

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

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

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Abstract. $C_{12}H_{24}O_6 \cdot CsNCS$, monoclinic, $P2_1/c$, $a = 12.063(6)$, $b = 8.409(4)$, $c = 22.370(11)$ Å, $\beta = 125.50(13)$, $M = 455.31$, $Z = 4$, $D_x = 1.637$, $D_m = 1.61$ g cm⁻³. The crystal is isostructural with the rubidium complex,

the only difference being that the caesium atom is displaced further (1.44 Å) from the mean plane of the hexaether.

Introduction. Recrystallization from aqueous methanol gave hygroscopic needles which had to be sealed from the atmosphere. These crystals are apparently different from the monohydrate described by Dale & Kristian-

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

Values are $\times 10^4$.

	x	y	z
Cs	112 (0)	1770 (0)	964 (0)
O(1)	-558 (5)	-483 (6)	1776 (3)
C(2)	502 (8)	-1139 (10)	2481 (4)
C(3)	1833 (9)	-1049 (11)	2590 (5)
O(4)	2230 (5)	547 (7)	2660 (3)
C(5)	3482 (9)	690 (11)	2730 (5)
C(6)	3855 (9)	2378 (11)	2790 (5)
O(7)	2861 (5)	3174 (7)	2150 (3)
C(8)	3215 (9)	4786 (11)	2125 (5)
C(9)	2158 (11)	5526 (13)	1425 (6)
O(10)	921 (6)	5525 (8)	1357 (3)
C(11)	-140 (9)	6400 (11)	742 (5)
C(12)	-1454 (9)	6200 (12)	656 (5)
O(13)	-1881 (5)	4603 (7)	473 (3)
C(14)	-3181 (10)	4348 (12)	333 (5)
C(15)	-3499 (9)	2627 (11)	245 (5)
O(16)	-2561 (5)	1865 (7)	913 (3)
C(17)	-2860 (9)	210 (11)	925 (5)
C(18)	-1839 (8)	-469 (10)	1648 (5)
N	2131 (8)	-138 (10)	660 (4)
C	2984 (9)	668 (11)	836 (5)
S	4312 (3)	1813 (3)	1108 (1)

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}
Cs	51	41	54	-1	34	0
O(1)	63	48	62	-3	45	4
C(2)	78	43	53	-3	39	10
C(3)	77	48	55	16	34	14
O(4)	62	49	68	6	41	0
C(5)	43	77	79	18	35	6
C(6)	39	80	77	6	33	-3
O(7)	50	61	77	-8	39	-8
C(8)	55	66	93	-26	50	-18
C(9)	97	56	102	-22	75	-6
O(10)	75	50	77	-6	49	5
C(11)	101	34	63	-4	44	1
C(12)	85	42	62	21	30	9
O(13)	70	44	69	12	36	0
C(14)	57	77	73	28	31	13
C(15)	49	76	70	7	28	-5
O(16)	45	57	63	-1	29	-11
C(17)	44	53	87	-21	42	-28
C(18)	72	46	85	-11	58	-10
N	95	79	87	-21	67	-35
C	69	81	51	23	38	-2
S	63	96	71	4	30	10

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sen (1972). Intensity measurements (4900 reflexions out to $\sin \theta/\lambda = 0.68 \text{ \AA}^{-1}$), structure analysis and refinement were carried out as for the rubidium complex (Dobler & Phizackerley, 1974). The final R was 0.032.* Positional parameters are given in Table 1, thermal parameters in Table 2, and calculated hydrogen positions in Table 3. Tables 4 and 5 contain bond distances and angles.

Discussion. The conformation of the hexaether is virtually indistinguishable from that in the rubidium complex; the caesium cation lies on the local threefold axis, 1.44 Å from the mean plane of the ring (Fig. 1) to give $\text{Cs} \cdots \text{O}$ distances of 3.04–3.27 Å (average

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30560 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

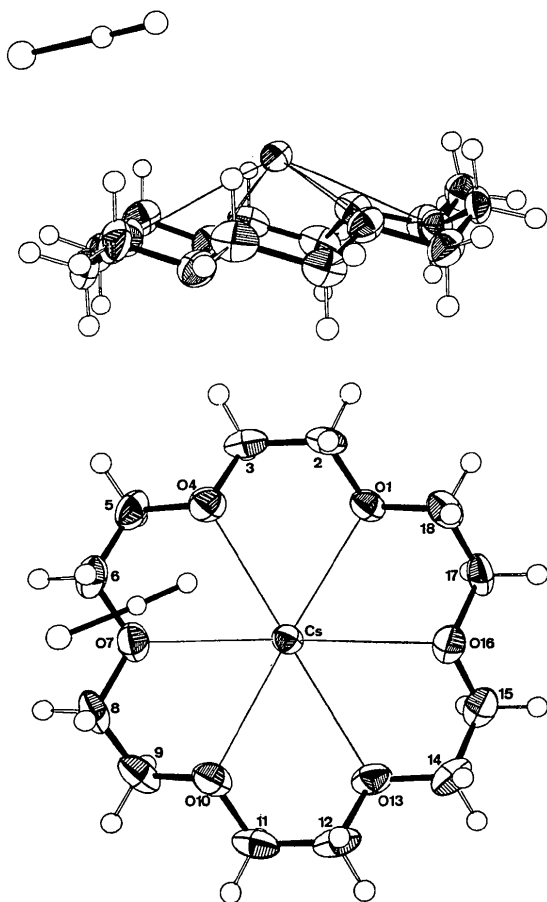


Fig. 1. Bottom: CsNCS complex viewed in direction normal to the mean plane, showing atom numbering. Top: view along a direction in the mean plane. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

