

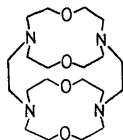
Short Communications

On the Crystal Structure of 7,16,21,26-Tetraoxa-1,4,10,13-tetraazatricyclo[11.5.5.5^{4,10}]octacosane in a Complex with Sodium Tetrafluoroborate at -150°C

P. GROTH

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

The syntheses of organic ligands consisting of two mono-aza-12-crown-4 rings linked together by a single alkane bridge between nitrogen bridgeheads,¹ and by two such bridges,² have recently been carried out. When free doubly *N,N'*-bridged bis(1,7-dioxo-4,10-diazacyclododecane) is contacted with a salt



solution containing Li, Na and K cations and Br and BF_4 anions, a complex with NaBF_4 crystallizes. ^{13}C NMR studies² show that the most likely conformation of the complexed ligand, with all nitrogen lone pairs pointing into the cavity, is not retained by the free ligand. A crystal structure investigation of the complex $\text{C}_{20}\text{H}_{40}\text{O}_4\text{N}_4 \cdot \text{NaBF}_4$ has been undertaken in order to obtain conformational evidence for this tricyclic molecule. The crystals belong to the monoclinic system with space group $P2_1/n$, cell dimensions $a=9.788(6)$ Å, $b=9.715(7)$ Å, $c=13.380(6)$ Å, $\beta=104.79(4)^\circ$, and $Z=2$ ($D_x=1.37$ g/cm³, $D_m=1.34$ g/cm³). With $2\theta_{\text{max}}=50^\circ$, $\text{MoK}\alpha$ -radiation, and an observed-unobserved cutoff at $2\sigma(I)$, 1106 independent reflections were recorded as observed on an automatic four-circle diffractometer at -150°C . No corrections for absorption or secondary extinction were applied (crystal size $0.2 \times 0.3 \times 0.3$ mm).

There can be no real center of symmetry with respect to carbon atoms in a given complexed

Table 1. Final fractional coordinates with estimated standard deviations. Hm,1 and Hm,2 are bonded to Cm.

ATOM	X	Y	Z
F1	.0866(8)	.0328(9)	-.0642(5)
F2	-.0367(8)	.1224(8)	-.0497(8)
F3	-.1424(6)	-.0228(7)	-.0679(4)
F4	.0121(8)	-.1042(10)	-.0620(7)
O1	.4643(3)	.6849(4)	1.1175(2)
O2	.2542(3)	.4672(3)	.8906(2)
N1	.3288(4)	.4198(5)	1.1125(3)
N2	.4034(4)	.7274(4)	.8964(3)
C1	.3403(41)	.5035(38)	1.1897(27)
C2	.3534(19)	.6552(21)	1.1652(12)
C3	.4668(16)	.8074(15)	1.0729(12)
C4	.3678(25)	.8190(44)	.9720(34)
C5	.2759(25)	.6863(25)	.8118(16)
C6	.1808(19)	.5964(22)	.8482(15)
C7	.1752(14)	.3747(14)	.9279(10)
C8	.1835(36)	.4199(21)	1.0371(30)
C9	.3619(24)	.2725(31)	1.1337(15)
C10	.5224(34)	.2486(37)	1.1832(29)
C11	.5822(27)	.1553(38)	1.0339(36)
C12	.6241(15)	.1916(14)	.9319(15)
C13	.5697(17)	.3557(22)	.7935(13)
C14	.6467(36)	.4502(37)	.8206(32)
C15	.7998(35)	.6341(18)	.9521(27)
C16	.8494(12)	.5434(14)	1.0480(12)
C17	.7803(19)	.4400(20)	1.1846(15)
C18	.7509(30)	.2894(25)	1.1502(17)
C19	.5979(25)	.6816(22)	.8088(13)
C20	.5211(32)	.7775(17)	.8559(22)
H	0.0000(0)	0.0000(0)	0.0000(0)
H01	.5000(0)	.5000(0)	1.0000(0)
H11	.425	.475	1.245
H12	.254	.490	1.217
H21	.370	.709	1.231
H22	.262	.686	1.117
H31	.564	.824	1.064
H32	.443	.880	1.119
H41	.369	.917	.949
H42	.272	.797	.980
H51	.309	.639	.755
H52	.224	.773	.782
H61	.098	.572	.789
H62	.146	.643	.903
H71	.215	.280	.926
H72	.075	.376	.884
H81	.121	.356	1.063
H82	.144	.515	1.032
H91	.298	.219	1.077
H92	.335	.251	1.201
H101	.493	.150	1.172
H102	.595	.261	1.248
H111	.483	.124	1.018
H112	.646	.081	1.072
H121	.503	.110	.883
H122	.727	.214	.946
H131	.438	.405	.748
H132	.593	.272	.757
H141	.718	.481	.757

Table 1. Continued.

h142	.779	.395	.864
h151	.784	.730	.971
h152	.474	.633	.911
h161	.938	.585	1.092
h162	.869	.449	1.025
h171	.724	.461	1.236
h172	.483	.449	1.218
h181	.782	.228	1.212
h182	.805	.267	1.099
h191	.668	.751	.802
h192	.567	.627	.742
h201	.540	.873	.883
h202	.481	.781	.778

ligand, only with respect to the heteroatoms and to the middle of each C—C bond. Since these bonds are not eclipsed, the —CH₂—CH₂— units have chirality, and this must be of the same sign for all

four units of a given ring. For simple steric reasons also the two bridge units are forced to take the same chirality which in turn is imposed on the other ring. A center of symmetry would have inverted the chirality of diametrically placed units. The fact that there are only two formula units in the cell therefore demands disorder of the tricyclic ligand (and the tetrafluoro borate anion as well).

