

## 1,4,7,10,13,16-Hexaazacyclooctadecanehexahydrogennitratemonohydrate

T. N. Margulis and L. J. Zompa

Department of Chemistry, University of Massachusetts-Boston, Boston, Massachusetts 02125

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The crystal structure of the anion-complexing agent, 1,4,7,10,13,16-hexaazacyclooctadecanehexahydrogennitratemonohydrate, has been determined by a single-crystal x-ray diffraction study. Nitrate and water are bound strongly to the hexacyclen ring by hydrogen-bonds and ion-ion interactions. The hexacyclen ring has a conformation which is relatively independent of its crystallographic environment.

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The cyclic hexaamine 1,4,7,10,13,16-hexaazacyclooctadecane (hexacyclen) forms complexes with many anionic species [1,2]. In several cases, particularly with nitrate and chloride ions, it has been shown that hexacyclen must be at least tetraprotonated to bind anions. This unusual propensity of hexacyclen to bind anions even in aqueous solution has prompted several crystallographic studies of hexacyclen salts [1,3]. Previously studied compounds are mixed hexacyclen salts containing both nitrate and chloride with the latter being found in positions near the ring opening. While the nitrate is more strongly bound than chloride in aqueous solution, in the solid state [2] it tends to be a hydrogen-bonded inter-ring crosslinking agent (sometimes along with water molecules). In order to further characterize the nitrate-ring interactions we synthesized 1,4,7,10,13,16-hexaazacyclooctadecanehexahydrogennitratemonohydrate and now present its crystal structure.

## Discussion.

The crystal structure, viewed along [100] is shown in Figure 1.

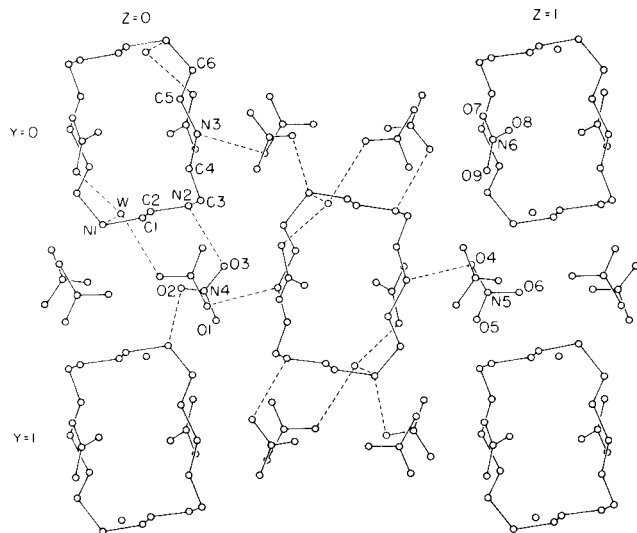


Figure 1. Crystal structure viewed along [100].

Oxygen atoms of the nitrate are held to ring nitrogen atoms either directly by strong H-bonds (O...H-N distances 2.83-2.86 Å) or by H-bonding to water which is H-bonded to the ring. In addition there are numerous short O...N distances with no clearly associated H atom. These we attribute to either bifurcated H-bonds or N<sup>+</sup>...O<sup>-</sup> columbic attractions. Two nitrate oxygen atoms, O7 and O9, have larger thermal motion than any other atom and are not involved in H-bonds or other short distances with the ring. The conformation of the ring, which lies on a center of symmetry, is shown in Figure 2.

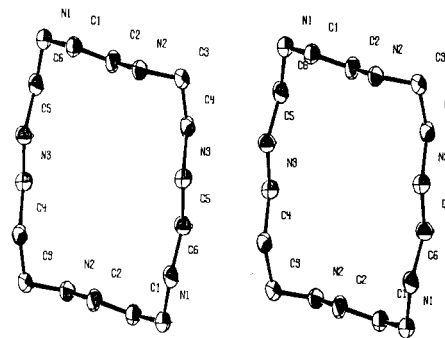


Figure 2. Stereoscopic view of hexacyclen ring.

