

Short Communication

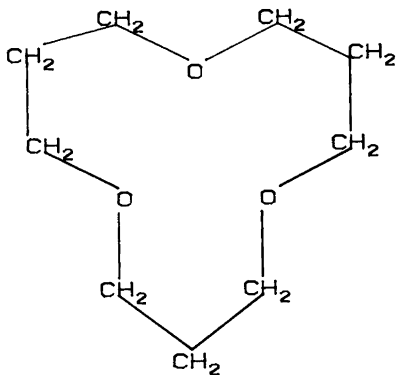
The Crystal Structure of (Thiocyanato-*M*) (1,5,9-trioxacyclododecane)lithium at -150°C

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Alkali salt complexes of 1,5,9-trioxacyclodode-



cane have been investigated by Dale *et al.*¹ NMR spectroscopic studies suggested that the complexing ring adopts a non-angular conformation with D_3 symmetry. An X-ray crystal structure investigation of the title compound was undertaken in order to establish the conformation of the 12-membered ring.

The crystals of $\text{C}_9\text{H}_{18}\text{O}_3 \cdot \text{LiSCN}$ belong to the monoclinic system with space group $P2_1$, cell dimensions $a = 7.037(4)$, $b = 13.233(5)$, $c = 7.106(7)$ Å, $\beta = 104.84(6)^{\circ}$ and $Z = 2$ ($D_x = 1.24$ g cm^{-3} , $D_m = 1.23$ g cm^{-3}). Using $2\theta_{\text{max}} = 50^{\circ}$ and $\text{MoK}\alpha$ radiation, and choosing an observed-unobserved cutoff at $2.5\sigma(I)$, a total of

Table 1. Final fractional coordinates (e.s.d.'s in parentheses) and equivalent thermal parameters for non-hydrogen atoms.

Atom	x	y	z	U_{eq}^a
S	0.1102(2)	0.1720	0.0659(2)	0.034
C	0.2089(7)	0.0824(4)	0.2183(7)	0.022
N	0.2809(7)	0.0207(4)	0.3298(7)	0.030
Li ⁺	0.4460(11)	-0.0786(8)	0.5011(14)	0.025
O1	0.6862(5)	-0.0398(3)	0.6922(5)	0.026
C1	0.8736(9)	-0.0603(5)	0.6561(9)	0.032
C2	0.8496(9)	-0.0823(6)	0.4469(10)	0.038
C3	0.7609(8)	-0.1865(5)	0.3820(9)	0.031
O2	0.5557(5)	-0.1845(3)	0.3793(6)	0.030
C4	0.4622(9)	-0.2821(4)	0.3486(10)	0.034
C5	0.2695(10)	-0.2781(5)	0.4076(10)	0.038
C6	0.2934(9)	-0.2666(5)	0.6213(11)	0.040
O3	0.3402(6)	-0.1627(3)	0.6738(6)	0.031
C7	0.3971(9)	-0.1469(6)	0.8768(10)	0.037
C8	0.4853(9)	-0.0412(5)	0.9191(10)	0.038
C9	0.6928(8)	-0.0328(5)	0.8959(8)	0.032

^a $U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3$.

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1086 observed reflections were recorded on an automatic diffractometer at ca. -150°C . No corrections for absorption or secondary extinction were applied (crystal size $0.4 \times 0.4 \times 0.2$ mm). The structure was solved by direct methods² and refined by full-matrix least-squares techniques.³ Weights in least-squares were calculated 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. Anisotropic temperature factors were used for non-hydrogen atoms. The maximum r.m.s. amplitudes of thermal vibration range from 0.19 to

Table 2. Bond distances (\AA), bond angles ($^{\circ}$) and torsion angles ($^{\circ}$) with e.s.d.'s in parentheses.

Distance		Distance	
S - C	1.635(6)	C - N	1.160(8)
Li ⁺ - N	1.958(9)	Li ⁺ - O1	1.946(9)
Li ⁺ - O2	1.910(9)	Li ⁺ - O3	1.940(9)
O1 - C1	1.432(7)	O1 - C9	1.439(7)
C1 - C2	1.482(9)	C2 - C3	1.535(9)
C3 - O2	1.440(7)	O2 - C4	1.440(7)
C4 - C5	1.520(9)	C5 - C6	1.492(9)
C6 - O3	1.440(8)	O3 - C7	1.411(8)
C7 - C8	1.529(9)	C8 - C9	1.515(9)
Angle		Angle	
S - C - N	178.3(5)	C - N - Li ⁺	169.4(6)
N - Li ⁺ - O1	121.8(6)	N - Li ⁺ - O2	117.1(6)
N - Li ⁺ - O3	121.0(5)	O1 - Li ⁺ - O2	97.5(5)
O1 - Li ⁺ - O3	96.7(5)	O2 - Li ⁺ - O3	97.5(5)
O1 - C1 - C2	110.1(5)	C1 - C2 - C3	114.3(6)
C2 - C3 - O2	108.4(5)	C3 - O2 - C4	113.7(5)
O2 - C4 - C5	109.4(5)	C4 - C5 - C6	114.1(6)
C5 - C6 - O3	108.6(6)	C6 - O3 - C7	113.1(5)
O3 - C7 - C8	109.4(6)	C7 - C8 - C9	113.6(6)
O1 - C9 - C8	108.8(5)	C1 - O1 - C9	113.5(5)
Torsion angle			
C9 - O1 - C1 - C2	171.1(7)		
C1 - O1 - C9 - C8	-164.0(7)		
O1 - C1 - C2 - C3	-73.7(6)		
C1 - C2 - C3 - O2	72.2(6)		
C2 - C3 - O2 - C4	-171.3(7)		
C3 - O2 - C4 - C5	163.1(7)		
O2 - C4 - C5 - C6	-68.9(6)		
C4 - C5 - C6 - O3	77.5(6)		
C5 - C6 - O3 - C7	-170.3(7)		
C6 - O3 - C7 - C8	168.0(7)		
O3 - C7 - C8 - C9	76.4(7)		
C7 - C8 - C9 - O1	70.3(6)		

