

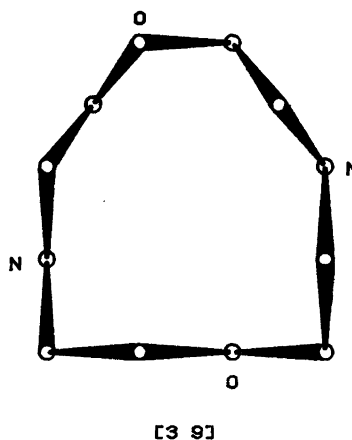
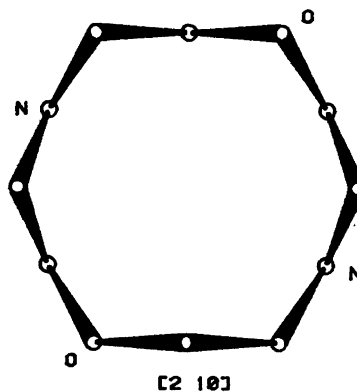
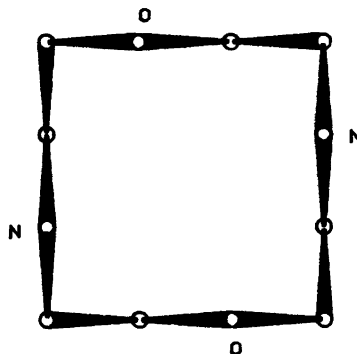
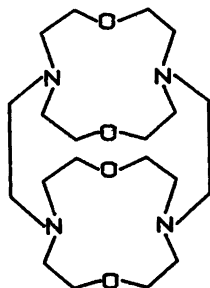
## Short Communication

### The Crystal Conformation of 7,16,21,26-Tetraoxa-1,4,10,13-tetraazatricyclo[11.5.5.5.<sup>4,10</sup>]octacosane in a Complex with Potassium Thiocyanate at $-130\text{ }^{\circ}\text{C}$

P. GROTH

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

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



is contacted with a salt solution containing  $\text{K}^+$  cations and  $\text{SCN}^-$  anions, a complex crystallizes.<sup>1</sup>  $^{13}\text{C}$  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  $\text{NaBF}_4$ <sup>3</sup> 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<sup>4</sup> is an entirely different one, the diangular  $[2\ 10]$ . The crystal structure of the dihydrochloride tetrahydrate<sup>4</sup> is disordered with two ring conformations,  $[3\ 3\ 3\ 3]$  and  $[3\ 9]$ .

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

ATOM	X	Y	Z
K4	.9705( 1)	.1240( 2)	.1250( 1)
S	.4944( 2)	.1294( 4)	.1229( 4)
C	.495( 1)	.1465( 14)	.1717( 4)
N	.493( 1)	.1421( 12)	.2053( 3)
O1	1.0659( 6)	.0518( 6)	.0665( 2)
O2	.8677( 7)	.1924( 7)	.0571( 2)
O5	1.1059( 6)	.0040( 6)	.1705( 2)
O4	.8945( 7)	.2345( 6)	.1799( 2)
N1	1.0965( 6)	.2662( 6)	.0786( 3)
N2	.9463( 7)	-.0574( 8)	.0949( 2)
N5	1.1270( 8)	.2566( 8)	.1669( 3)
N4	.8609( 6)	-.0046( 7)	.1754( 3)
C1	1.0194( 10)	.3211( 10)	.0542( 3)
C2	.9415( 12)	.2535( 11)	.0545( 3)
C3	.8062( 10)	.1423( 12)	.0579( 3)
C4	.7595( 10)	.0267( 10)	.0949( 3)
C5	.9165( 10)	-.0943( 9)	.0576( 3)
C6	1.0455( 11)	-.0699( 10)	.0659( 3)
C7	1.1728( 11)	.0799( 10)	.0366( 3)
C8	1.1602( 10)	.1954( 11)	.0562( 4)
C9	1.1554( 10)	.3553( 10)	.1057( 3)
C10	1.2065( 9)	.2652( 10)	.1422( 3)
C11	1.1620( 10)	.1676( 11)	.1360( 3)
C12	1.2091( 10)	.0594( 10)	.1619( 3)
C13	1.0505( 10)	-.0477( 10)	.2029( 3)
C14	.9571( 10)	-.0947( 9)	.1667( 3)
C15	.8197( 10)	.0900( 10)	.2081( 3)
C16	.7692( 11)	.1740( 11)	.1960( 3)
C17	.5646( 11)	.2760( 10)	.2069( 3)
C18	1.0597( 10)	.3206( 10)	.1696( 3)
C19	.7676( 9)	-.0506( 10)	.1527( 3)
C20	.7963( 9)	-.1053( 10)	.1151( 3)

