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

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Abstract. $C_{12}H_{24}O_6 \cdot RbNCS$, monoclinic, $P2_1/c$, $a = 11 \cdot 982(6)$, $b = 8 \cdot 347(4)$, $c = 21 \cdot 996(11)$ Å, $\beta = 125 \cdot 16(13)$, $M = 407 \cdot 87$, $Z = 4$, $D_x = 1 \cdot 506$, $D_m = 1 \cdot 50$. The hexaether has a conformation with effective D_{3d} ($\overline{3}m$) symmetry, but the rubidium ion is displaced by about 1·2 Å from the mean plane of the ligand so that the six Rb$\cdots$O distances are no longer equal. Two additional Rb$\cdots$N contacts complete the coordination of the cation.

Introduction. Intensity measurements (3500 reflexions out to $\sin \theta/\lambda = 0 \cdot 62$ Å^{-1}) were carried out as for the sodium complex (Dobler, Dunitz & Seiler 1974), except that backgrounds were estimated from a smooth experimental curve. The structure was solved by the heavy-atom method and refined by least-squares calculations with unit weights. Positions of hydrogen atoms were estimated from stereochemical considerations and included in the structure model but were not refined. The thiocyanate anion is disordered with

about 80% in one orientation, 20% in the antiparallel one. In the latter refinement stages, the positions of the NCS atoms were held constant, the occupancy factors being allowed to vary. The final R was 0·045.†‡ Positional parameters are given in Table 1, vibration tensors in Table 2, and calculated positions of hydrogen atoms in Table 3.

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

Values are × 10⁴.

	x	y	z
Rb	122 (1)	1826 (1)	1039 (0)
O(1)	−557 (4)	−524 (5)	1773 (2)
C(2)	470 (7)	−1214 (9)	2474 (4)
C(3)	1812 (7)	−1147 (9)	2576 (4)
O(4)	2225 (5)	469 (6)	2649 (2)
C(5)	3484 (7)	584 (9)	2726 (4)
C(6)	3858 (8)	2301 (10)	2783 (4)
O(7)	2850 (5)	3115 (6)	2135 (3)
C(8)	3231 (8)	4721 (9)	2122 (4)
C(9)	2182 (9)	5467 (11)	1403 (5)
O(10)	929 (5)	5443 (6)	1318 (3)
C(11)	−92 (8)	6379 (9)	724 (4)
C(12)	−1416 (8)	6179 (9)	635 (4)
O(13)	−1854 (5)	4568 (6)	446 (3)
C(14)	−3152 (8)	4354 (10)	312 (4)
C(15)	−3485 (8)	2600 (10)	222 (4)
O(16)	−2536 (4)	1818 (6)	894 (2)
C(17)	−2882 (7)	173 (9)	898 (4)
C(18)	−1848 (7)	−524 (9)	1643 (4)
N	1911	−96	608
C	2881	632	813
S	4260	1667	1104
N′	4591	1920	1171
C′	3622	1193	966
S′	2242	157	675

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Table 2. *Vibration-tensor components (Å²) of the non-hydrogen atoms*

Values are × 10³.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	52	41	65	2	37	8
O(1)	60	42	54	−2	40	4
C(2)	81	37	51	−4	40	6
C(3)	69	46	54	11	31	10
O(4)	59	41	66	8	42	5
C(5)	52	63	73	16	39	7
C(6)	40	74	73	7	33	1
O(7)	46	54	70	−2	34	0
C(8)	57	57	87	−16	49	−6
C(9)	82	48	88	−17	59	−3
O(10)	66	45	72	−2	43	9
C(11)	92	28	61	−4	41	0
C(12)	77	34	53	15	31	7
O(13)	62	37	64	7	34	−1
C(14)	56	60	68	21	29	8
C(15)	45	67	66	2	23	−3
O(16)	46	47	58	−3	27	−10
C(17)	51	43	78	−14	45	−17
C(18)	72	39	73	−10	55	−8
N	72	52	80	−43	63	−33
C	98	70	56	32	55	11
S	66	104	68	9	32	8
N′	66	104	68	9	32	8
C′	98	70	56	32	55	11
S′	72	52	80	−43	63	−33

Discussion. The highly symmetrical (D_{3d}) conformation of the hexaether is the same as that found in the potassium thiocyanate complex (Seiler, Dobler & Dunitz 1974), but the larger rubidium ion is displaced from the centre by about 1·2 Å towards the thiocyanate anions (see Fig. 1). The C–C distances (average 1·489 Å) are even shorter than in the potassium complex, prob-

Table 3. *Fractional coordinates of the hydrogen atoms calculated assuming local C_{2v} symmetry of the methylene groups with C–H = 1·0 Å, H–C–H = 110°*

Values are × 10^3.

	x	y	z
H(2)	53	−60	288
H(2)*	23	−236	249
H(3)	251	−175	304
H(3)*	172	−163	213
H(5)	421	1	319
H(5)*	338	10	228
H(6)	394	279	322
H(6)*	475	239	284
H(8)	331	534	253
H(8)*	413	472	218
H(9)	245	660	140
H(9)*	210	485	99
H(11)	19	753	83
H(11)*	−21	603	26
H(12)	−129	645	111
H(12)*	−212	690	23
H(14)	−313	478	74
H(14)*	−386	493	−15
H(15)	−443	245	9
H(15)*	−343	215	−18
H(17)	−381	11	80
H(17)*	−288	−43	51
H(18)	−181	14	203
H(18)*	−211	−165	166

ably due to larger internal motion but possibly also because of the different weighting systems used in the refinements.

