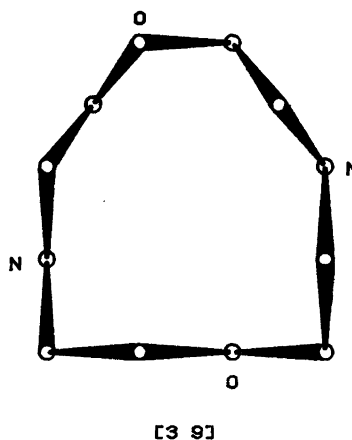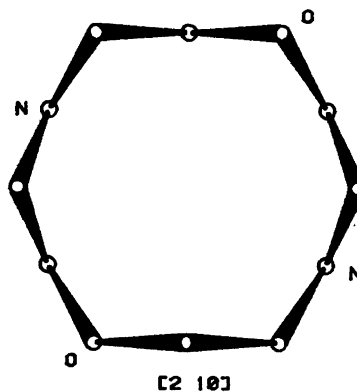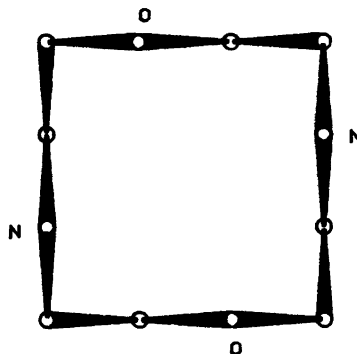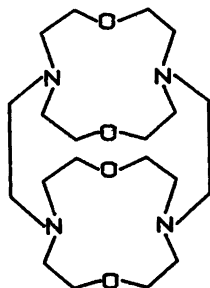# Short Communication

The Crystal Conformation of 7,16,21,26-Tetraoxa-1,4,10,13-tetra-azatricyclo[11.5.5.5.^{4,10}]octacosane in a Complex with Potassium Thiocyanate at −130 °C

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When free doubly N,N'-bridged bis(1,7-dioxa-4,10-diazacyclododecane)

is contacted with a salt solution containing K^{+} cations and SCN^{-} anions, a complex crystallizes.[1] ^{13}C NMR studies show that the most likely conformation of the complexed ligand, with all nitrogen lone pairs pointing into the cavity, [3 3 3 3],[2] is not retained by the free ligand. An X-ray crystal structure determination of the complex with NaBF$_4$[3] confirms the expected cubic arrangement of the eight donor atoms with identical helicity of the ten ethylene units in each molecule and the quadrangular [3 3 3 3] ring conformation. As predicted by NMR, the ring conformation in the crystals of the free ligand[4] is an entirely different one, the diangular [2 10]. The crystal structure of the dihydrochloride tetrahydrate[4] is disordered with two ring conformations, [3 3 3 3] and [3 9].

[2 10]

[3 9]

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

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

The results for the KSCN complex are now presented.

The crystals belong to the orthorhombic system with space group $P\,b\,c\,a$ and cell dimensions $a=11.834(8)$, $b=12.444(6)$, $c=34.38(2)$ Å, and $Z=8$ ($D_x=1.31$ g cm^{-3}, $D_m=1.26$ g cm^{-3}). With $2\theta_{max}=50°$ and MoKα-radiation 3537 independent reflections were measured on an automatic four-circle diffractometer at $ca.-130$ °C. The crystal quality was miserable, and only 1465 reflections were regarded as observed (using an observed-unobserved cutoff at $2.5\sigma(I)$). No corrections for absorption or secondary extinction were applied (crystal size 0.2×0.3×0.1 mm).

The structure was solved by direct methods[5] and refined by full-matrix least squares technique.[6] (All programs used, except those for phase determination, are included in Ref. 6.) Hydrogen atom positions were calculated. Anisotropic temperature factors were used for non-hydrogen atoms. Weights in least squares were calculated from the standard deviations in intensities 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 relatively high ($R=7.8\%$, $R_w=6.2\%$), probably due to the poor crystal quality. The principal thermal vibration ellipsoids correspond to maximum r.m.s. amplitudes between 0.16 and 0.30 Å. Final fractional coordinates with estimated standard deviations for non-hydrogen atoms are given in Table 1.
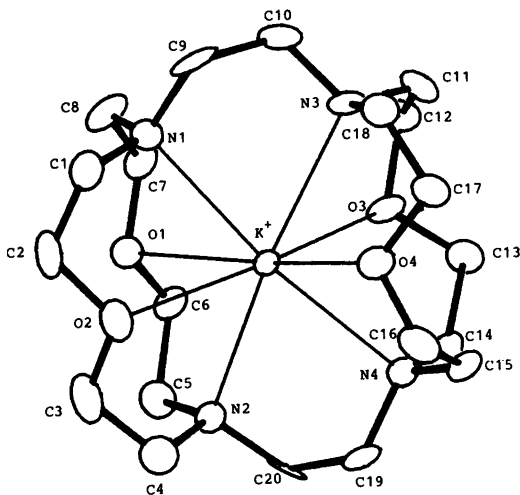

Fig. 1. Schematic drawing showing the numbering of atoms.

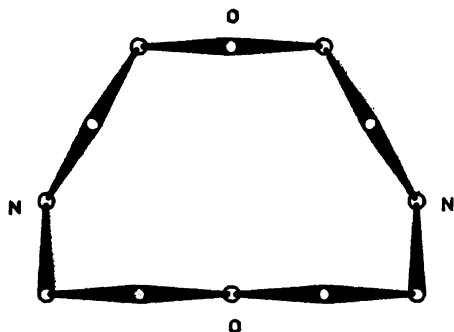*Table 3.* Dihedral angles with estimated standard deviations.

