# On the Crystal Structure of the (1:1) Complex between Lithium Thiocyanate and 1,5,9,13-Tetraoxacyclohexadecane at −150 °C

P. GROTH

Department of Chemistry, University of Oslo, Oslo 3, Norway

Some lithium salt complexes of 1,5,9,13-tetraoxacyclohexadecanes have been investigated by Dale and Krane.[1] Due to the easy interpretation of their spectra, the low-temperature NMR-spectroscopic study was limited to complexes of the octamethyl derivative; the stoichiometry of the crystalline complexes being (1:1) for LiBr and LiI, and (2:1) for LiSCN. One of the conclusions arrived at was that the conformation of the complexing ring had to be entirely different from the "square" diamond lattice conformation established for the uncomplexed 1,5,9,13-tetraoxacyclohexadecane (I),[2]
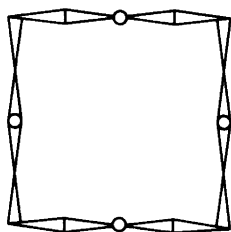
(I)

and the suggested conformation for the complexes with lithium salts was:
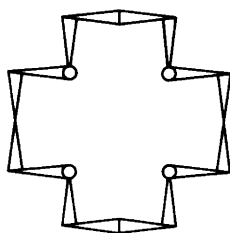
(II)

The quality of the (2:1) LiSCN complex crystals received for structure determined was bad. By

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

recrystallization from methanol somewhat better crystals were obtained. An X-ray crystal structure investigation was undertaken in order to clarify the conformational problems of the 16-membered ring.

The crystals belong to the monoclinic system with space group $P2_1/c$ and cell dimensions $a=9.319(3)$ Å, $b=9.278(3)$ Å, $c=18.287(5)$ Å, $\beta=94.11(2)°$. The measured and calculated densities ($D_m=1.18$ g cm^{-3}, $D_x=1.24$ g cm^{-3}, $Z=4$) showed that the recrystallization product was a (1:1) complex of $LiSCN-(CH_2-CH_2-CH_2-O)_4$.

With $2\theta_{max}=50°$ and MoKα-radiation 2535 independent reflections were measured on an automatic four-circle diffractometer at −150 °C Using an observed-unobserved cutoff at $2.5\sigma(I)$, 1408 reflections were recorded as observed. No corrections for absorption or secondary extinction were applied (crystal size $0.4 \times 0.5 \times 0.3$ mm).

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

ATOM	X	Y	Z
O1	.7174(7)	−.2090(6)	.6409(3)
O2	.5078(5)	.0020(8)	.6370(2)
O3	.7279(7)	.2225(6)	.6306(3)
O4	.9394(5)	−.0117(8)	.6344(2)
C1	.6129(10)	−.3004(9)	.6708(4)
C2	.5088(9)	−.2130(9)	.7115(4)
C3	.4192(9)	−.1080(10)	.6649(4)
C4	−.4186(10)	.1058(10)	.5960(4)
C5	.5097(10)	.1961(10)	.5498(4)
C6	.6137(9)	.2977(9)	.5903(4)
C7	.8442(10)	.3187(9)	.6527(5)
C8	.9567(9)	.2385(9)	.7000(4)
C9	1.0353(9)	.1220(10)	.6611(4)
C10	1.0153(9)	−.0981(10)	.5989(4)
C11	.9098(9)	−.1989(10)	.5576(4)
C12	.8201(10)	−.2906(10)	.6057(4)
LI+	.7277(13)	−.4897(19)	−.1657(6)
S	−.7888(2)	.0087(3)	.9308(1)
C13	.7657(7)	.0140(10)	.8404(4)
N	.7512(6)	.0133(9)	.7774(3)
H11	.663	−.371	.705
H12	.559	−.354	.630
H21	.565	−.157	.750
H22	.442	−.281	.734
H31	.346	−.063	.695
H32	.369	−.161	.623
H41	.370	.169	.631
H42	.345	.054	.564
H51	.444	.255	.516
H52	.567	.129	.520
H61	.560	.357	.625
H62	.656	.363	.554
H71	.807	.401	.681
H72	.858	.356	.608
H81	.908	.192	.741
H82	1.029	.310	.720
H91	1.111	.079	.696
H92	1.082	.166	.619
H101	1.075	−.154	.636
H102	1.079	−.052	.564
H111	.966	−.265	.527
H112	.843	−.139	.525
H121	.886	−.339	.644
H122	.769	−.365	.574

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

DISTANCE	(Å)	DISTANCE	(Å)
O1 - C1	1.43(1)	O1 - C12	1.41(1)
O2 - C3	1.43(1)	O2 - C4	1.45(1)
O3 - C6	1.43(1)	O3 - C7	1.44(1)
O4 - C9	1.42(1)	O4 - C10	1.42(1)
C1 - C2	1.50(1)	C2 - C3	1.51(1)
C4 - C5	1.50(1)	C5 - C6	1.51(1)
C7 - C8	1.51(1)	C8 - C9	1.51(1)
C10 - C11	1.52(1)	S - C13	1.65(1)
C13 - N	1.15(1)	C11 - C12	1.52(1)
LI+ - O1	2.08(2)	LI+ - O2	2.08(1)
LI+ - O3	2.07(2)	LI+ - O4	2.09(1)
LI+ - N	2.04(1)		

