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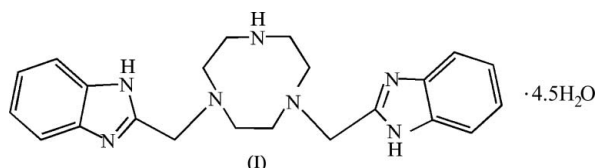
Key indicators

Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
Disorder in solvent or counterion
 R factor = 0.066
 wR factor = 0.142
Data-to-parameter ratio = 18.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.1,4-Bis(1*H*-benzimidazol-2-ylmethyl)-1,4,7-triazacyclononane 4.5-hydrate

The title compound, $\text{C}_{22}\text{H}_{27}\text{N}_7 \cdot 4.5\text{H}_2\text{O}$, crystallizes with two molecules of 1,4-bis(benzimidazol-2-ylmethyl)-1,4,7-triazacyclononane and nine disordered water molecules in the asymmetric unit. Each triazacyclononane group exhibits an intramolecular $\text{N}-\text{H} \cdots \text{N}$ hydrogen bond. The crystal packing is dominated by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds between organic molecules and water molecules, and also between water molecules.

Comment

In recent years, *N*-functionalized 1,4,7-triazacyclononane ligands have attracted attention owing to their versatile and efficient functions as ligands (Wainwright, 1997). A number of ligands derived from *N*-functionalized 1,4,7-triazacyclononane and their complexes have been employed, namely the derivatives of 1,4,7-triazacyclononane with pendent pyridyl (Tamura *et al.*, 2000), imidazolyl (Vaira *et al.*, 2000), pyrazolyl (Vaira *et al.*, 1994) aminophenyl (Fallis *et al.*, 2000) and benzimidazolyl (Li *et al.*, 2005) groups and some others. However, the crystal structures of the *N*-functionalized 1,4,7-triazacyclononane ligands are rarely reported. We report here the crystal structure of the 4.5-hydrate of 1,4-bis(benzimidazole-2-yl-methyl)-1,4,7-triazacyclononane, (I).



The asymmetric unit comprises two molecules of 1,4-bis(benzimidazole-2-yl-methyl)-1,4,7-triazacyclononane and nine water molecules. The characteristic geometrical parameters of the 1,4,7-triazacyclononane and benzimidazole groups (Fig. 1) are [$d_{\text{av}}(\text{C}-\text{N}) = 1.462$ (3) Å, $\theta_{\text{av}}(\text{C}-\text{N}-\text{C}) = 115.75$ (18)°] and [$d_{\text{av}}(\text{C}-\text{N}) = 1.357$ (3) Å]. The dihedral angles between the two benzimidazole planes in the two molecules are 37.9 (2) and 40.8 (2)°, indicating their almost identical overall conformations. Within each of the two triazacyclononane rings, there is an intramolecular hydrogen bond of the $\text{N}-\text{H} \cdots \text{N}$ type (Table 1). The water molecules are hydrogen bonded to each other using all potential donor and acceptor sites (Table 1).

Experimental

The title compound was prepared by a literature method (Li *et al.*, 2005). Crystals suitable for X-ray analysis were obtained by diffusion of diethyl ether into a solution in EtOH/H₂O (5:1) over a period of

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two weeks. During the crystallization experiment the amount of ethanol was five times larger than that of water, but the crystal structure does not include ethanol as a solvent. However, nine disordered water molecules are present in the asymmetric unit; water molecules are more polar and act as better proton donors and acceptors in hydrogen bonding.

Crystal data

$C_{22}H_{27}N_7 \cdot 4.5H_2O$
 $M_r = 470.58$
 Monoclinic, $P2_1/c$
 $a = 7.4815$ (5) Å
 $b = 21.5452$ (14) Å
 $c = 37.968$ (3) Å
 $\beta = 91.261$ (1)°
 $V = 6118.5$ (7) Å³

$Z = 8$
 $D_x = 1.022$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.07$ mm⁻¹
 $T = 294$ (2) K
 Block, yellow
 $0.30 \times 0.26 \times 0.24$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.97$, $T_{\max} = 0.98$

63905 measured reflections
 12024 independent reflections
 7076 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\text{max}} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.142$
 $S = 0.96$
 12024 reflections
 658 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.22P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2C \cdots N3$	0.90	2.26	2.772 (3)	116
$N7-H7 \cdots O8$	0.86	2.23	3.082 (4)	173
$N9-H9A \cdots N10$	0.90	2.34	2.833 (2)	114
$N9-H9A \cdots O14$	0.90	2.58	3.371 (4)	147
$N11-H11A \cdots O3$	0.86	2.19	3.043 (4)	171
$N13-H13A \cdots O12$	0.86	1.95	2.774 (4)	160
$O5-H5E \cdots O7$	0.85	2.55	3.087 (5)	122
$O6-H6C \cdots N14$	0.85	2.29	2.789 (2)	118
$O9-H9F \cdots N6$	0.85	2.01	2.771 (2)	148
$O10-H10D \cdots O8$	0.85	2.52	3.171 (5)	134
$O11-H11D \cdots N5$	0.85	2.29	2.729 (2)	113
$O15-H15E \cdots O6$	0.85	2.21	3.051 (2)	169
$O15-H15C \cdots N12$	0.85	2.12	2.885 (3)	150
$N4-H4 \cdots O3^i$	0.86	2.26	3.094 (4)	164
$O2-H2E \cdots N2^i$	0.85	2.49	3.033 (4)	123
$O6-H6E \cdots O1^{ii}$	0.85	2.41	3.079 (3)	136
$O9-H9E \cdots O1^{ii}$	0.85	2.59	3.168 (3)	126
$O11-H11B \cdots O13^{iii}$	0.85	2.36	3.065 (2)	141
$O13-H13B \cdots O9^{iv}$	0.85	2.58	3.2128 (19)	133
$O13-H13C \cdots O12^v$	0.85	2.33	3.137 (4)	159

