organic compounds

Intermolecular interactions, disorder and twinning in ciprofloxacin–2,2-difluoroethanol (2/3) and ciprofloxacin–water (3/14.5)

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The antibiotic ciprofloxacin [systematic name: 1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-4-ium-1-yl)-1,4-dihydroquinoline-3-carboxylate], has been crystallized as a 2:3 solvate with 2,2-difluoroethanol, $2C_{17}H_{18}FN_3O_3 \cdot 3C_2H_4O_2$, (I), and as a 3:14.5 hydrate, $3C_{17}H_{18}FN_3O_3 \cdot 14.5H_2O$, (II). The structure of (I) was determined using synchrotron X-ray diffraction data and refined as a two-component nonmerohedral twin. Both structures contain several independent molecules in the asymmetric unit: (I) contains two zwitterionic ciprofloxacin molecules and three difluoroethanol solvent molecules, while (II) contains three zwitterionic ciprofloxacin molecules and a mixture of ordered and disordered water molecules. The intermolecular interactions were analysed using fingerprint plots derived from Hirshfeld surfaces, providing a detailed description of the unique environment of each independent ciprofloxacin molecule.

Comment

Ciprofloxacin (Cf) belongs to the quinolone class of semi-synthetic antibiotics (Turel, 2002; Mitscher, 2005). A search of the Cambridge Structural Database (Version 5.31 with updates to May 2010; Allen, 2002) reveals 68 crystal structures containing the Cf molecule. These include the structures of the anhydrous form (Fabbiani *et al.*, 2009; Mahapatra *et al.*, 2010), a hexahydrate (Turel *et al.*, 1997; Fabbiani & Dittrich, 2008), hydrated sodium salts crystallized under high-pressure conditions and recoverable to ambient pressure (Fabbiani *et al.*, 2009), a lactate sesquihydrate (Prasanna & Guru Row, 2001), a hemi-methanolate (Li *et al.*, 2006), a hydrochloride 1.34-hydrate (Turel & Golobič, 2003), and several coordination complexes with group II or lanthanide elements.
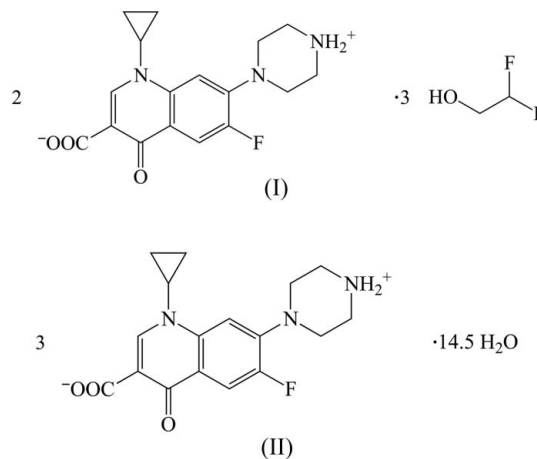
While the crystal structures of coordination complexes of Cf often contain more than one Cf molecule in the asymmetric unit, (I) and (II) are the only examples known to date of noncoordination complexes where this is the case: two and three independent Cf molecules are found in (I) and (II), respectively (Figs. 1 and 2). Some differences in torsion angles are observed for the Cf molecules in the two structures (Table 1), indicating conformational variations in the relative orientation of the piperazinium ring and, in particular, of the cyclopropyl and carboxylate groups relative to the planar dihydroquinoline ring structure. In both (I) and (II), Cf exists as a zwitterion. Previous literature (Główka *et al.*, 2003) has suggested that an in-plane conformation for quinolones, as observed for (I), is predominantly associated with a proton-ated carboxyl group, with exceptions being characterized by significant differences in C—O bond lengths compared with those normally observed in zwitterions. For (I) and (II), we are
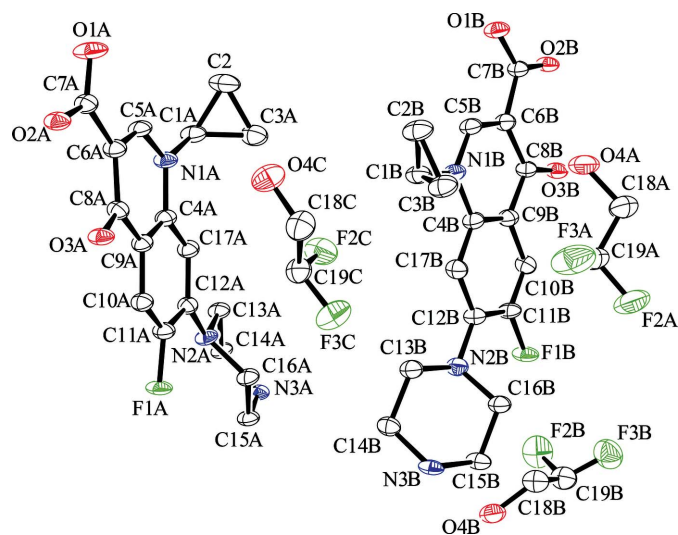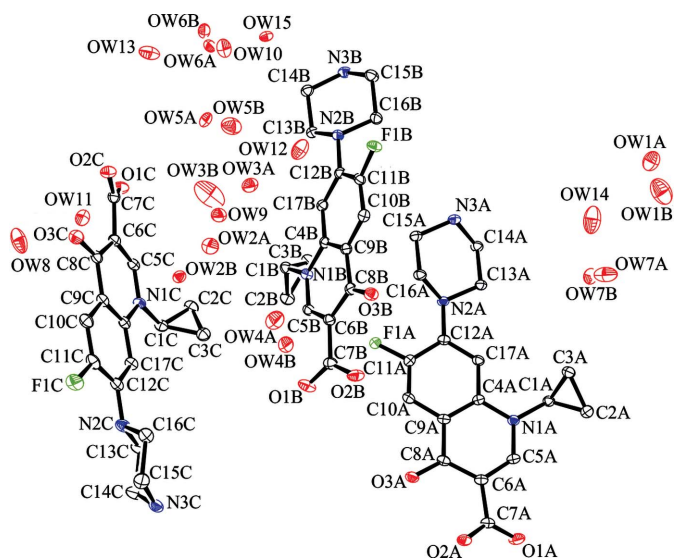

Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. Suffixes A, B and C denote symmetry-independent molecules.
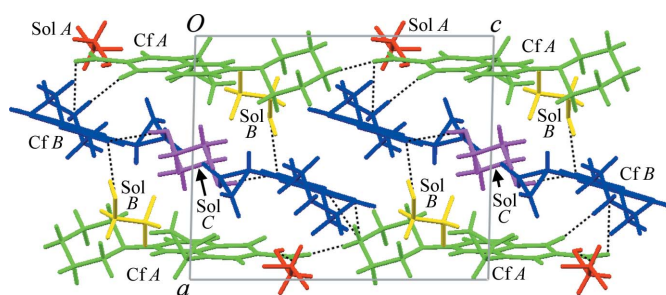
Figure 2
The asymmetric unit of (II), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. For Cf, suffixes A, B and C denote symmetry-independent molecules. For the water molecules (OW), suffixes A and B denote disordered parts.

Figure 3
The crystal packing of (I), viewed along the b axis, illustrating the hydrogen-bonded arrangements of Cf molecules A (green in the electronic version of the paper) and B (blue). Symmetry-independent solvent molecules are coloured differently and labelled (in the electronic version of the paper, molecule A is red, molecule B is yellow and molecule C is magenta). O—H···O and N^+—H···O hydrogen bonds are shown as dashed lines.

confident of our zwitterionic assignment on the basis of: (i) the observed bond lengths of the carboxylate group, which, although significantly different for most of the molecules, are well below the expected value of 1.31 Å for a C—OH single bond in a carboxylic acid (Allen *et al.*, 1987), and (ii) the fact that the H atoms of the NH_2^+ groups are visible in difference Fourier maps.

