

Crystal Structure Analysis of 1,4,7,10-Tetra-(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane Hydrate at -150°C

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^{13}C NMR spectroscopy¹ indicates conformational differences of 1,4,7,10-tetra-(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane as a hydrate and in its complexes with Li^+ , Na^+ and K^+ . Some single crystal X-ray analyses have been carried out in order to seek more precise information about these differences. The results for the hydrate are now reported.

The crystals of $(\text{C}_{16}\text{H}_{36}\text{O}_4\text{N}_4) \cdot \text{H}_2\text{O}$ are triclinic with space group $P1$ and cell dimensions (for Dirichlet's reduced cell) $a = 7.022(2)$, $b = 9.680(3)$, $c = 14.709(5)$ Å, $\alpha = 97.38(2)$, $\beta = 92.10(3)$, $\gamma = 96.99(2)^{\circ}$. There are two formula units in the cell ($D_x = 1.24$ g cm^{-3} , $D_m = 1.22$ g cm^{-3}), 2221 observed reflections were recorded on an automatic four-circle diffractometer at *ca.* -150°C ($2\theta_{\text{max}} = 50^{\circ}$, MoK α -radiation, ω -scan). No corrections for absorption or secondary extinction were applied (crystal size $0.2 \times 0.3 \times 0.3$ mm).

The structure was solved by direct methods² and refined by full-matrix least-squares technique.^{3,*}

Methylene hydrogen atom positions were calculated, the others were localized in a difference Fourier map. Anisotropic temperature factors were introduced for O, N and C atoms. Weights in least squares were 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. The form factors used were those of Hanson *et al.*⁴ except for hydrogen.⁵ The final R -value was 5.6% (weighted value 4.2%) for 2221 observed reflections.

Final fractional coordinates with estimated standard deviations may be found in Table 1. Bond distances and angles and dihedral angles with standard deviations (calculated from the correlation matrix of the final least squares refinement cycle) are listed in Table 2. Fig. 1 is a schematic drawing of the ring showing the numbering of atoms. Bond distances and angles have normal values within estimated limits of error. The torsional angles of Table 2 show that the 12-membered ring has the

Table 1. Final fractional coordinates with estimated standard deviations. HmN is bonded to Cm, HOM to Om, and HWm to OW.

ATOM	X	Y	Z
OW	.9175(3)	.7650(2)	.7198(1)
O1	.9469(3)	.2979(2)	.6176(1)
O2	.9180(3)	.7988(2)	.5414(1)
O3	1.1405(3)	1.2367(2)	.7786(1)
O4	1.1733(3)	.7504(2)	.8612(1)
N1	.6148(3)	.5413(2)	.7145(1)
N2	.5400(3)	.8420(2)	.6326(1)
N5	.7182(3)	.9747(2)	.8126(1)
N4	.7636(3)	.7026(2)	.9029(1)
C1	.4742(4)	.5534(3)	.6391(2)
C2	.3947(4)	.6946(3)	.6452(2)
C3	.4870(4)	.9466(3)	.6747(2)
C4	.5154(4)	.9720(3)	.7790(2)
C5	.7280(4)	.9570(3)	.9110(2)
C6	.6458(4)	.8429(3)	.9339(2)
C7	.6523(4)	.5627(3)	.8871(2)
C8	.5170(4)	.5363(3)	.8018(2)
C9	.7061(4)	.4126(3)	.6921(2)
C10	.8594(4)	.4240(3)	.6225(2)
C11	.5745(4)	.8457(3)	.5352(2)
C12	.7735(4)	.8841(3)	.5201(2)
C13	.8304(4)	1.1093(3)	.8000(2)
C14	1.0428(4)	1.1023(3)	.7897(2)
C15	.9275(4)	.7029(3)	.9681(2)
C16	1.0991(4)	.6546(3)	.9205(2)
H11	.3601(4)	.474(3)	.638(2)
H12	.548(4)	.540(3)	.579(2)
H21	.340(4)	.713(3)	.706(2)
H22	.277(4)	.681(3)	.597(2)
H31	.343(4)	.956(3)	.661(2)
H32	.566(4)	1.023(3)	.646(2)
H41	.434(4)	.894(3)	.806(2)
H42	.474(4)	1.067(3)	.800(2)
H51	.657(4)	1.026(3)	.946(2)
H52	.858(4)	.978(3)	.934(2)
H61	.507(4)	.781(3)	.906(2)
H62	.632(4)	.820(3)	1.001(2)
H71	.577(4)	.546(3)	.943(2)
H72	.743(4)	.492(3)	.883(2)
H81	.426(4)	.610(3)	.807(2)
H82	.444(4)	.442(3)	.800(2)
H91	.604(4)	.328(3)	.670(2)
H92	.771(4)	.392(3)	.748(2)
H101	.957(4)	.505(3)	.641(2)
H102	.810(4)	.439(3)	.562(2)
H111	.464(4)	.857(3)	.506(2)
H112	.561(4)	.718(3)	.501(2)
H121	.797(4)	.900(3)	.451(2)
H122	.801(4)	.989(3)	.553(2)
H131	.809(4)	1.189(3)	.849(2)
H132	.783(4)	1.142(3)	.747(2)
H141	1.036(4)	1.034(3)	.736(2)
H142	1.103(4)	1.070(3)	.846(2)
H151	.896(4)	.648(3)	1.022(2)
H152	.968(4)	.799(3)	.996(2)
H161	1.071(4)	.555(3)	.888(2)
H162	1.198(4)	.650(3)	.967(2)
H01	.978(4)	.270(3)	.562(2)
H02	.946(4)	.796(3)	.600(2)
H03	1.087(4)	1.257(3)	.732(2)
H04	1.089(4)	.752(3)	.845(2)
HW1	.830(4)	.700(3)	.722(2)
HW2	.847(4)	.827(3)	.745(2)

