organic compounds

An ice-like water hexamer with $\bar{3}$ symmetry in the hydrogen-bonded structure of 2,3,5,6-tetrafluoro-1,4-bis(imidazol-1-ylmethyl)benzene dihydrate

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An ice-like hexameric water cluster, stabilized by the flexible bis-imidazolyl compound 2,3,5,6-tetrafluoro-1,4-bis(imidazol-1-ylmethyl)benzene (Fbix), is found in the trigonal $R\bar{3}$ crystal structure of the title compound, $C_{14}H_{10}F_4N_4 \cdot 2H_2O$ or Fbix·2H$_2$O. The Fbix molecule lies about an inversion centre with one water molecule in the asymmetric unit in a general position. A cyclic chair-like hexameric water cluster with $\bar{3}$ symmetry is generated with a hydrogen-bonded O···O distance within the hexamer of 2.786 (3) Å. The Fbix molecule adopts a *trans* conformation, where the imidazole ring makes a dihedral angle of 70.24 (11)° with the central tetrafluorinated aromatic ring. Each water hexamer is connected by six Fbix molecules through intermolecular O—H···N hydrogen bonds [N···O = 2.868 (3) Å] to yield a three-dimensional supramolecular network with primitive cubic (pcu) topology. Large voids in each single pcu network lead to fourfold interpenetrated aggregates of Fbix·2H$_2$O.

Comment

In recent years there have been many systematic and successful studies of the crystal engineering of organic crystals, and evidence has been published demonstrating the molecular recognition of hydrogen-bonding and/or other noncovalent interactions (Desiraju, 1995; Hosseini, 2005). In the field of water chemistry, intense efforts have focused on unravelling the structural morphologies of water aggregates to improve the understanding of the nature of water–water interactions in bulk water or ice (Ludwig, 2001). Small water clusters, $(H_2O)_n$ where n = 3–8, have been extensively studied and structurally characterized; numerous water clusters including tetramers (Zhang, Tian *et al.*, 2007; Xu *et al.*, 2008), pentamers (Ma *et al.*, 2004), hexamers (Ye *et al.*, 2004; Mukhopadhyay & Bernal, 2005; Siddiqui *et al.*, 2008) and octamers (Doedens *et al.*, 2002)

reveal various conformations in the crystal hosts in the solid state. Among these, the water hexamer is of great interest since it represents the smallest possible unit that can exhibit some of the properties found in bulk water (Gregory *et al.*, 1997). Moreover, at the transition from two- to three-dimensional structures the water hexamer behaves by adopting ring (chair and boat), book, bag, cage and prism conformations with nearly equal energy by the energetic discrimination of 0.7 kcal mol^{-1} (Ludwig, 2000, 2001). This realization has prompted considerable interest in the structural characterization of water hexamers trapped in hydrate clathrates (Moorthy *et al.*, 2002; Mukhopadhyay & Bernal, 2005).


(I)
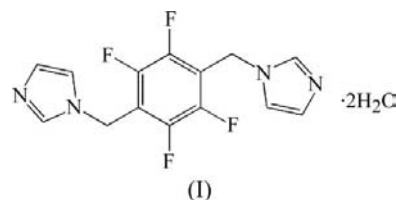
Imidazole-containing ligands such as 1,4-bis(imidazol-1-ylmethyl)benzene (bix) (Hoskins *et al.*, 1997*a,b*; Fan *et al.*, 2005), 1,1-(1,4-butanediyl)bis(imidazole) (bbix) (Ma *et al.*, 2000; Duncan *et al.*, 1996), 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib) (Liu & Tong, 2002) and related species have been used to generate a rich variety of metal–organic architectures with interesting structural topologies and potential properties, as well as many hydrogen-bonding aggregates (Aakeröy *et al.*, 2005, 2006; Zhang, Gembicky *et al.*, 2007; Xu *et al.*, 2008). Considering the weak intermolecular forces among fluorinated compounds, Shreeve and co-workers have reported three novel coordination polymers constructed from transition metals with 2,3,5,6-tetrafluoro-1,4-bis(imidazol-1-ylmethyl)benzene (Fbix) (Gao *et al.*, 2006). In the process of exploring the structural diversity and recognition pattern of the Fbix building block, we isolated its dihydrate, Fbix·2H$_2$O, (I). We describe herein the formation and structural features of the cyclic water hexamer with an ice-like chair conformation and its assembly into a cubic supramolecular network through O—H···N linkages with the Fbix crystal host.

