

## Short Communications

### The Crystal Structure of the (2:1) Complex between 1,4,7,10-Tetra-(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane and Lithium Chloride Dihydrate at $-150^{\circ}\text{C}$

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The complexation properties of 1,4,7,10-tetra-(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane have been studied in various solvents by titration with dry salt, monitored by  $^{13}\text{C}$  NMR spectroscopy.<sup>1</sup> The  $^{13}\text{C}$  signal for the ring carbons was found to move only moderately upfield on complexation, suggesting a similar ring conformation in the hydrate and in the three cation complexes with  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ . The signals for the side-chain  $\text{NCH}_2$

carbons on the other hand, indicated conformational differences for the side-chains. In order to clarify these conformational differences, the hydrate and some cation complexes have been studied by single crystal X-ray diffraction methods. The results for the dihydrated (2:1) complex with lithium chloride are now presented.

The crystals are monoclinic with space group  $P1_1/n$  and cell dimensions  $a=10.388(6)$ ,  $b=19.719(5)$ ,  $c=11.778(12)$  Å,  $\beta=91.00(5)^{\circ}$ . There are four formula units,  $(\text{C}_{16}\text{H}_{36}\text{O}_4\text{N}_4) \cdot (\text{LiCl})_2 \cdot (\text{H}_2\text{O})_2$ , in the cell ( $D_x=1.29$  g cm $^{-3}$ ,  $D_m=1.22$  g cm $^{-3}$ ). 2387 observed reflections were recorded on an automatic four-circle diffractometer at ca.  $-150^{\circ}\text{C}$  ( $2\theta_{\text{max}}=50^{\circ}$ , MoK $\alpha$ -radiation,  $\omega$ -scan). The crystal size was  $0.3 \times 0.3 \times 0.1$  mm, and no corrections for absorption or secondary extinction were made.

The structure was solved by direct methods<sup>2</sup> and refined by full-matrix least-squares technique.<sup>3,\*</sup> Weights in least squares were obtained from the

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

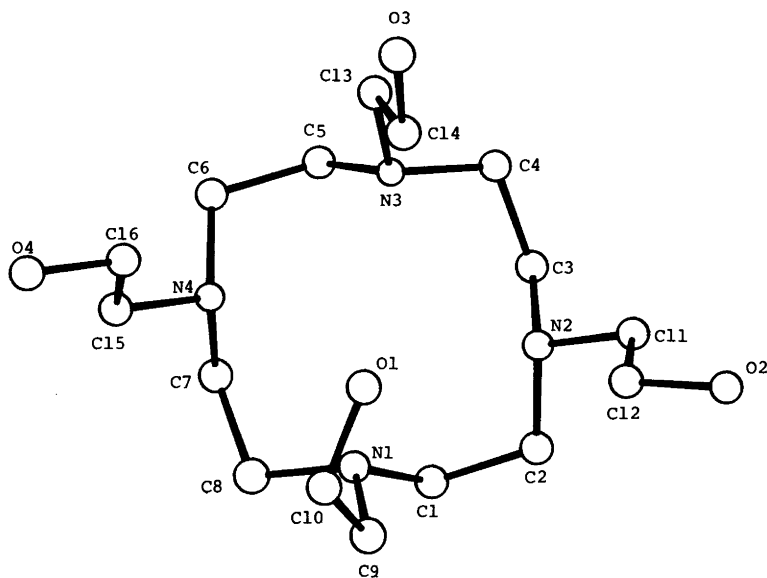


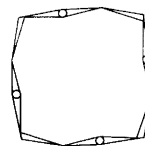
Fig. 1. Schematic drawing of the ligand showing the numbering of atoms.

Table 1. Final fractional coordinates with estimated standard deviations. Hmn is bonded to Cm, HOM, to Om, and HWmn to OWm.