The structure was solved by direct methods³ and refined by full-matrix least squares technique.^{4,*} The weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02 C_N)^2]^{1/2}$, where C_T is the total number of counts and C_N the net count.

*All programs used (except those for phase determination) are included in this reference.

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

DISTANCE		(Å)	DISTANCE		(Å)
N1 - C1	1.30	(3)	C1 - C2	1.52	(4)
O1 - C2	1.42	(2)	O1 - C3	1.33	(2)
C3 - C4	1.45	(5)	N2 - C4	1.45	(4)
N2 - C5	1.51	(2)	C5 - C6	1.45	(4)
O2 - C6	1.48	(2)	O2 - C7	1.36	(1)
C7 - C8	1.51	(4)	N1 - C8	1.52	(4)
N1 - C9	1.48	(3)	C9 - C10	1.56	(4)
C10 - N2	1.45	(4)	N2 - C11	1.46	(4)
C11 - C12	1.56	(5)	C12 - O1	1.53	(2)
O1 - C13	1.37	(2)	C13 - C14	1.51	(4)
C14 - N1	1.60	(3)	N1 - C15	1.43	(3)
C15 - C16	1.53	(3)	C16 - O2	1.46	(1)
O2 - C17	1.33	(2)	C17 - C18	1.54	(3)
C18 - N2	1.49	(3)	N1 - C19	1.49	(2)
C19 - C20	1.44	(4)	N2 - C20	1.48	(3)
NA+ - O1	2.47	(1)	NA+ - O2	2.50	(1)
NA+ - N1	2.64	(1)	NA+ - N2	2.65	(1)
B - F1	1.39	(1)	B - F2	1.37	(1)
B - F3	1.47	(1)	B - F4	1.33	(1)

ANGLE		(°)	ANGLE		(°)
C1 - N1 - C8	114.	(2)	N1 - C1 - C2	116.	(3)
O1 - C2 - C1	114.	(2)	C2 - O1 - C3	119.	(1)
O1 - C3 - C4	114.	(2)	N2 - C4 - C3	112.	(2)
C4 - N2 - C5	113.	(1)	N2 - C5 - C6	113.	(2)
O2 - C6 - C5	110.	(1)	C6 - O2 - C7	116.	(1)
O2 - C7 - C8	106.	(1)	N1 - C8 - C7	117.	(2)
C1 - N1 - C9	119.	(2)	C8 - N1 - C9	105.	(1)
N1 - C9 - C10	112.	(2)	C9 - C10 - N2	108.	(2)
C10 - N2 - C11	111.	(2)	C11 - N2 - C18	106.	(1)
C12 - C11 - N2	112.	(2)	C11 - C12 - O1	108.	(2)
C12 - O1 - C13	111.	(1)	C14 - C13 - O1	109.	(2)
C13 - C14 - N1	112.	(2)	C14 - N1 - C15	113.	(2)
C15 - C16 - N1	110.	(2)	C15 - C16 - O2	113.	(2)
C16 - O2 - C17	113.	(1)	C18 - C17 - O2	115.	(2)
C17 - C18 - N2	109.	(1)	C10 - N2 - C18	111.	(2)
C18 - N1 - C19	112.	(1)	C14 - N1 - C19	104.	(2)
C20 - C19 - N1	109.	(2)	N2 - C20 - C19	119.	(2)
C4 - N2 - C20	114.	(1)	C5 - N2 - C20	113.	(1)
F1 - B - F2	112.	(1)	F1 - B - F3	106.	(1)
F1 - B - F4	112.	(1)	F2 - B - F3	105.	(1)
F2 - B - F4	114.	(1)	F3 - B - F4	106.	(1)