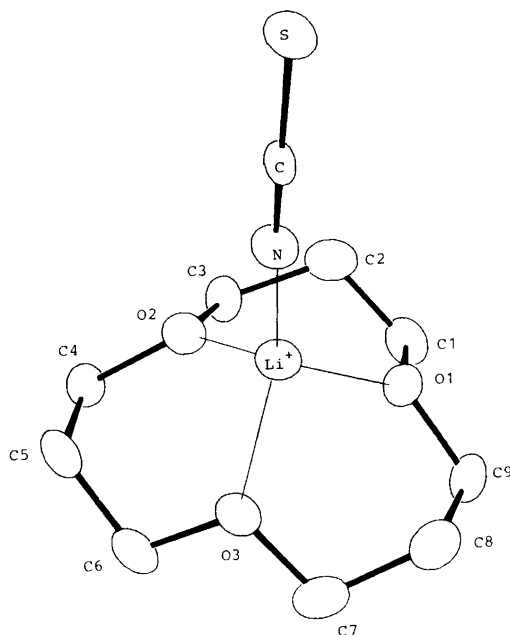
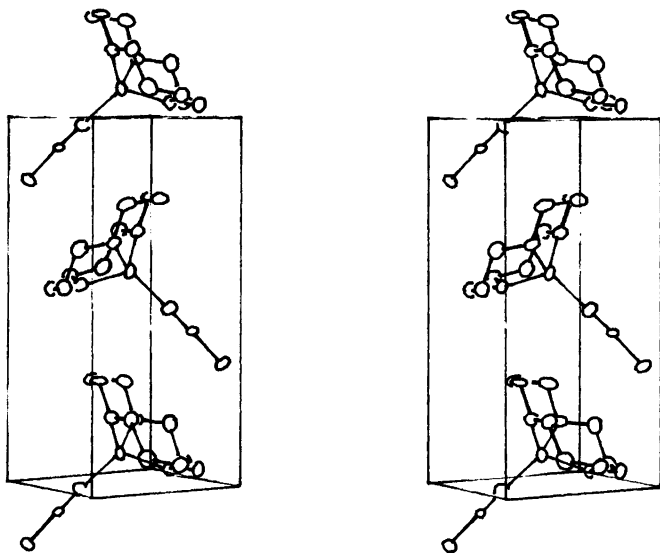


Fig. 1. Perspective drawing of the complex showing the numbering of atoms.

0.26 \AA . Hydrogen atoms positions were calculated and refined with isotropic temperature factors. The final R -value was 5.2% ($R_w = 5.9\%$) for 1086 observed reflections. Final fractional coordinates with estimated standard deviations for the non-hydrogen atoms are listed in Table 1. Bond distances, bond angles and torsion angles, with estimated standard deviations, may be found in Table 2. Fig. 1 is a perspective drawing of the complex showing the numbering of atoms, and Fig. 2 is a stereo view of the unit cell contents.

The C-C and C-O bond distances and angles agree within error limits with those of the (1:1) complex of lithium thiocyanate with 1,5,9,13-tetraoxacyclohexadecane,⁴ in which the lithium ion is pentacoordinated with an average coordination bond length of 2.072 \AA . In the present complex, the lithium cation is coordinated to three oxygen atoms of the cyclic triether at distances 1.910 – 1.946 \AA , and to the thiocyanate anion with a Li⁺-N distance of 1.958 \AA . These bond lengths correspond to typical values reported for tetrahedral coordination of lithium.⁵ The lithium ion is displaced 0.96 \AA out of the plane of the three

Fig. 2. Stereo view of the unit cell contents.



oxygens towards the thiocyanate anion. The torsion angles (Table 2) confirm that the 12-membered cyclic ligand adopts a conformation with approximately C_{3v} symmetry.

Lists of thermal parameters, hydrogen atom parameters, and observed and calculated structure factors are available from the author on request.

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