

Hierarchy of hydrogen bonding in bis(1,4,7-trioxa-10-azoniacyclododecane) bis(4-aminobenzoate) trihydrate

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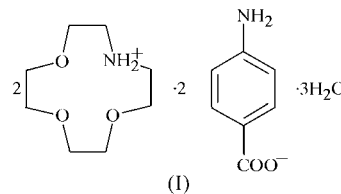
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In the title compound, $2C_8H_{18}NO_3^+ \cdot 2C_7H_6NO_2^- \cdot 3H_2O$, proton transfer occurs from the carboxylic acid group of the 4-aminobenzoic acid (PABA) molecule to the amine group of the macrocycle, resulting in the formation of a salt-like adduct. The anions are combined into helical chains which are further bound by the water molecules into sheets. The macrocyclic cations are situated between these layers and are bound to the anions both directly and *via* bridging water molecules. The structure exhibits a diverse system of hydrogen bonding.

Comment

The title compound, (I), was investigated as part of a study of hydrogen bonding in systems containing biologically important molecules and macrocyclic ligands. A search of the Cambridge Structural Database (Version 5.26, plus three 2005 updates; Allen, 2002) revealed a number of 4-aminobenzoic acid (PABA) cocrystals in neutral (Lynch *et al.*, 1992*b*; Lynch & McClenaghan, 2001; Moreno-Fuquen *et al.*, 2003), cationic (protonated on the amino group; Benali-Cherif *et al.*, 2002; Lynch *et al.*, 1992*a*) and anionic forms (deprotonated on the carboxylic acid group; Smith *et al.*, 1999). Only three examples are known so far for PABA cocrystals with O-containing crown ethers, *viz.* with 18-crown-6 (Elbasyouny *et al.*, 1983) and with two *cis* isomers of dicyclohexyl-18-crown-6 (Fonari *et al.*, 1994), which revealed that both complexes are adducts with a 1:2 stoichiometry, with the amino group of PABA responsible for the N—H...O(crown) hydrogen bonds. A robust dimeric carboxyl $R_2^2(8)$ homosynthon (Desiraju, 1995) was responsible for the PABA molecules associating into dimers. We report here the first example, (I), of a PABA cocrystal with the mixed N,O-macrocycle 1,4,7-trioxa-10-azacyclododecane.

Compound (I) is a salt-like adduct due to protonation of the macrocycle by PABA molecules. The asymmetric unit contains two tightly held cation–anion pairs, designated as *A* and *B*, and three water molecules (Fig. 1). Molecular dimensions are unexceptional.



The macrocyclic cations have an *exo–endo* orientation of the $>NH_2^+$ ammonium functionality, with one H atom involved in an intramolecular bifurcated N—H...O hydrogen bond inside the macrocycle and the second H atom involved in intermolecular hydrogen bonding with the PABA anions. The macrocycles have slightly different conformations and shapes, the heteroatoms being coplanar to within 0.39 Å in macrocycle *A* and 0.14 Å in macrocycle *B*. The mutual arrangement in the cation–anion units is described by the dihedral angle between the planes through the planar PABA skeleton and through four heteroatoms of the macrocycle, with a value of 48.9 (1)° in unit *A* and 62.9 (1)° in unit *B*.

In the *A* and *B* cation–anion units, the components are held together through a pair of N—H($>NH_2^+$)...O(COO[−]) and C—H...O(COO[−]) hydrogen bonds (Table 1). The N—H...O hydrogen bonds, with N2...O2 separations of 2.697 (2) and 2.735 (2) Å in units *A* and *B*, respectively, are the shortest of all those that sustain the structure. Each carboxylate group acts in a chelate mode *via* an $R_2^2(8)$ ring. This heterosynthon substitutes the planar robust centrosymmetric $R_2^2(8)$ homosynthon typical for two carboxyl groups. The environments of the macrocyclic cations are different in this structure, and whilst cation *A* does not have any direct contacts with water molecules, water molecule O1W interacts with cation *B* as a single H-atom donor and a single H-atom acceptor.

Although the mode of cation–anion interaction is similar in the *A* and *B* units, the structural functions of the *A* and *B* PABA anions are quite different in the supramolecular structure organization. PABA *A* anions are linked *via* N—

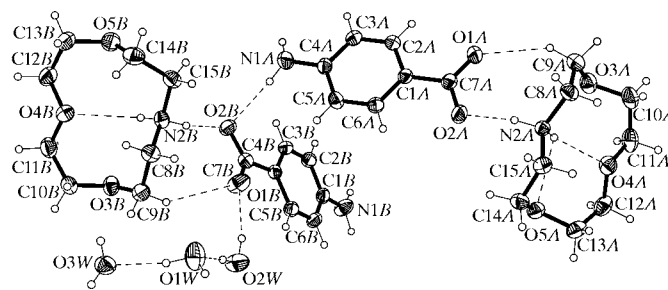


Figure 1

The asymmetric unit of (I), showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and hydrogen bonds are indicated by dashed lines.