The asymmetric unit of (I) comprises one Fbix molecule on an inversion centre at $(\frac{1}{3}, \frac{1}{6}, \frac{2}{3})$ and one lattice water molecule in a general position near the unit-cell origin; a perspective view with the atom-numbering scheme is shown in Fig. 1. The Fbix molecule adopts a *trans* conformation with a dihedral angle of 70.24 (11)° between the terminal imidazole ring and the central tetrafluorinated benzene plane. The $R\bar{3}$ space-group symmetry generates a hexameric cluster of water molecules with $\bar{3}$ symmetry and a perfect chair arrangement of the O atoms (Fig. 2). Within the chair-like hexameric cluster, each water molecule is simultaneously involved in interactions with symmetry-related water molecules (see Table 1), leading to a head-to-tail $R_6^6(12)$ hydrogen-bonding pattern (Etter, 1990). The hydrogen-bonded O···O distance within the water hexamer [2.786 (3) Å] is comparable with the value in ice I_h (2.759 Å) at 183 K (Eisenberg & Kauzmann, 1969) and is

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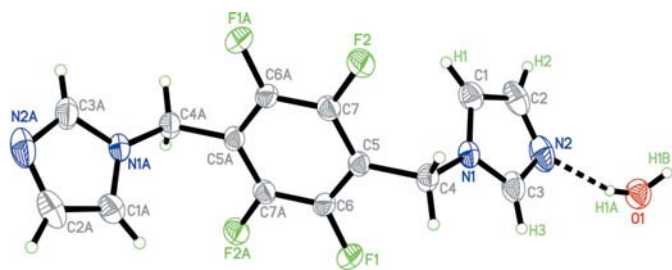
Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line represents a hydrogen bond. [Symmetry code: (A) $-x + \frac{2}{3}, -y + \frac{1}{3}, -z + \frac{4}{3}$.]
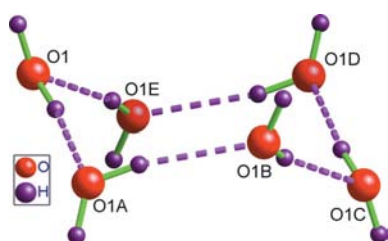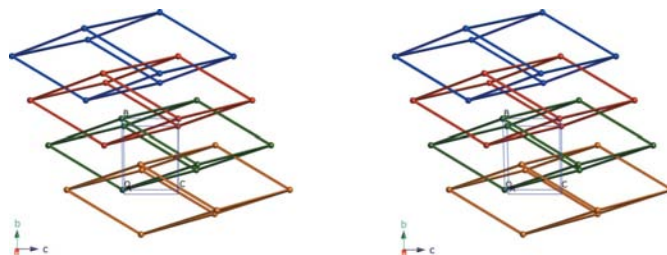

Figure 2
Representation of the chair conformation of the water hexamer [symmetry codes: (A) $x - y, x, -z$; (B) $-y, x - y, z$; (C) $-x, -y, -z$; (D) $-x + y, -x, z$; (E) $y, -x + y, -z$].

shorter than the value in liquid water (2.85 Å) (Narten *et al.*, 1982). The O···O···O···O torsion angles in the hexamer are ±63.54 (2)° and the O···O···O angle [107.95 (7)°] is close to the corresponding value of 109.3° for the preferred tetrahedral geometry in hexagonal ice. By way of contrast, a similar water hexamer crystallizing in the same $R\overline{3}$ space group as (I) has an almost ideal planar system (Moorthy *et al.*, 2002) with an O···O distance of 2.906 (5) Å, an O···O···O angle of 120.0 (2)° and O···O···O···O torsion angles of ±3.0 (2)°.

