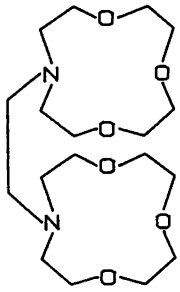
The Crystal Conformation of the (1:1) Complex between Lithium Thiocyanate and 10,10′-Ethylene Bis(1,4,7-trioxa-10-azacyclododecane) at −130 °C

P. GROTH

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

The syntheses of organic ligands of two mono-aza-12-crown-4 rings linked together by a single alkylene bridge between nitrogen bridgeheads have been reported.[1]

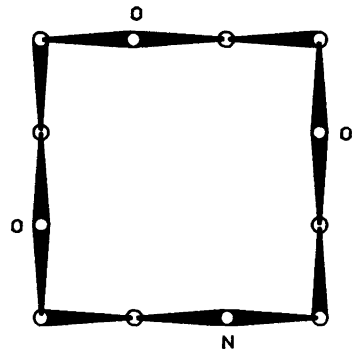


When the free *N,N′*-bridged bis(1,4,7-trioxa-10-azacyclododecane) is allowed to react with salt solutions containing Li^+, Na^+ or K^+ cations and SCN^- anions, stable complexes are obtained. Since no definite conclusions about ring conformations could be drawn from ^{13}C NMR studies of the free ligand and its complexes, X-ray crystallographic investigations have been undertaken. The results for the LiSCN complex are now presented.

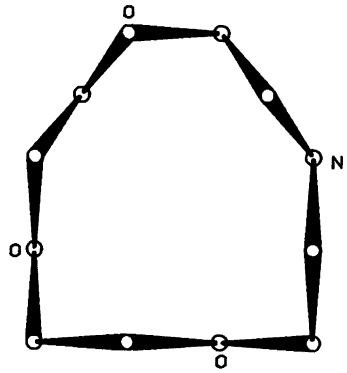
The crystals of $C_{18}H_{36}N_2O_6 \cdot LiSCN$ belong to the monoclinic system with space group $P2_1/c$ and cell dimensions a=12.222(5), b=22.754(7), c=16.482(4) Å, β=100.02(2)°. There are two independent complexes in the asymmetric unit (D_x=1.30 g cm^{-3} for Z=8, D_m=1.24 g cm^{-3}).

With $2\theta_{max}$=50° and Mo$K\alpha$-radiation 8723 independent reflections were measured on an automatic four-circle diffractometer at *ca.* −130 °C. Using an observed−unobserved cutoff at 2.5$\sigma(I)$, 5087 reflections were regarded as observed. No corrections for absorption or secondary extinction were applied (crystal size 0.4×0.7×0.2 mm).

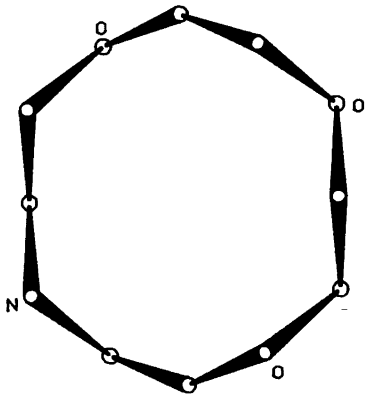
The structure was solved by direct methods[2] and refined by the full-matrix least squares technique.[3] [All programs used (except those for phase determination) are included in Ref. 3.] Hydrogen atom positions were calculated. Anisotropic temperature factors were used for non-hydrogen atoms and weights in least squares were



[3 3 3 3]



[3 9]



[6 6]

