

The Crystal Conformations of 7,16,21,26-Tetraoxa-1,4,10,13-tetraazatricyclo[11.5.5.5^{4,10}]octacosane and its Dihydrochloride Tetrahydrate

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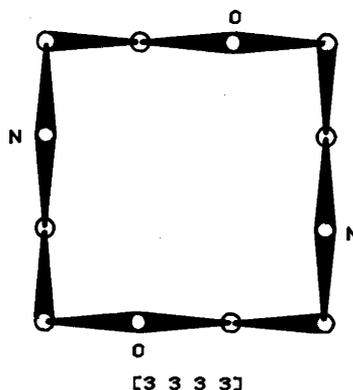
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The crystals of the title compound are monoclinic with space group $P2_1/c$ and cell dimensions $a=9.093(2)$, $b=12.940(3)$, $c=9.976(2)$ Å, $\beta=108.76(2)^\circ$. Those of the dihydrochloride tetrahydrate are orthorhombic with space group $Fdd2$ and cell dimensions $a=39.72(1)$, $b=16.999(5)$, $c=8.386(2)$ Å. Data were collected on an automatic four circle diffractometer at room temperature. The structures were solved by direct methods and refined by full-matrix least squares technique. The ring conformation in the free ligand is [2 10]. The dihydrochloride tetrahydrate structure is disordered, with two ring conformations, [3 3 3 3] and [3 9].

The syntheses of organic ligands of two monoaza-12-crown-4 rings linked together by a single alkylene bridge between nitrogen bridgeheads,¹ and by two such bridges,² have been reported.

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. An X-ray crystal structure determination of the complex with NaBF_4 ³ confirms the expected cubic arrangement of the eight donor atoms and identical helicity of the ten ethylene units in each molecule. The conformation of the bis(1,7-dioxo-4,10-diazacyclododecane) ring is the quadrangular [3 3 3 3]⁴ with approximate C_4 symmetry.



Since space-filling molecular models do not allow much conformational choice for this tricyclic molecule, and no definite conclusion could be reached from NMR studies, an X-ray crystal structure determination of the free ligand, $\text{C}_{20}\text{H}_{40}\text{N}_4\text{O}_4$, (I), has been undertaken. The free ligand is liberated by pyrolysis of the Na^+ complex. Along with the free ligand, a small amount of a higher melting substance could be

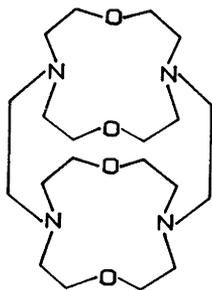


Table 1. Final fractional coordinates for (I) with estimated standard deviations. Hm1 and Hm2 are bonded to Cm.

ATOM	X	Y	Z
O1	.3062(4)	.5923(2)	.4695(4)
O2	.1588(8)	.3081(3)	.4696(4)
N1	.2983(4)	.4723(3)	.7175(4)
N2	.0209(5)	.5393(3)	.2468(4)
C1	.4254(7)	.5358(5)	.7038(7)
C2	.3731(8)	.6270(5)	.6099(7)
C3	.2171(8)	.6663(5)	.3771(7)
C4	.1308(8)	.6189(5)	.2374(6)
C5	.0906(7)	.4379(4)	.2825(6)
C6	.0740(7)	.3981(4)	.4181(6)
C7	.3017(14)	.3206(8)	.5705(10)
C8	.3262(9)	.3838(6)	.7125(8)
C9	-.1233(7)	.5433(6)	.4297(7)
C10	-.2596(7)	.4950(6)	.4581(6)
H11	.488(5)	.491(3)	.671(4)
H12	.483(5)	.559(3)	.794(5)
H21	.444(5)	.667(4)	.611(5)
H22	.301(5)	.683(3)	.650(5)
H31	.275(5)	.717(3)	.365(5)
H32	.155(5)	.695(3)	.420(5)
H41	.199(5)	.593(3)	.494(4)
H42	.078(5)	.667(3)	.480(5)
H51	.197(5)	.438(3)	.289(4)
H52	.044(5)	.397(3)	.245(5)
H61	-.029(5)	.381(3)	.407(4)
H62	.092(5)	.454(3)	.482(4)
H71	.281(9)	.343(4)	.500(7)
H72	.353(5)	.269(4)	.577(5)
H81	.426(5)	.347(3)	.765(5)
H82	.238(5)	.322(3)	.715(5)
H91	-.110(5)	.503(3)	.055(5)
H92	-.158(5)	.614(3)	.132(4)
H101	-.238(5)	.424(3)	.464(5)
H102	-.352(5)	.505(3)	.070(4)

Table 2. Final fractional coordinates for (II) with estimated standard deviations Hm1 and Hm2 are bonded to Cm. HWm1 and HWm2 are bonded to OWm and HCl comes from the hydrochloride.

