

Bis(tetramethylammonium) bis(2,4,5-carboxybenzoate)–benzene-1,2,4,5-tetracarboxylic acid (1/1)

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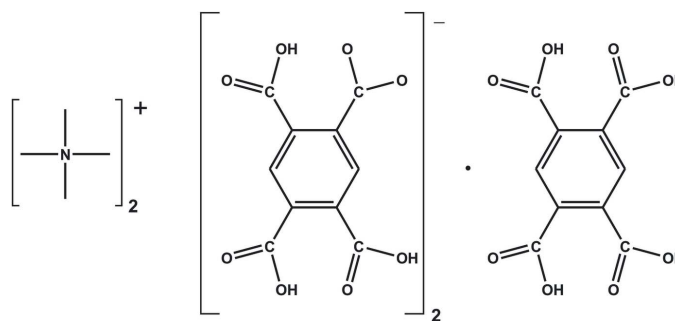
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.041; wR factor = 0.098; data-to-parameter ratio = 12.1.

The asymmetric unit of the title compound, $2\text{C}_4\text{H}_{12}\text{N}^+ \cdot 2\text{C}_{10}\text{H}_5\text{O}_8^- \cdot \text{C}_{10}\text{H}_6\text{O}_8$, consists of a tetramethylammonium cation, an anion derived from the singly deprotonated pyromellitic acid anion, 2,4,5-carboxybenzoate (H_3bta^-), and one-half of a benzene-1,2,4,5-tetracarboxylic acid (H_4bta) molecule, which has the centroid of the aromatic ring positioned at a crystallographic centre of inversion. The H_4bta and H_3bta^- residues are involved in an extensive intermolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bonding network, which leads to a three-dimensional supramolecular structure containing one-dimensional channels running parallel to the [001] crystallographic direction. These channels house the tetramethylammonium cations.

Related literature

For general background on supramolecular assemblies of organic molecules mediated by hydrogen bonds, see: Dale *et al.* (2004); Fabelo *et al.* (2005); Ruiz-Pérez *et al.* (2004); Steed & Atwood (2000). For literature relevant to this communication and published by our group, see: Cunha-Silva *et al.* (2007); Paz & Klinowski (2003); Paz *et al.* (2002); Shi *et al.* (2007). For the Cambridge Structural Database, see: Allen (2002). For graph-set notation, see: Bernstein *et al.* (1995)



Experimental

Crystal data

$2\text{C}_4\text{H}_{12}\text{N}^+ \cdot 2\text{C}_{10}\text{H}_5\text{O}_8^- \cdot \text{C}_{10}\text{H}_6\text{O}_8$
 $M_r = 908.72$
 Monoclinic, $P2_1/c$
 $a = 9.4282$ (4) Å
 $b = 18.7286$ (8) Å
 $c = 11.3175$ (5) Å
 $\beta = 107.053$ (2)°

$V = 1910.55$ (14) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹
 $T = 150$ (2) K
 $0.14 \times 0.12 \times 0.12$ mm

Data collection

Bruker Kappa APEXII diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)
 $T_{\min} = 0.982$, $T_{\max} = 0.984$

19608 measured reflections
 3736 independent reflections
 2523 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.099$
 $S = 1.00$
 3736 reflections
 308 parameters
 5 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O}2-\text{H}2 \cdots \text{O}6^{\text{i}}$	0.959 (10)	1.637 (11)	2.5885 (18)	171 (2)
$\text{O}4-\text{H}4 \cdots \text{O}11^{\text{ii}}$	0.941 (10)	1.806 (12)	2.7166 (19)	162 (2)
$\text{O}7-\text{H}7 \cdots \text{O}6$	0.962 (10)	1.483 (10)	2.4334 (19)	169 (2)
$\text{O}10-\text{H}10 \cdots \text{O}5^{\text{iii}}$	0.938 (10)	1.764 (11)	2.6890 (18)	168 (2)
$\text{O}12-\text{H}12 \cdots \text{O}8^{\text{iv}}$	0.957 (10)	1.600 (11)	2.5308 (19)	163 (2)

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

Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2; data reduction: SAINT-Plus (Bruker, 2005); program(s) used to solve structure: SHELXTL (Bruker 2001); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2444).