Like the previous hexacyclen salts we have studied the ring is relatively flat with a standard deviation from the mean plane of 0.5 Å (maximum deviation = 0.75 Å). A comparison of the torsion angles (Table 4) of these compounds with 1,4,7,10,13,16-hexaazacyclooctadecanetetrahydrogennitratetetradihydrogenchloride [3] shows that the rings are remarkably similar in conformation. The average deviation in torsion angles between matched atoms in the two compounds is 4.0° with a standard deviation of 2.0°. Thus the hexaprotonated hexacyclen ring has a conformation relatively independent of crystalline environment. The tetraprotonated amine salt, 1,4,7,10,13,16-hexaazacyclooctadecanedihydrogennitratehydrogenchloridedihydrate [2] also contains a ring that is approximately planar but with a substantially different conformation.

In pH-potentiometric studies of hexacyclen in aqueous

solution we have observe a slow reaction in the formation of  $H_3L^{3+}$  from  $H_4L^{4+}$ . This indicates that at least in aqueous solution some type of conformational change occurs in the hexacyclen ring as the species goes from the anion non-complexing to the complexing form. In future studies we hope to show the details of this conformational change by examining the crystal structure of some non-complexing rings.

Table I

## Crystallographic Data

Molecular Formula	$C_{12}H_{30}N_6 \cdot 6HNO_3 \cdot H_2O$
Space Group	$P2_1/c$
a, Å	$8.300 \pm 0.007$
b, Å	$11.559 \pm 0.010$
c, Å	$15.329 \pm 0.018$
$\beta$ , degrees	$100.50 \pm 0.08$
Z	2 formula weights/unit cell
$\rho_{x\text{-ray}}$ , $g\text{cm}^{-3}$	0.7516

Table 2

## Atomic coordinates with e.s.d.'s in parentheses

C(1)	0.3141(6)	0.2851(4)	0.0170(3)
C(2)	0.4949(6)	0.2570(4)	0.0342(3)
C(3)	0.7300(6)	0.2252(4)	0.1632(3)
C(4)	0.8016(6)	0.1227(4)	0.1218(3)
C(5)	0.8081(6)	-0.0908(4)	0.1100(4)
C(6)	0.7326(6)	-0.2010(4)	0.1405(3)
N(1)	0.7527(5)	-0.2989(4)	0.0796(3)
N(2)	0.5474(5)	0.2403(3)	0.1318(3)
N(3)	0.7579(5)	0.0096(3)	0.1607(3)
N(4)	0.4843(5)	0.5232(4)	0.1739(3)
N(5)	0.0114(6)	0.5281(5)	0.8600(3)
N(6)	0.6978(6)	0.0249(5)	0.8724(4)
O(1)	0.4642(6)	0.6222(4)	0.2004(3)
O(2)	0.5572(5)	0.5079(3)	0.1105(4)
O(3)	0.4343(5)	0.4382(3)	0.2106(2)
O(4)	-0.0156(6)	0.4358(4)	0.8159(3)
O(5)	-0.0613(5)	0.6179(4)	0.8299(3)

O(6)	0.1100(5)	0.5284(3)	0.9321(2)
O(7)	0.7750(9)	-0.0521(7)	0.8502(5)
O(8)	0.5820(4)	-0.0010(3)	0.9108(3)
O(9)	0.7226(9)	0.1233(6)	0.8555(4)
O(W)	0.9347(5)	0.2707(4)	0.9694(3)
HCl(1)	0.296(4)	0.355(3)	0.040(3)
HCl(2)	0.256(5)	0.221(4)	0.038(3)
HC2(1)	0.558(4)	0.330(3)	0.017(2)
HC2(2)	0.517(5)	0.182(3)	0.004(2)
HC3(1)	0.777(4)	0.289(3)	0.143(2)
HC3(2)	0.754(4)	0.223(3)	0.234(2)
HC4(1)	0.761(5)	0.113(4)	0.042(3)
HC4(2)	0.918(7)	0.132(5)	0.148(3)
HC5(1)	0.762(5)	-0.070(4)	0.031(3)
HC5(2)	0.911(7)	-0.096(5)	0.122(4)
HC6(1)	0.784(5)	-0.209(4)	0.211(3)
HC6(2)	0.619(4)	-0.186(3)	0.141(2)
HN1(1)	0.859(6)	-0.316(4)	0.076(3)
HN1(2)	0.720(5)	-0.349(3)	0.099(2)
HN2(1)	0.499(5)	0.178(4)	0.154(3)
HN2(2)	0.520(7)	0.310(6)	0.181(4)
HN3(1)	0.827(5)	0.009(3)	0.228(3)
HN3(2)	0.626(10)	0.012(7)	0.187(5)
HOW(1)	0.926(7)	0.370(5)	0.005(4)
HOW(2)	0.878(6)	0.273(5)	0.951(3)