The supramolecular architecture of both structures is dominated by three-dimensional hydrogen-bonding patterns, with different hydrogen-bonding capabilities satisfied by the symmetry-independent Cf molecules. Hydrogen-bond parameters are given in Tables 2 and 3. In (I), both Cf molecules form similarly bifurcated N—H···O(carboxylate) hydrogen bonds that define crosslinked chains of molecules A and B running in nearly perpendicular directions along the c and b axes, respectively. Symmetry-equivalent chains stack pairwise *via* face-to-face π–π interactions. Each of the three symmetry-independent 2,2-difluoroethanol molecules donates a hydrogen bond to the carboxylate O atom antiperiplanar to the carbonyl group: 2,2-difluoroethanol molecules B and C to Cf molecule B, and 2,2-difluoroethanol molecule A to Cf molecule A. These hydrogen bonds, together with weaker C—H···F and C—H···O interactions, contribute to the formation of the three-dimensional network (Fig. 3). The conformation of the hydroxy group differs in the three independent 2,2-difluoroethanol molecules, with values for the C19—C18—O4—H4 torsion angle of 151, 98 and 160° for molecules A, B and C, respectively.

Although significant disorder is observed for the water molecules in (II), hydrogen bonds involving the Cf molecules are well defined, since the majority of water molecules interacting directly with Cf are ordered and their H-atom positions could be assigned from the experimental data. As in (I), each of the symmetry-independent Cf molecules forms infinite

hydrogen-bonded N—H···O(carboxylate) chains. In (II), however, the hydrogen bonds in these chains are not bifurcated and involve N—H34 rather than N—H33. In addition, rather than being nearly orthogonal to each other, the chains all run along the a axis. Crosslinking of the chains occurs *via* a second set of N—H···O(carbonyl) hydrogen bonds, leading to the formation of trimers about a pseudo-3_1 screw axis. This is in marked contrast with the structure of Cf hexahydrate, which forms a layered structure with no direct Cf···Cf contacts
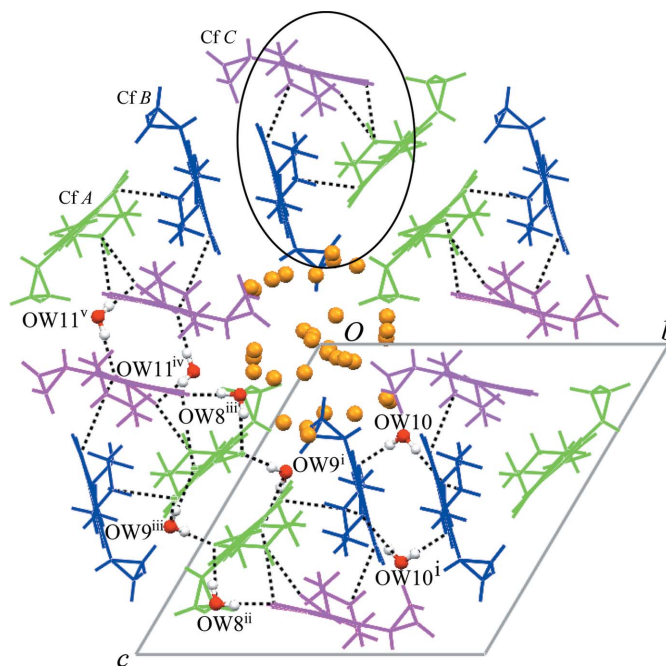
Figure 4
The crystal packing of (II), viewed along the a axis, illustrating the hexameric arrangement of trimeric hydrogen-bonded columns of Cf molecules A (green in the electronic version of the paper), B (blue) and C (magenta). Hydrogen bonds are shown as dashed lines, and the pseudo-3_1 screw axis is highlighted in the upper part of the diagram. Fully occupied water molecules OW8–OW11, which are hydrogen bonded to Cf molecules, are shown as balls and sticks. Disordered water molecules occupying the channel along the a axis are depicted as orange spheres. [Symmetry codes: (i) −x + 1, −y + 1, −z + 1; (ii) −x, −y + 1, −z + 1; (iii) x − 1, y − 1, z; (iv) −x + 1, −y, −z; (v) x, y − 1, z.]
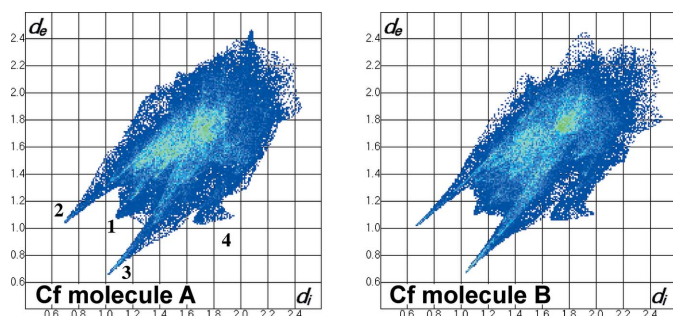
Figure 5
Fingerprint plots of Cf molecules A and B in (I). Close contacts are labelled as follows: 1 = H···H, 2 = H···O, 3 = O···H and 4 = C···H.