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Bis(tetramethylammonium) bis(2,4,5-carboxybenzoate)-benzene-1,2,4,5-tetracarboxylic acid (1/1)

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Comment

Crystal Engineers aim to design functional materials with overall properties which are uniquely directed by the physical and chemical properties of the employed building blocks. In this context, an important strategy used to control the self-assembly processes is based on the use of reliable intermolecular interactions, such as strong and highly directional hydrogen bonds (Steed & Atwood, 2000). Pyromellitic acid (benzene-1,2,4,5-tetracarboxylic acid, H₄bta) has been widely used in the isolation of novel organic crystals, as revealed by a systematic search of the Cambridge Structural Database (Version 5.28, 3 updates - August 2007; Allen, 2002). Indeed, the four symmetrically located carboxylic acid groups confer on this organic molecule predictable and interesting supramolecular properties (Ruiz-Pérez *et al.*, 2004; Fabelo *et al.*, 2005; Dale *et al.*, 2004). As part of our on-going research in the field of Crystal Engineering (Cunha-Silva *et al.*, 2007; Shi *et al.*, 2007), in particular in the use of organic ligands based on carboxylic acid groups (Paz & Klinowski, 2003; Paz *et al.*, 2002), we have recently isolated the title compound, [NMe₄]⁺₂ (H₃bta)⁻₂·(H₄bta), as a secondary product.

The asymmetric unit of I comprises one [NMe₄]⁺ cation, one H₃bta⁻ anion and half of a H₄bta molecule which has the centroid of the aromatic ring (*C_g*) positioned at a crystallographic centre of inversion (Figure 1). H₃bta⁻ anions (moiety type A) and H₄bta molecules (moiety type B) close pack along the [001] direction of the unit cell in a AABAAB_∞ alternate fashion, mediated by a series of weak π⋯π offset stacking interactions having *C_g*⋯*C_g* distances of 3.762 (2) Å (for A⋯A), 3.927 (2) Å (for A⋯B) and 3.910 (2) Å (for B⋯A). However, the crystal packing of I is essentially mediated by the extensive hydrogen bonding network composed of strong and highly directional O—H⋯O hydrogen bonds involving the two crystallographic independent residues of pyromellitic acid (Table 1). Indeed, while each H₄bta molecule interacts with six neighbouring H₃bta⁻ anions, each H₃bta⁻ is instead connected to three H₄bta plus another two symmetry-related H₃bta⁻. The resulting complicated hydrogen bond connectivity leads to the formation of supramolecular *R*₅⁵(31) rings (Bernstein *et al.*, 1995), which are further interconnected into helices running parallel to the [001] direction of the unit cell (Figure 2 and Table 1). This supramolecular arrangement distributes the H₃bta⁻ and H₄bta chemical moieties in such a way that the anionic framework contains a one-dimensional channels (also running parallel to the [001] direction) which houses the charge-balancing [NMe₄]⁺ cations (Figure 3). Besides the electrostatic interactions, these cationic moieties are further stabilized inside the channels by a series of weak C—H⋯O interactions, with C⋯O distances ranging from 3.161 (3) to 3.663 (3) Å (not shown).

Experimental

2,6-Dihydroxybenzoic acid (0.308 g, 2 mmol) and benzene-1,2,4,5-tetracarboxylic acid (0.510 g, 2 mmol) were mixed in distilled water (*ca* 20 ml). Tetramethylammonium hydroxide (solution of 25%; 2 mmol) and manganese chloride tetrahydrate (0.101 g, 0.5 mmol) were added, and the resulting mixture was refluxed for 5 h. The solvent from the final pale yellow

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solution was allowed to slowly evaporate, at ambient temperature, over a period of 10 months. Large single-crystals of the title compound, suitable for X-ray diffraction, were directly harvested from the crystallization vial.

Refinement

H atoms associated with the carboxylic acid groups were markedly visible from difference Fourier maps and were included in the final structural model with the O—H distances restrained to 0.95 (1) Å, and assuming an isotropic displacement behaviour with U_{iso} fixed at 1.5 times U_{eq} of the parent O atom. All remaining H atoms were located at idealized positions and refined with $U_{\text{iso}}=1.2\times U_{\text{eq}}(\text{C})$.