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

All H atoms were positioned geometrically and refined as riding ($C-H = 0.93$ and 0.97 Å, $N-H = 0.86-0.90$ Å, and $O-H = 0.85-0.92$ Å). $U_{\text{iso}}(H)$ values were set at $1.2U_{\text{eq}}(C,O,N)$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

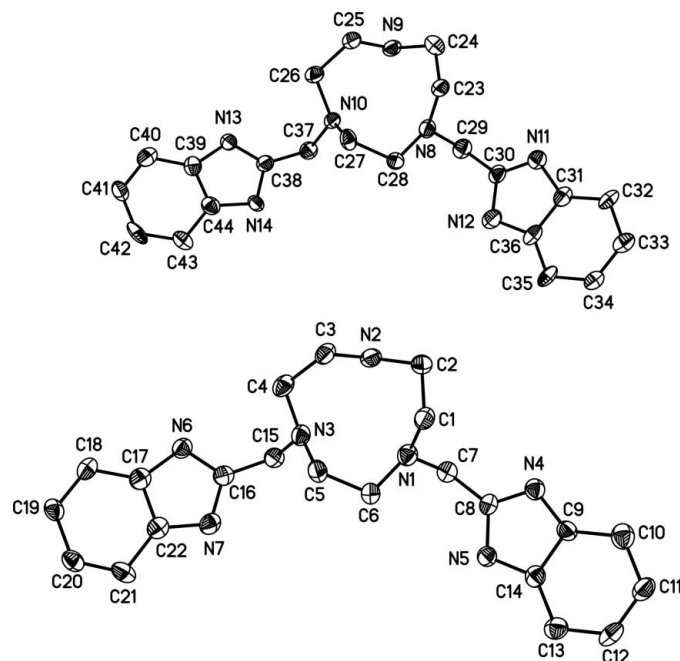


Figure 1

Views of the two independent molecules, with the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level. H atoms and water molecules have been omitted.

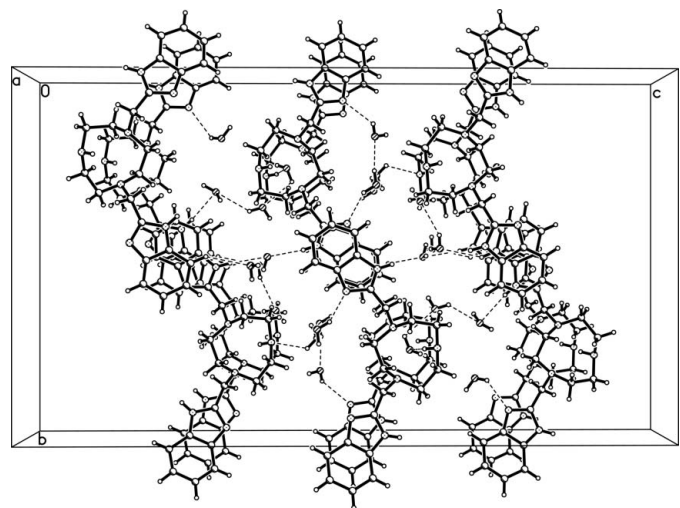


Figure 2

View of the crystal packing along the a axis. Hydrogen bonds are shown as dashed lines.

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References

- Bruker (2000). SMART, SAINT, SADABS and SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.
 Fallis, I. A., Farley, R. D., Malik, K. M. A., Murphy, D. M. & Smith, H. J. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3632–3639.

Li, Q. X., Luo, Q. H., Li, Y. Z., Duan, C. Y. & Tu, Q. Y. (2005). *Inorg. Chim. Acta*, **358**, 504–512.

Tamura, M., Urano, Y., Kikuchi, K., Higuchi, T., Hirobe, M. & Nagano, T. (2000). *J. Organomet. Chem.* **611**, 586–592.

Vaira, M. D., Mani, F. & Stoppioni, P. (1994). *J. Chem. Soc. Dalton Trans.* pp. 3739–3743.

Vaira, M. D., Mani, F. & Stoppioni, P. (2000). *Inorg. Chim. Acta*, **303**, 61–69.

Wainwright, K. P. (1997). *Coord. Chem. Rev.* **166**, 35–90.