

four C–O bonds lie in a very narrow range, 1.403–1.408 Å.

A stereoscopic drawing (Johnson, 1965) of the molecular packing is shown in Fig. 2. The planar zigzag segments of molecules related by the operation $x \rightarrow \frac{1}{2} + x, y \rightarrow y, z \rightarrow \frac{1}{2} - z$ run antiparallel to one another, leading to electrostatically favourable dipole-dipole interactions.

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

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Abstract. $C_{12}H_{24}O_6 \cdot NaNCS \cdot H_2O$, monoclinic, $P2_1/c$, $a = 12.316$ (6), $b = 13.737$ (7), $c = 11.215$ (6) Å, $\beta = 105.32$ (11)°, $M = 363.40$, $Z = 4$, $D_x = 1.32$ g cm⁻³. The hexaether adopts a highly irregular conformation in which five approximately coplanar atoms surround the sodium cation. A distorted pentagonal bipyramidal coordination of the cation is completed by the remaining oxygen of the hexaether and by a water molecule.

Introduction. Intensity measurements were made from a crystal of dimensions 0.4 × 0.4 × 0.4 mm with a four-circle diffractometer (Hilger and Watts Y290, graphite monochromator, Mo $K\alpha$ radiation, $\theta/2\theta$ scan, background measurements at beginning and end of each scan). 3160 reflexions were measured out to $\sin \theta/\lambda = 0.62$ Å⁻¹. The structure was solved by direct methods and refined by least-squares with the modified weighting system described by Dunitz & Seiler (1973). Methylene hydrogen positions were calculated from stereochemical considerations but were held constant during refinement. The two hydrogen atoms of the H₂O molecule were located from an ($F_o - F_c$) synthesis but not subsequently refined. Table 1 lists coordinates of heavy atoms from the final cycle with $r = 36$ Å², Table 2 the corresponding vibration tensors. Hydrogen positions are given in Table 3. The final R was 0.081 (0.053, weighted).* Atomic scattering factors were

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30557 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Values are × 10⁴.

	<i>x</i>	<i>y</i>	<i>z</i>
Na	2800 (0)	–580 (0)	1356 (0)
O(1)	2454 (1)	–2452 (1)	1046 (1)
C(2)	1306 (1)	–2739 (1)	650 (2)
C(3)	696 (1)	–2243 (1)	1471 (1)
O(4)	793 (1)	–1226 (1)	1343 (1)
C(5)	376 (1)	–710 (1)	2233 (1)
C(6)	454 (1)	358 (1)	2007 (1)
O(7)	1606 (1)	583 (1)	2121 (1)
C(8)	1785 (1)	1594 (1)	2076 (2)
C(9)	2996 (1)	1748 (1)	2063 (1)
O(10)	3293 (1)	1199 (1)	1121 (1)
C(11)	2785 (2)	1542 (1)	–100 (2)
C(12)	3037 (2)	829 (2)	–992 (2)
O(13)	2502 (1)	–65 (1)	–799 (1)
C(14)	2715 (2)	–856 (2)	–1518 (2)
C(15)	3871 (2)	–1299 (2)	–1031 (2)
O(16)	4127 (1)	–1458 (1)	276 (1)
C(17)	4252 (1)	–2446 (2)	679 (2)
C(18)	3137 (2)	–2970 (1)	423 (2)
N	6364 (2)	–776 (2)	4593 (3)
C	7296 (1)	–768 (1)	4558 (1)
S	8612 (0)	–770 (0)	4535 (0)
O(HOH)	3977 (1)	–589 (1)	3349 (1)

taken from *International Tables for X-ray Crystallography* (1962).

Discussion. The structural unit, with atom numbering, is shown in Fig. 1. Although 13 of the 18 ring-members are arranged as in the symmetrical D_{3d} conformation observed in the K⁺ complex (Seiler, Dobler & Dunitz,