Figures

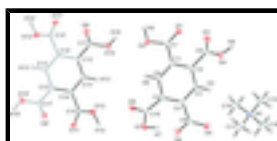


Fig. 1. Chemical moieties composing the asymmetric unit of I (black-filled bonds), showing the labelling scheme for all atoms. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are shown as small spheres with arbitrary radii. Symmetry transformation used to generate equivalent atoms: (i) $-x, -y, -z$.

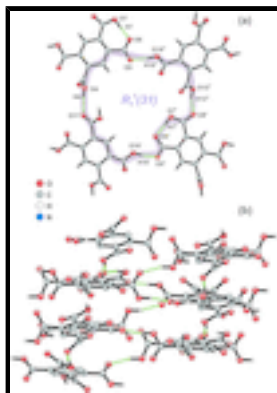


Fig. 2. Schematic representation of the O—H...O connections between adjacent H₃bta⁻ and H₄bta residues leading to (a) $R_5^S(31)$ rings which are further interconnected along the [001] direction of the unit cell into (b) helical chains surrounding the channels present in the crystal structure. For geometrical details on the represented hydrogen bonds (dashed green lines) see Table 1. Symmetry transformations used to generate equivalent atoms: (i) $I + x, y, I + z$; (ii) $I + x, I/2 - y, I/2 + z$; (iii) $-x, I/2 + y, I/2 - z$.

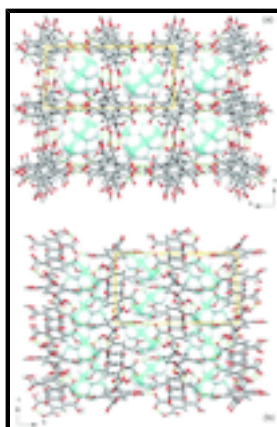


Fig. 3. Crystal packing of the title compound viewed in perspective along the (a) [001] and (b) [100] directions of the unit cell. O—H...O hydrogen bonds are represented as dashed green lines and the [NMe₄]⁺ cations in space-filling mode.

Bis(tetramethylammonium) bis(2,4,5-carboxybenzoate)–benzene-1,2,4,5-tetracarboxylic acid solvate (1/1)

Crystal data

$2\text{C}_4\text{H}_{12}\text{N}^+ \cdot 2\text{C}_{10}\text{H}_5\text{O}_8^- \cdot \text{C}_{10}\text{H}_6\text{O}_8$

$F(000) = 948$

$M_r = 908.72$	$D_x = 1.580 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2ybc	Cell parameters from 2577 reflections
$a = 9.4282 (4) \text{ \AA}$	$\theta = 2.9\text{--}23.2^\circ$
$b = 18.7286 (8) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$c = 11.3175 (5) \text{ \AA}$	$T = 150 \text{ K}$
$\beta = 107.053 (2)^\circ$	Block, colourless
$V = 1910.55 (14) \text{ \AA}^3$	$0.14 \times 0.12 \times 0.12 \text{ mm}$
$Z = 2$	

Data collection

Bruker X8 KappaCCD APEXII diffractometer	3736 independent reflections
Radiation source: fine-focus sealed tube graphite	2523 reflections with $I > 2\sigma(I)$
ω/φ scans	$R_{\text{int}} = 0.061$
Absorption correction: multi-scan (SADABS; Shelldrick, 1998)	$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 3.8^\circ$
$T_{\text{min}} = 0.982$, $T_{\text{max}} = 0.984$	$h = -11 \rightarrow 9$
19608 measured reflections	$k = -22 \rightarrow 23$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.099$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$
3736 reflections	where $P = (F_o^2 + 2F_c^2)/3$
308 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
5 restraints	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Special details

