

On the Crystal Structure of the (1:1) Complex between Lithium Thiocyanate and 1,4,7,10-Tetraoxacyclododecane at Room Temperature

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For 1,4,7,10-tetraoxacyclododecane (12-crown-4) the quadrangular [3 3 3 3]* conformation of C_4 symmetry [Fig. 1 (a)] was first demonstrated by IR and NMR spectroscopy on the (1:1) LiSCN complex.¹ Subsequently, this ring conformation has been found by X-ray diffraction for the NaCl,² NaOH,³ and CaCl₂⁴ complexes, while the CuCl₂ complex⁵ has a completely different and strained biangular [4 8] conformation [Fig. 1 (b)]. In the crystals of Mg(H₂O)₆Cl₂C₈H₁₀O₄,⁶ as well as in the crystalline crown ether itself,⁷ a centrosymmetric biangular [6 6] conformation with two pseudo-corners [Fig. 1 (c)] was found. An X-ray crystallographic investigation of LiSCN-(CH₂-CH₂-O)₄ has been undertaken in order to supplement the spectroscopic conformational evidence.

Attempts to collect data at low temperature were prohibited by crystal break-down on cooling. The crystals belong to the orthorhombic system with space group No. 33 ($Pna2_1$) or No. 62 ($Pnma$) and cell dimensions: $a=14.350(1)$, $b=11.810(2)$, $c=7.623(1)$ Å. 904 observed reflections were measured on an automatic four circle diffractometer at room temperature ($2\theta_{\max}=50^\circ$, MoK α -radiation).

Direct phase determination⁸ was carried out in space group $Pna2_1$ and the structure was refined by

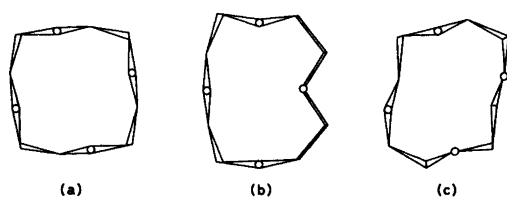


Fig. 1. Observed conformations for 1,4,7,10-tetraoxacyclododecane.

* 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.

fullmatrix least squares technique.^{9,*} Anisotropic temperature factors were introduced for non-hydrogen atoms. Hydrogen positions were calculated, but not refined. 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. The R -value arrived at was 6.7% ($R_w=6.9\%$) for 904 observed reflections.

The calculated principal axes of anisotropic thermal vibrations were extremely large for the carbon atoms of the cyclic tetraether with maximum r.m.s. amplitudes ranging from 0.41 to 0.64 Å and corresponding B -values of 13.51 and 31.95 Å², respectively. A Fourier map based upon the phases corresponding to $R=6.7\%$ gave split peaks for three of the ring carbon atoms. These findings point towards disorder phenomena. However, although the R -value decreased to 5.2% by introducing "half atoms" with positions calculated from the differences between the largest and the smallest principal axes of the thermal vibration ellipsoids,¹⁰ some of the bond distances arrived at were rather awkward. An inspection of the coordinate list

Table 1. Final fractional coordinates with estimated standard deviations. Hn,1 and Hn,2 are bonded to Cn.

ATOM	X	Y	Z
S	0.5358(1)	0.2500	0.7101(1)
C9	0.6210(2)	0.2500	0.5695(4)
N	0.6817(2)	0.2500	0.4705(3)
LI+	0.7853(3)	0.2500(10)	0.3020(6)
O1	0.8290(12)	0.0891(11)	0.2262(21)
O2	0.9205(1)	0.2500	0.3942(3)
O3	0.8271(8)	0.4162(7)	0.2241(13)
O4	0.7398(1)	0.2500	0.0475(3)
C1	0.9246(7)	0.0832(8)	0.1984(9)
C2	0.9547(7)	0.1327(9)	0.3795(11)
C3	0.9776(6)	0.3318(9)	0.3167(12)
C4	0.9177(8)	0.4313(8)	0.2951(14)
C5	0.8279(6)	0.4231(7)	0.0428(13)
C6	0.7471(7)	0.3579(11)	-0.0224(17)
C7	0.7801(6)	0.1615(13)	-0.0600(13)
C8	0.7724(5)	0.0592(6)	0.0649(11)
H11	0.946	0.131	0.098
H12	0.947	0.004	0.181
H21	1.024	0.132	0.389
H22	0.927	0.086	0.476
H31	1.001	0.305	0.200
H32	1.032	0.350	0.394
H41	0.951	0.485	0.217
H42	0.910	0.466	0.414
H51	0.887	0.390	-0.004
H52	0.823	0.504	0.005
H61	0.753	0.351	-0.153
H62	0.689	0.401	0.007
H71	0.847	0.178	-0.090
H72	0.744	0.149	-0.170
H81	0.798	-0.010	0.008
H82	0.706	0.046	0.098