In the present system, the other H atom of each water molecule is connected to the Fbix molecule *via* an O1—H1*A*···N2 hydrogen bond (see Table 1). From the viewpoint of topology, each discrete cyclic water hexamer, acting as a six-connected node, is linked by the bi-connected Fbix spacer to generate a three-dimensional supramolecular network (Fig. 3). The topology is as follows: the motif of the water hexamer connected to six Fbix linkers is represented as joining six other hexamers through O—H···N interactions, which results in a six-connected net with the Schläfli symbol $4^{12}.6^3$ (that represents primitive cubic topology), the net being somewhat offset. Because of the large void in each single net with the adjoining hexameric centre-to-centre distance separated by the Fbix linker [19.858 (11) Å], the final fourfold interpenetrated structure of this type is realized through a translation vector $[\frac{1}{3}, -\frac{1}{3}, -\frac{1}{3}]$ of *circa* 11.10 Å, according to the calculation in *TOPOS* (Blatov, 2004), as illustrated in Fig. 4. All the independent nets are related by this single vector and the whole fourfold interpenetrated array is generated by translating the primitive single net three times, which has a PIC (primitive
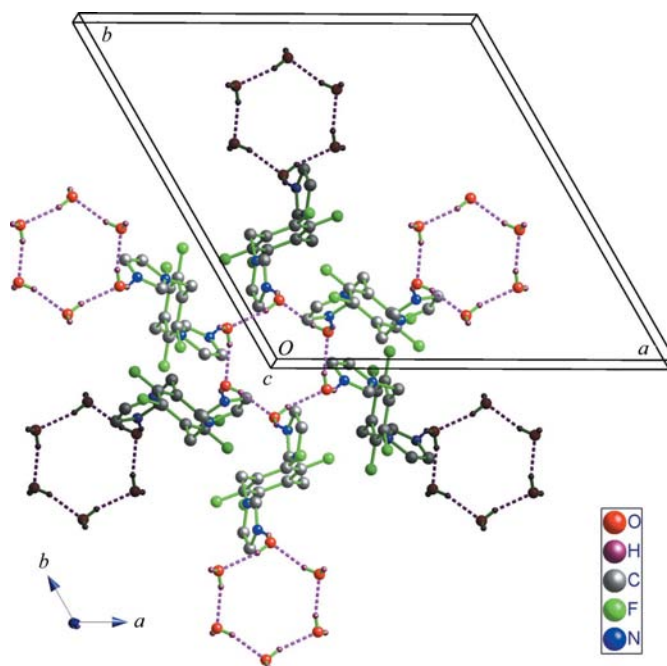
Figure 3
Self-assembly of the water hexamers and Fbix molecules by O—H···N interactions into an extended three-dimensional supramolecular arrangement.

Figure 4
A stereoview of the fourfold interpenetrated network. Each ball represents an $R_6^6(12)$ hydrogen-bonded water hexamer.

interpenetration cell) with the unit-cell vectors $[\frac{4}{3}, -\frac{4}{3}, -\frac{4}{3}]$, [0, 1, 0] and [1, 0, 0] (Blatov, 2004).

Experimental

Crystal data

$C_{14}H_{10}F_4N_4 \cdot 2H_2O$	$Z = 9$
$M_r = 346.29$	Mo $K\alpha$ radiation
Trigonal, $R\overline{3}$	$\mu = 0.13$ mm^{-1}
$a = 17.753$ (10) Å	$T = 297$ K
$c = 12.756$ (7) Å	$0.24 \times 0.22 \times 0.22$ mm
$V = 3482$ (3) Å^3	

Data collection

Bruker APEXII CCD
   diffractometer
Absorption correction: multi-scan
   (*SADABS*; Sheldrick, 2003)
   $T_{min} = 0.969$, $T_{max} = 0.971$

8266 measured reflections
1518 independent reflections
1327 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.134$
$S = 1.05$
1518 reflections

109 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A$$\cdots$N2	0.82	2.08	2.867 (3)	162
O1—H1$B$$\cdots$O1^{i}	0.82	1.98	2.786 (3)	166

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

All H atoms bound to C atoms were assigned to calculated positions, with C—H = 0.93 (aromatic) and 0.97 Å (methylene), and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of the water molecule were firstly located in a difference Fourier map and then refined with distance restraints O—H = 0.820 (1) Å and H$\cdots$H = 1.430 (1) Å, and finally constrained to ride on the O atom with [$U_{iso}(H) = 1.5U_{eq}(O)$].

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* and *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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