Experimental. See dedicated section in the main paper

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -

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factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.23459 (15)	-0.18900 (7)	0.41351 (13)	0.0243 (4)
O2	0.03177 (16)	-0.19106 (7)	0.25030 (14)	0.0306 (4)
H2	0.059 (2)	-0.2395 (6)	0.241 (2)	0.046*
O3	0.45044 (15)	-0.07193 (7)	0.43306 (13)	0.0222 (4)
O4	0.38326 (15)	-0.05971 (7)	0.60719 (13)	0.0228 (3)
H4	0.4840 (12)	-0.0655 (11)	0.6516 (18)	0.034*
O5	0.07842 (15)	0.17226 (7)	0.47794 (13)	0.0233 (4)
O6	-0.07866 (16)	0.17604 (7)	0.28878 (13)	0.0261 (4)
O7	-0.27358 (15)	0.09642 (7)	0.17213 (13)	0.0201 (3)
H7	-0.1913 (17)	0.1273 (9)	0.2101 (18)	0.030*
O8	-0.32512 (15)	-0.01671 (7)	0.19026 (13)	0.0226 (3)
O9	0.22586 (15)	0.16081 (7)	0.01694 (14)	0.0246 (4)
O10	-0.00003 (15)	0.19454 (7)	0.02169 (13)	0.0226 (4)
H10	0.038 (2)	0.2382 (7)	0.004 (2)	0.034*
O11	-0.34327 (15)	-0.06460 (7)	-0.22544 (13)	0.0223 (3)
O12	-0.39830 (15)	0.00769 (8)	-0.08721 (14)	0.0270 (4)
H12	-0.5011 (12)	0.0024 (12)	-0.1315 (18)	0.041*
C1	0.0979 (2)	-0.08162 (9)	0.34901 (17)	0.0127 (4)
C2	0.2037 (2)	-0.03525 (10)	0.42177 (17)	0.0129 (4)
C3	0.1658 (2)	0.03604 (10)	0.43179 (17)	0.0136 (4)
H3	0.2361	0.0669	0.4851	0.016*
C4	0.0279 (2)	0.06330 (9)	0.36590 (17)	0.0134 (4)
C5	-0.0786 (2)	0.01648 (10)	0.29062 (17)	0.0137 (4)
C6	-0.0402 (2)	-0.05506 (10)	0.28629 (17)	0.0137 (4)
H6	-0.1123	-0.0870	0.2379	0.016*
C7	0.1305 (2)	-0.15936 (10)	0.34274 (18)	0.0158 (5)
C8	0.3601 (2)	-0.05876 (10)	0.48645 (19)	0.0160 (5)
C9	0.0077 (2)	0.14282 (10)	0.38080 (19)	0.0161 (4)
C10	-0.2354 (2)	0.03281 (10)	0.21461 (18)	0.0157 (4)
C11	0.1018 (2)	0.14644 (10)	0.01977 (17)	0.0142 (4)
C12	0.0487 (2)	0.07093 (10)	0.01737 (17)	0.0123 (4)
C13	-0.0993 (2)	0.05489 (10)	-0.04131 (17)	0.0132 (4)
H13	-0.1680	0.0928	-0.0691	0.016*
C14	-0.1490 (2)	-0.01526 (10)	-0.06025 (17)	0.0123 (4)
C15	-0.3083 (2)	-0.02798 (10)	-0.13252 (18)	0.0141 (4)
N1	0.46132 (18)	0.23095 (8)	0.82066 (15)	0.0209 (4)
C16	0.5398 (3)	0.17774 (12)	0.9150 (2)	0.0412 (7)
H16A	0.6108	0.2024	0.9837	0.062*
H16B	0.5929	0.1438	0.8775	0.062*
H16C	0.4675	0.1520	0.9459	0.062*
C17	0.5693 (3)	0.27012 (13)	0.7714 (2)	0.0380 (6)
H17A	0.5170	0.3070	0.7135	0.057*