## EXPERIMENTAL

The 1,4,7,10,13,16-hexaazacyclooctadecanehexahydrogennitratemonohydrate was prepared by adding 8 M nitric acid to a solution of the pure ligand. Slow evaporation of this solution gave colorless needles suitable for X-ray crystallographic studies. The crystal used for all data collection was  $0.3 \times 0.1 \times 0.1$  mm and was sealed in a 0.3 mm capillary. Standard reflections did not change during data collection. Diffraction data ( $2\theta$  maximum =  $150^\circ$ ) were collected at room temperature on a computer-controlled Nicolet P2<sub>1</sub> diffractometer operated in a  $\theta$ - $2\theta$  scan mode with graphite monochromator and  $CuK_\alpha$  ( $\lambda = 1.54178$  Å) radiation. No correction for absorption or extinction were made.

Table 3

Bond Distances (Å) and Angles (Deg) (a) for  $H_6L(NO_3)_6 \cdot H_2O$  Ring Atoms

N1-C1	1.492	C6'-N1'-C1	118.3
C1-C2	1.511	N1'-C1-C2	112.0
C2-N2	1.493	C1-C2-N2	107.6
N2-C3	1.514	C2-N2-C3	115.2
C3-C4	1.516	N2-C3-C4	113.8
C4-N3	1.509	C3-C4-N3	111.7
N3-C5	1.498	C4-N3-C5	110.8
C5-C6	1.531	N3-C5-C6	108.6
C6-N1'	1.495	C5-C6-N1	110.0
Nitrate Ion			
N4-O1	1.235	O1-N4-O2	120.1
N4-O2	1.249	O2-N4-O3	119.3
N4-O3	1.241	O3-N4-O1	120.6
N5-O4	1.261	O4-N5-O5	118.6
N5-O5	1.247	O5-N5-O6	121.4
N5-O6	1.250	O6-N5-O4	120.0
N6-O7	1.182	O7-N6-O8	117.3
N6-O8	1.252	O8-N6-O9	120.5
N6-O9	1.193	O9-N6-O7	122.1

(a) Estimated standard deviations are approximately 0.004 Å in bond distance and 0.5 deg in bond angles.

#### Solution of the Structure.

The structure was solved by direct methods [4] and difference syntheses. All H atoms were located from a difference map. In the final full-

Table 4

A Comparison of Torsion Angles between  $H_6L(NO_3)_4Cl_2$  [3] and  $H_6L(NO_3)_6 \cdot H_2O$ 

$H_6L(NO_3)_4Cl_2$ (a)		$H_6L(NO_3)_6 \cdot H_2O$	
N1-C1-C2-N2	173.8	N1-C1'-C2'-N2'	177.8
C1-C2-N2-C3	177.7	C1'-C2'-N2'-C3'	173.1
C2-N2-C3-C4	65.3	C2'-N2'-C3'-C4'	59.1
N2-C3-C4-N3	69.7	N2'-C3'-C4'-N3'	74.8
C3-C4-N3-C5	-178.1	C3'-C4'-N3'-C5'	-171.6
C4-N3-C5-C6	169.0	C4'-N3'-C5'-C6'	169.3
N3-C5-C6-N1'	-165.4	N3'-C5'-C6'-N1'	-169.1
C5-C6-N1'-C1'	58.7	C5'-C6'-N1'-C1	56.6
C6-N1'-C1'-C2'	59.8	C6'-N1'-C1-C2	56.4

(a) Atoms are labeled here as they were in the original paper [3]. The torsion angles N3-C5-C6-N1 and C5-C6-N1-C1 were misprinted in that work.

matrix least-squares calculations the heavy atoms were refined anisotropically and H atoms refined isotropically to  $R = 0.068$  for 1612 observed reflections [5]. A final difference map showed no significant peaks. Crystallographic data is presented in Table 1. The atomic coordinates are shown in Table 2 and bond distance and angles are listed in Table 3.

#### REFERENCES AND NOTES

- [1] B. Dietrich, M. Hosseini, J. M. Lehn and R. B. Sessions, *J. Am. Chem. Soc.*, **103**, 1282 (1981).
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- [4] P. Main, S. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfsen, "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction", University of York, York, England and Louvain, Louvain, Belgium, 1978.
- [5] Lists of structure factors and thermal parameters are available from the Authors upon request.