H \cdots O hydrogen bonds to form a $C(8)$ helical chain running parallel to the [010] direction (Fig. 2). Each PABA B anion, acting as a single H-atom donor and a single H-atom acceptor, links a pair of PABA A anions separated by translation along the same direction, thus forming the outer surface of the helix. Propagation of these four hydrogen bonds generates a chain of fused $R_4^1(22)$ rings. Water molecule O3W acts as a double

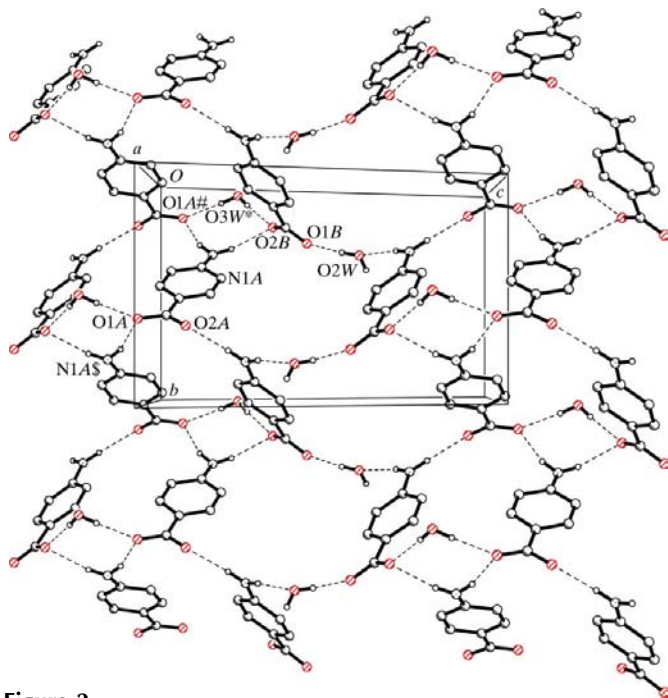


Figure 2
Part of the crystal structure of (I), showing the linking of the [010] chains by the water molecules. Atoms marked with an asterisk (*), a hash (#) or a dollar sign (\$) are at the symmetry positions $(-x, y - \frac{1}{2}, -z + 1)$, $(-x, y - \frac{1}{2}, -z)$ and $(-x, y + \frac{1}{2}, -z)$, respectively.

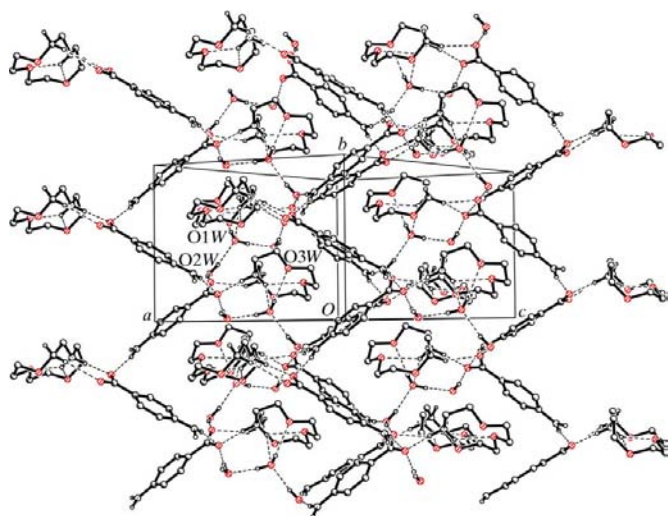


Figure 3
Part of the crystal structure of (I), showing the linking of the sheets by the cations. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Dashed lines indicate hydrogen bonds.

hydrogen-bond donor to atom O1A at $(x, y, z + 1)$ and atom O2B at $(-x, y + \frac{1}{2}, -z + 1)$, thus generating a second type of ring, *viz.* $R_4^2(8)$, to stabilize the helix further (Fig. 2). Water molecule O2W acts as a single donor towards atom O1B at $(-x, y + \frac{1}{2}, -z + 1)$ and as a single acceptor towards atom N2B at $(-x, y - \frac{1}{2}, -z + 1)$, combining two neighbouring helices into an anionic sheet *via* $R_6^0(26)$ fused rings (Fig. 2).

The anionic sheets are linked into a continuous framework by the cations and the water molecules, which play a vital role in the association of the cationic and anionic components into a three-dimensional network. Three water molecules themselves formulate a three-membered water cluster, *viz.* O3W \cdots O1W \cdots O2W, with O \cdots O separations of 2.736 (3) and 2.846 (3) Å, whose terminal members contact with PABA anions, while the bridging O1W water molecule is associated with the B macrocyclic cation *via* O1W \cdots O5B and N1B \cdots O1W hydrogen bonds (Table 1). Thus, the incorporation of the macrocyclic cations between the anionic sheets occurs *via* direct cation–anion contacts (for A and B pairs) and *via* a mediating water molecule for the macrocyclic B cation (Fig. 3).

