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4,11-Bis(acetamido)-7,14-dimethyl-4,11-diaza-1,8-diazoniacyclotetradecane diperchlorate dihydrate

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Key indicators

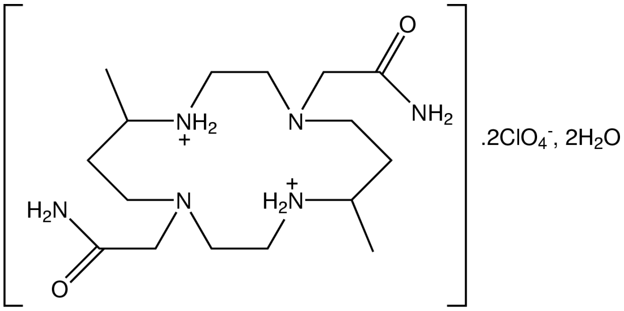
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.130
Data-to-parameter ratio = 20.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound features a doubly protonated dimethyl- and bis(methylcarboxamide)-substituted tetraazacyclotetradecane with the pendant arms disposed over the cavity, an arrangement that is facilitated by intramolecular hydrogen-bonding interactions. The dication occupies a special position about an inversion centre, whereas the ClO_4^- anion and the water molecule are in general positions, thus forming a crystal with the overall composition $C_{16}H_{36}N_6O_2^{2+}\cdot 2ClO_4^-\cdot 2H_2O$. The crystal structure is stabilized by a variety of hydrogen-bonding contacts involving the dication, perchlorate anion and solvent water molecule.

Comment

The crystal structure of the title compound, (I), comprises dications, perchlorate anions and solvent water molecules in the ratio 1:2:2. The cation (Fig. 1) occupies a special position about an inversion centre so that the four N atoms within the macrocycle are coplanar. Protonation occurs at the N1 atom and this is reflected in the systematic differences in the N1—C and N4—C bond distances (Table 1). The pendant acetamide groups lie to either side of the N_4 plane and are orientated so as to place the carbonyl O atoms over the cavity of the macrocycle.



(I)

This configuration is stabilized by hydrogen-bonding interactions involving the N1-bound H1n atoms which are directed towards the inside of the cavity. Thus, O4″ is equally separated from H1n and the symmetry-related H1n^i atoms, indicating that each H1n atom is bifurcated and that a hydrogen-bonded H_2O_2 square is formed perpendicular to the N_4 plane [symmetry code: (i) $-x$, $-y$, $-z$]. Geometric details of the hydrogen-bonding system in the structure of the title compound are given in Table 2.

The O4″ atom also forms an acceptor interaction with the solvent water molecule and the other water-bound H atom

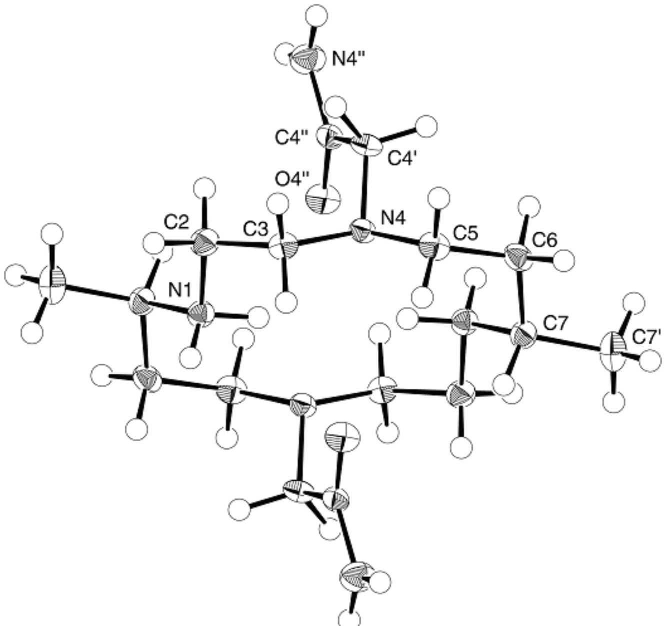


Figure 1
The molecular structure and crystallographic numbering scheme for the dication in (I). Displacement ellipsoids are shown at the 50% probability level (Johnson, 1976).

forms a donor interaction to a perchlorate O atom. The solvent water molecule is also involved in an acceptor interaction with the cationic NH_2 group of the macrocycle. Each of the amide H atoms forms a donor interaction with one of the perchlorate O atoms.