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

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

DISTANCE	(Å)	DISTANCE	(Å)
S - C9	1.63(1)	C9 - N	1.15(2)
N - Li+	1.96(1)	Li+ - O1	2.08(1)
Li+ - O2	2.06(1)	Li+ - O3	2.14(1)
Li+ - O4	2.05(1)	O1 - C1	1.39(2)
O1 - C8	1.52(2)	O2 - C2	1.47(1)
O2 - C3	1.46(1)	O3 - C4	1.42(2)
O3 - C5	1.38(2)	O4 - C6	1.38(1)
O4 - C7	1.45(1)	C1 - C2	1.56(2)
C3 - C4	1.47(2)	C5 - C6	1.48(2)
C7 - C8	1.54(2)		

ANGLE	(°)	ANGLE	(°)
C1 - O1 - C8	113.(1)	C2 - O2 - C3	115.(1)
C4 - O3 - C5	111.(1)	C6 - O4 - C7	115.(1)
O1 - C1 - C2	97.(1)	O2 - C2 - C1	109.(1)
O2 - C3 - C4	105.(1)	O3 - C4 - C3	119.(1)
O3 - C5 - C6	107.(1)	O4 - C6 - C5	114.(1)
O4 - C7 - C8	111.(1)	O1 - C8 - C7	106.(1)

DIHEDRAL ANGLE	(°)
C8 - O1 - C1 - C2	173.(1)
O1 - C1 - C2 - O2	-63.(1)
C3 - O2 - C2 - C1	-84.(1)
C2 - O2 - C3 - C4	162.(1)
O2 - C3 - C4 - O3	-46.(1)
C5 - O3 - C4 - C3	-89.(1)
C4 - O3 - C5 - C6	155.(1)
O3 - C5 - C6 - O4	-50.(1)
C7 - O4 - C6 - C5	-96.(1)
C6 - O4 - C7 - C8	173.(1)
O4 - C7 - C8 - O1	-60.(1)
C1 - O1 - C8 - C7	-74.(1)

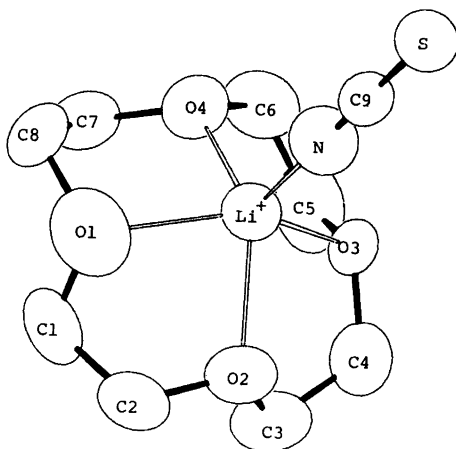


Fig. 2. Schematic drawing showing the coordination of the Li^+ ion and the conformation of cyclic tetraether. The mirror image ring has been left out for clarity. Li^+ , O2, O4, and the thiocyanate anion is in the mirror plane.

revealed that the four lithium thiocyanate atoms and two of the ring oxygens were nearly coplanar. Accordingly the coordinates and indices were transformed to fit space groups $Pnma$ with these six atoms in the mirror plane at $y=1/4$. Full-matrix least squares refinement converged at $R=4.1\%$ ($R_w=4.1\%$).

Final fractional coordinates with estimated standard deviations are given in Table 1. Maximum r.m.s. amplitudes of anisotropic vibrations range from 0.26 to 0.39 Å. Bond distances and angles and dihedral angles may be found in Table 2.

As shown in Fig. 2, the cyclic tetraether has the [3 3 3 3] conformation with the Li^+ ion coordinated to four oxygens and to the thiocyanate anion. The same type of coordination was found in the (1:1) complex between lithium thiocyanate and 1,5,9,13-tetraoxacyclohexadecane,¹¹ where the $\text{Li}^+ - \text{O}$ and $\text{Li}^+ - \text{N}$ bond distances agree with those of Table 2 within error limits.

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

1. Anet, F. A. L., Krane, J., Dale, J. and Kristiansen, P. O. *Acta Chem. Scand.* 27 (1973) 3395.
2. van Remoortere, F. P. and Boer, F. P. *Inorg. Chem.* 13 (1974) 2071.
3. Boer, F. P., Neuman, M. A., van Remoortere, F. P. and Steiner, E. C. *Inorg. Chem.* 13 (1974) 2826.
4. North, P. P., Steiner, E. C., van Remoortere, F. P. and Boer, F. P. *Acta Crystallogr. B* 32 (1976) 370.
5. van Remoortere, F. P., Boer, F. P. and Steiner, E. C. *Acta Crystallogr. B* 31 (1975) 1420.
6. Neuman, M. A., Steiner, E. C., van Remoortere, F. P. and Boer, F. P. *Inorg. Chem.* 14 (1975) 734.
7. Groth, P. *Acta Chem. Scand. A* 32 (1978) 279.
8. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
9. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
10. Kartha, G. and Ahmed, F. R. *Acta Crystallogr.* 13 (1960) 532.
11. Groth, P. *Acta Chem. Scand. A* 35 (1981) 460.

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