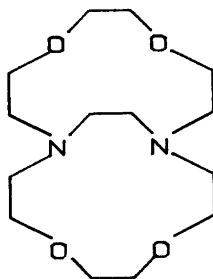


The Crystal Conformation of 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.2]eicosane in Complexes with NaSCN and KSCN at $-130\text{ }^{\circ}\text{C}$

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The aim of the single crystal X-ray crystallographic investigations of the molecule 4,7,13,15-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane and its complexes with LiSCN, NaSCN and KSCN, is to study dissimilarities of this molecule and to correlate the findings with ^{13}C



NMR results.¹ Crystal structure determinations of the free ligand and the Li^+ complex have been reported earlier.^{2,3} The results for the Na^+ and K^+ complexes are now presented.

The crystals of $\text{C}_{14}\text{H}_{28}\text{N}_2\text{O}_4 \cdot \text{NaSCN}$ and $\text{C}_{14}\text{H}_{28}\text{N}_2\text{O}_4 \cdot \text{KSCN}$ are both monoclinic with space group $P2_1/m$ and $Z=2$. The cell dimensions are $a=8.318(3)$, $b=11.921(7)$,

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

ATOM	X	Y	Z
NA+	.9391(1)	.2500(0)	.8974(1)
S	1.4841(1)	.2500(0)	1.2992(1)
C	1.3506(3)	.2500(0)	1.1335(2)
N	1.2590(3)	.2500(0)	1.0159(2)
O1	.8998(1)	.1324(1)	1.0821(1)
O2	.9590(1)	.1307(1)	.7043(1)
N1	.6665(1)	.1235(1)	.7896(1)
C1A	.6822(12)	.0453(15)	.9062(21)
C2A	.7354(5)	.0884(4)	1.0487(4)
C3A	.9430(7)	.2109(4)	1.2099(4)
C4A	.6568(7)	.0791(4)	.6615(5)
C5A	.8313(8)	.0384(4)	.6682(5)
C6A	.9606(7)	.1887(5)	.5849(5)
C7A	.5118(5)	.2028(4)	.7676(5)
C1B	.6279(12)	.0581(16)	.8928(21)
C2B	.7935(5)	.0252(3)	1.0208(4)
C3B	.8521(7)	.1773(4)	1.1813(5)
C4B	.7103(7)	.0333(4)	.6966(5)
C5B	.8052(7)	.0851(4)	.6102(5)
C6B	1.0483(6)	.2016(5)	.6372(5)
C7B	.5220(6)	.1860(4)	.6990(5)

Table 2. Final fractional coordinates for non-hydrogen atoms with estimated standard deviations for the KSCN complex.

ATOM	X	Y	Z
K+	.5043(1)	.2500(0)	.8765(1)
S	.9217(1)	.2500(0)	1.3371(1)
C	.8657(4)	.2500(0)	1.1743(3)
N	.8275(4)	.2500(0)	1.0583(3)
O1	.4726(2)	.3684(1)	.6439(1)
O2	.3844(2)	.3671(2)	1.0636(1)
N1	.1807(2)	.3758(1)	.7843(2)
C1A	.2297(11)	.4647(6)	.6784(6)
C2A	.3084(7)	.4454(5)	.5756(6)
C3A	.5378(11)	.2936(7)	.5509(7)
C4A	.1213(5)	.4495(3)	.8850(4)
C5A	.2894(7)	.4792(4)	.9946(5)
C6A	.3054(8)	.3296(5)	1.1480(5)
C7A	.0371(7)	.3437(4)	.7104(5)
C1B	.1703(11)	.4210(6)	.6642(6)
C2B	.3504(9)	.4598(5)	.6468(5)
C3B	.4485(12)	.3461(6)	.5258(6)
C4B	.2040(6)	.4496(3)	.8968(4)
C5B	.2200(8)	.4093(4)	1.0375(5)
C6B	.3948(9)	.2783(4)	1.1828(4)
C7B	.0286(6)	.2929(4)	.7854(6)

Table 3. Torsion angles with estimated standard deviations for the NaSCN complex.