As to be expected, the sodium and boron atoms are situated at centres of inversion. The four fluor atoms were given multiplicities 0.5 in order to satisfy the symmetry requirements. Anisotropic temperature factors were introduced for F, C, N and C atoms. Refinement converged at $R=12.2\%$. The principal axes of the thermal vibration ellipsoids for the carbon atoms corresponded to maximum r.m.s. amplitudes between 0.4 and 0.6 Å, while those of the other atoms were normal. Positions of "half-carbon atoms" were calculated from the differences between maximum and minimum principal axes of the thermal vibrational ellipsoids.⁵ Corresponding "half-hydrogen" atom positions were calculated and included in the structure factor calculations, but not refined. The final R -value was 7.1% ($R_w=5.1\%$) for 1106 observed reflections. The maximum r.m.s. anisotropic thermal vibrational amplitudes arrived at range from 0.25 to 0.27 Å for the oxygen and nitrogen atoms, confirming that these atoms are non-participant in the disorder phenomena. For the half-carbons of the 12-membered rings the corresponding range is 0.25–0.34 Å. In spite of the relatively poor crystal quality, these values seem to justify the conclusion that the bis(1,7-dioxo-4,10-diazacyclododecane) rings occur in equal amounts as two enantiomorphous forms. The fact that the four bridge half-atoms have amplitudes between 0.35 and 0.52 Å might suggest a more complicated type

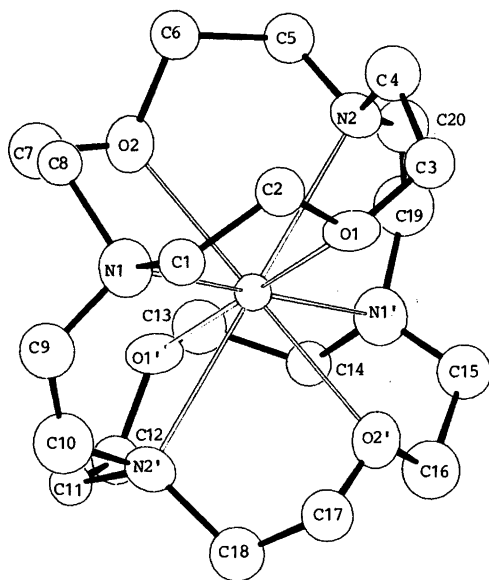


Fig. 1. Schematic drawing of the complex. For clarity, only one of the enantiomers is drawn.

of disorder for the tricyclic ligand as a whole, but this cannot be stated with confidence.

Final fractional coordinates with estimated standard deviations are given in Table 1. Bond distances and angles are listed in Table 2, while torsional angles may be found in Table 3.

Within the large limits of error bond distances and angles may be regarded as normal.

The torsional angles of Table 3 correspond to the quadrangular conformation for the bis(1,7-dioxo-4,10-diazacyclododecane) ring with approximate C_4 symmetry.

Fig. 1 is a schematic drawing showing the conformation of the tricyclic ligand with the expected cubic arrangement of the eight donor atoms. For clarity, only one of the enantiomers is drawn.

Lists of thermal parameters and observed and calculated structure factors are available from the author.

Table 3. Dihedral angles with estimated standard deviations.

DIHEDRAL ANGLE	(°)	
C8 - N1 - C1 - C2	-76. (3)	
N1 - C1 - C2 - O1	-54. (4)	
C3 - O1 - C2 - C1	166. (2)	
C4 - C3 - O1 - C2	-78. (2)	
N2 - C4 - C3 - O1	-66. (3)	
C5 - N2 - C4 - C3	153. (2)	
C6 - C5 - N2 - C4	-69. (2)	ring
N2 - C5 - C6 - O2	-61. (2)	
C7 - O2 - C6 - C5	180. (1)	
C8 - C7 - O2 - C6	-84. (2)	
N1 - C8 - C7 - O2	-62. (2)	
C7 - C8 - N1 - C1	156. (2)	
C9 - N1 - C1 - C2	160. (2)	
C9 - N1 - C8 - C7	-73. (2)	
C10 - C9 - N1 - C1	-68. (3)	
C10 - C9 - N1 - C8	163. (3)	
N1 - C9 - C10 - N2	-71. (3)	bridge
C9 - C10 - N2 - C11	-78. (3)	
C9 - C10 - N2 - C18	165. (2)	
C10 - N2 - C11 - C12	165. (2)	
C17 - C18 - N2 - C10	-84. (2)	
C18 - N2 - C11 - C12	-75. (3)	
N2 - C11 - C12 - O1	-55. (2)	
C11 - C12 - O1 - C13	178. (2)	
C12 - O1 - C13 - C14	-84. (2)	
O1 - C13 - C14 - N1	-56. (3)	
C13 - C14 - N1 - C15	153. (2)	ring
C16 - C15 - N1 - C14	-78. (3)	
N1 - C15 - C16 - O2	-59. (2)	
C15 - C16 - O2 - C17	171. (1)	
C16 - O2 - C17 - C18	-79. (2)	
O2 - C17 - C18 - N2	-61. (2)	
C17 - C18 - N2 - C11	155. (2)	
C19 - N1 - C15 - C16	165. (2)	
C19 - N1 - C14 - C13	-85. (3)	
C20 - C19 - N1 - C15	-80. (3)	
C20 - C19 - N1 - C14	158. (2)	
N2 - C20 - C19 - N1	-64. (3)	bridge
C20 - N2 - C4 - C3	-78. (3)	
C20 - N2 - C5 - C6	161. (1)	
C19 - C20 - N2 - C4	160. (3)	
C19 - C20 - N2 - C5	-71. (3)	

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