Table 2. *Vibrational-tensor components (\AA^2) of the non-hydrogen atoms*

Values are $\times 10^3$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	38	39	34	0	8	0
O(1)	41	49	61	-1	20	-17
C(2)	46	38	53	-5	10	-9
C(3)	40	38	52	-6	15	3
O(4)	46	35	40	-2	19	1
C(5)	43	49	41	-1	21	-2
C(6)	34	47	48	6	13	-5
O(7)	37	35	52	1	14	-4
C(8)	55	33	59	2	19	-8
C(9)	56	37	48	-12	11	-10
O(10)	46	44	37	-3	11	0
C(11)	98	39	40	0	11	7
C(12)	71	64	42	-19	23	-5
O(13)	52	49	41	-3	11	-1
C(14)	61	65	43	0	6	-11
C(15)	63	88	44	19	24	1
O(16)	44	65	45	4	14	-2
C(17)	40	66	63	17	16	2
C(18)	57	48	70	8	27	-11
N	50	81	81	-10	18	5
C	50	41	41	-8	10	0
S	47	69	51	-5	13	-3
O(HOH)	52	77	44	14	2	-3

1974), the overall conformation of the ring is obviously irregular. In particular, one oxygen atom, O(13), lies 1.95 \AA out of the mean plane of the other five. The torsion angles about C-C bonds are all close to $\pm 60^\circ$ (*sc*), those about C-O bonds are mostly close to ± 60 or 180° (*ap*) but one C-O torsion angle is 115° (*ac*). Bond angles at O atoms range from 111.5 to 116.5° (average 113.3°), those at C atoms from 106.0 to 113.6° (average 109.2°); the bond angles in the irregular part of the ring are markedly wider than those in the regular part.

The sodium ion is coordinated to the six O atoms of the hexaether at distances of 2.45–2.62 \AA and to a water molecule at 2.32 \AA . The resulting coordination polyhedron is a distorted pentagonal bipyramid.

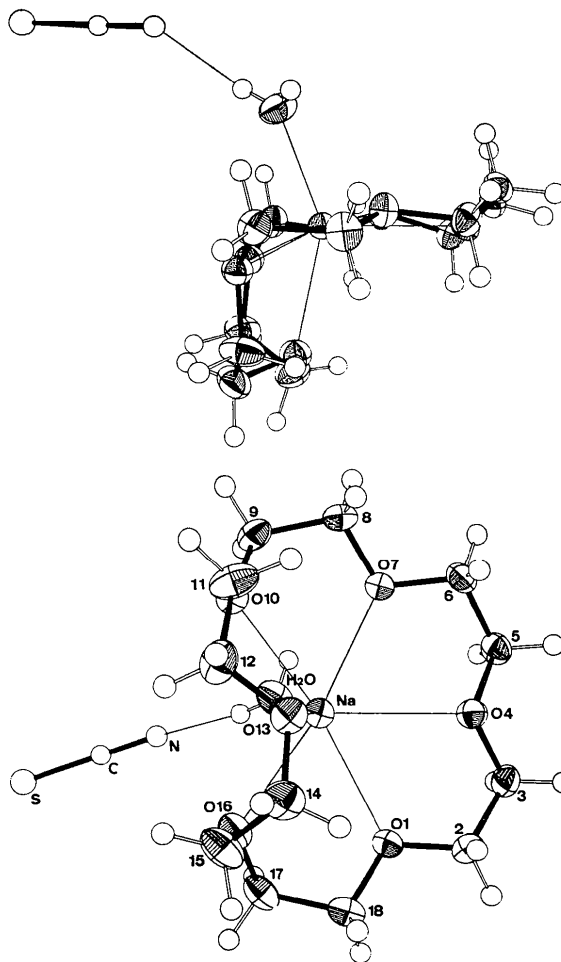


Fig. 1. Bottom: $\text{NaNCS}\cdot\text{H}_2\text{O}$ complex viewed in a direction normal to the mean plane through five O atoms, showing atom numbering. Top: view along a direction in the mean plane. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

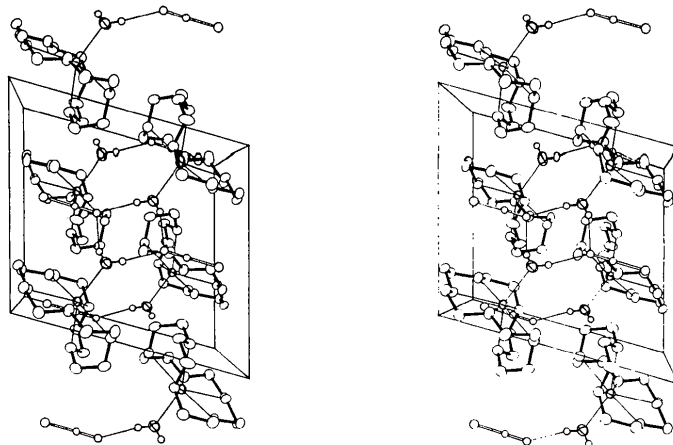


Fig. 2. Stereoscopic view (Johnson, 1965) of the crystal structure looking along the b axis. The c axis is vertical.

