107.65 (14)	175.91 (13)
C(18)	O(1)	C(2)	C(3)	1.465 (2)	115.53 (13)	173.94 (13)
O(4)	C(5)	C(6)	O(7B)			10.7 (6)
C(5)	C(6)	O(7B)	C(8B)		118.4 (5)	-175.6 (7)
C(6)	O(7B)	C(8B)	C(9B)	1.289 (9)	119.5 (9)	-152.7 (9)
O(7B)	C(8B)	C(9B)	O(10B)	1.488 (13)	106.9 (9)	-65.1 (15)
C(8B)	C(9B)	O(10B)	C(11)	1.495 (11)	107.5 (9)	-108.0 (15)
C(9B)	O(10B)	C(11)	C(12)	1.39 (3)	123.3 (17)	-152.1 (14)
O(10B)	C(11)	C(12)	O(13)	1.42 (3)	106.7 (11)	-65.9 (8)
Involving the carbonyl O atoms						
O(19)	C(2)	O(1)	C(18)	1.199 (2)	124.17 (15)	-3.8 (2)
O(19)	C(2)	C(3)	O(4)		121.85 (15)	-163.54 (14)
O(20)	C(6)	C(5)	O(4)	1.196 (2)	121.92 (14)	-157.34 (18)
O(20)	C(6)	O(7A)	C(8A)		126.66 (18)	-4.8 (4)
O(20)	C(6)	O(7B)	C(8B)		118.6 (5)	-7.2 (11)

The bond lengths, bond angles and torsion angles of the macrocycle are listed in Table 2. The ring contains a polyether grouping [C(8), C(9), ... C(17), C(18)] and a diester grouping [C(18), O(1), ... O(7), C(8)] which has an ether bridge [C(2) to C(6)]. There is good agreement in bond lengths and angles between the complexed (conformation *A* only) and uncomplexed ligands (Dalley & Larson, 1979a). The average differences between corresponding features are 0.009 (9) Å for bond distances and 1.1 (9)° for bond angles. The polyether portions of the resolved molecules have typical C-C and C-O distances [averages: 1.494 (5) and 1.420 (14) Å, respectively]. Bond angles are also typical with an average of 109.0 (14)° for C-centered and 112.3 (15)° for O-centered angles. The geometries of the ester groups are consistent with ester groups in both cyclic and non-cyclic ester-containing molecules (Dalley & Larson, 1979a,b; Kroon & Kanters, 1973).

The K⁺ cation is situated at the center of the ring at an average of 2.75 (5) Å [the sum of the van der Waals radius of O and ionic radius of K⁺ is 2.73 Å (Pauling, 1960)] from the ring O atoms and 0.1765 (4) and 0.2443 (4) Å below the least-squares planes of these atoms in conformations *A* and *B*, respectively. The K⁺ ion is also coordinated to two thiocyanates (Fig. 2), one on either side of the polyether ring. The K-anion distances are: K-N(*A*), 2.873 (5); K-N(*B*'), 2.939 (23); K-S(*A*'), 3.3550 (14); K-S(*B*),

Table 3. *Least-squares planes of donor atoms in conformations A and B and deviations of selected atoms from those planes*

$$\text{Equation for A: } -7.69545x + 0.10791y + 14.99808z = 9.23592; \\ \sigma = 0.13$$

$$\text{Equation for B: } -7.60959x + 0.67365y + 14.98514z = 9.41976; \\ \sigma = 0.19$$

	A	B
O(1)	-0.0106 (10) Å	-0.0172 (10) Å
O(4)	0.0879 (10)	-0.0547 (10)
O(7)	-0.011 (3)	0.207 (10)
O(10)	-0.134 (8)	-0.29 (2)
O(13)	0.2040 (10)	0.2110 (10)
O(16)	-0.1359 (10)	-0.0608 (10)
O(19)	-1.3261 (11)	-1.3363 (11)
O(20)	1.4925 (13)	1.1972 (13)
K ⁺	-0.1765 (4)	-0.2443 (4)

3.124 (8) Å. Fig. 2 illustrates the oscillating motion of the cation in the cavity. The mean-squared amplitude of vibration in the direction perpendicular to the plane of the molecule is nearly twice those of the other two directions.

The effect of complexation on the conformation of the crown molecule can be seen when comparing torsion-angle values, the donor-atom least-squares plane (see Table 3) and the shape of the cavity of the non-complexed ligand with similar features of the potassium complex. The torsion angles about the O(4)–C(5) and C(18)–O(1) bonds change from 72 and -161° in the free ligand to -169 and 176° in the complex. These changes cause the two carbonyl O atoms to go from very different environments in the free molecule to a similar environment with respect to the macrocycle in the complex. Thus, O(19) and O(20) are 2.25 and -0.31 Å respectively from the donor-atom least-squares plane in the uncomplexed ring while in the complexed ligand the two carbonyl O atoms are approximately equidistant from the similarly defined plane but on opposite sides of the ring (Table 3). These observations support the observed carbonyl stretching frequencies for the two compounds (Izatt *et al.*, 1977). The average deviation of donor atoms from the least-squares plane of conformation A is 0.10 (8) Å and of conformation B is 0.14 (11) Å. Both values are considerably less than the deviation found in the

uncomplexed ligand of 0.37 Å. The O...O distances across the ring range from 5.42–5.57 Å in the complex whereas in the free ligand the range is greater (5.30 to 5.51 Å). These distances indicate that the cavity expanded slightly and became more circular on complexation.

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References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- CAMPBELL, M. L., DALLEY, N. K. & SIMONSEN, S. H. (1981). *Acta Cryst.* **B37**, 1747–1750.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- DALLEY, N. K. & LARSON, S. B. (1979a). *Acta Cryst.* **B35**, 1901–1903.
- DALLEY, N. K. & LARSON, S. B. (1979b). *Acta Cryst.* **B35**, 2428–2430.
- DOBLER, M. & PHIZACKERLEY, R. P. (1974). *Acta Cryst.* **B30**, 2746–2748.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., pp. 202–207. Birmingham: Kynoch Press.
- IZATT, R. M., LAMB, J. D., ASAY, R. E., MAAS, G. E., BRADSHAW, J. S., CHRISTENSEN, J. J. & MOORE, S. S. (1977). *J. Am. Chem. Soc.* **99**, 6134–6136.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KROON, J. & KANTERS, J. A. (1973). *Acta Cryst.* **B29**, 1278–1283.
- MAAS, G. E., BRADSHAW, J. S., IZATT, R. M. & CHRISTENSEN, J. J. (1977). *J. Org. Chem.* **42**, 3937–3941.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd ed. Ithaca: Cornell Univ. Press.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination. A Practical Guide*, pp. 454–458. New York: Macmillan.