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3,6,9,16,19,22-Hexaazatricyclo-[22.2.2.2^{11,14}]triaconta-11,13,24,-26(1),27,29-hexaene pentahydrate

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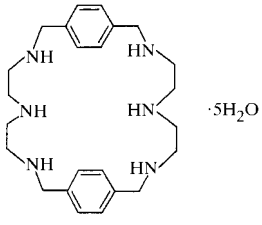
In the title macrocyclic polyamine, $C_{24}H_{38}N_6\cdot5H_2O$, the centrosymmetric polyamine molecules are stacked in rows, and between these molecules there are channels along the *a* axis. The intermolecular hydrogen bonds formed between the water and polyamine, together with those formed between water molecules, generate an extensive hydrogen-bonding network.

Comment

Macrocyclic complexes play a key role in the modelling of metallobiosites (Fenton & Ōkawa, 1993), and in the development of systems for activating substrate molecules (Vigato *et al.*, 1990). Our current studies focus on macrocyclic polyamines in which the relative positions of the donor atoms in the ring are designed to hold pairs of coordinated transition metal ions at specified distances. The distance between these two metal ions is considered to be an important factor in



(I)

increasing the efficiency in activation of substrates. Recently, it was reported that the binuclear complexes of the title compound, (I), and its analogues can accelerate the hydrolysis of bis(*p*-nitrophenyl)phosphate and adenosine triphosphate (Ragunathan & Schneider, 1996; Lu *et al.*, 1998). On the other hand, these compounds and their metal complexes are good receptors for inorganic phosphates and ribonucleic acid (Nation *et al.*, 1996; Li *et al.*, 1997). Therefore, the structure of the title compound may prove useful both for understanding the mechanisms of hydrolysis and for the design of new compounds.

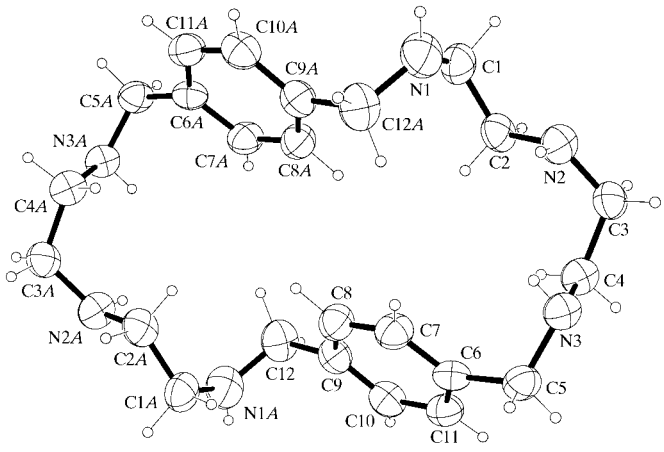


Figure 1
Structure of the title compound showing 50% probability displacement ellipsoids with the numbering scheme (suffix *A* indicates atoms at $1-x$, $1-y$, $1-z$). The water molecules were omitted for clarity.

Fig. 1 is the *ORTEP*II (Johnson, 1976) representation of compound (I). The centrosymmetric macrocycle adopts a chair-like conformation, with one diethylene triamine moiety flipped down and the other flipped up. Although in its analogue 3,7,11,19,23,27-hexaazatricyclo[27.3.1.1^{13,17}]tetratriaconta-1(32),13,15,17(34),29(33),30-hexaene hexahydrobromide dihydrate, (II), the molecule is still in the chair conformation, it is the two phenyl rings that are flipped down and flipped up and lie nearly perpendicular to the plane of the macrocyclic arms (Liobet *et al.*, 1994). These differences may depend both on the different states of protonation and on the different placing of the aromatic substituents, *para* in (I)