The aforementioned hydrogen-bonding network results in a structure that may be described as being comprised of alternating stacks of cations, and anions and water molecules aligned along the *c* direction.

Experimental

The 1,8-bis(acetamido)-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane compound was prepared in the following manner: 7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane (Fairbank *et al.*, 1985) (2.28 g, 0.01 mol) in ethanol (20 ml) was added to a solution of 2-chloroacetamide (4.68 g, 0.05 mol) and triethylamine (6.07 g, 0.06 mol) also in ethanol (30 ml). The mixture was then refluxed for one day. After the solution had been allowed to stand for three days, a quantity of colourless crystals precipitated. These were recrystallized from a water/acetonitrile (1:1, 20 ml) mixture. Crystals of the title compound were isolated as colourless blocks from the attempted reaction of 1,8-bis(acetamido)-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane and zinc perchlorate in aqueous medium.

Crystal data

$C_{16}H_{36}N_6O_2^{2+}\cdot 2ClO_4^{-}\cdot 2H_2O$
$M_r = 579.43$
Monoclinic, *C*2/*c*
$a = 16.576$ (3) Å
$b = 10.877$ (6) Å
$c = 14.314$ (2) Å
$\beta = 90.25$ (1)°
$V = 2581$ (1) Å^3
$Z = 4$

$D_x = 1.491$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 7.5$–14.6°
$\mu = 0.32$ mm^{-1}
$T = 173$ K
Block, colourless
0.36 × 0.23 × 0.13 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
4647 measured reflections
2965 independent reflections
1545 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\rm max} = 27.5°$

$h = -21 \rightarrow 8$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 18$
3 standard reflections every 400 reflections intensity decay: 1.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.130$
$S = 0.98$
2965 reflections
144 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O4″—C4″	1.241 (3)	N4″—C4″	1.331 (4)
N1—C2	1.495 (4)	C2—C3	1.519 (4)
N1—C7$^{\rm i}$	1.507 (3)	C4′—C4″	1.516 (4)
N4—C3	1.471 (3)	C5—C6	1.521 (4)
N4—C4′	1.463 (3)	C6—C7	1.521 (4)
N4—C5	1.481 (3)	C7—C7′	1.520 (4)
C2—N1—C7$^{\rm i}$	114.7 (2)	O4″—C4″—C4′	120.9 (2)
C4′—N4—C3	111.7 (2)	N4″—C4″—C4′	115.9 (3)
C4′—N4—C5	110.2 (2)	N4—C5—C6	113.3 (2)
C3—N4—C5	108.6 (2)	C7—C6—C5	114.8 (2)
N1—C2—C3	111.7 (2)	C7′—C7—C6	112.2 (2)
N4—C3—C2	114.0 (2)	C7′—C7—N1$^{\rm i}$	111.1 (2)
N4—C4′—C4″	113.3 (2)	C6—C7—N1$^{\rm i}$	108.1 (2)
O4″—C4″—N4″	123.2 (3)		

Symmetry code: (i) $-x, -y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1n···O4″	0.93	2.53	3.083 (3)	118
N1—H1n···O4″$^{\rm i}$	0.93	2.54	3.079 (3)	118
O1*w*—H2o···O4″	0.99	1.76	2.744 (3)	176
O1*w*—H1o···O12$^{\rm ii}$	0.90	2.02	2.903 (3)	166
N1—H2n···O1*w*$^{\rm iii}$	0.88	1.92	2.768 (3)	163
N4″—H3n···O13$^{\rm iv}$	0.95	2.27	3.110 (4)	148
N4″—H4n···O11$^{\rm v}$	0.95	2.26	3.122 (4)	151

Symmetry codes: (i) $-x, -y, -z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $x, -y, \frac{1}{2} + z$; (iv) $x, 1 - y, z - \frac{1}{2}$; (v) $-x, 1 - y, -z$.

The C-bound H atoms were placed in geometrically calculated positions and included in the final refinement in the riding-model approximation with an overall displacement parameter. The O- and N-bound H atoms were located from a difference Fourier map but were not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Fairbank, M. G., Norman, P. R. & McAuley, A. (1985). *Inorg. Chem.* **24**, 2639–2644.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1996). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1997). *TEXSAN for Windows*. Version 1.05. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

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