Experimental

To obtain complex (I), 1,4,7-trioxa-10-azacyclododecane (175 mg, 0.1 mmol) and PABA (137 mg, 1 mmol) were dissolved in a water–methanol (6 ml, 1:5 *v/v*) mixture at 337 K. The reaction mixture was then allowed to stand until crystals were deposited. These were filtered off and recrystallized from a mixture of methanol (2 ml), butanol (1 ml), ethyl acetate (2 ml) and heptane (2 ml) to give yellow crystals of (I) (m.p. 387–388 K). Analysis calculated for $C_{30}H_{54}N_4O_{13}$: C 53.08, H 8.02, N 8.25%; found: C 53.02, H 8.09, N 8.30%. 1H NMR (DMSO- d_6 , 300 MHz): δ 3.48 (*m*, 32H, CH_2N , CH_2O , aza-12-crown-4), 7.11 (*m*, 8H, CH, Ph).

Crystal data

$2C_8H_{18}NO_3^+ \cdot 2C_7H_6NO_2^- \cdot 3H_2O$
 $M_r = 678.77$
 Monoclinic, $P2_1$
 $a = 12.541$ (3) Å
 $b = 9.5315$ (19) Å
 $c = 15.989$ (3) Å
 $\beta = 110.91$ (3) $^\circ$
 $V = 1785.4$ (7) Å 3
 $Z = 2$

$D_x = 1.263$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 5927 reflections
 $\theta = 1.4$ – 24.2 $^\circ$
 $\mu = 0.10$ mm $^{-1}$
 $T = 293$ (2) K
 Prism, yellow
 $0.29 \times 0.23 \times 0.21$ mm

Data collection

Bruker SMART CCD diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical using intensity measurements (SADABS; Sheldrick, 1996)
 $T_{min} = 0.745$, $T_{max} = 1.000$
 17540 measured reflections

3714 independent reflections
 2856 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.031$
 $\theta_{max} = 26.0$ $^\circ$
 $h = -15 \rightarrow 15$
 $k = -11 \rightarrow 11$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.062$
 $S = 1.00$
 3714 reflections
 480 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.12$ e Å $^{-3}$
 $\Delta\rho_{min} = -0.11$ e Å $^{-3}$

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

<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>
N1A—H1...O2B	0.89 (2)	2.14 (2)	3.015 (3)	168 (2)
N1A—H2...O1A ⁱ	0.88 (2)	2.18 (2)	3.024 (3)	159 (2)
N2A—H3...O2A	0.94 (2)	1.77 (2)	2.697 (2)	170 (2)
N2A—H4...O4A	0.92 (2)	2.09 (2)	2.847 (2)	139 (2)
N2A—H4...O5A	0.92 (2)	2.45 (2)	2.839 (2)	106 (1)
C9A—H9A...O1A	0.97	2.46	3.305 (3)	146
N1B—H5...O2A ⁱⁱ	0.90 (2)	2.12 (2)	3.011 (3)	169 (2)
N1B—H6...O2W ⁱⁱⁱ	0.90 (2)	2.18 (2)	3.065 (3)	167 (2)
N2B—H7...O4B	0.91 (2)	2.46 (2)	3.126 (2)	131 (2)
N2B—H7...O1W ^{iv}	0.91 (2)	2.55 (2)	3.183 (3)	127 (2)
N2B—H8...O2B	0.94 (2)	1.80 (2)	2.735 (2)	170 (2)
N2B—H8...O1B	0.94 (2)	2.60 (2)	3.324 (3)	134 (2)
C9B—H9C...O1B	0.97	2.48	3.280 (3)	140
O1W—H11W...O5B ^v	0.92 (2)	2.20 (3)	2.943 (3)	138 (4)
O1W—H12W...O3W	0.93 (2)	1.83 (2)	2.736 (3)	166 (4)
O2W—H21W...O1B	0.86 (2)	1.92 (2)	2.770 (3)	167 (3)
O2W—H22W...O1W	0.88 (2)	1.98 (3)	2.846 (3)	171 (3)
O3W—H31W...O2B ^v	0.84 (2)	1.92 (2)	2.751 (3)	170 (3)
O3W—H32W...O1A ^{vi}	0.83 (2)	1.94 (2)	2.770 (3)	173 (3)

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

C-bound H atoms were placed in calculated positions, with C—H distances of 0.93 or 0.97 Å, and were treated using a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. N-bound and water H atoms were located in a difference Fourier map and were then allowed to refine isotropically, subject to similarity restraints for N—H and O—H distances in amino groups, ammonia groups and water molecules, and with an angular H—O—H restraint for the O2W molecule (H...H = 1.46 Å), as well as a floating origin restraint. In the absence of species heavier than oxygen, no significant anomalous dispersion was observed. Friedel pairs were therefore merged.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3002). Services for accessing these data are described at the back of the journal.

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