ATOM	X	Y	Z
CL-	.40228(5)	.50381(15)	.49801
OW1	.0963(1)	.6915(3)	.4827(10)
OW2	.4072(1)	.1856(2)	.5118(11)
O1	.7599(1)	.1822(3)	.0335(10)
N1	.6967(1)	.1668(3)	.2478(14)
N2	.6884(1)	.3366(3)	.2513(13)
C1	.7060(2)	.1077(5)	.1254(15)
C2	.7265(2)	.1414(5)	-.0104(14)
C3	.7822(2)	.0997(5)	.0277(15)
C4	.6848(2)	.3726(5)	.0891(13)
C5	.6600(1)	.2804(6)	.2815(15)
C6	.6647(2)	.2035(5)	.2016(13)
C7	.6949(2)	.1279(5)	.4051(14)
C10	.6909(2)	.3985(6)	.3829(13)
O2A	.7469(1)	.3944(4)	.4174(10)
O2B	.7455(3)	.3327(10)	.4686(25)
C8A	.7256(3)	.1392(8)	.5028(21)
C8B	.7296(8)	.1008(20)	.4566(43)
C9A	.7166(2)	.3821(6)	.4956(21)
C9B	.7116(11)	.3622(26)	.5174(75)
HW11	.106	.713	.563
HW12	.079	.667	.528
HW21	.393	.205	.435
HW22	.403	.133	.487
H11	.685	.085	.080
H12	.719	.066	.178
H21	.715	.190	-.051
H22	.728	.101	-.097
H31	.785	.081	-.085
H32	.774	.056	.096
H41	.669	.418	.095
H42	.675	.332	.014
H51	.639	.304	.215
H52	.659	.271	.102
H61	.664	.212	.086
H62	.646	.168	.236
H71A	.692	.070	.387
H72A	.675	.150	.464
H71B	.680	.081	.397
H72B	.686	.166	.485
H81A	.723	.113	.608
H82A	.730	.197	.521
H81B	.738	.063	.377
H82B	.727	.076	.563
H91A	.715	.328	.535
H92A	.715	.420	.588
H91B	.698	.317	.563
H92B	.715	.403	.601
A101	.669	.400	.410
A102	.695	.450	.332
B101	.668	.412	.422
B102	.702	.447	.341
HCL	.711	.224	.313

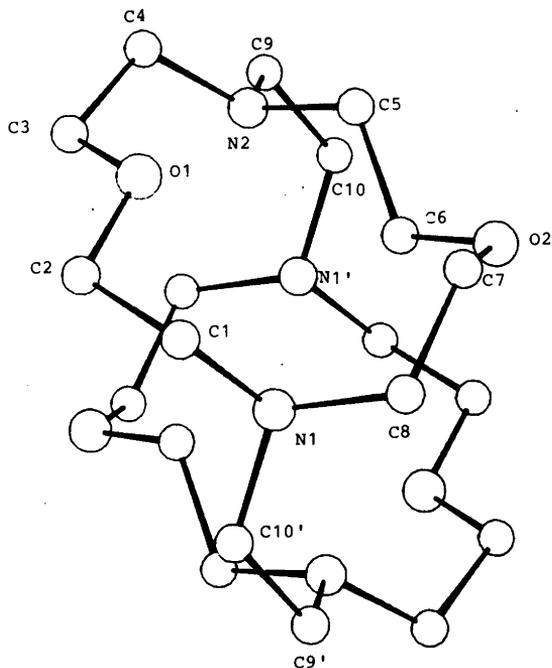


Fig. 1. Schematic drawing of (I) showing the numbering of atoms.