(Turel *et al.*, 1997). The trimers in (II) are arranged in a hexameric fashion centred about the inversion centre at the unit-cell origin (Fig. 4). This arrangement creates channels approximately 4.5 Å in diameter that contain predominantly disordered water molecules ($OW1$–$OW7$ and $OW15$), as well as those that were modelled as ordered but exhibit the largest displacement parameters ($OW12$–$OW14$). The better defined water molecules, $OW8$–$OW11$, act as hydrogen-bond donor bridges, linking molecules within a trimer ($OW8$) and pairs of symmetry-related molecules ($OW9$–$OW11$), thereby connecting the trimers (Fig. 4 and Table 3). Within the hexameric arrangement, face-to-face π–π interactions link symmetry-equivalent Cf hydrogen-bonded chains in a manner similar to that found for the pairwise stacks of hydrogen-bonded chains in (I), albeit at slightly larger interplanar separations [3.4854 (8), 3.4980 (9) and 3.6165 (7) Å for pairwise stacks of molecules A, B and C, respectively, in (II); 3.2642 (14) and 3.4023 (14) Å for molecules A and B, respectively, in (I)]. As in the structure of (I), there are a number of C—H···O, C—H···F and C—H···π interactions that contribute to the stability of the structure.

Hirshfeld surfaces (Spackman & Byrom, 1997; McKinnon *et al.*, 1998) and fingerprint plots (Spackman & McKinnon, 2002) have been shown to be useful tools for comparing and elucidating intermolecular interactions of molecules in different crystalline environments, including symmetry-independent molecules in the asymmetric unit (McKinnon *et al.*, 2004, 2007). The analysis of fingerprint plots is restricted here to the structure of (I), since several water H atoms are missing from the structure of (II). Fingerprint plots for the two symmetry-independent Cf molecules and three symmetry-independent

2,2-difluoroethanol molecules in (I) are shown in Figs. 5 and 6, respectively. At first glance, the plots for Cf look quite similar in shape, which reflects the not-too-dissimilar packing environment around the two molecules. On closer inspection, the 'thickness' and point density of some features, *e.g.* the long spikes denoting hydrogen bonding or the regions at high values of d_e and d_i, are distinct for each molecule. The asymmetry about the plot diagonal is typical of a structure that contains more than one molecule in the crystallographic asymmetric unit. Some interactions, *e.g.* H···H, O···H, H···O and C···H, labelled in Fig. 5 as 1, 2, 3 and 4, respectively, manifest themselves with characteristic features in the plots. For instance, it is immediately obvious that two distinct C···H interactions, namely π···H, are present, and on comparison with the plots shown in Fig. 6, the complementary H···π interactions are visible, *viz.* Cf molecule A with solvent molecule C, and Cf molecule B with solvent molecule A, while solvent molecule B does not participate in such contacts. The diffuse set of points labelled 5 in Fig. 6 corresponds to H···H contacts involved in a cyclic interaction; hydroxy atoms $O4A$ and $H4A$ of solvent molecule A are approximately coplanar with atoms $O1A$ and $H5A$ of Cf molecule A, so that, in addition to the stronger $O4A$—$H4A$···$O1^v$ hydrogen bond, a much weaker $C5A$—$H5A$···$O4^v$ interaction [$C5A$···$O4^v$ = 3.669 (5) Å; symmetry code: (v) $-x + 1$, $-y + 1$, $-z + 2$] is also present.

