

The Crystal Conformation of 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.2]eicosane Lithium Thiocyanate Hemihydrate at $-130\text{ }^{\circ}\text{C}$

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A reaction providing a novel type of bicyclic ligand with strong affinity for alkali cations has been described.¹ ^{13}C NMR studies of the thiocyanates showed that the K^+ complex is somewhat stronger than the Li^+ complex, although both are a great deal weaker than the Na^+ complex.

X-Ray crystal structure determinations have been carried out in order to verify that both rings of the Na^+ complex have the expected quadrangular [3 3 3] conformation,² and also

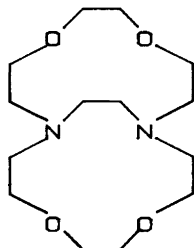


Table 1. Final fractional coordinates for non-hydrogen atoms with estimated standard deviations.

ATOM	X	Y	Z
O1	.0914(2)	.2212(1)	.2571(1)
O2	.2780(1)	.2861(1)	.4305(1)
O3	.4919(2)	.2927(1)	.2823(1)
O4	.3060(2)	.2240(1)	.1094(1)
N1	.1312(2)	.3676(1)	.1232(1)
N2	.3239(2)	.4389(1)	.3133(1)
C1	-.0013(3)	.3518(2)	.1451(2)
C2	-.0176(3)	.2497(2)	.1698(2)
C3	.0559(3)	.2186(1)	.3583(2)
C4	.1868(2)	.2131(1)	.4426(2)
C5	.2360(3)	.3758(1)	.4602(2)
C6	.3293(3)	.4462(1)	.4284(2)
C7	.4569(3)	.4580(1)	.2927(2)
C8	.5535(3)	.3775(1)	.3309(2)
C9	.5405(3)	.2646(2)	.4912(2)
C10	.4429(3)	.1919(2)	.1325(2)
C11	.2744(3)	.2903(2)	.0229(2)
C12	.1368(3)	.3296(2)	.0177(2)
C13	.1720(3)	.4663(1)	.1320(2)
C14	.2158(3)	.4981(1)	.2486(2)
Li+	.2751(5)	.2952(3)	.2518(1)
SA	.7367(2)	.0461(1)	.2783(2)
CA	.6453(6)	-.0067(3)	.1694(1)
NA	.5941(8)	-.0440(5)	.0824(6)
SB	.9486(1)	-.0055(1)	.4736(1)
CB	.8242(6)	.0232(4)	.3687(1)
NB	.7272(6)	.0324(4)	.2993(1)
OW	.5843(6)	-.0451(4)	.1068(5)

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

DISTANCE	(Å)	DISTANCE	(Å)
O1 - C2	1.429(3)	O1 - C3	1.435(4)
O2 - C4	1.436(3)	O2 - C5	1.439(3)
O3 - C8	1.440(3)	O5 - C9	1.457(4)
O4 - C10	1.430(4)	O4 - C11	1.439(4)
N1 - C1	1.466(4)	N1 - C12	1.475(4)
N1 - C13	1.474(3)	N2 - C6	1.470(4)
N2 - C7	1.472(4)	N2 - C14	1.475(4)
C1 - C2	1.518(4)	C3 - C4	1.498(4)
C5 - C6	1.513(4)	C7 - C8	1.520(4)
C9 - C10	1.508(4)	C11 - C12	1.499(5)
C13 - C14	1.523(4)	SA - CA	1.659(7)
CA - NA	1.234(10)	SB - CB	1.646(6)
CB - NB	1.162(8)	O1 - L1+	2.161(6)
O2 - L1+	2.255(6)	O5 - L1+	2.151(6)
O4 - L1+	2.222(6)	N1 - L1+	2.205(5)
N2 - L1+	2.210(5)	NA' - OW	2.942(7)
NB - OW	2.773(9)		