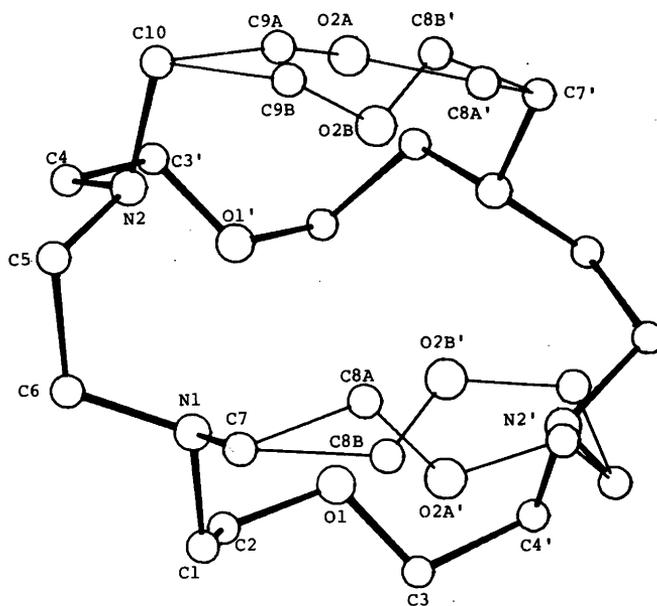


Fig. 2. Schematic drawing of the ligand of (II) showing the numbering of atoms.

Table 3. Bond distances and angles and torsion angles for (I) with estimated standard deviations.

DISTANCE		(Å)	DISTANCE		(Å)
O1 - C2	1.41	(1)	O1 - C3	1.39	(1)
O2 - C6	1.40	(1)	O2 - C7	1.37	(1)
N1 - C1	1.46	(1)	N1 - C8	1.43	(1)
N1 - C10'	1.46	(1)	N2 - C4	1.46	(1)
N2 - C5	1.45	(1)	N2 - C9	1.45	(1)
C1 - C2	1.49	(1)	C3 - C4	1.49	(1)
C5 - C6	1.50	(1)	C7 - C8	1.47	(1)
C9 - C10	1.49	(1)			
ANGLE		(°)	ANGLE		(°)
C2 - O1 - C3	114.	(1)	C6 - O2 - C7	117.	(1)
C1 - N1 - C8	113.	(1)	C1 - N1 - C10'	109.	(1)
C8 - N1 - C10'	114.	(1)	C4 - N2 - C5	114.	(1)
C4 - N2 - C9	113.	(1)	C5 - N2 - C9	116.	(1)
N1 - C1 - C2	114.	(1)	O1 - C2 - C1	109.	(1)
O1 - C3 - C4	111.	(1)	N2 - C4 - C3	113.	(1)
N2 - C5 - C6	112.	(1)	O2 - C6 - C5	114.	(1)
O2 - C7 - C8	124.	(1)	N1 - C8 - C7	116.	(1)
N2 - C9 - C10	115.	(1)	N1 - C10' - C9'	119.	(1)
DIIHEDRAL ANGLE		(°)			
C2 - O1 - C3 - C4	-174.	(1)			
C3 - O1 - C2 - C1	164.	(1)			
C6 - O2 - C7 - C8	64.	(2)			
C7 - O2 - C6 - C5	96.	(1)			
C1 - N1 - C8 - C7	-78.	(1)			
C8 - N1 - C1 - C2	138.	(1)			
C1 - N1 - C10' - C9'	110.	(1)			
C10' - N1 - C1 - C2	-94.	(1)			
C8 - N1 - C10' - C9'	-122.	(1)			
C10' - N1 - C8 - C7	156.	(1)			
C4 - N2 - C5 - C6	120.	(1)			
C5 - N2 - C4 - C3	-85.	(1)			
C4 - N2 - C9 - C10	-157.	(1)			
C9 - N2 - C4 - C3	140.	(1)			
C5 - N2 - C9 - C10	69.	(1)			
C9 - N2 - C5 - C6	-107.	(1)			
N1 - C1 - C2 - O1	-68.	(1)			
O1 - C3 - C4 - N2	62.	(1)			
N2 - C5 - C6 - O2	-174.	(1)			
O2 - C7 - C8 - N1	-74.	(2)			
N2 - C9 - C10 - N1'	53.	(1)			

isolated, which turned out to be the dihydrochloride tetrahydrate, $C_{20}H_{40}O_4N_4 \cdot 2HCl \cdot 4H_2O$, (II). Presumably this arises from a contamination of hydrochloride in the crude Na^+ complex. A crystal structure investigation of this compound has also been carried out.

