

Acta Cryst. (1974). B30, 2744

Potassium Thiocyanate Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane

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(Received 27 June 1974; accepted 5 July 1974)

Abstract. $C_{12}H_{24}O_6 \cdot KNCS$, monoclinic, $P2_1/c$, $a = 8.190(4)$, $b = 14.285(7)$, $c = 7.775(4)$, Å $\beta = 99.19(10)^\circ$, $M = 361.50$, $Z = 2$, $D_x = 1.34$ g cm $^{-3}$. The potassium ion occupies a crystallographic centre of symmetry and is coordinated to the six oxygen atoms of the hexaether, which has effective $D_{3d}(3m)$ symmetry. The thiocyanate anions are disordered and interact only weakly with the cations.

Introduction. Intensity measurements (1930 reflexions out to $\sin \theta/\lambda = 0.68$ Å $^{-1}$), structure analysis and refinement were carried out as for the sodium complex (Dobler, Dunitz & Seiler, 1974). The parameters of the disordered thiocyanate group were held constant during the later refinement cycles with modified weights. Table 1 lists coordinates of heavy atoms from the final refinement cycle with $r = 14$ Å 2 , Table 2 the corresponding vibration tensors. Hydrogen positions,

calculated from stereochemical considerations, are given in Table 3. The final R was 0.042 (0.058, weighted).*

Discussion. Fig. 1 shows the very regular ring conformation and coordination. The six oxygen atoms lie

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30558 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates (and estimated standard deviations) of the non-hydrogen atoms

	Values are $\times 10^4$.		
	<i>x</i>	<i>y</i>	<i>z</i>
K	0 (0)	0 (0)	0 (0)
O(1)	713 (2)	-1797 (1)	1232 (2)
C(2)	2412 (3)	-2040 (1)	1594 (3)
C(3)	3312 (2)	-1267 (1)	2649 (2)
O(4)	3222 (2)	-447 (1)	1619 (2)
C(5)	4029 (3)	318 (1)	2558 (3)
C(6)	3927 (2)	1150 (2)	1354 (4)
O(7)	2270 (2)	1472 (1)	1004 (2)
C(8)	2071 (3)	2211 (1)	-228 (3)
C(9)	304 (3)	2544 (1)	-468 (3)
S, N	-1330 (0)	-5 (0)	3637 (0)
C	-258 (0)	-1 (0)	4754 (0)

Table 2. Vibration-tensor components (Å 2) of the non-hydrogen atoms

	Values are $\times 10^3$.					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	45	33	70	-4	-16	11
O(1)	52	32	55	6	5	0
C(2)	57	43	54	16	9	2
C(3)	51	52	49	11	-1	7
O(4)	43	49	45	3	0	3
C(5)	44	61	66	-2	-12	0
C(6)	40	58	87	-12	8	4
O(7)	44	43	48	-6	7	3
C(8)	60	43	54	-14	11	5
C(9)	72	33	47	1	6	-1
S, N	71	69	77	2	4	-8
C	36	45	81	1	6	-4

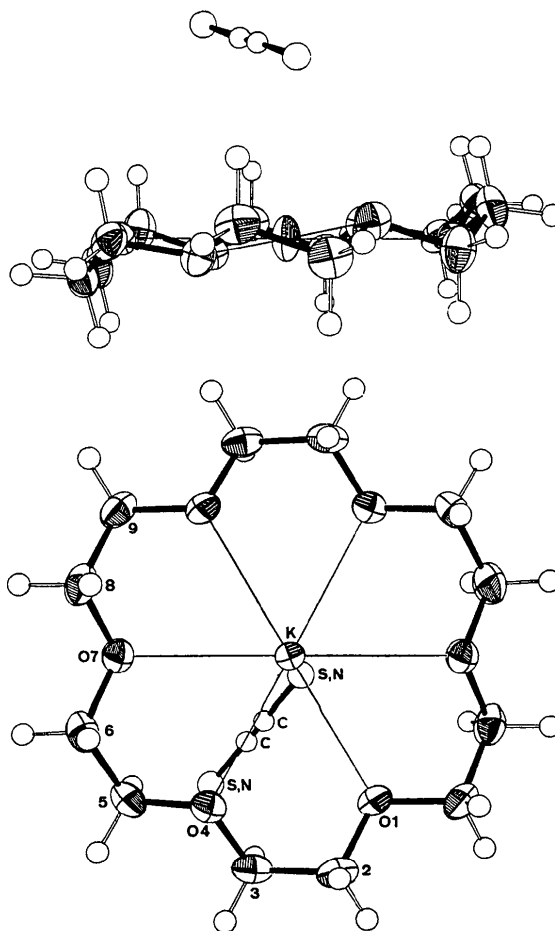


Fig. 1. Bottom: KNCS complex viewed in direction normal to the mean plane, showing atom numbering. Top: view along a direction in the mean plane. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