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

DISTANCE (Å)		DISTANCE (Å)	
S - C	(1.69( 2))	S - C	(1.69( 2))
O1 - C8	1.42( 1)	O1 - C8	1.42( 1)
O2 - C2	1.47( 1)	O2 - C2	1.47( 1)
O5 - C12	1.46( 1)	O5 - C12	1.46( 1)
O4 - C18	1.45( 1)	O4 - C18	1.45( 1)
N1 - C4	1.45( 2)	N1 - C4	1.45( 2)
N1 - C9	1.46( 2)	N1 - C9	1.46( 2)
N2 - C5	1.45( 1)	N2 - C5	1.45( 1)
N5 - C10	1.46( 2)	N5 - C10	1.46( 2)
N5 - C18	1.50( 2)	N5 - C18	1.50( 2)
N4 - C15	1.47( 1)	N4 - C15	1.47( 1)
C1 - C2	1.47( 2)	C1 - C2	1.47( 2)
C5 - C8	1.58( 2)	C5 - C8	1.58( 2)
C9 - C10	1.54( 2)	C9 - C10	1.54( 2)
C13 - C14	1.52( 2)	C13 - C14	1.52( 2)
C17 - C18	1.49( 2)	C17 - C18	1.49( 2)
ANGLE (°)			
S - C - N	179.( 2)	S - C - N	179.( 2)
C2 - O2 - C5	112.( 1)	C2 - O2 - C5	112.( 1)
C16 - O4 - C17	114.( 1)	C16 - O4 - C17	114.( 1)
C1 - N1 - C9	111.( 1)	C1 - N1 - C9	111.( 1)
C4 - N2 - C5	112.( 1)	C4 - N2 - C5	112.( 1)
C5 - N2 - C20	115.( 1)	C5 - N2 - C20	115.( 1)
C10 - N5 - C18	111.( 1)	C10 - N5 - C18	111.( 1)
C14 - N4 - C15	110.( 1)	C14 - N4 - C15	110.( 1)
C15 - N4 - C19	112.( 1)	C15 - N4 - C19	112.( 1)
O2 - C2 - C1	110.( 1)	O2 - C2 - C1	110.( 1)
N2 - C4 - C5	115.( 1)	N2 - C4 - C5	115.( 1)
O1 - C6 - C5	106.( 1)	O1 - C6 - C5	106.( 1)
N1 - C8 - C7	115.( 1)	N1 - C8 - C7	115.( 1)
N5 - C10 - C9	114.( 1)	N5 - C10 - C9	114.( 1)
O5 - C12 - C11	110.( 1)	O5 - C12 - C11	110.( 1)
N4 - C14 - C15	112.( 1)	N4 - C14 - C15	112.( 1)
O4 - C18 - C15	113.( 1)	O4 - C18 - C15	113.( 1)
N5 - C18 - C17	114.( 1)	N5 - C18 - C17	114.( 1)
N2 - C20 - C19	116.( 1)	N2 - C20 - C19	116.( 1)
ANGLE (°)			
C6 - O1 - C7	114.( 1)	C6 - O1 - C7	114.( 1)
C12 - O5 - C13	112.( 1)	C12 - O5 - C13	112.( 1)
C1 - N1 - C8	114.( 1)	C1 - N1 - C8	114.( 1)
C8 - N1 - C9	112.( 1)	C8 - N1 - C9	112.( 1)
C4 - N2 - C20	111.( 1)	C4 - N2 - C20	111.( 1)
C10 - N5 - C11	112.( 1)	C10 - N5 - C11	112.( 1)
C14 - N4 - C18	109.( 1)	C14 - N4 - C18	109.( 1)
N1 - C1 - C2	115.( 1)	N1 - C1 - C2	115.( 1)
O2 - C5 - C4	113.( 1)	O2 - C5 - C4	113.( 1)
N2 - C5 - C6	110.( 1)	N2 - C5 - C6	110.( 1)
O1 - C7 - C8	112.( 1)	O1 - C7 - C8	112.( 1)
N1 - C9 - C10	117.( 1)	N1 - C9 - C10	117.( 1)
N5 - C11 - C12	112.( 1)	N5 - C11 - C12	112.( 1)
O5 - C13 - C14	109.( 1)	O5 - C13 - C14	109.( 1)
N4 - C15 - C18	111.( 1)	N4 - C15 - C18	111.( 1)
O4 - C17 - C18	108.( 1)	O4 - C17 - C18	108.( 1)
N4 - C19 - C20	118.( 1)	N4 - C19 - C20	118.( 1)