Experimental

Ciprofloxacin (Sigma Aldrich) was used as received. Single crystals were obtained by recrystallization from 2,2-difluoroethanol for (I) or from water–NaOH at *ca* pH 12 for (II) by slow evaporation of saturated solutions under ambient conditions. Crystals of (II) were identified from a mixture also containing crystals of the known Cf hexahydrate. They can be easily distinguished by their characteristic thick block habit, compared with the thin plates typically displayed by the hexahydrate. While we have not studied in detail the conditions under which preferential or controlled crystallization of (II) occurs, we have also observed concomitant crystallization of the two hydrates from water–NaOH (*ca* pH 12) at the lower temparature of 278 K. These crystals appear to be stable when kept suspended in solution for weeks under ambient conditions. Crystals of (II) have also been obtained by crystallization from an aqueous Ba(OH)$_2$ solution.

For (I), several crystals of various size were screened and all were found to be two-component twins. Smaller crystals were found to be
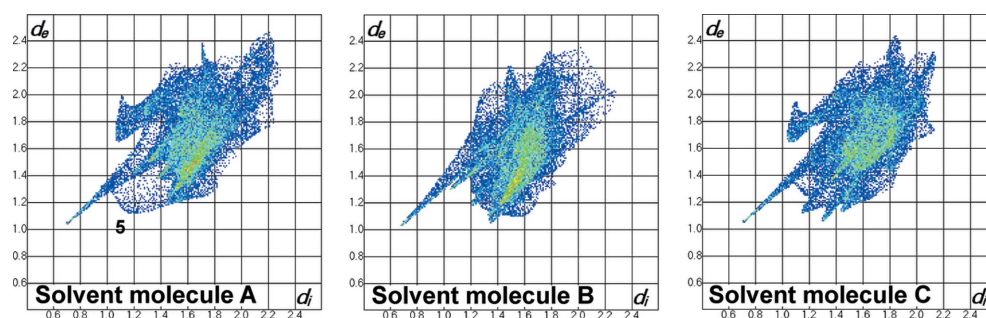
Figure 6
Fingerprint plots of solvent molecules A, B and C in (I). Close contacts are labelled as follows: 5 = H···H.

better suited for data collection in terms of low mosaicity and good reflection profiles, *e.g.* absence of peak splitting, though data resolution was limited even using a synchrotron source. The nonmerohedral twin law corresponds to a twofold rotation about the [011] direct-lattice direction. The fractional contribution of the major component was refined to 0.519 (2).

Compound (I)

Crystal data

$2C_{17}H_{18}FN_3O_3 \cdot 3C_2H_4F_2O$
$M_r = 908.84$
Triclinic, $P\bar{1}$
$a = 10.9848$ (4) Å
$b = 13.9800$ (4) Å
$c = 13.9802$ (4) Å
$\alpha = 105.6488$ (18)°
$\beta = 90.352$ (2)°

$\gamma = 93.364$ (2)°
$V = 2063.22$ (11) Å^3
$Z = 2$
Synchrotron radiation
$\lambda = 0.7000$ Å
$\mu = 0.13$ mm^{-1}
$T = 120$ K
$0.1 \times 0.08 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2008*a*)
$T_{min} = 0.58$, $T_{max} = 0.74$

51821 measured reflections
7072 independent reflections
5962 reflections with $I > 2\sigma(I)$
$R_{int} = 0.08$

Table 1
Selected torsion angles (°) for the Cf molecules in (I) and (II).