H17B	0.6169	0.2366	0.7284	0.057*
H17C	0.6449	0.2925	0.8398	0.057*
C18	0.3829 (3)	0.28289 (12)	0.8791 (2)	0.0363 (6)
H18A	0.3321	0.3185	0.8178	0.054*
H18B	0.4551	0.3068	0.9480	0.054*
H18C	0.3101	0.2576	0.9100	0.054*
C19	0.3527 (3)	0.19388 (13)	0.7173 (2)	0.0407 (7)
H19A	0.2768	0.1710	0.7480	0.061*
H19B	0.4039	0.1576	0.6827	0.061*
H19C	0.3054	0.2286	0.6531	0.061*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0200 (8)	0.0142 (8)	0.0316 (9)	0.0039 (6)	-0.0034 (7)	-0.0003 (7)
O2	0.0315 (9)	0.0129 (8)	0.0342 (9)	0.0053 (7)	-0.0112 (7)	-0.0103 (7)
O3	0.0153 (8)	0.0235 (8)	0.0284 (9)	0.0023 (6)	0.0075 (7)	-0.0020 (7)
O4	0.0156 (8)	0.0316 (9)	0.0170 (8)	0.0017 (7)	-0.0018 (6)	0.0010 (7)
O5	0.0261 (9)	0.0126 (7)	0.0266 (8)	-0.0005 (6)	0.0007 (7)	-0.0038 (6)
O6	0.0302 (9)	0.0113 (7)	0.0286 (9)	-0.0004 (7)	-0.0044 (7)	0.0043 (6)
O7	0.0165 (8)	0.0153 (8)	0.0230 (8)	0.0021 (6)	-0.0026 (6)	0.0015 (6)
O8	0.0126 (8)	0.0185 (8)	0.0333 (9)	-0.0013 (7)	0.0016 (7)	-0.0031 (7)
O9	0.0148 (8)	0.0176 (8)	0.0406 (9)	-0.0036 (6)	0.0067 (7)	0.0040 (7)
O10	0.0218 (8)	0.0110 (8)	0.0369 (9)	-0.0001 (6)	0.0116 (7)	0.0006 (7)
O11	0.0166 (8)	0.0250 (8)	0.0204 (8)	-0.0002 (6)	-0.0022 (6)	-0.0061 (7)
O12	0.0100 (7)	0.0323 (9)	0.0360 (9)	0.0011 (7)	0.0024 (7)	-0.0143 (7)
C1	0.0145 (11)	0.0107 (10)	0.0143 (10)	0.0014 (8)	0.0065 (9)	0.0008 (8)
C2	0.0133 (10)	0.0132 (10)	0.0123 (10)	0.0014 (8)	0.0042 (9)	0.0031 (8)
C3	0.0135 (11)	0.0121 (10)	0.0145 (10)	-0.0021 (8)	0.0030 (9)	-0.0011 (8)
C4	0.0169 (11)	0.0121 (10)	0.0126 (10)	-0.0012 (9)	0.0064 (9)	0.0004 (8)
C5	0.0130 (10)	0.0132 (10)	0.0161 (10)	-0.0005 (8)	0.0061 (9)	0.0005 (8)
C6	0.0150 (11)	0.0124 (10)	0.0139 (10)	-0.0030 (8)	0.0044 (9)	-0.0014 (8)
C7	0.0160 (11)	0.0141 (11)	0.0165 (11)	-0.0006 (9)	0.0036 (9)	-0.0016 (9)
C8	0.0180 (11)	0.0073 (10)	0.0215 (12)	-0.0026 (9)	0.0038 (9)	-0.0008 (9)
C9	0.0140 (11)	0.0128 (10)	0.0227 (11)	-0.0015 (9)	0.0071 (10)	0.0013 (9)
C10	0.0146 (11)	0.0160 (11)	0.0161 (11)	0.0020 (9)	0.0038 (9)	-0.0022 (9)
C11	0.0134 (11)	0.0142 (10)	0.0122 (10)	0.0012 (9)	-0.0008 (8)	0.0023 (8)
C12	0.0127 (10)	0.0126 (10)	0.0129 (10)	-0.0013 (8)	0.0056 (8)	-0.0016 (8)
C13	0.0126 (10)	0.0115 (10)	0.0153 (10)	0.0037 (8)	0.0037 (8)	0.0030 (8)
C14	0.0102 (10)	0.0137 (10)	0.0134 (10)	-0.0010 (8)	0.0041 (8)	-0.0001 (8)
C15	0.0121 (10)	0.0090 (10)	0.0199 (12)	0.0011 (8)	0.0028 (9)	0.0045 (9)
N1	0.0201 (10)	0.0169 (9)	0.0256 (10)	-0.0021 (8)	0.0064 (8)	0.0002 (8)
C16	0.0388 (15)	0.0307 (14)	0.0453 (16)	0.0095 (12)	-0.0015 (13)	0.0120 (12)
C17	0.0345 (14)	0.0419 (15)	0.0453 (16)	-0.0130 (12)	0.0239 (13)	-0.0084 (12)
C18	0.0479 (16)	0.0242 (13)	0.0494 (17)	0.0059 (11)	0.0342 (14)	0.0049 (11)
C19	0.0358 (15)	0.0397 (15)	0.0369 (15)	-0.0158 (12)	-0.0043 (12)	-0.0037 (12)

supplementary materials

Geometric parameters (Å, °)