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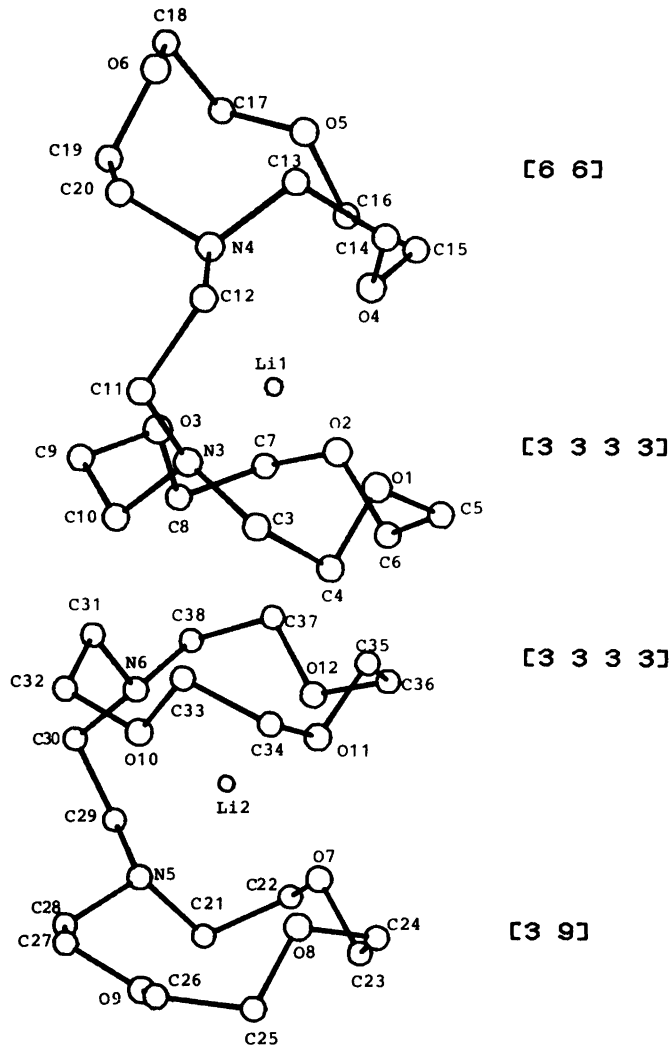

Fig. 1. Schematic drawing showing the numbering of atoms.

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. H-atoms were refined with isotropic temperature factors. The final R-value was 4.2 % (R_w=3.6 %) for 5087 observed reflections. Maximum r.m.s. amplitudes range from 0.15 to 0.22 Å. Final fractional coordinates for non-hydrogen atoms are listed in Table 1.

Fig. 1 is a schematic drawing of the ligands and the Li^+ cations with their numbering. The bond distances and angles are normal within estimated error limits. From the list of torsion angles (Table 2), it may be seen that the four 12-membered rings adopt three different conformations. One from each complex has the most common [3 3 3 3] conformation.[4] The [3 9] conformation of the third ring has been observed earlier,[5] while the fourth, which may be described as [6 6], corresponds to that of the free 12-crown-4.[6]

Cation contacts together with the angles between them are given in Table 3. The typical Li^+---O distance for four-fold coordination is