ATOM	X	Y	Z
CL1	.65790(11)	.58664(6)	.43090(9)
CL2	.74642(11)	.59245(6)	.05965(9)
LI1+	.7372(7)	.1339(3)	-.2249(6)
LI2+	.9342(7)	.0764(3)	-.7332(6)
OW1	.7726(3)	.2865(2)	-.2427(4)
OW2	.8228(3)	-.0028(1)	-.7579(4)
O1	.9161(3)	.1616(1)	-.2036(3)
O2	.8510(3)	.1555(1)	-.4971(2)
O3	.9202(3)	-.0649(1)	-.4710(3)
O4	.9822(3)	.0881(1)	-.5768(2)
N1	.6996(3)	.2364(1)	-.2501(3)
N2	.6309(3)	.1543(1)	-.0542(3)
N3	.6299(3)	.0418(1)	-.2247(2)
N4	.6850(3)	.1269(1)	-.4192(2)
C1	.5885(5)	.2548(2)	-.1806(4)
C2	.5963(5)	.2272(2)	-.0605(4)
C3	.5172(4)	.1421(2)	-.0821(3)
C4	.5556(4)	.0411(2)	-.1187(3)
C5	.5398(4)	.0460(2)	-.3225(3)
C6	.6060(4)	.0653(2)	-.4325(3)
C7	.6024(4)	.1890(2)	-.4251(4)
C8	.6696(5)	.2482(2)	-.3719(4)
C9	.8186(4)	.2709(2)	-.2128(4)
C10	.9347(4)	.2291(2)	-.2437(4)
C11	.6789(4)	.1389(2)	.0612(4)
C12	.8178(4)	.1578(2)	.0782(4)
C13	.7125(4)	-.0194(2)	-.2301(4)
C14	.8415(4)	-.0052(2)	-.1749(4)
C15	.7814(4)	.1288(2)	-.5093(4)
C16	.8970(4)	.0851(2)	-.4819(4)
H11	.512(3)	.237(2)	-.217(3)
H12	.580(3)	.304(2)	-.185(3)
H21	.514(4)	.238(2)	-.023(3)
H22	.663(3)	.252(2)	-.018(3)
H31	.468(3)	.134(2)	-.150(3)
H32	.480(3)	.111(2)	-.016(3)
H41	.476(3)	.014(2)	-.132(3)
H42	.610(3)	.022(1)	-.064(3)
H51	.469(3)	.078(1)	-.308(3)
H52	.493(3)	.000(2)	-.329(3)
H61	.533(3)	.069(1)	-.493(3)
H62	.658(3)	.030(2)	-.455(3)
H71	.514(4)	.178(2)	-.587(3)
H72	.581(4)	.195(2)	-.507(3)
H81	.617(3)	.287(2)	-.379(3)
H82	.760(4)	.260(2)	-.410(3)
H91	.815(3)	.278(2)	-.128(3)
H92	.822(3)	.317(1)	-.246(3)
H101	1.015(4)	.250(2)	-.211(3)
H102	.947(4)	.229(2)	-.325(3)
H111	.663(3)	.089(2)	.077(3)
H112	.620(3)	.159(1)	.119(3)
H121	.836(4)	.203(2)	.054(3)
H122	.878(4)	.127(2)	.032(3)
H131	.725(3)	-.034(2)	-.308(3)
H132	.669(4)	-.055(2)	-.193(3)
H141	.830(4)	.012(2)	-.094(3)
H142	.883(3)	.030(2)	-.219(3)
H151	.813(4)	.175(2)	-.515(3)
H152	.738(4)	.112(2)	-.584(3)
H161	.882(4)	.037(2)	-.468(4)
H162	.943(3)	.106(2)	-.412(3)
HO1	.975(5)	.150(2)	-.173(5)
HO2	.838(5)	.186(3)	.230(5)
HO3	.904(4)	-.085(2)	-.118(4)
HO4	1.048(4)	.092(2)	-.566(4)
HW11	.763(5)	.310(2)	.188(4)
HW12	.748(5)	.304(2)	.295(4)
HW21	.829(4)	-.028(2)	-.793(4)
HW22	.815(6)	-.022(3)	-.682(5)

standard deviations in intensities,  $\sigma(I)$ , 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. Methylene hydrogen atom positions were calculated while those of the hydroxyl groups and the water molecules were localized in a difference Fourier map. The form factors were those of Hanson *et al.*,<sup>4</sup> except for hydrogen.<sup>5</sup> Anisotropic temperature factors were introduced for O, N and C atoms. Standard deviations in bond distances and angles were calculated from the correlation matrix of the final least-squares refinement cycle. The final  $R$ -value was 5.4% ( $R_w = 3.8\%$ ) for 2387 observed reflections.

Final fractional coordinates with estimated standard deviations are given in Table 1. Bond distances and angles and torsional angles may be found in Table 2. In Table 3 coordination bonds and hydrogen bonds are listed. The dihedral angles of Table 2 show that the ring conformation is [3 3 3 3].<sup>6\*</sup> There are one *gauche* and three *anti*



[3 3 3 3]

$N-C-C-O$  torsional angles. This is illustrated in Fig. 1 which also shows the numbering of atoms. It may be seen that the  $N-C-C$  planes of all four side-chains are tilted towards the "corner" atoms of the ring.

Fig. 2 is a stereoscopic view showing the complex with the hydrogen bonding system. One of the lithium cations is coordinated to four nitrogen atoms and to the oxygen of the *gauche* side-chain. The other is coordinated to three different *anti* side-chain oxygen atoms of three different symmetry related ligands, and to one of the water molecules. Cl 1 and Cl 2 receive four and three hydrogen bonds, respectively, donated by the water molecules and the side-arm hydroxyl groups. Finally, the third *anti* side-chain hydroxyl group donates its hydrogen to one of the water molecules. Bond distances and angles have normal values within estimated limits of error.

