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1,4,7,11,14,17-Hexaazacycloicosane-9,19-diol hexahydrobromide

Feng Liang,[a] Yi-Zhi Li,[b] Cheng-Tai Wu[a]* and Si-Min Liu[a]

[a]Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China, and [b]Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: llyyjz@nju.edu.cn

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The crystal structure of 1,4,7,11,14,17-hexaazacycloicosane-9,19-diol hexahydrobromide, $C_{14}H_{34}N_6O_2 \cdot 6HBr$, shows the macrocycle to be centrosymmetric. A three-dimensional network, leading to the formation of channels, is formed owing to the presence of both intermolecular and intramolecular hydrogen-bonding interactions between the constituents of the structure.

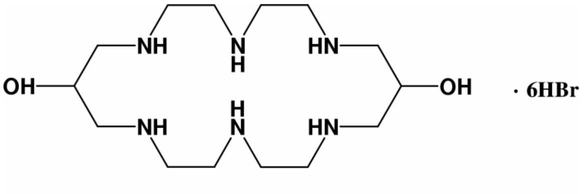
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.039
wR factor = 0.088
Data-to-parameter ratio = 17.9

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

Comment

Organic materials containing large cavities or channels with controlled sizes, shapes and chemical environments have received much attention in recent years because of their potential applications in separation, catalysis, and optoelectronics. Various organic building blocks have been used to assemble a variety of porous three-dimensional networks with hydrogen bonding (Venkataraman *et al.*, 1994; Brunet *et al.*, 1997; Russell *et al.*, 1997).



(I)

We have reported the synthesis of the title compound, (I) (Xue *et al.*, 1998). The structures of a series of novel hydroxy macrocyclic polyamines (Liu, Xue, Wu *et al.*, 1996) and their complexing properties with transition metal ions, such as copper(II) (Liu, Xue, Fu *et al.*, 1996) and nickel(II) (Liu *et al.*, 1997), have been reported. Recently, our interest has been directed towards the self-assembly of macrocyclic compounds utilizing functional groups. To better understand the structural characteristics of the macrocyclic precursors, the crystal structure of (I) has been investigated.

The X-ray crystal structural study indicated the presence of layers which are defined by macrocyclic rings. The HBr molecules, which are largely anchored between adjacent layers (Fig. 1), play an important role in connecting these two-dimensional structures. A range of Br—H···N, N—H···Br, O—H···Br hydrogen bonding is observed in the assembled structure (Table 1). In addition to these, N—H···Br hydrogen bonding has also been observed (Table 1). A three-dimensional network is formed by both intermolecular and intramolecular hydrogen-bonding interactions in the unit cell. The most interesting feature of the crystal structure is that the macrocycles are arranged in such a way to produce an

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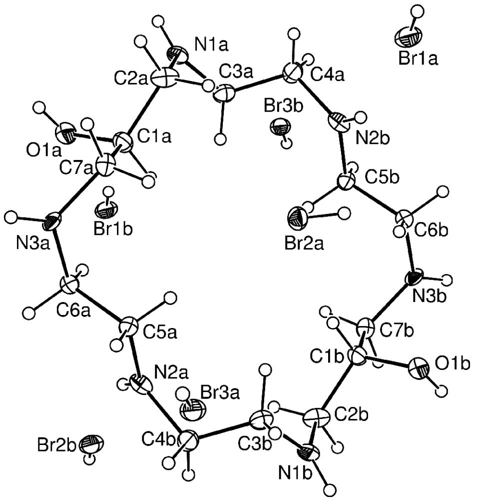

Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 30% probability level (Bruker, 1997). The macrocycle is disposed about a centre of inversion.

arrangement with channels extended along the *b* axis (Fig. 3). The channels are occupied by HBr molecules that form a complicated hydrogen-bonding network among themselves. In this structure, the macrocycle functions as a bulky linear bifunctional building block. The HBr molecules 'cement' these to form a column. This novel structure may provide further insight into designing new porous materials, as well as other supramolecular architectures.

Experimental

The title compound (Xue *et al.*, 1998) was heated so that it dissolved in a minimum amount of water. This was followed by the addition of acetone and ethanol (5:1). The solution was allowed to stand at room temperature for 5–6 months to furnish colourless crystals.