O1—C7	1.205 (2)	C5—C6	1.392 (3)
O2—C7	1.320 (2)	C5—C10	1.507 (3)
O2—H2	0.959 (10)	C6—H6	0.9500
O3—C8	1.205 (2)	C11—C12	1.498 (3)
O4—C8	1.319 (2)	C12—C13	1.391 (3)
O4—H4	0.941 (10)	C12—C14 ⁱ	1.395 (3)
O5—C9	1.236 (2)	C13—C14	1.390 (3)
O6—C9	1.280 (2)	C13—H13	0.9500
O7—C10	1.296 (2)	C14—C12 ⁱ	1.395 (3)
O7—H7	0.962 (10)	C14—C15	1.503 (3)
O8—C10	1.231 (2)	N1—C19	1.482 (3)
O9—C11	1.210 (2)	N1—C18	1.489 (3)
O10—C11	1.321 (2)	N1—C16	1.489 (3)
O10—H10	0.938 (10)	N1—C17	1.489 (3)
O11—C15	1.217 (2)	C16—H16A	0.9800
O12—C15	1.298 (2)	C16—H16B	0.9800
O12—H12	0.957 (10)	C16—H16C	0.9800
C1—C6	1.380 (3)	C17—H17A	0.9800
C1—C2	1.395 (3)	C17—H17B	0.9800
C1—C7	1.494 (3)	C17—H17C	0.9800
C2—C3	1.395 (3)	C18—H18A	0.9800
C2—C8	1.507 (3)	C18—H18B	0.9800
C3—C4	1.392 (3)	C18—H18C	0.9800
C3—H3	0.9500	C19—H19A	0.9800
C4—C5	1.415 (3)	C19—H19B	0.9800
C4—C9	1.517 (3)	C19—H19C	0.9800
C7—O2—H2	111.2 (15)	C14 ⁱ —C12—C11	120.69 (16)
C8—O4—H4	112.9 (13)	C12—C13—C14	121.57 (17)
C10—O7—H7	106.7 (12)	C12—C13—H13	119.2
C11—O10—H10	105.5 (13)	C14—C13—H13	119.2
C15—O12—H12	114.8 (13)	C13—C14—C12 ⁱ	119.26 (17)
C6—C1—C2	118.85 (17)	C13—C14—C15	118.14 (16)
C6—C1—C7	120.19 (17)	C12 ⁱ —C14—C15	122.53 (16)
C2—C1—C7	120.92 (17)	O11—C15—O12	126.05 (18)
C1—C2—C3	119.21 (17)	O11—C15—C14	122.25 (17)
C1—C2—C8	122.22 (16)	O12—C15—C14	111.59 (16)
C3—C2—C8	118.52 (17)	C19—N1—C18	109.77 (18)
C4—C3—C2	121.91 (17)	C19—N1—C16	109.59 (17)
C4—C3—H3	119.0	C18—N1—C16	109.03 (17)
C2—C3—H3	119.0	C19—N1—C17	108.99 (17)
C3—C4—C5	118.80 (17)	C18—N1—C17	109.11 (17)
C3—C4—C9	115.37 (17)	C16—N1—C17	110.34 (18)
C5—C4—C9	125.82 (17)	N1—C16—H16A	109.5
C6—C5—C4	118.12 (17)	N1—C16—H16B	109.5
C6—C5—C10	113.39 (17)	H16A—C16—H16B	109.5