EXPERIMENTAL

Crystal and intensity data. The crystal data for (I) are: $a=9.093(2)$, $b=12.940(3)$, $c=9.976(2)$ Å, $\beta=108.76(2)^\circ$, $Z=2$, space group $P2_1/c$, $D_x=1.19$ g cm $^{-3}$, $D_m=1.17$ g cm $^{-3}$ (by flotation), $V=1111.44$ Å 3 , $\mu=1.55$ cm $^{-1}$ (MoK α), $\lambda(MoK\alpha)=0.71069$ Å. The crystal data for (II) are: $a=39.72(1)$, $b=16.999(5)$, $c=8.386(2)$ Å, $Z=8$, space group $Fdd2$, $D_x=1.28$ g cm $^{-3}$, $D_m=1.25$ g cm $^{-3}$ (by flotation), $V=5662.35$ Å 3 , $\mu=2.81$ cm $^{-1}$ (MoK α), $\lambda(MoK\alpha)=0.71069$ Å. Data were collected on an automatic four-circle diffractometer at room temperature by the ω -scan technique ($2\theta_{max}=50^\circ$) with MoK α radiation. The scan rate varied from 2 to 30° min $^{-1}$, depending on the intensity of the reflection. The intensities of two test reflections remeasured after every 100 reflections showed no significant changes during data collection for (II), while those of (I) varied considerably (up to 20%). The intensities were corrected for Lorentz and polarization effects, but no corrections for absorption or secondary extinction were made

(crystal sizes $0.4 \times 0.5 \times 0.2$ mm and $0.3 \times 0.6 \times 0.2$ mm for (I) and (II), respectively). With an observed-unobserved cutoff at $2\sigma(I)$, 975 reflections for (I) and 771 for (II) were regarded as observed.

Determination and refinement of the structures. The structures were solved by direct methods⁵ and refined by full-matrix least squares technique.⁶ All programs used (except those for phase determination) are included in Ref. 6. Anisotropic temperature factors were introduced for all non-hydrogen atoms in (I), and for all non-hydrogen atoms for which no disorder could be observed in (II). A difference Fourier map of (II) revealed the four water hydrogen atoms and, in addition, one small peak which was interpreted as the hydrochloride hydrogen. All other H-atom positions were calculated. The hydrogen atoms of (II) were not refined. Weights in least-squares were obtained 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. Occupancy factors of the disordered atoms in (II) were refined to $G_A=0.7$ and $G_B=0.3$. The final R -values were $R=8.3\%$ ($R_w=6.8\%$) for the 975 reflections of (I), and $R=5.6\%$ ($R_w=5.1\%$) for the 771 reflections of (II). Standard deviations in bond distances and angles and torsion angles were calculated from the correlation matrices of the final least-squares refinement cycles. Final fractional coordinates with estimated standard deviations are given in

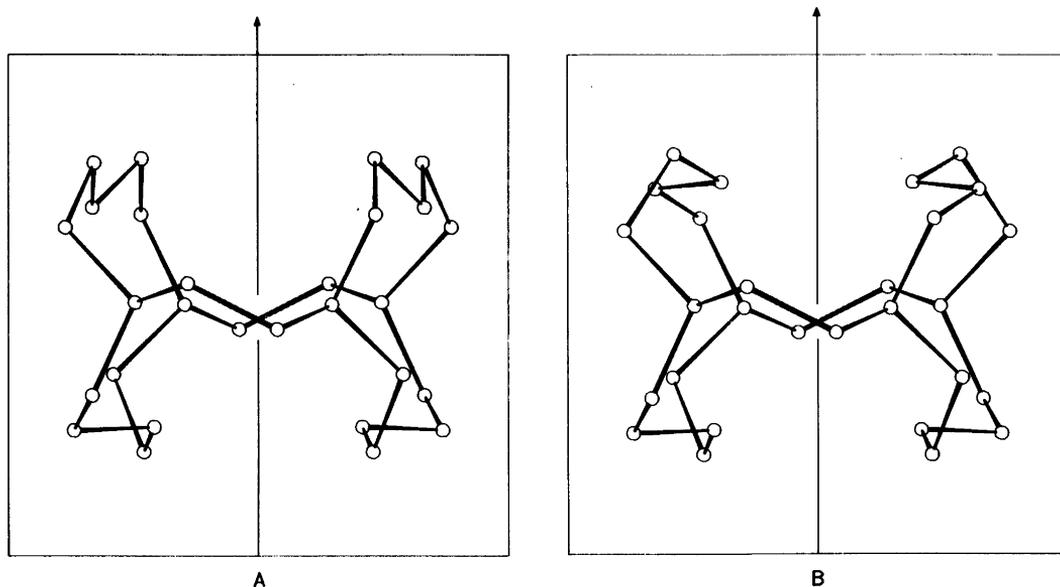


Fig. 3. Pure A- and B-ligands of (II) viewed roughly along the a -axis.