Crystal data

$C_{14}H_{34}N_6O_2 \cdot 6HBr$
$M_r = 803.92$
Orthorhombic, *Pbca*
$a = 12.340$ (1) Å
$b = 10.380$ (1) Å
$c = 20.321$ (2) Å
$V = 2602.9$ (4) Å^3
$Z = 4$
$D_x = 2.052$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3478 reflections
$\theta = 2.6$–$27.1°$
$\mu = 9.28$ mm^{-1}
$T = 293$ (2) K
Block, colourless
$0.3 \times 0.2 \times 0.2$ mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.124$, $T_{\max} = 0.156$
12529 measured reflections
2294 independent reflections
1680 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.084$
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 14$
$k = -12 \rightarrow 10$
$l = -23 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.088$
$S = 1.03$
2294 reflections
128 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.92$ e Å^{-3}
$\Delta\rho_{\min} = -0.75$ e Å^{-3}

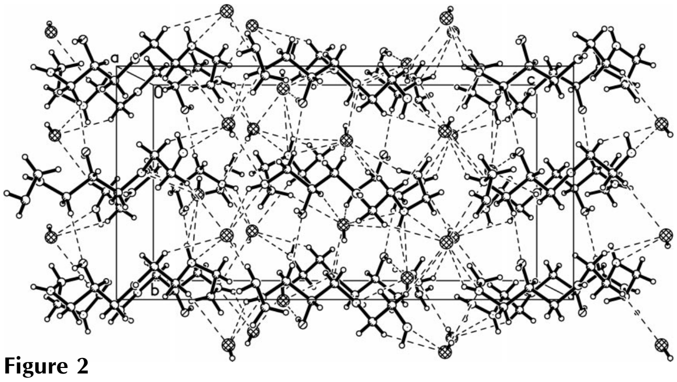

Figure 2
View of the packing, along the *a* axis, showing the hydrogen-bonding interactions.

Table 1
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
Br3—H3⋯N2$^{\rm i}$	0.87	2.64	3.267 (5)	130
N1—H1B⋯Br3$^{\rm ii}$	0.86	2.69	3.366 (5)	136
N2—H2C⋯Br1$^{\rm iii}$	0.86	2.63	3.404 (5)	151
N3—H3C⋯Br1$^{\rm iv}$	0.86	2.75	3.225 (4)	116
N3—H3C⋯Br2$^{\rm v}$	0.86	2.82	3.251 (5)	113
O1—H1D⋯Br1$^{\rm vi}$	0.82	2.48	3.300 (4)	175

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

All the H atoms except the H atoms of HBr were placed in calculated positions and included in the final refinement with overall displacement parameters; for N—H, $U_{\rm iso} = 1.2U_{\rm eq}$(parent atom), and for O—H and methylene H, $U_{\rm iso} = 1.5U_{\rm eq}$(parent atom), The H atoms of HBr were located from difference density maps and were refined as riding, using the instruction AFIX 3 (Bruker, 1997) with $U_{\rm iso} = 1.2U_{\rm eq}$(parent atom).

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

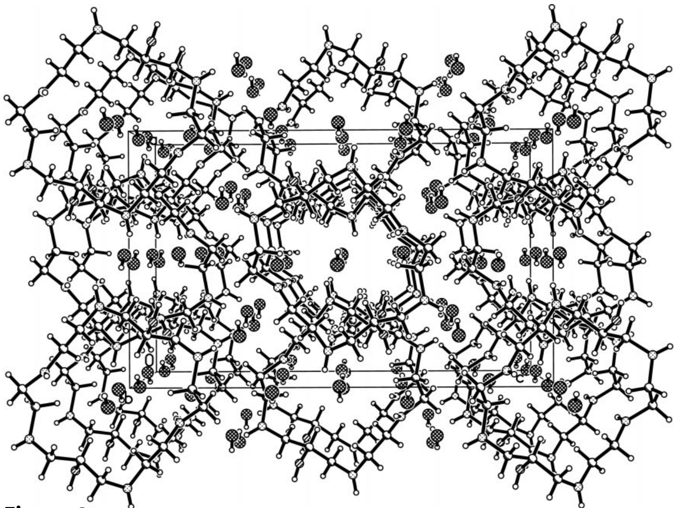

Figure 3
The arrangement of channels, extended along the *b* axis.

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References

Bruker (1997). *SMART, SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Brunet, P., Simard, M. & Wuest, J. D. (1997). *J. Am. Chem. Soc.* **119**, 2737–2739.

Liu, S. H., Xue, G. P., Fu, E. Q., Wu, C. T., Luo, B. S. & Chen, L. R. (1996). *Chin. J. Struct. Chem.* **15**, 315–316.

Liu, Y., Xue, G. P., Wu, C. T., Luo, B. S. & Chen, L. R. (1996). *Chin. J. Struct. Chem.* **15**, 371–372.

Liu, Y., Xue, G. P., Wu, C. T., Luo, B. S. & Chen, L. R. (1997). *Chin. J. Struct. Chem.* **16**, 338–339.

Russell, V. A., Evans, C. C., Li, W. & Ward, M. D. (1997). *Science*, **276**, 575–577.

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

Venkataraman, D., Lee, S., Zhang, J. & Moore, J. S. (1994). *Nature (London)*, **371**, 591–592.

Xue, G. P., Liu, Y. & Wu, C. T. (1998). *Chin. J. Chem.* **16**, 536–538.