The results for the KSCN complex are now presented.

The crystals belong to the orthorhombic system with space group  $Pbca$  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<sup>-3</sup>,  $D_m=1.26$  g cm<sup>-3</sup>). With  $2\theta_{\max}=50^\circ$  and MoK $\alpha$ -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  $0.2\times 0.3\times 0.1$  mm).

The structure was solved by direct methods<sup>5</sup> and refined by full-matrix least squares technique.<sup>6</sup> (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.

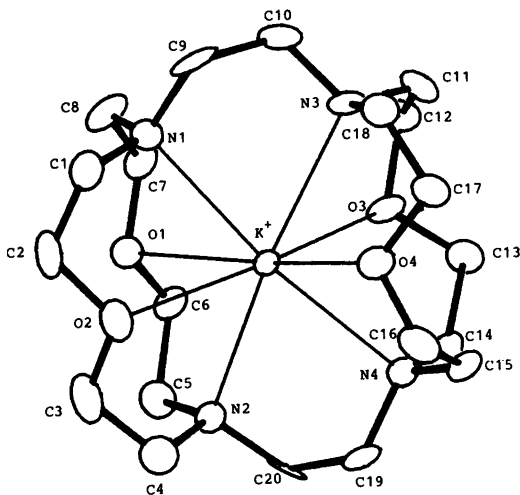


Fig. 1. Schematic drawing showing the numbering of atoms.

Table 3. Dihedral angles with estimated standard deviations.