Maximum root mean squares anisotropic thermal vibration amplitudes range from 0.15 to

\* A shorthand notation for conformational type, consisting of a series of numbers within brackets, each giving the number of bonds in one "side", starting with the shortest. The direction around the ring is so chosen that the following number is smallest possible.

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

DISTANCE		(Å)	DISTANCE		(Å)
O1 - C10	1.428( 6)		O2 - C12	1.438( 5)	
O3 - C14	1.434( 6)		O4 - C16	1.439( 6)	
N1 - C1	1.472( 6)		N1 - C8	1.481( 6)	
N1 - C9	1.472( 6)		N2 - C2	1.483( 6)	
N2 - C3	1.478( 6)		N2 - C11	1.471( 6)	
N3 - C4	1.479( 6)		N3 - C5	1.474( 6)	
N3 - C13	1.482( 6)		N4 - C6	1.473( 6)	
N4 - C7	1.481( 6)		N4 - C15	1.472( 6)	
C1 - C2	1.519( 7)		C3 - C4	1.520( 6)	
C5 - C6	1.525( 6)		C7 - C8	1.508( 7)	
C9 - C10	1.510( 7)		C11 - C12	1.500( 6)	
C13 - C14	1.506( 7)		C15 - C16	1.509( 7)	
ANGLE		(°)	ANGLE		(°)
C1 - N1 - C8	110.2( 4)		C1 - N1 - C9	112.5( 4)	
C8 - N1 - C9	112.2( 4)		C2 - N2 - C3	110.1( 4)	
C2 - N2 - C11	108.9( 4)		C3 - N2 - C11	110.2( 3)	
C4 - N3 - C5	109.1( 3)		C4 - N3 - C13	109.9( 4)	
C5 - N3 - C13	111.8( 4)		C6 - N4 - C7	110.2( 4)	
C6 - N4 - C15	109.2( 4)		C7 - N4 - C15	110.3( 4)	
N1 - C1 - C2	113.6( 4)		N2 - C2 - C1	113.7( 4)	
N2 - C3 - C4	111.6( 4)		N3 - C4 - C3	112.0( 4)	
N3 - C5 - C6	112.9( 4)		N4 - C6 - C5	112.0( 4)	
N4 - C7 - C8	111.0( 4)		N1 - C8 - C7	111.5( 4)	
N1 - C9 - C10	110.2( 4)		O1 - C10 - C9	108.5( 4)	
N2 - C11 - C12	112.4( 4)		O2 - C12 - C11	109.7( 4)	
N3 - C13 - C14	110.0( 4)		O3 - C14 - C13	111.3( 4)	
N4 - C15 - C16	112.3( 4)		O4 - C16 - C15	108.0( 4)	
DIIHEDRAL ANGLE		(°)	DIIHEDRAL ANGLE		(°)
C1 - N1 - C8 - C7	-85.8( 5)		C8 - N1 - C1 - C2	164.5( 4)	
C1 - N1 - C9 - C10	153.1( 4)		C9 - N1 - C1 - C2	-69.4( 5)	
C8 - N1 - C9 - C10	-81.9( 5)		C9 - N1 - C8 - C7	148.0( 4)	
C2 - N2 - C3 - C4	159.3( 4)		C2 - N2 - C11 - C12	-81.7( 5)	
C3 - N2 - C11 - C12	-78.4( 5)		C11 - N2 - C2 - C1	160.7( 4)	
C2 - N2 - C11 - C12	-81.7( 5)		C3 - N2 - C11 - C12	157.5( 4)	
C4 - N3 - C5 - C6	165.1( 4)		C11 - N2 - C3 - C4	-80.6( 5)	
C5 - N3 - C4 - C3	-82.2( 5)		C4 - N3 - C5 - C6	165.1( 4)	
C4 - N3 - C13 - C14	-89.7( 5)		C5 - N3 - C4 - C3	-82.2( 5)	
C13 - N3 - C4 - C3	154.9( 4)		C4 - N3 - C13 - C14	-89.7( 5)	
C5 - N3 - C13 - C14	119.0( 4)		C13 - N3 - C4 - C3	154.9( 4)	
C13 - N3 - C5 - C6	-73.1( 5)		C5 - N3 - C13 - C14	119.0( 4)	
C6 - N4 - C7 - C8	159.9( 4)		C13 - N3 - C5 - C6	-73.1( 5)	
C7 - N4 - C6 - C5	-79.7( 5)		C6 - N4 - C7 - C8	159.9( 4)	
C6 - N4 - C15 - C16	-81.2( 5)		C7 - N4 - C6 - C5	-79.7( 5)	
C15 - N4 - C6 - C5	159.0( 4)		C6 - N4 - C15 - C16	-81.2( 5)	
C7 - N4 - C15 - C16	157.5( 4)		C15 - N4 - C6 - C5	159.0( 4)	
C15 - N4 - C7 - C8	-79.4( 5)		C7 - N4 - C15 - C16	157.5( 4)	
N1 - C1 - C2 - N2	-47.7( 6)		C15 - N4 - C7 - C8	-79.4( 5)	
N2 - C3 - C4 - N3	-63.7( 5)		N1 - C1 - C2 - N2	-47.7( 6)	
N3 - C5 - C6 - N4	-51.9( 5)		N2 - C3 - C4 - N3	-63.7( 5)	
N4 - C7 - C8 - N1	-61.4( 5)		N3 - C5 - C6 - N4	-51.9( 5)	
N1 - C9 - C10 - O1	-51.0( 5)		N4 - C7 - C8 - N1	-61.4( 5)	
N2 - C11 - C12 - O2	167.5( 4)		N1 - C9 - C10 - O1	-51.0( 5)	
N3 - C13 - C14 - O3	175.5( 4)		N2 - C11 - C12 - O2	167.5( 4)	
N4 - C15 - C16 - O4	177.5( 4)		N3 - C13 - C14 - O3	175.5( 4)	
			N4 - C15 - C16 - O4	177.5( 4)	