DIHEDRAL ANGLE				(°)
C8 –	O1 –	C7 –	C8	−170.(1)
C7 –	O1 –	C8 –	C5	172.(1)
C2 –	O2 –	C5 –	C4	161.(1)
C5 –	O2 –	C2 –	C1	−169.(1)
C12 –	O5 –	C13 –	C14	175.(1)
C13 –	O5 –	C12 –	C11	−82.(1)
C16 –	O4 –	C17 –	C18	172.(1)
C17 –	O4 –	C16 –	C15	−81.(1)
C1 –	N1 –	C8 –	C7	−117.(1)
C8 –	N1 –	C1 –	C2	84.(1)
C1 –	N1 –	C9 –	C10	159.(1)
C9 –	N1 –	C1 –	C2	−169.(1)
C8 –	N1 –	C9 –	C10	−75.(1)
C9 –	N1 –	C8 –	C7	116.(1)
C4 –	N2 –	C5 –	C8	128.(1)
C5 –	N2 –	C4 –	C5	−81.(1)
C4 –	N2 –	C20 –	C19	−79.(1)
C20 –	N2 –	C4 –	C5	170.(1)
C5 –	N2 –	C20 –	C19	154.(1)
C20 –	N2 –	C5 –	C6	−105.(1)
C10 –	N3 –	C11 –	C12	−81.(1)
C11 –	N3 –	C10 –	C9	168.(1)
C10 –	N3 –	C18 –	C17	165.(1)
C18 –	N3 –	C10 –	C9	−72.(1)
C11 –	N3 –	C18 –	C17	−71.(1)
C18 –	N3 –	C11 –	C12	155.(1)
C14 –	N4 –	C15 –	C16	154.(1)
C15 –	N4 –	C14 –	C15	−72.(1)
C14 –	N4 –	C19 –	C20	−66.(1)
C19 –	N4 –	C14 –	C15	165.(1)
C15 –	N4 –	C19 –	C20	171.(1)
C19 –	N4 –	C15 –	C16	−85.(1)
N1 –	C1 –	C2 –	O2	84.(1)
O2 –	C5 –	C4 –	N2	−64.(1)
N2 –	C5 –	C6 –	O1	−75.(1)
O1 –	C7 –	C8 –	N1	61.(2)
N1 –	C9 –	C10 –	N3	−65.(1)
N3 –	C11 –	C12 –	O5	−62.(1)
O5 –	C13 –	C14 –	N4	−62.(1)
N4 –	C15 –	C16 –	O4	−62.(1)
O4 –	C17 –	C18 –	N3	−60.(1)
N4 –	C19 –	C20 –	N2	−65.(1)

The bond distances and angles of Table 2 do not deviate from normal values within the large estimated limits of error. Fig. 1 is a schematic drawing showing the numbering of atoms.

The torsion angles given in Table 3 show that the conformation of the 12-membered ring to the left (Fig. 1) may be described as the strained biangular [4 8], which was also found in crystals of the complex between CuCl and 1,4,7,10-tetraoxacyclododecane.[7]

Table 4. Coordination distances and angles with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)
K+ – O1	2.84(1)	K+ – O2	2.89(1)
K+ – O5	2.75(1)	K+ – O4	2.58(1)
K+ – N1	2.76(1)	K+ – N2	2.84(1)
K+ – N5	2.84(1)	K+ – N4	2.74(1)

ANGLE	(°)	ANGLE	(°)
O1 – K+ – O2	68.(1)	O1 – K+ – O5	94.(1)
O1 – K+ – O4	171.(1)	O1 – K+ – N1	64.(1)
O1 – K+ – N2	65.(1)	O1 – K+ – N5	114.(1)
O1 – K+ – N4	121.(1)	O2 – K+ – O5	159.(1)
O2 – K+ – O4	107.(1)	O2 – K+ – N1	66.(1)
O2 – K+ – N2	67.(1)	O2 – K+ – N5	129.(1)
O2 – K+ – N4	121.(1)	O5 – K+ – O4	94.(1)
O5 – K+ – N1	111.(1)	O5 – K+ – N2	101.(1)
O5 – K+ – N5	64.(1)	O5 – K+ – N4	94.(1)
O4 – K+ – N1	109.(1)	O4 – K+ – N2	121.(1)
O4 – K+ – N5	65.(1)	O4 – K+ – N4	69.(1)
N1 – K+ – N2	116.(1)	N1 – K+ – N5	89.(1)
N1 – K+ – N4	172.(1)	N2 – K+ – N5	164.(1)
N2 – K+ – N4	69.(1)	N5 – K+ – N4	104.(1)

The other ring has the familiar [3 3 3 3] conformation with approximate C_4 symmetry. Fig. 1 illustrates the eight-coordination of the potassium cation. It should be pointed out that one of its contacts (Table 4) K^+---O4=2.58 Å, is unusually short.

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

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3. Groth, P. *Acta Chem. Scand.* A 35 (1981) 717.
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5. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr.* A 27 (1971) 368.
6. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
7. van Remoortere, F. P., Boer, F. P. and Steiner, E. C. *Acta Crystallogr.* B 31 (1975) 1420.