The rubidium ion is coordinated to the six oxygens of the hexaether (Rb···O, 2·93–3·15 Å, average 3·024 Å) and to two thiocyanate anions (Rb···N(S), 3·23 and 3·31 Å), which show a preference (*circa* 80%) for coordination through nitrogen. Each thiocyanate forms a bridge between two cations leading to the formation of centrosymmetric dimers (Fig. 1). Bridging thiocyanate groups also occur in the isomorphous caesium thiocyanate complex of the hexaether (Dobler

Table 4. *Bond distances (Å), bond angles (°) and torsion angles (°) 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)				1·428	112·5	−179·1
O(1)–C(2)–C(3)–O(4)				1·491	109·4	67·3
C(2)–C(3)–O(4)–C(5)				1·414	109·3	−178·3
C(3)–O(4)–C(5)–C(6)				1·420	110·9	178·6
O(4)–C(5)–C(6)–O(7)				1·485	108·9	−60·9
C(5)–C(6)–O(7)–C(8)				1·403	109·9	−173·1
C(6)–O(7)–C(8)–C(9)				1·422	112·3	175·5
O(7)–C(8)–C(9)–O(10)				1·476	109·6	59·6
C(8)–C(9)–O(10)–C(11)				1·401	108·9	168·8
C(9)–O(10)–C(11)–C(12)				1·404	114·1	175·4
O(10)–C(11)–C(12)–O(13)				1·492	110·5	−63·5
C(11)–C(12)–O(13)–C(14)				1·417	109·3	−176·4
C(12)–O(13)–C(14)–C(15)				1·417	110·9	−172·0
O(13)–C(14)–C(15)–O(16)				1·500	109·1	64·0
C(14)–C(15)–O(16)–C(17)				1·404	108·8	171·8
C(15)–O(16)–C(17)–C(18)				1·435	112·9	−177·6
O(16)–C(17)–C(18)–O(1)				1·491	108·6	−63·6
C(17)–C(18)–O(1)–C(2)				1·402	110·1	−178·6

Table 5. *Distances (Å) and angles (°) involving the rubidium and thiocyanate ions*

Rb···O(1)	2·938		Rb···N	3·226	
Rb···O(4)	3·146		Rb···N′	3·314	
Rb···O(7)	2·929				
Rb···O(10)	3·122		N–C–S	1·148	1·634	180·0
Rb···O(13)	2·998		N′–C′–S′	1·148	1·634	180·0
Rb···O(16)	3·012				

& Phizackerley, 1974), in an analogous complex with a tetramethyldibenzo derivative of the hexaether (Truter, 1973) and in bis(potassium thiocyanate)dibenzo-24-crown-8 (Fenton, Mercer, Poonia & Truter, 1972).

The measured density and the absence of residual peaks in the final $(F_o - F_c)$ synthesis show that the crystals described here are anhydrous, in contrast to the monohydrate described by Dale & Kristiansen (1972).
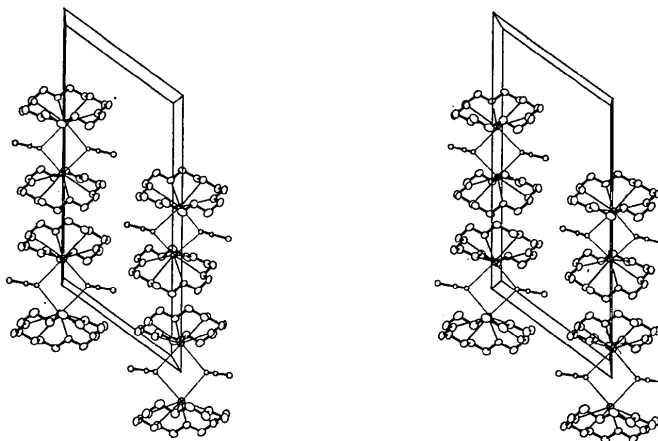

Fig. 1. Stereoscopic view (Johnson, 1965) of the crystal structure looking along the *b* axis. The *c* axis is vertical.

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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, $P2_1/c$, $a = 12\cdot063(6)$, $b = 8\cdot409(4)$, $c = 22\cdot370(11)$ Å, $\beta = 125\cdot50(13)$, $M = 455\cdot31$, $Z = 4$, $D_x = 1\cdot637$, $D_m = 1\cdot61$ 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 × 10⁴.

	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 × 10³.

	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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