

# On the Crystal Structure of the (1:1) Complex between 1,4,7,10,13-Pentaoxacyclopentadecane and Sodium Thiocyanate Hemihydrate at $-150^{\circ}\text{C}$

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1,4,7,10,13-Pentaoxacyclopentadecane (15-crown-5) forms (2:1) sandwich-type complexes cesium<sup>1</sup> and barium<sup>2</sup> cations. In the  $\text{BaBr}_2$  complex two different quinquangular ring formations [33333]\* (Fig. 1a) and [23343] (Fig. 1b) occur. The crystalline substance with  $\text{CuBr}_2 \cdot 3\text{H}_2\text{O}$  is not a cation complex, but a molecular complex with two cation-coordinated water molecules and a uniaxial ring conformation (Fig. 1c). <sup>13</sup>C NMR investigations<sup>4</sup> suggest that the complexing conformation is close to the quinquangular one (Fig. 1a) not only with the larger cations, forming (2:1) sandwich complexes, but also with sodium and lithium. A crystal structure analysis of  $\text{C}_{10}\text{H}_{20}\text{O}_5 \cdot \text{NaSCN} \cdot \frac{1}{2}\text{H}_2\text{O}$  has been undertaken in order to supplement the conformational evidence for the cyclic pentaether.

The crystals are monoclinic with space group  $P2_1/n$  and cell dimensions:  $a = 10.907(4)$ ,  $b = 8.043(3)$ ,  $c = 17.182(4)$  Å, and  $\beta = 93.80(3)^{\circ}$ . There are two formula units in the cell ( $D_x = 1.37$  g/cm<sup>3</sup>,  $D_m = 1.34$  g/cm<sup>3</sup>). 1826 observed reflections were recorded on an automatic four-circle diffractometer at  $c_a$ .

\*A shorthand notation for conformational type, consisting of a series of numbers within brackets, each giving the number of bonds in one "side", starting with the shortest. The direction around the ring is so chosen that the following number is smallest possible.

Table 1. Final fractional coordinates with estimated standard deviations. The hydrogen atoms  $A_{n,m}$  and  $B_{n,m}$  are bonded to  $C_nA$  and  $C_nB$ , respectively.

ATOM	X	Y	Z
NA+	1.0086( 1)	0.2178( 1)	0.9505( 1)
O1A	0.9071( 5)	0.2423( 8)	0.7274( 3)
O2A	0.9854( 5)	0.5160( 8)	0.8093( 3)
O3A	1.1264( 6)	0.4007( 7)	0.9392( 3)
O4A	1.1894( 4)	0.0717( 6)	0.9141( 2)
O5A	1.1213( 4)	0.7669( 6)	0.7557( 2)
C1A	0.8708( 7)	0.4024(11)	0.7009( 5)
C2A	0.8649( 8)	0.5123(10)	0.7717( 4)
C3A	0.9933( 9)	0.6024(10)	0.8828( 5)
C4A	1.1188( 8)	0.5734(11)	0.9208( 4)
C5A	1.2490( 7)	0.3465(13)	0.9588( 4)
C6A	1.2434( 6)	0.1654(10)	0.9776( 4)
C7A	1.2730(12)	0.9319(18)	0.8627( 8)
C8A	1.2003(12)	-0.0548(16)	0.7914( 7)
C9A	1.0204( 9)	-0.0026(13)	0.7068( 5)
C10A	0.9508( 8)	0.1376(12)	0.6681( 5)
O1B	0.9204( 5)	0.1910( 7)	0.7131( 3)
O2B	0.9586( 6)	0.4902( 7)	0.7889( 3)
O3B	1.0920( 5)	0.4453( 8)	0.9275( 3)
O4B	1.2230( 4)	0.1917( 5)	0.8715( 2)
O5B	1.0799( 4)	-0.0367( 6)	0.7844( 2)
C1B	0.8858( 7)	0.3429(10)	0.6751( 4)
C2B	0.8503( 6)	0.4624(11)	0.7366( 5)
C3B	0.9351( 7)	0.5916(10)	0.8546( 4)
C4B	1.0558( 9)	0.6066(10)	0.9027( 5)
C5B	1.2201( 7)	0.4328(11)	0.9494( 4)
C6B	1.2549( 7)	0.2544(12)	0.9492( 4)
C7B	1.2646(16)	0.0152(22)	0.8537(10)
C8B	1.2123(11)	-0.0283(16)	0.7799( 7)
C9B	1.0170( 8)	-0.0715(12)	0.7113( 5)
C10B	0.9876( 8)	0.0830(12)	0.6651( 4)
SA	0.6030( 2)	0.1994( 3)	0.9625( 1)
C11A	0.7459( 7)	0.1801(10)	0.9373( 4)
NA	0.8455( 5)	0.1593( 8)	0.9202( 3)
SB	0.5771( 2)	0.2458( 3)	0.9672( 1)
C11B	0.7014( 7)	0.2259(10)	0.9245( 4)
NB	0.7965( 6)	0.2124( 9)	0.8945( 3)
OW	1.0030( 8)	0.3543(11)	0.9726( 4)
A11	0.788	0.396	0.672
A12	0.932	0.447	0.666
A21	0.806	0.465	0.808
A22	0.839	0.626	0.756
A31	0.931	0.559	0.917
A32	0.981	0.724	0.874
A41	1.131	0.641	0.970
A42	1.183	0.604	0.884
A51	1.283	0.410	1.006
A52	1.301	0.366	0.914