ANGLE	(°)	ANGLE	(°)
C2 - O1 - C3	113.4(2)	C4 - O2 - C5	112.5(2)
C8 - O3 - C9	112.9(2)	C10 - O4 - C11	113.2(3)
C1 - N1 - C12	111.6(2)	C1 - N1 - C13	115.0(2)
C12 - N1 - C13	110.6(2)	C6 - N2 - C7	111.3(2)
C6 - N2 - C14	111.2(2)	C7 - N2 - C14	112.6(2)
N1 - C1 - C2	110.2(3)	O1 - C2 - C1	109.7(2)
O1 - C3 - C4	106.1(2)	O2 - C4 - C3	111.6(2)
O2 - C5 - C6	106.2(2)	N2 - C6 - C5	110.8(2)
N2 - C7 - C8	110.6(2)	O3 - C8 - C7	109.0(2)
O3 - C9 - C10	106.6(2)	O4 - C10 - C9	111.6(2)
O4 - C11 - C12	108.1(3)	N1 - C12 - C11	110.4(3)
N1 - C13 - C14	111.8(2)	N2 - C14 - C13	112.1(2)
SA - CA - NA	170.4(7)	SB - CB - NB	169.7(6)
NB - OW - NA'	130.0(7)		

Table 3. Dihedral angles with estimated standard deviations.

DIHEDRAL ANGLE	(°)
C2 - O1 - C3 - C4	-169.2(2)
C3 - O1 - C2 - C1	99.8(3)
C4 - O2 - C5 - C6	-172.1(2)
C5 - O2 - C4 - C3	71.9(3)
C8 - O3 - C9 - C10	-165.3(2)
C9 - O3 - C8 - C7	100.0(3)
C10 - O4 - C11 - C12	-171.3(2)
C11 - O4 - C10 - C9	74.9(3)
C1 - N1 - C12 - C11	-143.8(2)
C12 - N1 - C1 - C2	72.6(3)
C1 - N1 - C13 - C14	74.4(3)
C13 - N1 - C1 - C2	-162.0(2)
C12 - N1 - C13 - C14	-159.7(3)
C13 - N1 - C12 - C11	89.5(3)
C6 - N2 - C7 - C8	72.9(3)
C7 - N2 - C6 - C5	-145.1(2)
C6 - N2 - C14 - C13	-159.5(2)
C14 - N2 - C6 - C5	88.5(3)
C7 - N2 - C14 - C13	75.8(3)
C14 - N2 - C7 - C8	-161.5(2)
N1 - C1 - C2 - O1	55.9(3)
O1 - C3 - C4 - O2	55.2(3)
O2 - C5 - C6 - N2	56.9(3)
N2 - C7 - C8 - O3	54.2(3)
O3 - C9 - C10 - O4	52.5(3)
O4 - C11 - C12 - N1	54.2(3)
N1 - C13 - C14 - N2	54.9(3)

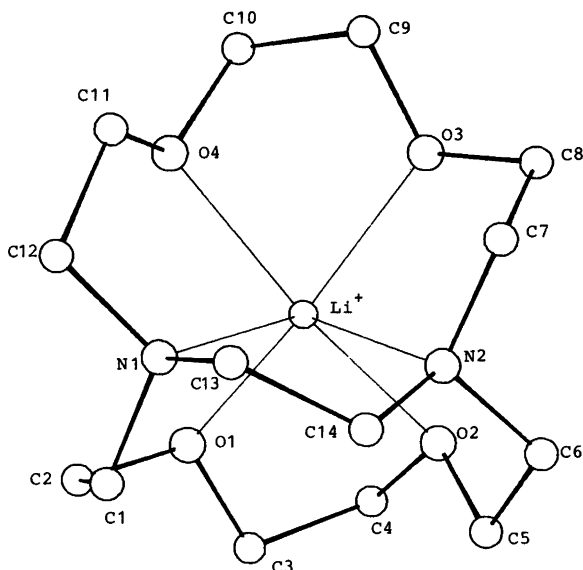


Fig. 1. Perspective drawing of the complex showing the numbering of atoms.

to settle the ring conformational problems for the free ligand and the complexes with LiSCN and KSCN. A crystal structure determination of the free ligand has recently been reported.³ The results for the LiSCN complex are now presented.