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

ATOM	X	Y	Z
S1	.54174(6)	.59958(5)	.27285(4)
C1	.54294(20)	.60887(14)	.17550(17)
N1	.54507(19)	.61484(10)	.10567(14)
S2	.95751(6)	.65010(5)	.74845(4)
C2	.97469(20)	.62751(14)	.84996(18)
N2	.98585(18)	.62470(10)	.92149(15)
LI1	.5245(5)	.1554(1)	.6955(2)
LI2	-.0489(5)	.1249(2)	.2624(2)
O1	.58794(15)	.21719(7)	.61869(10)
O2	.58708(14)	.19502(7)	.82255(10)
O3	.42917(15)	.08085(7)	.84790(10)
O4	.50908(14)	.21582(7)	.77975(10)
O5	.57850(14)	.17215(7)	.90247(10)
O6	.51097(15)	.07884(7)	.98454(10)
O7	-.09501(14)	.18957(7)	.16548(10)
O8	.14571(15)	.17572(8)	.18429(11)
O9	.04545(14)	.06948(8)	.08621(11)
O10	.07758(15)	.06888(7)	.32969(10)
O11	.08168(14)	.18659(7)	.32765(10)
O12	-.14220(15)	.18451(7)	.35255(10)
N3	.65924(16)	.10158(9)	.64695(12)
N4	.64857(16)	.11592(9)	.82485(12)
N5	-.16011(16)	.06557(9)	.15415(12)
N6	-.15555(18)	.08182(9)	.33580(12)
C3	.71747(20)	.14551(12)	.80101(15)
C4	.65820(21)	.18851(11)	.55715(15)
C5	.50255(22)	.25857(11)	.58555(16)
C6	.59490(22)	.22687(12)	.55415(16)
C7	.28757(21)	.14915(12)	.60029(16)
C8	.34412(21)	.09598(12)	.57879(15)
C9	.50168(22)	.05566(11)	.65128(16)
C10	.59800(22)	.05758(11)	.59245(16)
C11	.75928(20)	.07578(12)	.71595(16)
C12	.75508(20)	.11078(12)	.79185(16)
C13	.64858(20)	.16541(12)	.87952(15)
C14	.61555(21)	.22092(11)	.85104(16)
C15	.41581(22)	.24521(11)	.80419(16)
C16	.35529(22)	.19985(12)	.82655(16)
C17	.5259(22)	.11918(12)	.91852(16)
C18	.40040(22)	.08587(12)	.98002(16)
C19	.51820(21)	.05001(11)	.88788(16)
C20	.65298(20)	.05848(11)	.88855(15)
C21	-.19901(21)	.11042(12)	.09101(15)
C22	-.20217(21)	.17055(12)	.12892(16)
C23	-.05475(24)	.21888(12)	.10667(17)
C24	.08595(24)	.22690(12)	.14585(17)
C25	.17957(25)	.14476(12)	.09655(17)
C26	.16045(22)	.08018(12)	.10577(16)
C27	.01271(22)	.01755(11)	.12528(16)
C28	-.11210(21)	.01484(11)	.11657(15)
C29	-.25507(21)	.04612(11)	.19226(16)
C30	-.21717(21)	.01856(12)	.27625(16)
C31	-.07291(20)	.05280(11)	.59707(15)
C32	.02901(20)	.01595(11)	.58208(15)
C33	.15609(20)	.09618(12)	.59105(15)
C34	.18205(20)	.15594(11)	.55470(16)
C35	.04217(22)	.21867(12)	.59011(17)
C36	-.07807(22)	.25589(11)	.55556(17)
C37	-.17855(21)	.15815(11)	.40077(16)
C38	-.25228(20)	.09915(12)	.56977(15)

Table 2. Dihedral angles with estimated standard deviations.

DIHEDRAL ANGLE	(°)		
C4 - O1 - C5 - C6	90.5(5)	C20 - N4 - C12 - C11	77.9(5)
C5 - O1 - C4 - C5	-175.2(2)	C15 - N4 - C20 - C19	70.8(5)
C6 - O2 - C7 - C8	84.0(5)	C20 - N4 - C15 - C14	-155.9(2)
C7 - O2 - C8 - C5	-162.2(2)	C21 - N5 - C28 - C27	95.2(5)
C9 - O5 - C9 - C10	96.9(2)	C28 - N5 - C21 - C22	-155.7(2)
C9 - O5 - C8 - C7	-171.4(2)	C21 - N5 - C29 - C30	-159.8(2)
C14 - O4 - C15 - C16	-114.5(2)	C29 - N5 - C21 - C22	85.2(5)
C15 - O4 - C14 - C15	106.1(2)	C28 - N5 - C29 - C30	90.0(5)
C16 - O5 - C17 - C18	160.1(2)	C29 - N5 - C28 - C27	-144.1(2)
C17 - O5 - C16 - C15	-162.0(2)	C30 - N6 - C31 - C32	78.2(5)
C18 - O6 - C19 - C20	167.7(2)	C31 - N6 - C30 - C29	-151.5(2)
C19 - O8 - C18 - C17	-90.7(5)	C30 - N6 - C38 - C37	-158.1(2)
C22 - O7 - C25 - C24	-170.8(2)	C38 - N6 - C30 - C29	82.8(2)
C25 - O7 - C22 - C21	84.8(5)	C31 - N6 - C38 - C37	76.6(5)
C24 - O8 - C25 - C26	-159.1(2)	C38 - N6 - C31 - C32	-158.9(2)
C25 - O8 - C24 - C25	79.8(5)	N5 - C5 - C4 - O1	57.7(5)
C26 - O9 - C27 - C28	169.0(2)	O1 - C5 - C6 - O2	59.2(5)
C27 - O9 - C28 - C25	-155.0(2)	O2 - C7 - C8 - O5	64.7(5)
C32 - O10 - C35 - C34	-169.8(2)	O5 - C9 - C10 - N5	57.8(5)
C35 - O10 - C32 - C31	88.2(2)	N5 - C11 - C12 - N4	64.4(5)
C34 - O11 - C35 - C36	-164.8(2)	N4 - C15 - C14 - O4	58.4(5)
C35 - O11 - C34 - C33	86.7(5)	O4 - C15 - C16 - O5	71.5(5)
C36 - O12 - C37 - C39	-172.1(2)	O5 - C17 - C18 - O6	-48.4(5)
C37 - O12 - C38 - C35	90.1(5)	O6 - C19 - C20 - N4	-85.7(5)
C5 - N5 - C10 - C9	-155.2(2)	N5 - C21 - C22 - O7	64.1(5)
C10 - N5 - C5 - C4	77.4(5)	O7 - C25 - C24 - O8	64.9(5)
C5 - N5 - C11 - C12	87.5(2)	O8 - C25 - C26 - O9	71.0(5)
C11 - N5 - C5 - C4	-157.6(2)	O9 - C27 - C28 - N5	-57.7(5)
C10 - N5 - C11 - C12	-147.2(2)	N5 - C29 - C30 - N6	62.1(5)
C11 - N5 - C10 - C9	90.8(5)	N6 - C31 - C32 - O10	57.5(5)
C12 - N4 - C15 - C14	82.2(5)	O10 - C35 - C34 - O11	55.5(5)
C15 - N4 - C12 - C11	-159.9(2)	O11 - C35 - C36 - O12	57.9(5)
C12 - N4 - C20 - C19	-166.4(2)	O12 - C37 - C38 - N6	57.9(5)