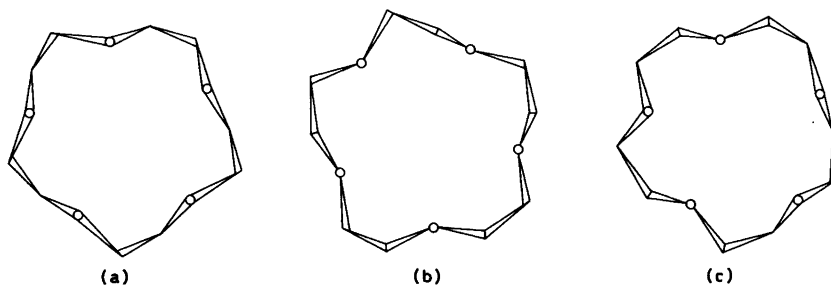


Fig. 1. Crystal structures of 1,4,7,10,13-pentaoxacyclopentadecane (a) and (b) as a (2:1) complex with  $\text{BaBr}_2$  and (c) as a (1:1) adduct with  $\text{CuBr}_2$  hydrate.

Table 1. Continued.

A61	1.194	0.150	1.024
A62	1.329	0.124	0.990
A71	1.338	-0.044	0.887
A72	1.316	0.136	0.845
A81	1.153	-0.150	0.811
A82	1.260	-0.095	0.754
A91	0.965	-0.069	0.730
A92	1.053	-0.075	0.666
A101	0.879	0.095	0.635
A102	1.006	0.204	0.636
B11	0.815	0.323	0.636
B12	0.957	0.388	0.648
B21	0.782	0.415	0.766
B22	0.822	0.570	0.712
B31	0.872	0.538	0.826
B32	0.906	0.774	0.837
B41	1.046	0.679	0.949
B42	1.120	0.655	0.870
B51	1.237	0.480	1.003
B52	1.268	0.496	0.911
B61	1.210	0.193	0.988
B62	1.346	0.264	0.962
B71	1.235	-0.062	0.896
B72	1.356	0.011	0.856
B81	1.244	-0.139	0.763
B82	1.232	0.057	0.740
B91	0.938	-0.130	0.721
B92	1.069	-0.145	0.681
B101	0.935	0.055	0.617
B102	1.064	0.139	0.650

For the present complex,  $Z=2$  in space group  $P2_1/n$  implies a disordered structure. The  $E$ -map obtained using direct methods<sup>5</sup> contained some split peaks corresponding to "half-atoms". These were refined isotropically while anisotropic temperature factors were introduced for the others. Full-matrix least squares refinement<sup>6\*</sup> converged at  $R=16\%$ . Except for that of  $\text{Na}^+$ , all the maximum r.m.s. amplitudes were extremely large. With positions calculated from the differences between the largest and smallest principal axes of the thermal vibration ellipsoids,<sup>7</sup> half-atoms (with isotropic temperature factors) were introduced for all atoms but sodium. Except for those of the water molecule, half-hydrogen atom positions were calculated and included in the structure factor calculations, but not refined. The final  $R$ -value was  $7.0\%$  ( $R_w=5.0\%$ ) for 1826 observed reflections. Weights in least squares were obtained from the standard deviations in intensities,  $\sigma(I)$ , taken as  $\sigma(I) = [C_T + (0.02C_N)^2]^{1/2}$  where  $C_T$  is the total number of counts, and  $C_N$  the net count.