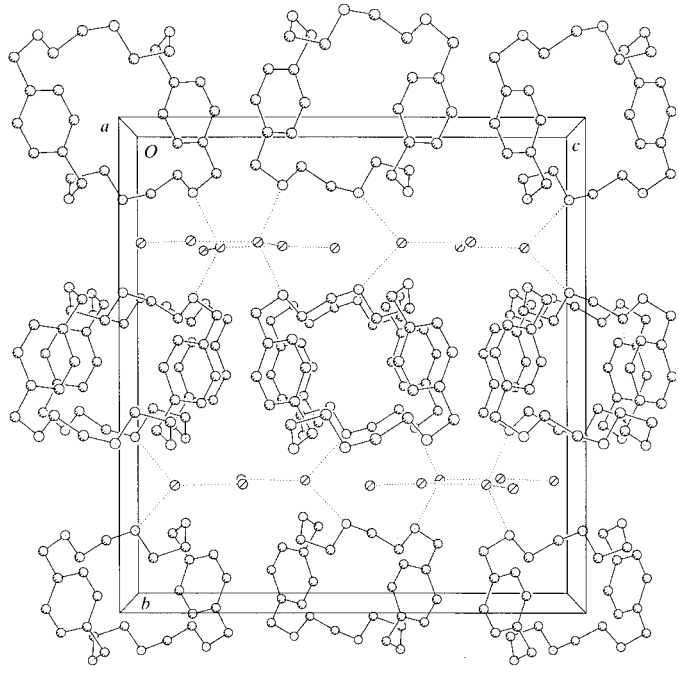


Figure 2
The unit cell of the title compound with H atoms omitted for clarity.

and *meta* in (II). The C—C and C—N bond lengths in (I) are almost equal to those in (II). In the crystal, the macrocyclic molecules are arranged in stacks (Fig. 2), and the macrocycles of the molecules form an apparent channel along the *a* axis. The water molecules (O11, O12, O14, O15 and their symmetry-related partners) link different polyamine molecules by hydrogen bonds (Table 2) to form a supermolecule.

Experimental

The title compound was synthesized in a procedure similar to that used by Chen & Martell (1991). To an MeCN solution of diethylene triamine an equivalent amount of terephthalaldehyde was added slowly at room temperature. Several hours later, a white precipitate was obtained. The white solid was reduced with sodium borohydride in ethanol for 5 h. The solvent was then removed *in vacuo*, and the residue was extracted with chloroform. The product was purified by recrystallization from MeCN, the pure compound dissolved in an appropriate amount of hot water and single crystals suitable for crystallographic analysis were obtained by crystallization from water.

Crystal data

$C_{24}H_{38}N_6{\cdot}5H_2O$
M_r = 500.68
Orthorhombic, *Pnma*
a = 7.451 (3) Å
b = 19.709 (6) Å
c = 18.587 (8) Å
V = 2729.6 (18) Å^3
Z = 4
D_x = 1.218 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 29 reflections
θ = 7.80–9.17°
μ = 0.086 mm^{-1}
T = 293 (2) K
Prism, colourless
0.40 × 0.20 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
3241 measured reflections
2474 independent reflections
1770 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25°
$h = -1 \rightarrow 8$
$k = -23 \rightarrow 1$
$l = -1 \rightarrow 22$
3 standard reflections
every 97 reflections
intensity decay: 4.94%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.197
S = 1.027
2474 reflections
244 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.1131P)^2 + 1.2637P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.451 (4)	C1—C2	1.513 (4)
N2—C2	1.463 (3)	C3—C4	1.513 (4)
N2—C3	1.466 (4)	C5—C6	1.511 (4)
N3—C4	1.455 (4)	C9—C12	1.526 (4)
N3—C5	1.475 (4)		
C2—N2—C3	114.0 (2)	N3—C5—C6	115.1 (2)
C4—N3—C5	114.3 (2)	C7—C6—C5	120.6 (2)
N1—C1—C2	116.8 (3)	C11—C6—C5	121.9 (3)
N2—C2—C1	111.6 (2)	C10—C9—C12	122.2 (3)
N2—C3—C4	116.4 (2)	C8—C9—C12	120.3 (3)
N3—C4—C3	111.8 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O15	0.84 (2)	2.29 (2)	3.097 (9)	162.4 (16)
N2—H2N···O13	0.85 (2)	2.27 (3)	3.115 (4)	172 (2)
N3—H3N···O13	0.85 (2)	2.58 (3)	3.361 (4)	153 (2)
O11—H21···N3	0.902 (16)	1.911 (16)	2.810 (3)	175 (2)
O12—H22···N2	0.901 (19)	2.03 (2)	2.903 (4)	162 (2)
O13—H23···O14^{i}	0.90 (3)	1.90 (3)	2.768 (6)	162 (3)
O14—H24···O11	0.898 (18)	1.96 (2)	2.850 (5)	169 (5)
O14—H34···O11^{ii}	0.90 (3)	1.93 (3)	2.825 (5)	177 (5)

Symmetry codes: (i) $x-1, y, z$; (ii) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{3}{2}-z$.

H atoms were found from the difference map and were refined isotropically with fixed isotropic displacement parameters $1.2U_{eq}$ of the atoms to which they are attached. To make the refinement stable, several restraints were used to fix the O—H and N—H bond distances as well as the H—O—H angles. No suitable positions were found from the difference map for the H atoms attached to the disordered O atoms O15 and O15′.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1091). Services for accessing these data are described at the back of the journal.

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