Table 3. Cation contacts together with the angles between them with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)
LI1 - O1	2.155(5)	LI1 - O2	2.287(5)
LI1 - O5	2.092(5)	LI1 - O4	1.988(5)
LI1 - N5	2.280(5)	LI1 - N4	2.558(5)
LI2 - O7	2.169(5)	LI2 - O10	2.185(5)
LI2 - O11	2.250(5)	LI2 - O12	2.224(5)
LI2 - N5	2.454(5)	LI2 - N6	2.585(5)
ANGLE	(°)	ANGLE	(°)
O1 - LI1 - O2	78.7(2)	O1 - LI1 - O5	125.1(2)
O1 - LI1 - O4	91.8(2)	O1 - LI1 - N5	77.7(2)
O1 - LI1 - N4	120.5(2)	O2 - LI1 - O5	76.8(2)
O2 - LI1 - O4	94.7(2)	O2 - LI1 - N5	128.6(2)
O2 - LI1 - N4	154.9(2)	O5 - LI1 - O4	155.9(2)
O5 - LI1 - N5	81.4(2)	O5 - LI1 - N4	104.2(2)
O4 - LI1 - N5	159.9(2)	O4 - LI1 - N4	78.9(2)
N5 - LI1 - N4	75.6(1)	O7 - LI2 - O10	148.1(2)
O7 - LI2 - O11	89.7(2)	O7 - LI2 - O12	85.4(2)
O7 - LI2 - N5	78.7(2)	O7 - LI2 - N6	155.5(2)
O10 - LI2 - O11	75.8(2)	O10 - LI2 - O12	119.1(2)
O10 - LI2 - N5	106.7(2)	O10 - LI2 - N6	77.5(2)
O11 - LI2 - O12	76.0(2)	O11 - LI2 - N5	161.4(2)
O11 - LI2 - N6	122.9(2)	O12 - LI2 - N5	116.5(2)
O12 - LI2 - N6	74.8(1)	N5 - LI2 - N6	75.1(1)

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. Although the average Li^+---O distance of Table 3 (2.168 Å) suggests hexacoordinated lithium, the mean value of the four Li^+---N contacts (2.418 Å) is indeed large, and the coordination number of Li^+ in the present complex is uncertain. The distances from Li^+ to the planes of the four hetero atoms of the [3 3 3 3]-rings are 1.00 Å and 1.11 Å, respectively. Distances to corresponding planes of the "partner" rings are 1.47 Å and 1.70 Å. The contacts LI1---O4 (1.988Å) and LI2---O7 (2.169 Å), show that the "partner" rings have adopted two different conformations, both offering satisfactory penta-coordination conditions. Whether the two remaining contacts, LI1---N4 (2.556 Å) and LI2---N5 (2.454 Å), correspond to weak interactions, cannot be judged.

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

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