Final fractional coordinates with estimated standard deviations are given in Table 1 and bond distances and angles may be found in Table 2. The torsional angles (listed in Table 3) show that the

$-150^\circ\text{C}$  ( $2\theta_{\text{max}}=50^\circ\text{C}$ ,  $\text{MoK}\alpha$ -radiation). No corrections for absorption or secondary extinctions were made (crystal size  $0.3 \times 0.3 \times 0.1$  mm).

\*All programs used (except those for phase determination) are included in this reference.

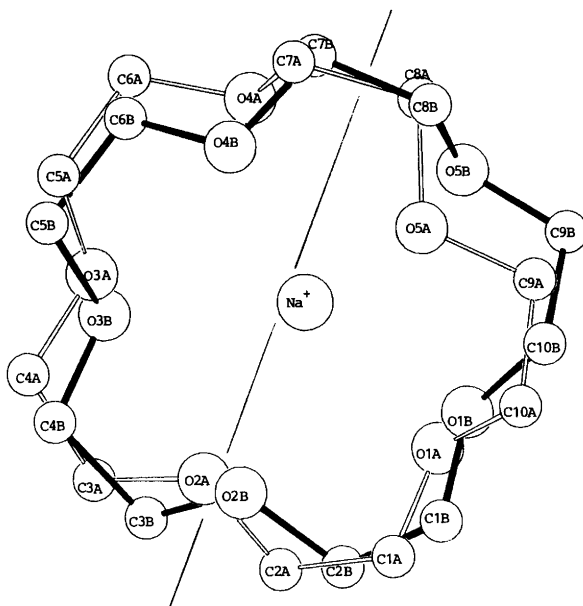


Fig. 2. Schematic drawing showing the conformation of the disordered cyclic pentaether.

Table 2. Bond distances and angles with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)
O1A - C10A	1.43(1)	O1B - C10B	1.43(1)
O1A - C1A	1.41(1)	O1B - C1B	1.42(1)
O2A - C2A	1.43(1)	O2B - C2B	1.45(1)
O2A - C3A	1.44(1)	O2B - C3B	1.43(1)
O3A - C4A	1.43(1)	O3B - C4B	1.41(1)
O3A - C5A	1.43(1)	O3B - C5B	1.43(1)
O4A - C6A	1.42(1)	O4B - C6B	1.45(1)
O4A - C7A	1.35(1)	O4B - C7B	1.53(2)
O5A - C8A	1.42(1)	O5B - C8B	1.45(1)
O5A - C9A	1.45(1)	O5B - C9B	1.42(1)
C1A - C2A	1.51(1)	C1B - C2B	1.50(1)
C3A - C4A	1.50(1)	C3B - C4B	1.51(1)
C5A - C6A	1.49(1)	C5B - C6B	1.48(1)
C7A - C8A	1.58(2)	C7B - C8B	1.40(2)
C9A - C10A	1.49(1)	C9B - C10B	1.50(1)
SA - C11A	1.65(1)	SB - C11B	1.59(1)
C11A - NA	1.16(1)	C11B - NB	1.19(1)
NA+ - O1A	2.33(1)	NA+ - O1B	2.50(1)
NA+ - O2A	2.51(1)	NA+ - O2B	2.48(1)
NA+ - O3A	2.42(1)	NA+ - O3B	2.40(1)
NA+ - O4A	2.49(1)	NA+ - O4B	2.35(1)
NA+ - O5A	2.43(1)	NA+ - O5B	2.49(1)
NA+ - NA	2.26(1)	NA+ - NB	2.48(1)
NA+ - OW	2.4(1)		

