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A novel (3,4,10)-connected three-dimensional hydrogen-bonded supramolecular network containing a cyclic water hexamer

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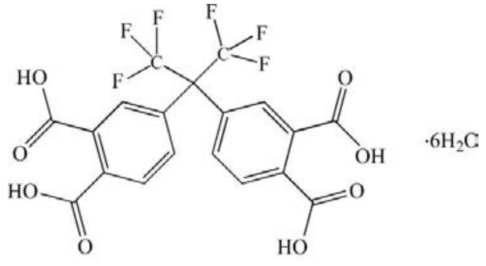
The title compound, 4,4′-(1,1,1,3,3,3-hexafluoroisopropylidene)-diphthalic acid hexahydrate, $C_{19}H_{10}F_6O_8 \cdot 6H_2O$, crystallizes in the centrosymmetric space group *Pbcn*, with half of the diphthalic acid residue and three water molecules in the asymmetric unit. The organic molecule is located on a crystallographic twofold axis. In the solid, cyclic water hexamers in chair conformations have crystallographically imposed inversion symmetry. Strong $O-H\cdots O$ hydrogen bonds between the hexamers and organic molecules result in a unique three-dimensional supramolecular network [$O\cdots O$ = 2.554 (2)–2.913 (2) Å]. This compound represents the first example of a (3,4,4,10)-connected four-nodal supramolecular topology with the Schläfli symbol $(4^3.5.6.7)_2(4^3.5^2.7)_2(4^3)_2(4^6.5^6.6^2.7^8.8^{14}.9^9)$.

Comment

Great attention has been paid to small water clusters both in theoretical and experimental studies, not only with the aim of understanding hydrogen-bonding interactions and the behavior of bulk water, but also as a result of their fascinating topology when associated with organic molecules or metal–organic frameworks (Ludwig, 2001; Ugalde *et al.*, 2000; Maheshwary *et al.*, 2001; Chesnut, 2002; Sadlej *et al.*, 1999; Custelcean *et al.*, 2000; López *et al.*, 2008). Many discrete water clusters, including tetramers, hexamers, octamers, decamers and higher clusters, have been identified. Among the water clusters, cyclic hexamers are of special interest because they are the building blocks of ice I_h (Ludwig, 2001) and are expected to be relevant to the structure of liquid water. Theoretical calculations suggest that several different isomers of the water hexamer, such as ring, book, cage, cyclic and prism, represent nearly isoenergetic clusters (Ludwig, 2001; Chesnut, 2002). However, understanding how the water clusters link into higher dimensional networks is still challenging. Recently, water clusters associated with organic, inorganic and metal–organic frameworks have been studied. One-dimensional aggregates such as water chains and tapes and a few examples of two- or three-dimensional polymers (Wang *et al.*, 2006; Michaelides *et al.*, 2003; Hu *et al.*, 2007; Mukhopadhyay *et al.*, 2005; Ye *et al.*, 2004; Neogi *et al.*, 2005; Zheng *et al.*, 2005; Ghosh *et al.*, 2004; Ghosh *et al.*, 2005; Ghosh *et al.*, 2003) have been described. In this contribution, we report the synthesis under hydrothermal conditions of 4,4′-(1,1,1,3,3,3-hexafluoroisopropylidene)diphthalic acid hexahydrate, (I), which contains an unexpected cyclic water hexamer in a chair conformation. Interestingly, a unique three-dimensional supramolecular network is formed by strong intermolecular $O-H\cdots O$ hydrogen bonds between these hexamers and the large organic residue. To our knowledge, this compound is the first example of a (3,4,4,10)-connected four-nodal supramolecular topology associated with the Schläfli symbol $(4^3.5.6.7)_2(4^3.5^2.7)_2(4^3)_2(4^6.5^6.6^2.7^8.8^{14}.9^9)$.



(I)

The asymmetric unit of (I) consists of one half of the 4,4′-(hexafluoroisopropylidene)diphthalic acid (H_4hfipdpt) molecule and three water molecules (Fig. 1). The benzene rings of the bent H_4hfipdpt molecule subtend a dihedral angle of 65.80 (1)°. As shown in Fig. 2, the carboxyl groups of H_4hfipdpt adopt *syn–syn* 1,3-μ_2-carboxyl and 1,1,3-μ_3-carboxyl coordination modes, which are crosslinked by different cyclic hexameric water clusters *via* strong intermolecular $O-H\cdots O$ hydrogen bonds. In each cyclic hexamer unit, the average $O\cdots O$ distance is 2.817 (4) Å, which is in the range of the corresponding values in ice I_h at 183 K