Table 3. Fractional coordinates of the hydrogen atoms calculated assuming local C_{2v} symmetry of the methylene groups with $\text{C-H} = 1.0 \text{ \AA}$, $\text{H-C-H} = 110^\circ$

Values are $\times 10^3$.

	x	y	z
H(2)	55	-52	288
H(2)*	29	-228	250
H(3)	253	-164	305
H(3)*	175	-153	216
H(5)	422	12	318
H(5)*	337	22	229
H(6)	392	286	322
H(6)*	475	247	286
H(8)	331	540	254
H(8)*	410	480	218
H(9)	243	665	141
H(9)*	205	490	101
H(11)	11	755	82
H(11)*	-25	601	29
H(12)	-132	647	113
H(12)*	-216	691	25
H(14)	-317	476	76
H(14)*	-389	492	-13
H(15)	-444	246	11
H(15)*	-343	218	-15
H(17)	-378	11	82
H(17)*	-284	-38	54
H(18)	-179	19	203
H(18)*	-211	-159	167

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	4	2-3	1-2-3	1-2-3-4
C(18)-O(1)-C(2)-C(3)	1.445	113.6	-177.6			
O(1)-C(2)-C(3)-O(4)	1.480	110.4	68.0			
C(2)-C(3)-O(4)-C(5)	1.402	109.6	-177.2			
C(3)-O(4)-C(5)-C(6)	1.431	111.3	179.0			
O(4)-C(5)-C(6)-O(7)	1.471	109.8	-62.5			
C(5)-C(6)-O(7)-C(8)	1.392	109.6	-173.3			
C(6)-O(7)-C(8)-C(9)	1.432	113.4	177.2			
O(7)-C(8)-C(9)-O(10)	1.466	110.4	60.9			
C(8)-C(9)-O(10)-C(11)	1.409	108.9	172.2			
C(9)-O(10)-C(11)-C(12)	1.424	113.9	173.7			
O(10)-C(11)-C(12)-O(13)	1.491	111.0	-66.2			
C(11)-C(12)-O(13)-C(14)	1.411	109.0	-176.1			
C(12)-O(13)-C(14)-C(15)	1.427	112.1	-172.3			
O(13)-C(14)-C(15)-O(16)	1.481	110.1	64.9			
C(14)-C(15)-O(16)-C(17)	1.400	108.6	173.0			
C(15)-O(16)-C(17)-C(18)	1.442	113.9	-179.0			
O(16)-C(17)-C(18)-O(1)	1.464	109.7	-65.5			
C(17)-C(18)-O(1)-C(2)	1.398	110.5	180.0			

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

$\text{Cs} \cdots \text{O}(1)$	3.041	$\text{Cs} \cdots \text{N}$	3.300
$\text{Cs} \cdots \text{O}(4)$	3.274	$\text{Cs} \cdots \text{N}'$	3.315
$\text{Cs} \cdots \text{O}(7)$	3.035		
$\text{Cs} \cdots \text{O}(10)$	3.271	N-C-S	1.098 1.652 177.5
$\text{Cs} \cdots \text{O}(13)$	3.097		
$\text{Cs} \cdots \text{O}(16)$	3.160		

3.146 Å). Eightfold coordination is completed by two nitrogen atoms (ordered thiocyanate anions) at 3.30 and 3.32 Å.

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

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Abstract. $C_{12}H_{24}O_6 \cdot Ca(NCS)_2$, monoclinic, $C2/c$, $a = 13.34$, $b = 10.69$, $c = 15.39$ Å, $\beta = 106.2^\circ$, $U = 2108$ Å³, $Z = 4$. Crystallized from chloroform/hexane. The structure is disordered.

Introduction. Intensity measurements (1700 reflexions) were carried out as for the sodium complex (Dobler, Dunitz & Seiler, 1974).^{*} The structure was solved by direct methods. The first E maps showed the calcium atoms (at symmetry centres) and linear thiocyanate groups, and subsequent F_o syntheses showed that the electron density in the mean plane of the hexaether was incompatible with a single orientation. The distribution of peaks was roughly similar to that found in the disordered potassium toluene-*p*-sulphonate complex (Groth, 1971).

Discussion. Each Ca^{2+} ion is surrounded by a nearly planar hexagon of oxygen atoms in at least two orientations related by rotation in the mean plane.

^{*} A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30561 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The $Ca^+ \cdots O$ distances are 2.56–2.74 Å. Hexagonal bipyramidal coordination is completed by the nitrogen atoms of the thiocyanate anions ($Ca^+ \cdots N$ 2.35 Å) which point approximately along the virtual threefold axis of the hexagon. Pairs of anions, belonging to different calcium ions, are related by the screw axes. The structure is fairly open.

A second crystal modification containing solvent of crystallization is obtained by cooling an aqueous acetone solution: monoclinic, $P2_1/c$, $a = 7.74$, $b = 14.09$, $c = 21.27$ Å, $\beta = 98.9^\circ$, $U = 2292$ Å³. The unit-cell volume points to a dihydrate, $C_{12}H_{24}O_6 \cdot Ca(NCS)_2 \cdot 2H_2O$ ($Z = 4$). These crystals disintegrate rapidly under X-radiation, even when enclosed in capillaries with mother liquor. They were not studied further.

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

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