$\theta_1 = $ C2—C1—N1—C5, $\theta_2 = $ C5—C6—C7—O1 and $\theta_3 = $ C11—C12—N2—C16.

Molecule	θ_1	θ_2	θ_3
(I), A	37.9 (5)	−3.0 (5)	−58.0 (4)
(I), B	−30.5 (6)	0.3 (5)	60.4 (4)
(II), A	−41.2 (2)	−24.3 (2)	52.7 (2)
(II), B	−35.8 (2)	−12.3 (2)	61.2 (2)
(II), C	26.9 (2)	20.4 (2)	−62.8 (2)

Table 2
Geometry of intermolecular interactions (Å, °) for (I).

All standard uncertainties were calculated using *PLATON* (Spek, 2009).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3A—H3A3$\cdots$O1A^i	0.90	2.58	3.176 (4)	125
N3A—H3A3$\cdots$O2A^i	0.90	1.86	2.758 (4)	173
N3A—H3A4$\cdots$O2B^{ii}	0.90	2.39	2.885 (4)	114
N3A—H3A4$\cdots$O3B^{ii}	0.90	1.85	2.717 (4)	162
N3B—H3B3$\cdots$O1B^{iii}	0.90	2.77	3.376 (4)	126
N3B—H3B3$\cdots$O2B^{iii}	0.90	1.82	2.724 (4)	179
N3B—H3B4$\cdots$O2A^{iv}	0.90	2.50	2.894 (4)	107
N3B—H3B4$\cdots$O3A^{iv}	0.90	1.79	2.687 (4)	171
O4A—H4A$\cdots$O1A^v	0.82	1.88	2.672 (4)	162
O4B—H4B$\cdots$O1B^{ii}	0.82	1.87	2.666 (4)	165
O4C—H4C$\cdots$O1B^v	0.82	1.93	2.733 (4)	168
C2A—H2A2$\cdots$F3B^{ii}	0.97	2.51	3.207 (5)	128
C14A—H14A$\cdots$O2A^{vi}	0.97	2.49	3.350 (5)	148
C14A—H14A$\cdots$O3A^{vi}	0.97	2.49	3.274 (4)	138
C16A—H16A$\cdots$O4B^{vii}	0.97	2.48	3.148 (5)	126
C1B—H1B$\cdots$F2C	0.98	2.45	3.200 (5)	133
C14B—H14D$\cdots$O2B^{ii}	0.97	2.34	3.295 (4)	170
C15B—H15D$\cdots$O2A^{iv}	0.97	2.51	3.131 (5)	122
C18B—H18D$\cdots$F1B	0.97	2.46	3.396 (5)	161

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

Table 3
Hydrogen-bond geometry (Å, °) for (II).