Table 3. Coordination bond distances and hydrogen bond distances with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)
CL1 - OW1	3.213(4)	CL1 - OW2'	3.159(5)
CL1 - O1'	3.096(4)	CL1 - O3'	3.106(4)
CL2 - OW1	3.184(5)	CL2 - OW2'	3.207(5)
CL2 - O4'	3.068(4)	LI1+ - O1	1.948(8)
LI1+ - N1	2.079(8)	LI1+ - N2	2.346(8)
LI1+ - N3	2.131(8)	LI1+ - N4	2.347(8)
LI2+ - OW2	1.927(9)	LI2+ - O2'	1.943(8)
LI2+ - O3'	1.941(8)	LI2+ - O4	1.922(8)
OW1 - O2	2.764(5)		

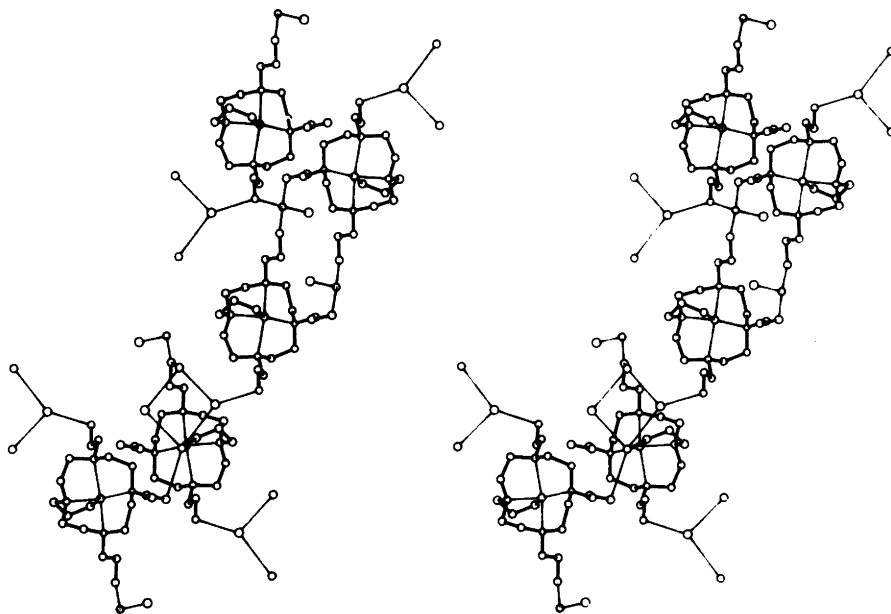


Fig. 2. Stereoscopic view of the complex illustrating the type of coordination and the hydrogen bonding system.

0.22 Å. C-H bond distances lay between 0.93 and 1.04 Å while O-H range from 0.70 to 0.81 Å.

Like for the Li-complexes of the 6-crown-18-ether,<sup>7</sup> the conformational problem for the ligand in a (1:1) water-free complex with Li<sup>+</sup> is not settled. In fact, considerable effort has been put into attempts to solve the structure of the (1:1) complex with LiSCN. It is, however, highly disordered, and no definite conclusions about the ligand conformation could be drawn.

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

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