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 $\times 10^3$.

	<i>x</i>	<i>y</i>	<i>z</i>
H(2)	97	-255	-22
H(2)*	125	-347	75
H(3)	-11	-244	123
H(3)*	105	-244	236
H(5)	-43	-89	215
H(5)*	84	-87	309
H(6)	0	52	115
H(6)*	18	74	262
H(8)	128	186	129
H(8)*	164	192	280
H(9)	310	246	192
H(9)*	348	155	289
H(11)	194	159	-23
H(11)*	309	220	-22
H(12)	273	105	-185
H(12)*	388	74	-80
H(14)	216	-137	-153
H(14)*	268	-61	-237
H(15)	390	-194	-145
H(15)*	446	-85	-120
H(17)	476	-278	24
H(17)*	461	-245	159
H(18)	278	-298	-49
H(18)*	327	-365	74
H(HOH)	465	-68	362
H(HOH)*	372	-22	377

As in the other structures in this series, the C-C bonds appear to be abnormally short (range 1.497–1.510 Å, average 1.503 Å) whereas the C-O bond distances are more or less normal (range 1.410–1.437 Å, average 1.423 Å). The rigid-body model (Schomaker & Trueblood, 1970) gives very poor agreement between observed and calculated U_{ij} values [$\langle(\Delta U_{ij})^2\rangle^{1/2} = 0.0063 \text{ \AA}^2$, $\langle\sigma^2(U_{ij})\rangle^{1/2} = 0.0006 \text{ \AA}^2$]. The vibration ellipsoids of some of the atoms, e.g. C(11), in the irregular part of the ring are large and anisotropic, suggesting that internal motions in this part of the molecule are by no means negligible.

The crystal structure (Fig. 2) is built from dimeric units formed by hydrogen bonding between the water molecules and the N atoms of the thiocyanate anions (O-H...N, 2.91, 3.09 Å).

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

Atoms	Distance	Angle	Torsion angle			
				1	2	3
C(18)-O(1)-C(2)-C(3)	1.421	112.2	173.0			
O(1)-C(2)-C(3)-O(4)	1.497	107.6	60.7			
C(2)-C(3)-O(4)-C(5)	1.413	108.5	-171.3			
C(3)-O(4)-C(5)-C(6)	1.425	111.4	-177.4			
O(4)-C(5)-C(6)-O(7)	1.497	108.5	-59.4			
C(5)-C(6)-O(7)-C(8)	1.424	107.7	-172.6			
C(6)-O(7)-C(8)-C(9)	1.410	111.9	-173.9			
O(7)-C(8)-C(9)-O(10)	1.509	107.7	52.4			
C(8)-C(9)-O(10)-C(11)	1.423	112.4	70.5			
C(9)-O(10)-C(11)-C(12)	1.426	113.9	-172.3			
O(10)-C(11)-C(12)-O(13)	1.491	108.2	63.4			
C(11)-C(12)-O(13)-C(14)	1.437	106.0	-176.0			
C(12)-O(13)-C(14)-C(15)	1.418	114.1	76.8			
O(13)-C(14)-C(15)-O(16)	1.511	113.6	46.6			
C(14)-C(15)-O(16)-C(17)	1.432	111.3	114.7			
C(15)-O(16)-C(17)-C(18)	1.426	116.5	-73.7			
O(16)-C(17)-C(18)-O(1)	1.510	112.1	-58.5			
C(17)-C(18)-O(1)-C(2)	1.419	107.1	166.5			

Table 5. Distances (Å) and angles ($^\circ$) involving the sodium and thiocyanate ions

Na...O(1)	2.614	N-C-S	1.159	1.628	178.8
Na...O(4)	2.623	N...O(HOH)	2.913		
Na...O(7)	2.474	N'...O(HOH)	3.087		
Na...O(10)	2.550				
Na...O(13)	2.452				
Na...O(16)	2.576				
Na...O(HOH)	2.321				

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