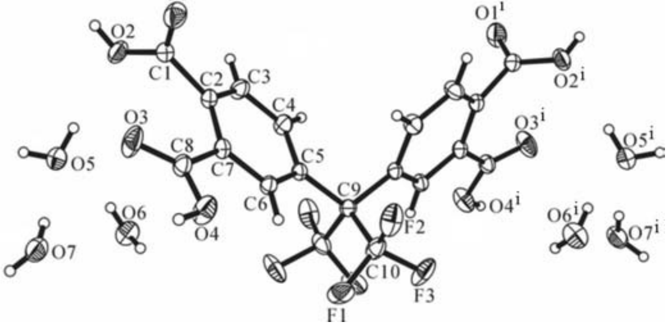


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]

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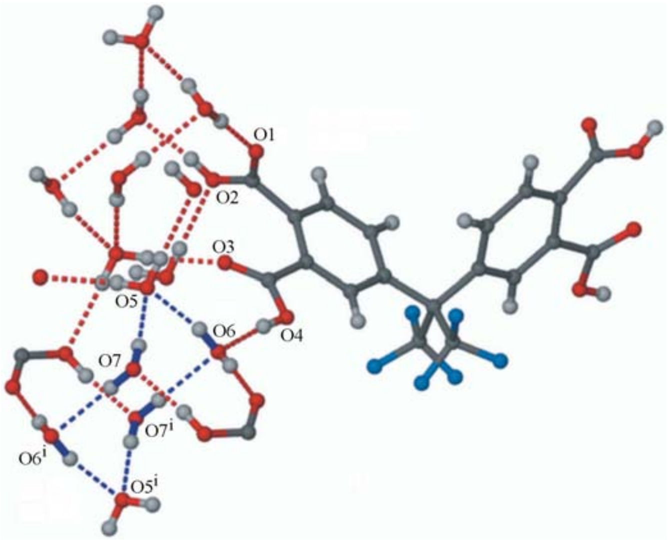

Figure 2
Perspective view showing the (3,4,4)-connected modes of the water hexamers, which are crosslinked with H_4hfipdpt *via* strong intermolecular O—H···O hydrogen bonds. The hexamer (in which waters are linked by blue dashed lines in the electronic version of the paper) consists of atoms O5, O6, O7, O5^i, O6^i and O7^i. [Symmetry code: (i) $-x + 2, -y + 1, -z$.]

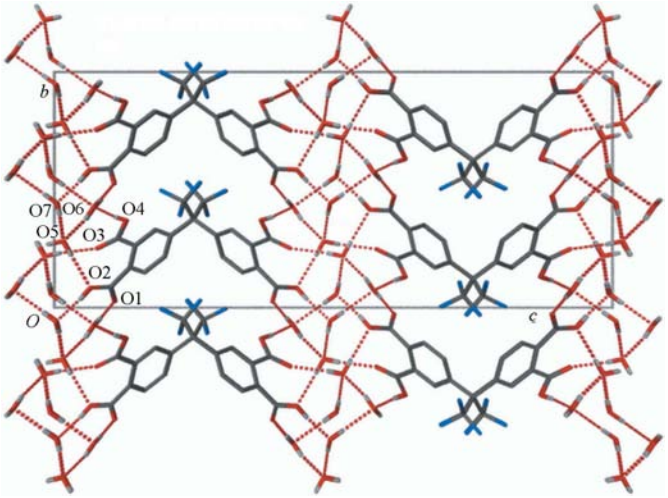

Figure 3
The extended structure of the three-dimensional supramolecular network of (I), viewed along the *a* axis. H atoms not involved in hydrogen bonding have been omitted for clarity.

[2.759 (2) Å; Ludwig, 2001] and liquid water [2.851 (3) Å; Ludwig, 2001]. The O···O···O angles range from 86.71 (5) to 107.85 (7)° and are narrower than the value of 109.3 (2)° in hexagonal ice (Ludwig, 2001; Michaelides *et al.*, 2003). The cyclic hexamer of water molecules has crystallographically imposed inversion symmetry and the O5, O6 and O7 water molecules of the hexamers adopt 4-, 4- and 3-connected modes, respectively. The hexamers in the subunits are cross-linked with different organic H_4hfipdpt molecules *via* strong intermolecular O—H···O hydrogen bonds [O···O = 2.554 (2)–2.913 (2) Å], which give rise to a unique three-dimensional hydrogen-bonded supramolecular network (Fig. 3). The geometric parameters of the hydrogen bonds are listed in Table 1. The resulting three-dimensional supramolecular framework exhibits an interesting (3,4,4,10)-connected topology. A calculation of the vertex symbol with the program *TOPOS* (Blatov *et al.*, 2000) shows that the title compound exhibits a unique (3,4,4,10)-connected four-nodal supramolecular topology with the Schläfli symbol $(4^3.5.6.7)_2(4^3.5^2.7)_2(4^3)_2(4^6.5^6.6^2.7^8.8^{14}.9^9)$ (Fig. 4).