C4—C5—C10	128.46 (17)	N1—C16—H16C	109.5
C1—C6—C5	123.02 (18)	H16A—C16—H16C	109.5
C1—C6—H6	118.5	H16B—C16—H16C	109.5
C5—C6—H6	118.5	N1—C17—H17A	109.5
O1—C7—O2	124.56 (18)	N1—C17—H17B	109.5
O1—C7—C1	123.77 (18)	H17A—C17—H17B	109.5
O2—C7—C1	111.67 (17)	N1—C17—H17C	109.5
O3—C8—O4	126.17 (19)	H17A—C17—H17C	109.5
O3—C8—C2	123.43 (18)	H17B—C17—H17C	109.5
O4—C8—C2	110.35 (16)	N1—C18—H18A	109.5
O5—C9—O6	123.75 (17)	N1—C18—H18B	109.5
O5—C9—C4	118.97 (17)	H18A—C18—H18B	109.5
O6—C9—C4	117.23 (17)	N1—C18—H18C	109.5
O8—C10—O7	120.75 (18)	H18A—C18—H18C	109.5
O8—C10—C5	118.01 (17)	H18B—C18—H18C	109.5
O7—C10—C5	121.19 (17)	N1—C19—H19A	109.5
O9—C11—O10	124.15 (18)	N1—C19—H19B	109.5
O9—C11—C12	122.01 (17)	H19A—C19—H19B	109.5
O10—C11—C12	113.81 (16)	N1—C19—H19C	109.5
C13—C12—C14 ⁱ	119.16 (16)	H19A—C19—H19C	109.5
C13—C12—C11	119.71 (16)	H19B—C19—H19C	109.5
C6—C1—C2—C3	1.7 (3)	C1—C2—C8—O4	-111.46 (19)
C7—C1—C2—C3	-175.72 (17)	C3—C2—C8—O4	70.9 (2)
C6—C1—C2—C8	-175.85 (17)	C3—C4—C9—O5	-28.3 (3)
C7—C1—C2—C8	6.7 (3)	C5—C4—C9—O5	152.83 (19)
C1—C2—C3—C4	-3.6 (3)	C3—C4—C9—O6	149.16 (18)
C8—C2—C3—C4	174.08 (17)	C5—C4—C9—O6	-29.7 (3)
C2—C3—C4—C5	2.6 (3)	C6—C5—C10—O8	22.3 (3)
C2—C3—C4—C9	-176.26 (17)	C4—C5—C10—O8	-155.63 (19)
C3—C4—C5—C6	0.1 (3)	C6—C5—C10—O7	-155.23 (17)
C9—C4—C5—C6	178.88 (17)	C4—C5—C10—O7	26.9 (3)
C3—C4—C5—C10	177.89 (18)	O9—C11—C12—C13	-146.62 (19)
C9—C4—C5—C10	-3.3 (3)	O10—C11—C12—C13	31.6 (2)
C2—C1—C6—C5	1.0 (3)	O9—C11—C12—C14 ⁱ	25.7 (3)
C7—C1—C6—C5	178.48 (17)	O10—C11—C12—C14 ⁱ	-156.07 (17)
C4—C5—C6—C1	-1.9 (3)	C14 ⁱ —C12—C13—C14	-1.2 (3)
C10—C5—C6—C1	179.95 (17)	C11—C12—C13—C14	171.26 (17)
C6—C1—C7—O1	-163.87 (19)	C12—C13—C14—C12 ⁱ	1.2 (3)
C2—C1—C7—O1	13.5 (3)	C12—C13—C14—C15	-175.65 (17)
C6—C1—C7—O2	16.4 (3)	C13—C14—C15—O11	123.1 (2)
C2—C1—C7—O2	-166.19 (17)	C12 ⁱ —C14—C15—O11	-53.6 (3)
C1—C2—C8—O3	71.0 (3)	C13—C14—C15—O12	-53.2 (2)
C3—C2—C8—O3	-106.6 (2)	C12 ⁱ —C14—C15—O12	130.02 (19)

Symmetry codes: (i) $-x, -y, -z$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 \cdots O6 ⁱⁱ	0.96 (1)	1.64 (1)	2.5885 (18)	171 (2)
O4—H4 \cdots O11 ⁱⁱⁱ	0.94 (1)	1.81 (1)	2.7166 (19)	162 (2)
O7—H7 \cdots O6	0.96 (1)	1.48 (1)	2.4334 (19)	169 (2)
O10—H10 \cdots O5 ^{iv}	0.94 (1)	1.76 (1)	2.6890 (18)	168 (2)
O12—H12 \cdots O8 ^v	0.96 (1)	1.60 (1)	2.5308 (19)	163 (2)

Symmetry codes: (ii) $-x, y-1/2, -z+1/2$; (iii) $x+1, y, z+1$; (iv) $x, -y+1/2, z-1/2$; (v) $-x-1, -y, -z$.