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

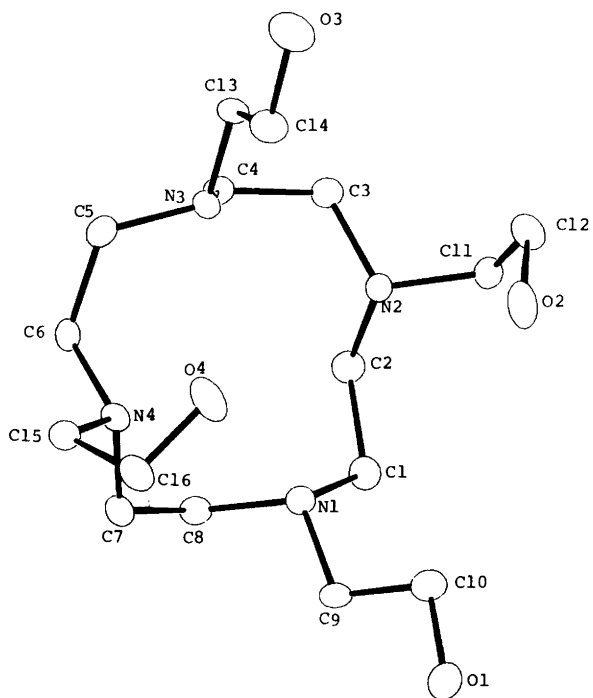


Fig. 1. Schematic drawing of the 12-membered ring showing the numbering of atoms.

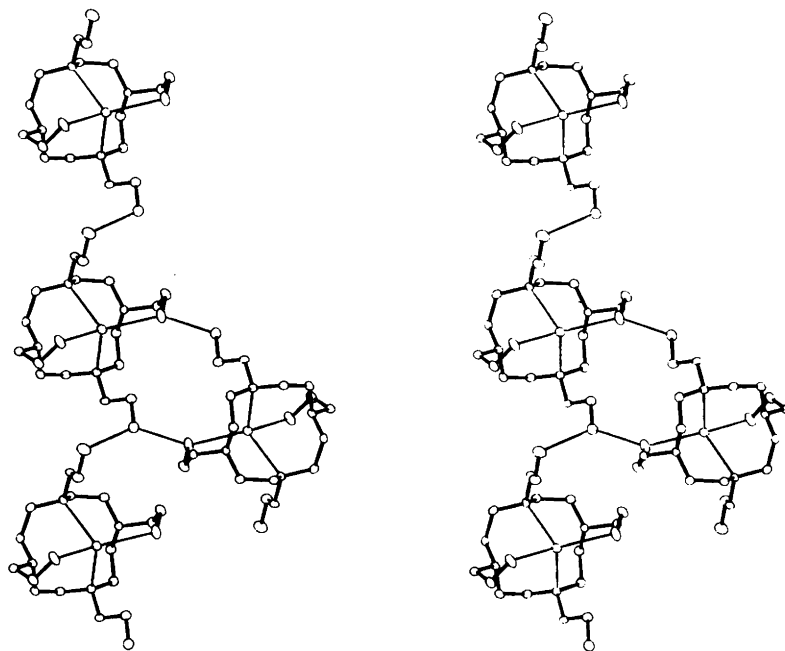


Fig. 2. Stereoscopic view showing the hydrogen bonding system.