The crystals of $C_{14}H_{28}N_2O_4 \cdot LiSCN \cdot \frac{1}{2}H_2O$ are monoclinic with space group $P2_1/n$, cell dimensions $a=10.201(3)$, $b=14.364(3)$, $c=12.855(4)$ Å, $\beta=104.44(3)$, and $Z=4$. ($D_x=1.32$ g cm^{-3} , $D_m=1.30$ g cm^{-3}). With $2\theta_{max}=50^\circ$, MoK α -radiation, and an observed-unobserved cutoff at $2.5\sigma(I)$, 2485 independent reflections were recorded as observed on an automatic four-circle diffractometer at *ca.* $-130^\circ C$. 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 methods⁴ and refined by full-matrix least squares technique.⁵ All programs used (except those for phase determination) are included in Ref. 5. The thiocyanate anion is disordered with about 50 % in each of two positions (labeled A and B, respectively). Anisotropic temperature factors were introduced for ordered non-hydrogen atoms, while those of the thiocyanate anions were refined with isotropic temperature factors. This led to a large negative value for NA and the corresponding Fourier map showed a splitted peak at that

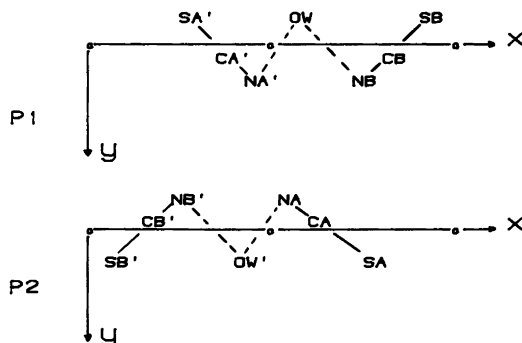
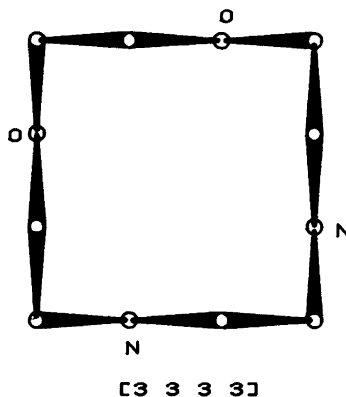


Fig. 2. Schematic drawing of the disordered thiocyanate anions.

position. By introducing the oxygen of an assumed "half" water molecule, the thermal parameters arrived at were reasonable. 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. Hydrogen atom positions were calculated. The final R -values were as high as $R=6.4$, $R_w=6.9\%$ for 2485 observed reflections, probably due to poor crystal quality.

Final fractional coordinates for non-hydrogen atoms are given in Table 1. Bond distances and angles and torsion angles may be found in Table 2 and Table 3, respectively. Fig. 1 is a perspective drawing of the complex, showing the numbering of atoms.

The dihedral angles of Table 3 show that both rings have chosen the familiar [3 3 3 3] conformation.



"Corner atoms" are C2, C4, C6 and C13 for the lower ring of Fig. 1, while C8, C10, C12 and C14 are the corners of the upper ring. Bond distances and angles are normal within estimated limits of error. It may be noted that Li^+ is hexacoordinated without any contact with the anion. The rather unusually high coordination number for Li^+ is reflected in the somewhat long coordination bonds of Table 2 (ranging from 2.151 to 2.255 Å).

The disorder may be described as a fifty-fifty mixture of unit cells with pairs of anions, in positions P1 and P2, respectively, linked by water bridges (Fig. 2).

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

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