Short Communications

The Crystal Conformation of 1,10-Dimethyl-7,16,21,26-Tetra-oxa-1,4,10,13-Tetraazatricyclo-[11.5.5.5.^{4,10}]octacosane Diiodide Hemihydrochloride Hemihydrate at -130 °C

P. GROTH

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

The crystal structures of the free doubly N, N'-bridged bis(1,7-dioxa-4,10-diazacyclododecane) and its dihydrochloride dihydrate have recently

been determined.¹ The free ligand was treated with methyl iodide in order to explore contingent effects on the ring conformation caused by methylation. As no definite conclusion on this point could be reached spectroscopically, an X-ray crystal structure analysis was undertaken. This revealed that the reaction product was contaminated with hydrochloride and had taken up water. The results of the analysis are now reported.

The crystals of $C_{22}H_{44}N_4O_4^{2+} \cdot 2I^- \cdot \frac{1}{2}HCl \cdot \frac{1}{2}H_2O$ belong to the monoclinic system with space group Cc, cell dimensions a=21.656(7), b=8.410(4), c=21.078(7) Å, $\beta=128.27(2)^\circ$, and Z=4 ($D_x=1.56$ g cm⁻³, $D_m=1.55$ g cm⁻³). With $2\theta_{max}=50^\circ$ and MoK_a -radiation 3778 independent reflections were measured on an automatic four-circle diffractometer at ca. -130 °C. Using an observed–unobserved cutoff at $2.5\sigma(I)$, 2261

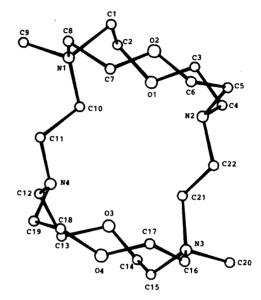


Fig. 1. Schematic drawing showing the numbering of atoms.

reflections were recorded as observed. The intensity data were corrected for absorption $[\mu=2.19~\text{mm}^{-1},\text{ crystal size }(0.3\times0.2\times0.1)\text{mm}]$. However, for unknown reasons the final R-values were about 1% higher than those arrived at when refining with uncorrected intensities, and therefore the latter were used.

The structure was solved by direct methods² and refined by full-matrix least squares technique.³ All programs used (except those for phase determination) are included in Ref. 3]. Methyl hydrogen atoms were localized in a difference Fourier map. A small peak (about 0.9 Å from N) was taken as the hydrochloride "half-hydrogen". Peaks corresponding to water half-hydrogens did not show up. Other H-atom positions were calculated. These atoms were included in structure factor calculations, but not refined. Anisotropic temperature factors were introduced for iodine and chlorine, while other non-hydrogen atoms were refined isotropically. Weights in least squares were calculated from the

1.54(2) 1.52(3) 1.52(3) 1.50(2) 1.54(2) 1.54(2) 1.54(2) 1.54(2) 1.54(2) 1.54(2)

Table 2. Bond distances and angles with estimated standard deviations. Table 1. Final fractional coordinates with estimated standard deviations for non-hydrogen

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8 8		Fí	(8194(48)	_ ,	(L)692.	N2 - C22 4.	1.48(2)	NS - C45	-
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						NS - C24 - C22	115.0 1)	N2 - C22 - C24	

116.(1) 109.(1) 107.(2) 109.(1) 118.(2)

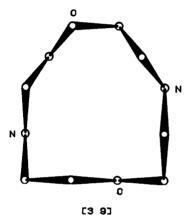
110.(1)

1.55(2) 1.40(5) 1.45(2)

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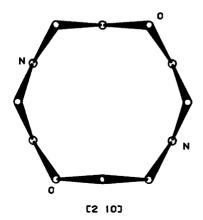
140.0 119.6

standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02 \ C_N)^2]^2$, where C_T is the total number of counts and C_N the net count. The final R-value was 3.5 % $(R_w = 4.3 \ \%)$ for 2261 observed reflections. Final fractional coordinates for non-hydrogen atoms are given in Table 1. Within the large estimated limits of error (due to the presence of iodine), the bond distances and angles of Table 2 are normal. Fig. 1 is a schematic drawing, showing the numbering of atoms. The torsional angles of Table 3 show that both 12-membered rings adopt the [3 9] conformation 4 which is different from the [2 10] conformation of the free ligand, 1 but has been observed earlier. 1,5,6



It may be pointed out that the torsion angles N1-C10-C11-N4 and N2-C22-C21-N3 are anti in the present compound, while corresponding dihedral angles are gauche in the four previously reported structures. 1,5,6

Although the H-atoms of the half-water molecule remain undetermined, it may be stated that



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Table 3. Dihedral angles with estimated standard deviations.