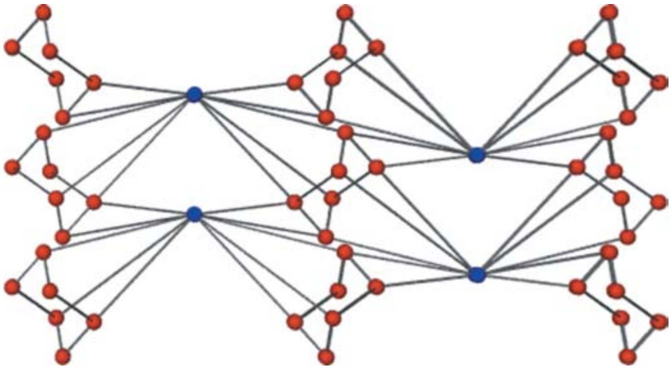

Figure 4
View of the (3,4,4,10)-connected four-nodal topology. 5- and 10-connected nodes denote H_4hfipdpt (darker spheres; blue in the electronic version of the paper) and all others are H_2O (lighter spheres; red).

The FT–IR spectrum was interpreted in the light of the structural results. The stretching frequency of the O—H bonds was observed at *ca* 3540 and 3400 cm^{-1}, which is due to both the hexameric water cluster and the carboxyl group. The first peak is close to the value of 3490 cm^{-1} reported for liquid water, while the second peak is slightly greater than both the value of the reported cyclic water hexamer (3335 cm^{-1}) formed in liquid helium and the measured band at 3359 cm^{-1} for the hexamer in an organic molecular crystal host because of the co-operative effects between the clusters and organic molecules (Custelcean *et al.*, 2000; Michaelides *et al.*, 2003; Buck & Huisken, 2000).

Experimental

A mixture of $Pb(NO_3)_2$ (108.7 mg, 0.33 mmol), 4,4′-bipyridine (18.8 mg, 0.12 mmol) and 4,4′-(hexafluoroisopropylidene)bis(phthalic anhydride) (69.6 mg, 0.16 mmol) in H_2O (8 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and heated at 443 K for 72 h. A crop of colorless single crystals of the title compound was obtained after cooling the solution to room temperature. Platelet-shaped crystals were collected and washed with distilled water. The yield is *ca* 55% based on 4,4′-(hexafluoroisopropylidene)bis(phthalic anhydride). IR (KBr, ν/cm^{-1}): 3540 (*vs*), 3400 (*vs*), 2930 (*w*), 2827 (*w*), 2653 (*w*), 2549 (*w*), 1973 (*m*), 1713 (*vs*), 1312 (*w*), 1254 (*w*), 1234 (*w*), 1072 (s), 982 (*s*), 840 (*s*), 795 (*m*), 750 (*w*), 703 (*w*), 658 (*w*), 600 (*w*).

Crystal data

$C_{19}H_{10}F_6O_8 \cdot 6H_2O$
$M_r = 588.37$
Orthorhombic, *Pbcn*
$a = 6.9425$ (14) Å
$b = 12.366$ (3) Å
$c = 29.220$ (6) Å
$V = 2508.5$ (9) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.16$ mm^{-1}
$T = 298$ (2) K
0.46 × 0.39 × 0.09 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.929$, $T_{\max} = 0.986$
22570 measured reflections
2852 independent reflections
2030 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.109$
$S = 1.02$
2852 reflections
178 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2B···O7$^{\rm i}$	0.82	1.74	2.554 (2)	171
O4—H4B···O6	0.82	1.81	2.629 (2)	173
O5—H1···O3$^{\rm ii}$	0.82	1.99	2.806 (2)	170
O5—H2···O2$^{\rm iii}$	0.82	2.10	2.913 (2)	173
O6—H3···O1$^{\rm iv}$	0.82	1.95	2.773 (2)	178
O6—H4···O5	0.82	1.95	2.760 (2)	169
O7—H5···O5	0.82	1.99	2.806 (2)	176
O7—H6···O6$^{\rm v}$	0.82	2.07	2.884 (2)	174

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

All water H atoms were positioned from Fourier difference maps and refined subject to the constraint O—H = 0.82 Å. The remaining H atoms were positioned geometrically and allowed to ride on their respective parent atoms at distances of C—H = 0.93 Å and O—H = 0.82 Å (for the carboxyl group), and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: EG3011). Services for accessing these data are described at the back of the journal.

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