Fig. 2

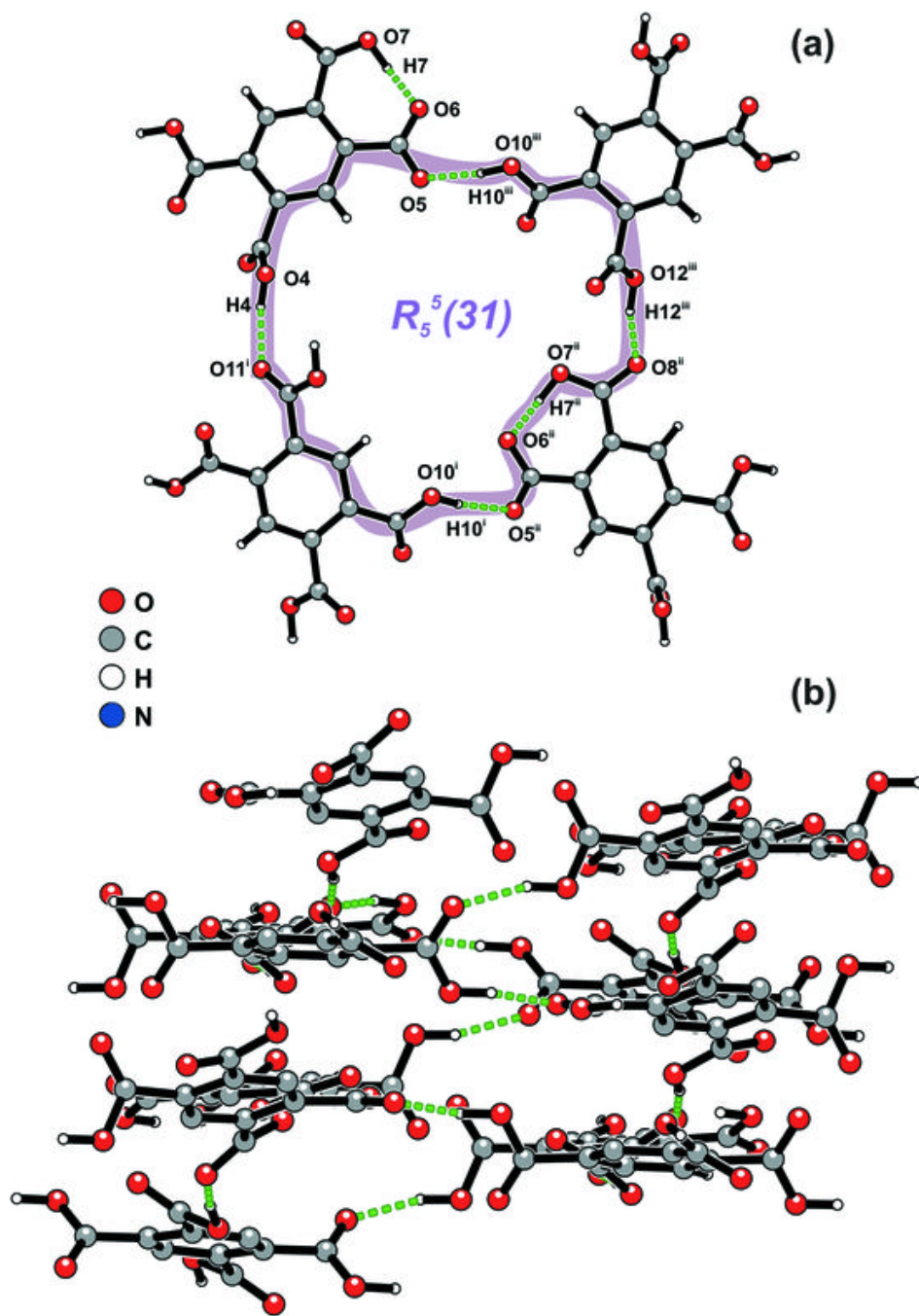


Fig. 3