ANGLE	(°)	ANGLE	(°)
C1A - O1A - C10A	114.(1)	C1B - O1B - C10B	113.(1)
C2A - O2A - C3A	114.(1)	C2B - O2B - C3B	113.(1)
C4A - O3A - C5A	113.(1)	C4B - O3B - C5B	113.(1)
C6A - O4A - C7A	111.(1)	C6B - O4B - C7B	117.(1)
C8A - O5A - C9A	114.(1)	C8B - O5B - C9B	113.(1)
O1A - C1A - C2A	107.(1)	O1B - C1B - C2B	108.(1)
O2A - C2A - C1A	107.(1)	O2B - C2B - C1B	107.(1)
O2A - C3A - C4A	108.(1)	O2B - C3B - C4B	106.(1)
O3A - C4A - C3A	107.(1)	O3B - C4B - C3B	108.(1)
O3A - C5A - C6A	107.(1)	O3B - C5B - C6B	108.(1)
O4A - C6A - C5A	112.(1)	O4B - C6B - C5B	107.(1)
O4A - C7A - C8A	107.(1)	O4B - C7B - C8B	108.(1)
O5A - C8A - C7A	107.(1)	O5B - C8B - C7B	108.(1)
O5A - C9A - C10A	108.(1)	C8B - C9B - C10B	107.(1)
O1A - C10A - C9A	108.(1)	O1B - C10B - C9B	107.(1)
SA - C11A - NA	177.(1)	SB - C11B - NB	178.(1)

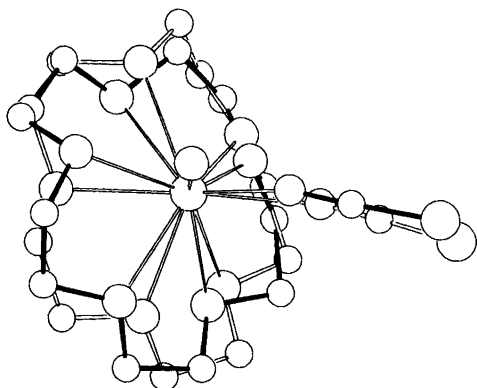


Fig. 3. Schematic drawing of the complex.

conformation of the cyclic pentaether is the uniaxial one of Fig. 1c with corner atoms C6A and C9A, respectively. An illustration is given in the schematic drawing, Fig. 2, from which it may be seen that the disorder of the ring arises from the presence of statistical pseudo mirror planes. In the somewhat overcrowded drawing of Fig. 3 it is attempted to give an impression of the disordered complex with the seven-coordinated sodium. Within the large limits of error, bond distances and angles may be regarded as normal.

Lists of thermal parameters and observed and calculated structure factors are available from the author.

Table 3. Dihedral angles with estimated standard deviations.

DHEDRAL ANGLE	(°)
C1A - O1A - C10A - C9A	165.(1)
C10A - O1A - C1A - C2A	-163.(1)
O1A - C1A - C2A - O2A	61.(1)
C3A - O2A - C2A - C1A	-174.(1)
C2A - O2A - C3A - C4A	171.(1)
O2A - C3A - C4A - O3A	-66.(1)
C5A - O3A - C4A - C5A	166.(1)
C4A - O3A - C5A - C6A	179.(1)
O3A - C5A - C6A - O4A	58.(1)
C7A - O4A - C6A - C5A	84.(1)
C6A - O4A - C7A - C8A	-174.(1)
O4A - C7A - C8A - O5A	65.(1)
C9A - O5A - C8A - C7A	-160.(1)
C8A - O5A - C9A - C10A	-176.(1)
O5A - C9A - C10A - O1A	-59.(1)
C1B - O1B - C10B - C9B	-179.(1)
C10B - O1B - C1B - C2B	-164.(1)
O1B - C1B - C2B - O2B	62.(1)
C3B - O2B - C2B - C1B	-175.(1)
C2B - O2B - C3B - C4B	180.(1)
O2B - C3B - C4B - O3B	-62.(1)
C5B - O3B - C4B - C3B	140.(1)
C4B - O3B - C5B - C6B	-162.(1)
O3B - C5B - C6B - O4B	58.(1)
C7B - O4B - C6B - C5B	173.(1)
C6B - O4B - C7B - C8B	173.(1)
O4B - C7B - C8B - O5B	-66.(1)
C9B - O5B - C8B - C7B	177.(1)
C8B - O5B - C9B - C10B	-88.(1)
O5B - C9B - C10B - C1B	-55.(1)

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