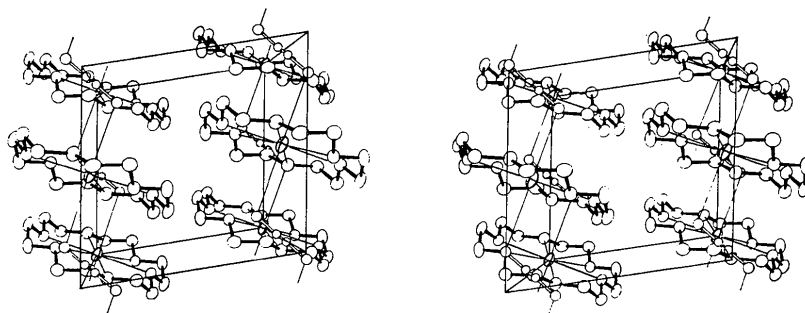


Fig. 2. Stereoscopic view of the crystal structure looking along the b axis. The c axis is vertical.

Table 3. Fractional coordinates of the hydrogen atoms calculated assuming local C_{2v} symmetry of the methylene groups with $C-H = 1.0 \text{ \AA}$, $H-C-H = 109^\circ$

Values are $\times 10^3$.

	x	y	z
H(2)	256	-264	224
H(2)*	285	-210	46
H(3)	274	-115	369
H(3)*	448	-145	305
H(5)	346	49	356
H(5)*	521	17	299
H(6)	468	165	186
H(6)*	427	93	21
H(8)	283	274	19
H(8)*	233	198	-138
H(9)	1	272	68
H(9)*	18	311	-127

alternately 0.19 \AA above and below their mean plane so that the coordination polyhedron around K^+ is actually a very flat octahedron ($K \cdots O$, 2.770 – 2.833 \AA , average 2.805 \AA). The C–C distances are again somewhat short (1.497 – 1.507 \AA , average 1.504 \AA), possibly because of internal motions in the ring. The rigid-body model gives rather poor agreement between observed and calculated U_{ij} values [$\langle (\Delta U_{ij})^2 \rangle^{1/2} = 0.0040 \text{ \AA}^2$, $\langle \sigma^2(U_{ij}) \rangle^{1/2} = 0.0010 \text{ \AA}^2$] and the vibration ellipsoids of the C atoms (Fig. 1) are noticeably anisotropic. Bond angles at O (111.6 – 112.9° , average 112.2°) are again larger than those at C (107.5 – 109.4° , average 108.5°).

The thiocyanate groups, which formally occupy crystallographic centres of symmetry, are disordered. The two terminal atoms (statistically N or S) are both 3.19 \AA from a K^+ ion, and the resulting alternation of anions and cations along the c axis is a prominent feature of the crystal structure (Fig. 2). Layers in the $(10\bar{2})$ planes contain interpenetrating roughly square

nets of complexed hexaether- K^+ cations and thiocyanate anions. The short contacts of 3.19 \AA connect the anions to cations of neighbouring layers and the whole arrangement can be regarded as a very distorted rocksalt-type structure.

Table 4. Bond distances (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$) in the centrosymmetric 18-membered ring

Atoms				Distance	Angle	Torsion angle
1	2	3	4	2-3	1-2-3	1-2-3-4
C(9)	O(1)	C(2)	C(3)	1.418	112.9	-170.8
O(1)	C(2)	C(3)	O(4)	1.497	108.1	-65.2
C(2)	C(3)	O(4)	C(5)	1.414	108.9	178.9
C(3)	O(4)	C(5)	C(6)	1.418	111.6	178.1
O(4)	C(5)	C(6)	O(7)	1.507	108.2	70.0
C(5)	C(6)	O(7)	C(8)	1.418	109.4	-175.5
O(7)	O(7)	C(8)	C(9)	1.417	112.0	-177.4
O(7)	C(8)	C(9)	O(1')	1.507	108.9	-65.3
C(8)	C(9)	O(1')	C(2')	1.424	107.5	-177.5

Table 5. Distances (\AA) involving the potassium and thiocyanate ions

$K \cdots O(1)$	2.770	(S, N)–C	1.12
$K \cdots O(4)$	2.811	(S, N)–(S, N)	2.78
$K \cdots O(7)$	2.833		
$K \cdots (S, N)$	3.19		

We thank Professor J. Dale for a sample of the compound. This work was supported by the Swiss National Fund for the Advancement of Scientific Research.

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