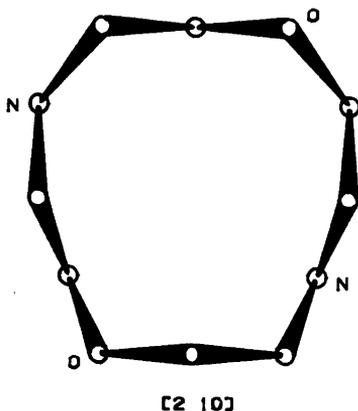
Table 4. Bond distances and angles and torsion angles for (II) with estimated standard deviations.

DISTANCE		(Å)	DISTANCE		(Å)
O1 - C2	1.42	(1)	O1 - C3	1.38	(1)
N1 - C1	1.48	(1)	N1 - C6	1.46	(1)
N1 - C7	1.48	(1)	N2 - C4	1.50	(1)
N2 - C5	1.50	(1)	N2 - C10	1.53	(1)
C1 - C2	1.51	(1)	C3 - C4'	1.49	(1)
C5 - C6	1.48	(1)	C7 - C8A	1.48	(2)
C7 - C8B	1.52	(3)	C10 - C9A	1.42	(2)
C10 - C9B	1.52	(1)	O2A - C9A	1.39	(1)
O2A - C8A'	1.43	(2)	O2B - C9B	1.49	(2)
O2B - C8B'	1.51	(4)			
ANGLE		(°)	ANGLE		(°)
C2 - O1 - C3	113.	(1)	C1 - N1 - C6	110.	(1)
C1 - N1 - C7	109.	(1)	C6 - N1 - C7	112.	(1)
C4 - N2 - C5	111.	(1)	C4 - N2 - C10	112.	(1)
C5 - N2 - C10	111.	(1)	N1 - C1 - C2	114.	(1)
O1 - C2 - C1	114.	(1)	O1 - C3 - C4'	108.	(1)
N2 - C4 - C3'	111.	(1)	N2 - C5 - C6	112.	(1)
N1 - C6 - C5	112.	(1)	N1 - C7 - C8A	113.	(1)
N1 - C7 - C8B	110.	(2)	N2 - C10 - C9A	113.	(1)
N2 - C10 - C9B	107.	(1)	C9A - O2A - C8A'	112.	(1)
C9B - O2B - C8B'	111.	(1)	C7 - C8A - O2A'	108.	(1)
C7 - C8B - O2B'	113.	(2)	C10 - C9A - O2A	106.	(1)
C10 - C9B - O2B	115.	(1)			
DIHEDRAL ANGLE		(°)			
C2 - O1 - C3 - C4'	-175.	(1)			
C3 - O1 - C2 - C1	85.	(1)			
C1 - N1 - C6 - C5	-159.	(1)			
C6 - N1 - C1 - C2	89.	(1)			
C1 - N1 - C7 - C8A	99.	(1)			
C1 - N1 - C7 - C8B	67.	(2)			
C7 - N1 - C1 - C2	-148.	(1)			
C6 - N1 - C7 - C8A	-140.	(1)			
C6 - N1 - C7 - C8B	-172.	(2)			
C7 - N1 - C6 - C5	80.	(1)			
C4 - N2 - C5 - C6	78.	(1)			
C5 - N2 - C4 - C3'	-156.	(1)			
C4 - N2 - C10 - C9A	-136.	(1)			
C4 - N2 - C10 - C9B	-152.	(1)			
C10 - N2 - C4 - C3'	79.	(1)			
C5 - N2 - C10 - C9A	100.	(1)			
C5 - N2 - C10 - C9B	84.	(1)			
C10 - N2 - C5 - C6	-156.	(1)			
N1 - C1 - C2 - O1	71.	(1)			
O1 - C3 - C4' - N2'	54.	(1)			
N2 - C5 - C6 - N1	56.	(1)			
N1 - C7 - C8A - O2A'	-61.	(2)			
N1 - C7 - C8B - O2B'	59.	(2)			
N2 - C10 - C9A - O2A	71.	(1)			
N2 - C10 - C9B - O2B	56.	(1)			
C9A - O2A - C8A' - C7'	176.	(1)			
C8A' - O2A - C9A - C10	-165.	(1)			
C9B - O2B - C8B' - C7'	-179.	(2)			
C8B' - O2B - C9B - C10	80.	(1)			

Tables 1 and 2. Lists of observed and calculated structure factors and thermal parameters are obtainable from the author.