DIHEDRAL ANGLE	(°)
C2A - O1 - C3A - C3B'	-74.(1)
C3A - O1 - C2A - C1A	163.(1)
N1 - C1A - C2A - O1	-62.(1)
C7A - N1 - C1A - C2A	-69.(1)
C1A - N1 - C7A - C7B'	156.(1)
N1 - C7A - C7B' - N1'	-64.(1)
C1B' - N1' - C7B' - C7A	-86.(1)
C7B' - N1' - C1B' - C2B'	160.(1)
N1' - C1B' - C2B' - O1'	-53.(1)
C3B' - O1' - C2B' - C1B'	-90.(1)
C2B' - O1' - C3B' - C3A	170.(1)
O1' - C3B' - C3A - O1	-58.(1)
C5A - O2 - C6A - C6B'	162.(1)
C6A - O2 - C5A - C4A	-89.(1)
N1 - C4A - C5A - O2	-60.(1)
C7A - N1 - C4A - C5A	159.(1)
C4A - N1 - C7A - C7B'	-73.(1)
C4B' - N1' - C7B' - C7A	160.(1)
C7B' - N1' - C4B' - C5B'	-77.(1)
N1' - C4B' - C5B' - O2'	-60.(1)
C6B' - O2' - C5B' - C4B'	168.(1)
C5B' - O2' - C6B' - C6A	-72.(1)
O2' - C6B' - C6A - O2	-62.(1)

Table 4. Torsion angles with estimated standard deviations for the KSCN complex.

DIHEDRAL ANGLE	(°)
C2A - O1 - C3A - C3B'	-76.(1)
C3A - O1 - C2A - C1A	166.(1)
N1 - C1A - C2A - O1	-64.(1)
C7A - N1 - C1A - C2A	-70.(1)
C1A - N1 - C7A - C7B'	160.(1)
N1 - C7A - C7B' - N1'	-70.(1)
C1B' - N1' - C7B' - C7A	-70.(1)
C7B' - N1' - C1B' - C2B'	155.(1)
N1' - C1B' - C2B' - O1'	-67.(1)
C3B' - O1' - C2B' - C1B'	-80.(1)
C2B' - O1' - C3B' - C3A	162.(1)
O1' - C3B' - C3A - O1	-60.(1)
C5A - O2 - C6A - C6B'	172.(1)
C6A - O2 - C5A - C4A	-79.(1)
N1 - C4A - C5A - O2	-58.(1)
C7A - N1 - C4A - C5A	159.(1)
C4A - N1 - C7A - C7B'	-89.(1)
C4B' - N1' - C7B' - C7A	157.(1)
C7B' - N1' - C4B' - C5B'	-50.(1)
N1' - C4B' - C5B' - O2'	-74.(1)
C6B' - O2' - C5B' - C4B'	157.(1)
C5B' - O2' - C6B' - C6A	-75.(1)
O2' - C6B' - C6A - O2	-60.(1)

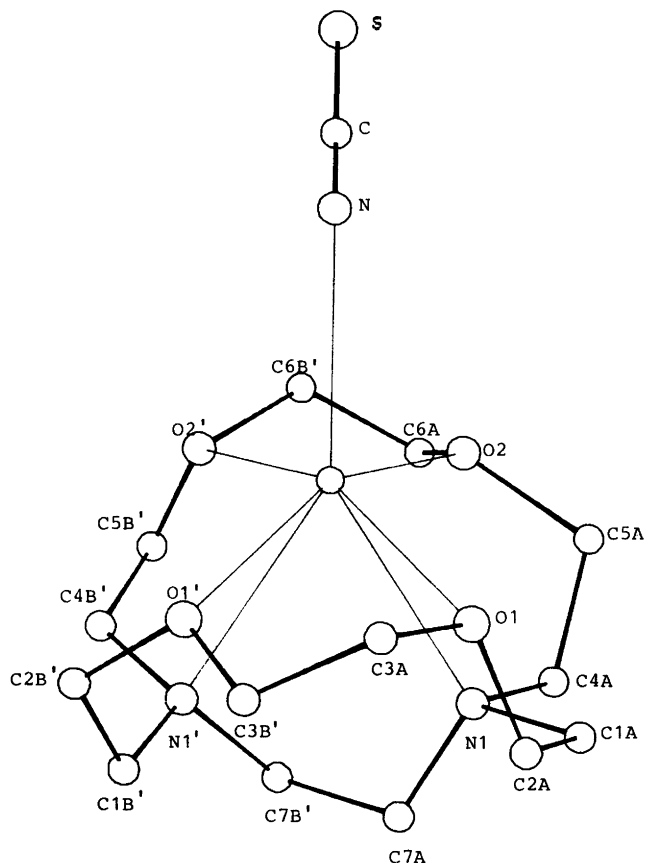


Fig. 1. Schematic drawing for one of the disordered ligands showing the numbering of atoms.