Di	HEDRAL ANGLE	(*)
C2 -	D1 - C3 - C4	149.(2)
C5 -	D1 - C2 - C1	-79.(2)
C6 -	02 - C7 - C8	-160.(1)
C7 -	02 - C6 - C5	(58.(1)
C15 -	05 - C14 - C15	-72.(2)
C14 ~	05 - C15 - C12	454.(1)
C17 ~	04 - C18 - C19	140.(1)
C18 -	04 - C17 - C16	-161.(2)
C1 -	N1 - C8 - C7	-82.(2)
CB -	N1 - C1 - C2	160.(2)
C9 -	N1 - C1 - C2	-88.(2)
C1 -	N1 - C10 - C11	-175.(1)
C10 -	N1 - C1 - C2	42.(2)
C9 -	N1 - C8 - C7	f62.(2)
C8 -	N1 - C10 - C11	67.(2)
C18 -	N1 - C8 - C7	59.(2)
C9 -	N4 C40 - C14	-49.(2)
C4 -	N2 - C5 - C6	154.(1)
C5 -	N2 - C4 - C5	-87.(2)
C4 -	N2 - C22 - C21	-82.(2)
C22 -	N2 - C4 - C5	156.(1)
C5 -	N2 - C22 - C21	(58.(1)
C22 -	N2 - C5 - C6	-88.(1)
C15 -	NS - C16 - C17	-76.(2)
C16 -	NS - C15 - C14	172.(1)
C2G -	NS - C15 - C14	-69.(2)
C15 -	NS - C21 - C22	475.(1)
C21 -	NS - C15 - C14	44.(2)
C20 -	NS - C16 - C17	(68.(2)
C18 -	NS - C21 - C22	55.(2)
C21 -	NS - C16 - C17	47.(2)
C20 -	NS - C21 - C22	-74.(2)
C11 -	N4 - C12 - C15	158.(1)
C12 -	N4 - C11 - C10	-80.(2)
C11 -	N4 - C19 - C18	-84.(2)
C19 -	N4 - C11 - C10	155.(1)
C12 -	N4 - C19 - C18	149.(1)
C (9 -	N4 - C12 - C13	-75.(2)
N1 -	C1 - C2 - O1	-77.(2)
01 -	C5 - C4 - N2	-65.(2)
N2 -	C5 - C6 - O2	-75.(2)
02 ~	C7 - C8 - N1	67.(2)
NI -	C10 - C11 - N4	(75.(1)
N4 -	C12 - C15 - 05	-75.(2)
05 ~	C14 - C15 - N5	-86.(2)
N5 -	C16 - C17 - 04	59.(2)
04 -	C18 - C19 - N1	-75.(2)
N5 -	C21 - C22 - N2	-175.(1)

it is bonded to O1 and O3. (OW···O1=2.81 Å, OW···O3=2.88 Å, O1···OW···O3=104°). The presence of an intra-molecular hydrogen bond between N2 and O1 is also probable (N2···O3=2.85 Å, N2-HCl=0.93 Å, O3···HCl=2.25 Å, N2-HCl···O1=120°).

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

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- 1. Groth, P. Acta Chem. Scand. B 38(1984). In
- press.

 2. Germain, G., Main, P. and Woolfson, M. M. Acta Crystallogr. A 27 (1971) 368.

 3. Groth, P. Acta Chem. Scand. 27 (1973) 1837.

- Dale, J. Acta Chem. Scand. 27 (1973) 1115.
 Groth, P. Acta Chem. Scand. A 38(1984) 183.
 Groth, P. Acta Chem. Scand. A 38 (1984). In

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