DISCUSSION

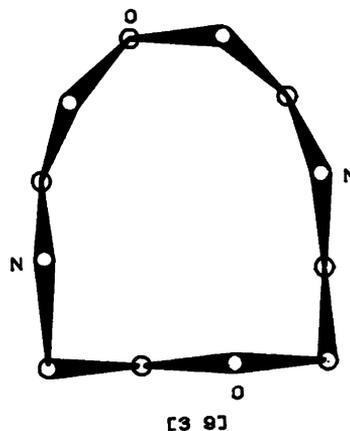
The free ligand, (I). Space group $P2_1/c$ with $Z=2$ demands C_1 symmetry of the ligand in an ordered structure. Fig. 1 is a schematic drawing showing the centrosymmetric molecule and the numbering of atoms. From the list of torsion angles (Table 3) it may be seen that the 12-membered ring adopts the diangular [2 10] conformation which is entirely different from the quadrangular [3 3 3 3] conformation of the NaBF_4 complex.³



It should be pointed out that an oxygen atom, O2, unexpectedly plays the role as one of the two ring "corners". However, the thermal parameters of the three atoms constituting the short "side" of the ring (O2, C7, C8), correspond to maximum r.m.s. amplitudes of 0.36, 0.52 and 0.34 Å, respectively. This clearly points towards disorder in that part of the ring. Further indications are the short bond distances O2-C7 and C7-C8 of 1.37 Å and 1.47 Å, respectively, and the large O2-C7-C8 angle of 124° (see Table 3). Positions of partial C and O atoms were calculated from the differences between maximum and minimum principal axes of the thermal vibration ellipsoids, and refined along with their occupancy factors. However, no significant improvement was obtained and a rather awkward geometry resulted. In spite of the unsuccessful attempt to introduce disorder, the findings mentioned above, and also the high final R -value of 8.3 %,

may imply some disorder although it cannot be properly handled with the present set of data.

The dihydrochloride tetrahydrate, (II). Space group $Fddd2$ with $Z=8$ demands C_2 symmetry of the ligand in an ordered structure. Fig. 2 is a schematic drawing of the disordered ligand showing the numbering of atoms. The bond distances and angles have normal values within error limits. From the list of torsion angles it may be seen that the two disordered 12-membered rings, labeled A and B, have different conformations. For A, it is the triangular [3 9] while B has the quadrangular [3 3 3 3] conformation.



The refinement of occupancy factors to about 70 % A-form and 30 % B-form implies that the crystals must contain a certain amount of pure A-ligands. Whether the rest of the mixture consists of ligands with one A- and one B-ring or pure B-ligands, or both, cannot be settled. In Fig. 3 A and B the pure A- and B-ligands are viewed approximately along the a -axis with the twofold axes of rotation indicated.

The peak in the difference Fourier map being interpreted as the hydrochloride hydrogen atom was found at distances 1.25 and 2.17 Å from N1 and N2, respectively. Although the angle N1-HCl-N2 is as small as 114°, the N1-N2 contact of 2.91 Å is significantly shorter than the corresponding distance in (I), N1-N2'=3.04 Å. This seems to justify the assumption of an intramolecular hydrogen bond in (II).

The chlorine anion accepts three hydrogen bonds from the water molecules, Cl-OW1=3.20 Å, Cl-OW2'=3.25 Å, Cl-OW2''=3.27 Å. These bond lengths correspond

roughly to those of sodium chloride dihydrate.⁸ No other short intermolecular contacts are observed.

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REFERENCES

1. Calverley, M. J. and Dale, J. J. *Chem. Commun.* (1981) 684.
2. Calverley, M. J. and Dale, J. J. *Chem. Commun.* (1981) 1084.
3. Groth, P. *Acta Chem. Scand. A* 35 (1981) 717.
4. Dale, J. *Acta Chem. Scand.* 27 (1973) 1115.
5. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
6. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
7. Kartha, G. and Ahmed, F. R. *Acta Crystallogr.* 13 (1960) 532.
8. Klewe, B. and Pedersen, B. *Acta Crystallogr. B* 30 (1974) 2363.

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