$c=10.177(4)$ Å, $\beta=111.90(3)^\circ$ for the NaSCN complex, and $a=7.799(2)$, $b=12.131(5)$, $c=10.301(2)$ Å, $\beta=103.28(2)^\circ$ for the KSCN complex. Data were collected on an automatic four-circle diffractometer at *ca.* -130°C using the ω -scan technique ($2\theta_{\text{max}}=50^\circ$) with MoK α radiation. With an observed-unobserved cutoff at $2.5\sigma(I)$, 1353 and 1414 reflections were regarded as observed for the Na $^+$ and K $^+$ complex, respectively. No corrections for absorption or secondary extinction were made (crystal sizes $0.4\times 0.5\times 0.2$ mm and $0.3\times 0.6\times 0.2$ mm). The structures were solved by direct methods⁴ and refined by full-matrix least squares.⁵ All programs used are included in Ref. 5, except those for phase determination. Although the intensity distribution [$N(z)$ -plot etc.] strongly indicated centro symmetric space groups for both complexes, attempts were made to solve and refine the structures in space group $P2_1$. However, the rather awkward geometrical and thermal parameters arrived at, as well as the final R -values of about 15 %, clearly pointed towards disordered structures in space group $P2_1/m$. For both complexes, the E -map corresponding to the best figure of merit contained several split peaks indicating disorder, which was to be expected from the space group and the number of complexes in the cell. Anisotropic temperature factors were used for all non-hydrogen atoms. Maximum r.m.s. amplitudes lay between 0.20 and 0.33 Å. Hydrogen atom positions were calculated. The occupancy factor $G=0.5$ was used for all disordered atoms. 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 final R -values were $R=3.6\%$ ($R_w=4.1\%$) for

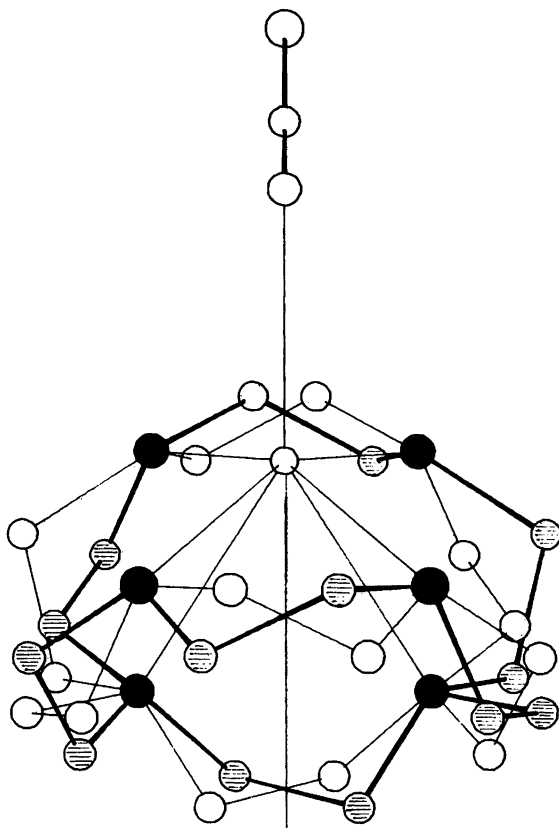
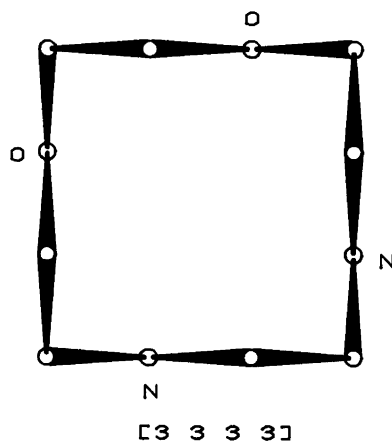


Fig. 2. Illustration of the disordered ligands.

the 1353 observed reflections of the NaSCN-complex, and $R=4.6\%$ ($R_w=6.1\%$) for the 1414 observed reflections of the KSCN-complex. Final fractional coordinates with estimated standard deviations for non-hydrogen atoms are given in Tables 1 and 2. Dihedral angles may be found in Tables 3 and 4, which show that the ring conformation is $[3\ 3\ 3\ 3]^6$ in both complexes.



This was also the preferred conformation in the LiSCN complex³ while that of the free ligand was [3 9].² A comparison of the numerical values of the torsion angles reveals particularly large changes in the *gauche* bonds at some of the "corner" atoms and in the bridge C–C bond. These changes efficiently narrow and open the cleft between the rings in order to adapt to the smaller Li⁺ cation and the larger K⁺ cation. Fig. 1 is a schematic drawing showing the numbering of atoms (for one of the ligands only). In Fig. 2 the disordered ligands, related by a mirror plane, are illustrated. No disorder could be observed for the hetero atoms.

A coordination number of seven is found for Na⁺ and K⁺, the anion being the seventh ligand. Na⁺ has attained its optimal coordination number and the ligand has little conformational strain. The K⁺ ion readily takes coordination numbers up to 10, and is here clearly rather naked next to the anion. The coordination bonds to Na⁺ vary between 2.46 and 2.60 Å while those to K⁺ range from 2.73 to 2.92 Å.

List of hydrogen atom coordinates, thermal parameters, bond distances and angles as well as observed and calculated structure factors, is available from the author.

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