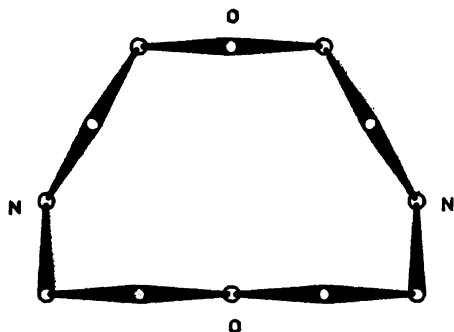
DIHEDRAL ANGLE		(°)
C8 - O1 - C7 - C6		-170.(1)
C7 - O1 - C6 - C5		172.(1)
C2 - O2 - C3 - C4		161.(1)
C3 - O2 - C2 - C1		-169.(1)
C12 - O5 - C13 - C14		173.(1)
C13 - O5 - C12 - C11		-82.(1)
C16 - O4 - C17 - C18		172.(1)
C17 - O4 - C16 - C15		-81.(1)
C1 - N1 - C8 - C7		-117.(1)
C8 - N1 - C1 - C2		84.(1)
C1 - N1 - C9 - C10		159.(1)
C9 - N1 - C1 - C2		-168.(1)
C8 - N1 - C9 - C10		-73.(1)
C9 - N1 - C8 - C7		116.(1)
C4 - N2 - C5 - C6		128.(1)
C5 - N2 - C4 - C3		-81.(1)
C4 - N2 - C20 - C19		-79.(1)
C20 - N2 - C4 - C3		170.(1)
C5 - N2 - C20 - C19		154.(1)
C20 - N2 - C5 - C6		-105.(1)
C10 - N5 - C11 - C12		-81.(1)
C11 - N5 - C10 - C9		168.(1)
C10 - N5 - C18 - C17		165.(1)
C18 - N5 - C10 - C9		-72.(1)
C11 - N5 - C18 - C17		-71.(1)
C18 - N5 - C11 - C12		155.(1)
C14 - N4 - C15 - C16		154.(1)
C15 - N4 - C14 - C13		-72.(1)
C14 - N4 - C19 - C20		-66.(1)
C19 - N4 - C14 - C13		163.(1)
C15 - N4 - C19 - C20		171.(1)
C19 - N4 - C15 - C16		-83.(1)
N1 - C1 - C2 - O2		84.(1)
O2 - C5 - C4 - N2		-64.(1)
N2 - C5 - C6 - O1		-73.(1)
O1 - C7 - C8 - N1		64.(2)
N1 - C9 - C10 - N5		-65.(1)
N5 - 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		-63.(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 the crystals of the complex between CuCl and 1,4,7,10-tetraoxacyclododecane.<sup>7</sup>

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

DISTANCE		(Å)	DISTANCE		(Å)
K <sup>+</sup>	O1	2.84(1)	K <sup>+</sup>	O2	2.83(1)
K <sup>+</sup>	O5	2.75(1)	K <sup>+</sup>	O4	2.58(1)
K <sup>+</sup>	N1	2.78(1)	K <sup>+</sup>	N2	2.81(1)
K <sup>+</sup>	N5	2.81(1)	K <sup>+</sup>	N4	2.74(1)
ANGLE		(°)	ANGLE		(°)
O1	- K <sup>+</sup> - O2	98.(1)	O1	- K <sup>+</sup> - O5	94.(1)
O1	- K <sup>+</sup> - O4	171.(1)	O1	- K <sup>+</sup> - N1	84.(1)
O1	- K <sup>+</sup> - N2	98.(1)	O1	- K <sup>+</sup> - N5	114.(1)
O1	- K <sup>+</sup> - N4	121.(1)	O2	- K <sup>+</sup> - O5	189.(1)
O2	- K <sup>+</sup> - O4	107.(1)	O2	- K <sup>+</sup> - N1	88.(1)
O2	- K <sup>+</sup> - N2	87.(1)	O2	- K <sup>+</sup> - N5	128.(1)
O2	- K <sup>+</sup> - N4	121.(1)	O5	- K <sup>+</sup> - O4	94.(1)
O5	- K <sup>+</sup> - N1	111.(1)	O5	- K <sup>+</sup> - N2	101.(1)
O5	- K <sup>+</sup> - N5	84.(1)	O5	- K <sup>+</sup> - N4	84.(1)
O4	- K <sup>+</sup> - N1	108.(1)	O4	- K <sup>+</sup> - N2	121.(1)
O4	- K <sup>+</sup> - N5	85.(1)	O4	- K <sup>+</sup> - N4	88.(1)
N1	- K <sup>+</sup> - N2	118.(1)	N1	- K <sup>+</sup> - N5	88.(1)
N1	- K <sup>+</sup> - N4	172.(1)	N2	- K <sup>+</sup> - N5	104.(1)
N2	- K <sup>+</sup> - N4	88.(1)	N5	- K <sup>+</sup> - 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)  $K^+ \cdots O4 = 2.58 \text{ \AA}$ , 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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