ANGLE	(°)	ANGLE	(°)
O1 - C1 - C2	111.(1)	C1 - O1 - C12	111.(1)
O1 - C12 - C11	113.(1)	O2 - C3 - C2	111.(1)
C3 - O2 - C4	110.(1)	O2 - C4 - C5	110.(1)
O3 - C6 - C5	112.(1)	C6 - O3 - C7	111.(1)
O3 - C7 - C8	110.(1)	O4 - C9 - C8	111.(1)
C9 - O4 - C10	111.(1)	O4 - C10 - C11	110.(1)
C1 - C2 - C3	115.(1)	C4 - C5 - C6	116.(1)
C7 - C8 - C9	115.(1)	C10 - C11 - C12	115.(1)
S - C13 - N	178.(1)		

DIHEDRAL ANGLE	(°)
C12 - O1 - C1 - C2	177.(1)
C11 - C12 - O1 - C1	166.(1)
C4 - O2 - C3 - C2	-177.(1)
C5 - C4 - O2 - C3	-164.(1)
C7 - O3 - C6 - C5	165.(1)
C8 - C7 - O3 - C6	175.(1)
C10 - O4 - C9 - C8	-179.(1)
C11 - C10 - O4 - C9	-169.(1)
O1 - C1 - C2 - C3	63.(1)
C1 - C2 - C3 - O2	-66.(1)
O2 - C4 - C5 - C6	-68.(1)
C4 - C5 - C6 - O3	69.(1)
O3 - C7 - C8 - C9	67.(1)
C7 - C8 - C9 - O4	-63.(1)
O4 - C10 - C11 - C12	-68.(1)
C10 - C11 - C12 - O1	70.(1)

The structure was solved by direct methods [3] and refined by full-matrix least squares technique.[4],* Hydrogen atom positions were calculated and not refined. Anisotropic temperature factors were introduced for non-hydrogen atoms and weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$, where C_T is the total number of counts and C_N the net count. The form factors used were those of Hanson *et al.*[5] except for hydrogen.[6] The final R-value was as high as 10.5 % ($R_w = 7.8$ %), probably due to the poor crystal quality. Final fractional coordinates with estimated standard deviations are given in Table 1. The principal thermal vibration ellipsoids for non-hydrogen atoms correspond to maximum r.m.s. amplitudes between 0.16 and 0.25 Å.

Bond distances, bond angles and dihedral angles

may be found in Table 2. The standard deviations, given in parentheses, are estimated from the correlation matrix of the final least squares refinement cycle.

Fig. 1 is a schematic drawing of the molecule which shows that the 16-membered ring adopts the conformation (II).

The bond distances and angles of Table 2 agree within error limits with those of 1,5,9,13-tetraoxacyclohexadecane itself,[2] while some of the corresponding torsional angles deviate significantly.

The lithium ion is coordinated to four oxygen atoms of the cyclic tetraether at distances 2.07 – 2.09 Å and to the thiocyanate anion with a Li+---N distance of 2.04 Å (Table 2). The complex is illustrated in Fig. 2 which shows that the lithium ion is displaced somewhat (0.55 Å) out of the plane of the four oxygens towards the thiocyanate anion. The
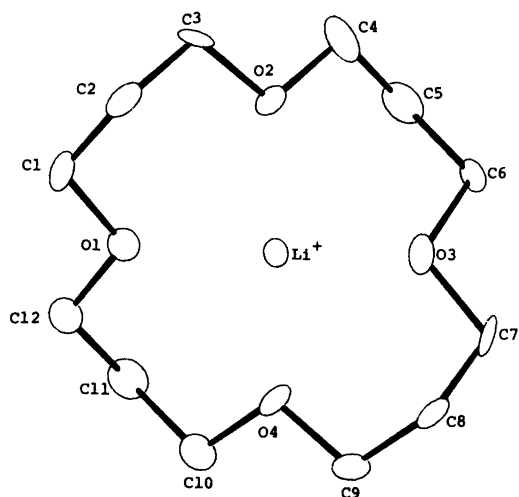
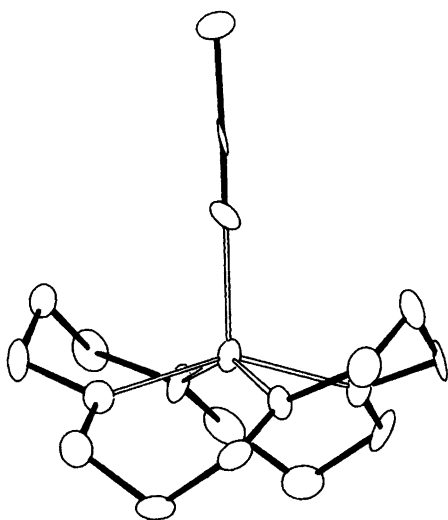*Fig. 1.* Schematic drawing of the 16-membered ring.

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

1. Dale, J. and Krane, J. *Chem. Commun.* (1972) 1012.
2. Groth, P. *Acta Chem. Scand.* 25 (1971) 725.
3. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystalogr. A* 27 (1971) 368.
4. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
5. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
7. Shannon, R. D. *Acta Crystallogr. A* 32 (1976) 751.
8. *International Table for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 258.
9. Moras, D. and Weiss, R. *Acta Crystallogr. B* 29 (1973) 400.

Fig. 2. Schematic drawing showing the coordination of the Li^+ ion.

typical $Li^+ {-}{-}{-}O$ distance for tetrahedral coordination is 1.97 Å,[7] while the corresponding average bond length for six-fold coordination is 2.16 Å.[8] In the cryptate complex $C_{14}H_{28}N_2O_4 \cdot LiI$,[9] where the lithium ion is coordinated to four oxygen atoms and two nitrogens, the average bond lengths are $Li{-}{-}{-}O = 2.13$ Å, and $Li{-}{-}{-}N = 2.28$ Å, respectively. The intermediate values obtained for the five-fold coordination of the present complex seem reasonable.