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

DISTANCE	(Å)	DISTANCE	(Å)	DIHEDRAL ANGLE (°)	
OW - O2	2.685(3)	OW - O4	2.727(3)	O1 - C10 - C9 - N1	173.2(2)
OW - N1	2.835(3)	OW - N3	2.839(3)	O2 - C12 - C11 - N2	69.9(3)
O1 - O3 ^m	2.852(3)	O1 - O2	2.658(3)	O3 - C14 - C13 - N3	-179.5(2)
O1 - C10	1.426(4)	O2 - C12	1.435(4)	O4 - C16 - C15 - N4	65.7(3)
O3 - C14	1.426(4)	O4 - C16	1.419(4)	C8 - N1 - C1 - C2	69.5(3)
N1 - C1	1.483(4)	N1 - C8	1.482(4)	C7 - C8 - N1 - C1	-164.7(2)
N1 - C9	1.475(4)	N2 - C2	1.467(4)	C9 - N1 - C1 - C2	-169.8(3)
N2 - C3	1.466(4)	N2 - C11	1.466(4)	C10 - C9 - N1 - C1	77.1(3)
N3 - C4	1.487(4)	N3 - C5	1.479(4)	C9 - N1 - C8 - C7	74.7(3)
N3 - C13	1.476(4)	N4 - C6	1.466(4)	C10 - C9 - N1 - C8	-161.9(2)
N4 - C7	1.465(4)	N4 - C15	1.470(4)	C3 - N2 - C2 - C1	-156.6(2)
C1 - C2	1.532(4)	C3 - C4	1.523(4)	C4 - C3 - N2 - C2	75.5(3)
C5 - C6	1.527(4)	C7 - C8	1.521(4)	C11 - N2 - C2 - C1	79.4(3)
C9 - C10	1.516(4)	C11 - C12	1.509(4)	C12 - C11 - N2 - C2	-153.3(2)
C13 - C14	1.513(4)	C15 - C16	1.509(4)	N2 - C2 - C1 - N1	67.0(3)
				C11 - N2 - C3 - C4	-159.9(2)
				C12 - C11 - N2 - C3	82.1(3)
				C5 - N3 - C4 - C3	-163.1(2)
				C6 - C5 - N3 - C4	68.2(3)
				C13 - N3 - C4 - C3	76.2(3)
				C14 - C13 - N3 - C4	-153.5(2)
				N3 - C4 - C3 - N2	61.1(3)
				C13 - N3 - C5 - C6	-170.8(2)
				C14 - C13 - N3 - C5	85.2(3)
				C7 - N4 - C6 - C5	-154.8(2)
				C8 - C7 - N4 - C6	72.6(3)
				C15 - N4 - C6 - C5	81.6(3)
				C16 - C15 - N4 - C6	-148.9(2)
				N4 - C6 - C5 - N3	70.0(3)
				C15 - N4 - C7 - C8	-162.8(2)
				C16 - C15 - N4 - C7	85.8(3)
				N4 - C7 - C8 - N1	63.2(3)
ANGLE	(°)	ANGLE	(°)		
O1 - C10 - C9	106.7(2)	O2 - C12 - C11	111.7(3)		
O3 - C14 - C13	110.8(3)	O4 - C16 - C15	111.4(2)		
N1 - C1 - C2	114.9(2)	C1 - N1 - C8	110.1(2)		
C1 - N1 - C9	109.5(2)	N1 - C8 - C7	114.3(2)		
C8 - N1 - C9	109.7(2)	N1 - C9 - C10	114.3(2)		
N2 - C2 - C1	113.2(2)	C2 - N2 - C3	111.6(2)		
C2 - N2 - C11	111.3(2)	N2 - C3 - C4	114.2(2)		
C3 - N2 - C11	110.6(2)	N2 - C11 - C12	112.7(2)		
N3 - C4 - C3	113.5(2)	C4 - N3 - C5	110.5(2)		
C4 - N3 - C13	109.9(2)	N3 - C5 - C6	115.8(2)		
C5 - N3 - C13	109.3(2)	N3 - C13 - C14	114.4(2)		
N4 - C6 - C5	112.9(2)	C6 - N4 - C7	112.5(2)		
C6 - N4 - C15	111.3(2)	N4 - C7 - C8	114.6(2)		
C7 - N4 - C15	109.9(2)	N4 - C15 - C16	111.8(2)		

[3333] conformation⁶ with two *anti* and two *gauche* N-C-C-O torsional angles.

As to be expected from the NMR studies,¹ the ring conformation corresponds to that of the dihydrated (2:1) complex with LiCl.⁶ The dissimilarity in conformation stems from the various number of *anti* and *gauche* side-chains (only one *gauche* chain in the Li-complex). It may be noted that all side-arms bend off towards the corner atoms. The same pattern was observed in the Li-complex.

Fig. 2 is a stereoscopic view which illustrates the hydrogen bonding system. The water molecule donates its two hydrogen atoms to N1 and N3, and accepts hydrogen bonds from the two *gauche* side-arms. It is thus completely encapsulated tetrahedrally. The hydroxyl groups of the *anti* chains are involved in two inter-molecular hydrogen bonds.

The principal thermal vibration ellipsoids for non-hydrogen atoms correspond to maximum r.m.s. amplitudes between 0.13 and 0.25 Å. The

C-H and O-H bond distance ranges are 0.93–1.06 and 0.83–0.88 Å, respectively.

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

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- Buøen, S., Dale, J., Groth, P. and Krane, J. *Chem. Commun.* 20 (1982) 1172.
- Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
- Groth, P. *Acta Chem. Scand.* 27 (1973) 3131.
- Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
- Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
- Groth, P. *Acta Chem. Scand. A* 37 (1983) 71.

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