

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: none
 2031 measured reflections
 578 independent reflections

539 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\text{max}} = 25^\circ$
 $h = -5 \rightarrow 6$
 $k = -12 \rightarrow 12$
 $l = -7 \rightarrow 7$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.098$
 $S = 1.082$
 578 reflections
 49 parameters
 H atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.134P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
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1,4,7,10,13,16,21,24-Octaazabicyclo-[8.8.8]hexacos-4,6,13,15,21,23-hexaene pentahydrate

VICKIE MCKEE AND JANE NELSON

School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland. E-mail: v.mckee@qub.ac.uk

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Abstract

The title compound, C₁₈H₃₀N₈·5H₂O, is a hexamine cryptand which crystallizes with pseudo-threefold symmetry, each strand having the *anti* conformation. Water molecules are hydrogen bonded to five of the six imine N atoms.

Comment

The title compound, hereinafter imBT·5H₂O, is a small azacryptand which acts as an efficient host for single main group (Apperley *et al.*, 1999), transition (Hunter *et al.*, 1990) or lanthanide (Bligh *et al.*, 1998) ions in redox states I–III, despite the presence of six imino functions which might normally be expected to be subject to metal-assisted hydrolysis in the presence of strong Lewis acids. While attempting to discover the effective limiting size of the cavity for group 13 cations, we treated the ligand with a number of cations in redox state +III, isolating products of acceptable purity for $M = \text{In}$ and Tl , though not for $M = \text{Ga}$. We also attempted synthesis of the Tl^{I} cryptate to discover whether the cryptand cavity could accommodate this cation, which is 0.2–0.3 Å larger than Hg^{II} or Sr^{II} but 0.1–0.2 Å smaller than Cs^{I} ; all three of these cations have previously been coordinated by this host. However, the expected Tl complex was not obtained and, as described in the *Experimental* section, the isolated product was imBT·5H₂O. Smith *et al.* (1993) have described the structure of imBT, but the pentahydrate has not previously been reported.

Table 1. Selected geometric parameters and hydrogen-bonding geometry (Å, °)

N1—C1	1.2847 (19)	N2—C3	1.450 (2)
N1—C2	1.4820 (19)	C1—C1'	1.479 (3)
N2—C1	1.3436 (19)	C3—C2	1.536 (2)
C1—N1—C2	105.66 (12)	N2—C1—C1'	120.31 (15)
C1—N2—C3	109.04 (13)	N2—C3—C2	101.51 (12)
N1—C1—N2	117.32 (14)	N1—C2—C3	106.44 (12)
N1—C1—C1'	122.37 (15)		

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...N1 ⁱⁱ	0.87 (2)	2.09 (2)	2.919 (2)	157 (2)
C2—H2B...N1 ⁱⁱⁱ	0.99	2.91	3.866 (2)	162
C3—H3B...N1 ^{iv}	0.99	2.97	3.684 (2)	130

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

The amine-H atom was located from difference maps and refined (with the atomic displacement parameter fixed at 0.05 Å²).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINTE* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL97*.

We are grateful to Professor Ward T. Robinson, University of Canterbury, Christchurch, New Zealand, for access to the diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1338). Services for accessing these data are described at the back of the journal.

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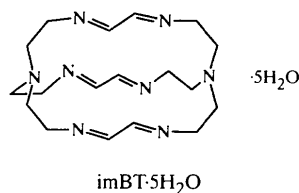


Fig. 1 shows the contents of the asymmetric unit. The cryptand shows pseudo-threefold symmetry and adopts a conformation very similar to that of the anhydrous compound (Smith *et al.*, 1993). In both cases, all the N=C—C=N units adopt the *anti* conformation and are close to planar (mean torsion angles 170.9 and 169.5° for imBT·5H₂O and imBT, respectively). The overall length of the cavity (N1···N2) is 7.029 (3) in imBT·5H₂O and 6.84 Å in imBT. In cryptate complexes, this bridgehead–bridgehead distance contracts as the width of the cavity expands to accommodate the metal ion guest; in [Hg(imBT)](ClO₄)₂, for example, the N1···N2 distance reduces to 6.15 (3) Å (Apperley *et al.*, 1999). The bond distances within the cryptand are unremarkable and there are no significant differences between the three strands. Larger hexamine cryptands (Drew *et al.*, 1995; Nelson *et al.*, 1998) and conjugated systems such as the triscarotenoid azacryptands (Lehn *et al.*, 1992) show interstrand (imine)CH— π interactions across the cavity and these seem to control their conformations (Drew *et al.*, 1995). This effect is not apparent in imBT, the imine protons being essentially tangential to the cavity. It is possible that this distinction arises from the short strand length.

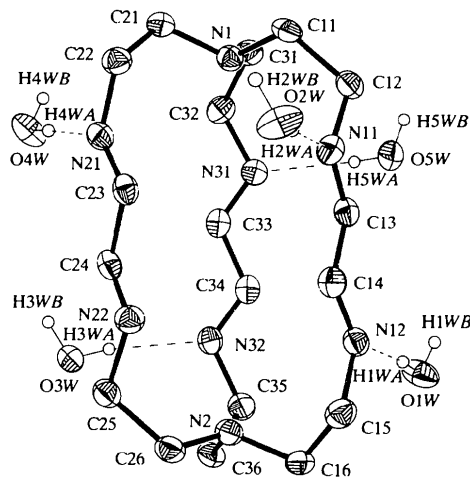


Fig. 1. A perspective view of the asymmetric unit of imBT·5H₂O, showing 50% probability displacement ellipsoids and the hydrogen-bonding. Non-water H atoms are omitted for clarity.

All of the imine lone pairs are divergent (directed out of the central cavity) and five of these are hydrogen-bonded to water molecules (Table 1). Each water

molecule makes two further hydrogen-bonds to other water molecules and the resulting hydrogen-bonded network cross-links the azacryptands in three dimensions (Fig. 2). In view of the frequently reported tendency of many imine groups to hydrolyse, it is noteworthy that imBT crystallizes as a pentahydrate and shows remarkable stability towards hydrolysis.

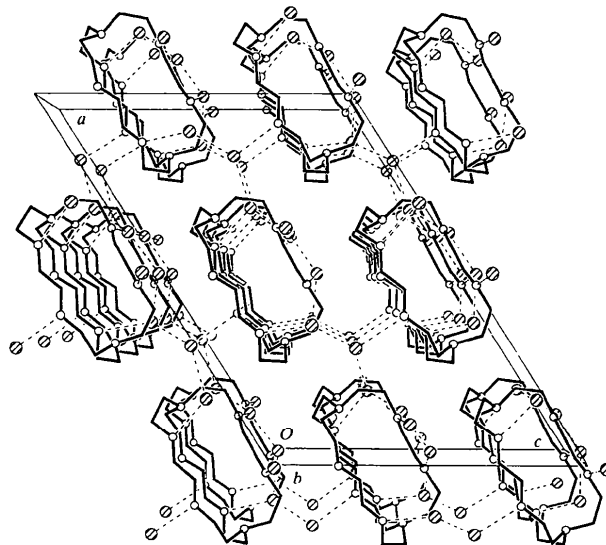


Fig. 2. Packing diagram for imBT·5H₂O, showing the hydrogen-bonding network. O atoms are shown as hatched circles and H atoms are omitted for clarity.

Experimental

The free cryptand (17.9 mg, 0.05 mmol), prepared as described by Smith *et al.* (1993), was dissolved in CHCl₃ (2 ml). EtOH (2 ml) was then added, followed by Tl(NO₃)₃·3H₂O (44.4 mg, 0.1 mmol) dissolved in H₂O (10 drops) and EtOH (1 ml). No change was observed on addition of the metal salt. The solution was left to evaporate in air to around one third of its original volume and then placed in an Et₂O atmosphere for crystallization by vapour diffusion. After 2 weeks, large colourless crystals suitable for X-ray crystallography were observed.

Crystal data

C₁₈H₃₀N₈·5H₂O
M_r = 448.58
 Monoclinic
Cc
a = 22.3117 (14) Å
b = 8.2925 (6) Å
c = 16.1711 (18) Å
 β = 122.532 (6)°
V = 2522.5 (4) Å³
Z = 4
D_x = 1.181 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 34 reflections
 θ = 5.45–12.47°
 μ = 0.087 mm⁻¹
T = 153 (2) K
 Block
 0.60 × 0.58 × 0.42 mm
 Colourless

Data collection

Siemens P4 diffractometer $\theta_{\max} = 25^\circ$
 ω scans $h = 0 \rightarrow 26$
 Absorption correction: none $k = -9 \rightarrow 1$
 2603 measured reflections $l = -19 \rightarrow 16$
 2273 independent reflections 3 standard reflections
 2074 reflections with every 97 reflections
 $I > 2\sigma(I)$ intensity decay: none
 $R_{\text{int}} = 0.015$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.068$
 $S = 1.052$
 2273 reflections
 311 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.6765P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$

Extinction correction:
SHELXL97 (Sheldrick, 1997)
 Extinction coefficient:
 0.0052 (4)
 Scattering factors from
International Tables for Crystallography (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter: not reliably determined

Table 1. *Hydrogen-bonding geometry* (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WA...N12	0.94 (3)	1.97 (3)	2.906 (3)	175 (3)
O1W—H1WB...O3W ^a	0.78 (3)	1.96 (3)	2.736 (3)	176 (3)
O2W—H2WA...N11	0.76 (3)	2.12 (3)	2.883 (3)	175 (3)
O2W—H2WB...O1W ⁱⁱ	0.80 (3)	1.99 (3)	2.788 (3)	176 (3)
O3W—H3WA...N32	0.83 (3)	2.07 (3)	2.885 (3)	170 (3)
O3W—H3WB...O5W ⁱⁱⁱ	0.88 (3)	1.83 (3)	2.711 (3)	176 (3)
O4W—H4WA...N21	0.87 (3)	2.05 (3)	2.928 (3)	178 (3)
O4W—H4WB...O2W ^{iv}	0.80 (3)	2.01 (3)	2.812 (3)	173 (3)
O5W—H5WA...N31	0.82 (3)	2.11 (4)	2.928 (3)	174 (3)
O5W—H5WB...O4W ^a	0.80 (3)	1.97 (4)	2.771 (3)	172 (3)

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

All non-H atoms were refined with anisotropic atomic displacement parameters. H atoms bonded to C atoms were placed at calculated positions, with isotropic displacement parameters riding on U_{eq} of the carrier atoms. H atoms bonded to O atoms were located from difference maps and refined with a common fixed atomic displacement parameter of 0.04 \AA^2 .

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1990a). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1339). Services for accessing these data are described at the back of the journal.

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C—H...O interactions in dimethyl 6,6'-dimethoxy-3,3',5,5'-tetramethylbiphenyl-2,2'-dicarboxylate

ALLISON J. DOBSON AND ROGER E. GERKIN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.ohio-state.edu

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Abstract

The title compound, C₂₂H₂₆O₆, crystallized in the centrosymmetric space group *Pbcn* with half of the molecule as the asymmetric unit (the molecular symmetry is 2). The H atoms of each of the four methyl groups in the asymmetric unit are disordered over two sites. Nine leading C—H...O interactions are present, with H...O distances ranging from 2.50 to 2.87 Å and C...O distances ranging from 3.157 (3) to 3.567 (3) Å. The various interaction chains form a three-dimensional network. The intramolecular angle between the biphenyl ring planes (twist angle) is 71.3 (1)°.

Comment

This report is one of a series on hydrogen-bonding and C—H...O interactions in aromatic compounds, and follows reports on other substituted biphenyls including, for example, biphenyl-3-carboxylic acid, 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid and 6,6'-dimethoxy-3,3',5,5'-tetramethylbiphenyl-2,2'-dimethanol (hereafter,