Only water–water contacts for which H-atom positions are available are included. All standard uncertainties were calculated using *PLATON* (Spek, 2009).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
Contacts involving Cf				
N3A—H3A3$\cdots$O2C^i	0.90	2.03	2.866 (2)	153
N3A—H3A3$\cdots$O3C^i	0.90	2.29	2.903 (2)	125
N3A—H3A4$\cdots$O2A^{ii}	0.90	1.80	2.684 (2)	166
N3B—H3B3$\cdots$O3A^{ii}	0.90	1.90	2.782 (3)	168
N3B—H3B4$\cdots$O2B^{ii}	0.90	1.76	2.660 (2)	173
N3C—H3C4$\cdots$O1C^{iii}	0.90	1.79	2.682 (2)	170
N3C—H3C3$\cdots$OW5A^{iii}	0.90	2.29	2.959 (4)	131
N3C—H3C3$\cdots$O3B^{iv}	0.90	2.10	2.859 (2)	142
OW8—H81$\cdots$O1A^{iv}	0.86 (1)	1.86 (1)	2.702 (2)	165 (3)
OW8—H82$\cdots$O3C	0.86 (3)	1.83 (3)	2.683 (2)	170 (3)
OW9—H91$\cdots$O2A^{iv}	0.86 (2)	2.07 (2)	2.836 (2)	149 (2)
OW9—H91$\cdots$O3A^{iv}	0.86 (2)	2.38 (2)	3.021 (2)	133 (2)
OW9—H92$\cdots$O1A^v	0.86 (2)	1.92 (2)	2.784 (2)	176 (2)
OW10—H101$\cdots$O1B^{ii}	0.86 (3)	1.96 (3)	2.816 (2)	179 (3)
OW10—H102$\cdots$O2B^i	0.87 (2)	1.99 (2)	2.826 (2)	158 (3)
OW10—H102$\cdots$O3B^i	0.87 (2)	2.52 (3)	3.091 (2)	126 (2)
OW11—H111$\cdots$O2C^{vi}	0.87 (3)	1.97 (3)	2.830 (2)	175 (2)
OW11—H112$\cdots$O1C	0.86 (1)	1.88 (1)	2.731 (2)	176 (2)
OW15—H152$\cdots$O1B^{ii}	0.82 (3)	1.99 (3)	2.787 (3)	163 (4)
Water–water contacts				
OW12—H121$\cdots$OW9^i	0.86 (3)	1.86 (3)	2.712 (2)	176 (3)
OW12—H122$\cdots$OW3A	0.84 (3)	2.20 (3)	2.825 (4)	131 (3)
OW12—H122$\cdots$OW5B	0.84 (3)	2.06 (3)	2.882 (5)	165 (3)
OW13—H131$\cdots$OW8^{vi}	0.86 (2)	1.96 (2)	2.803 (3)	166 (2)
OW13—H132$\cdots$OW1A^{vii}	0.85 (3)	2.16 (3)	2.930 (4)	150 (3)
OW13—H132$\cdots$OW6A	0.85 (3)	2.41 (3)	2.827 (5)	111 (2)
OW14—H141$\cdots$OW1A	0.89 (1)	2.25 (2)	2.910 (4)	131 (2)
OW14—H141$\cdots$OW1B	0.89 (1)	2.03 (3)	2.623 (5)	123 (3)
OW14—H142$\cdots$OW8^i	0.86 (4)	1.91 (4)	2.728 (4)	157 (3)
OW15—H151$\cdots$OW4A^i	0.85 (3)	1.91 (3)	2.75 (3)	170 (4)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $x - 1, y, z$; (iv) $-x, -y + 1, -z + 1$; (v) $x + 1, y + 1, z$; (vi) $-x + 1, -y + 1, -z$; (vii) $x, y, z - 1$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.202$
$S = 1.16$
7072 reflections
571 parameters

522 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Compound (II)

Crystal data

$3C_{17}H_{18}FN_3O_3 \cdot 14.5H_2O$
$M_r = 1255.26$
Triclinic, $P\bar{1}$
$a = 13.8760$ (12) Å
$b = 15.8760$ (13) Å
$c = 16.528$ (2) Å
$\alpha = 115.755$ (7)°
$\beta = 103.610$ (7)°

$\gamma = 102.325$ (5)°
$V = 2972.8$ (5) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 100$ K
$0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)
$T_{min} = 0.40$, $T_{max} = 0.43$

55842 measured reflections
12150 independent reflections
9655 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$

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The program *TWINABS* (Sheldrick, 2008*a*) was used to generate a merged reflection file for (I) in the *SHELXL* HKLF5 format (Sheldrick, 2008*b*). Data statistics were as follows: 20 118 data (4526 unique) for domain 1 only with mean $I/\sigma(I) = 14.3$; 20 116 data (4515 unique) for domain 2 only with mean $I/\sigma(I) = 14.5$; 7592 data (1975 unique) for both domains with mean $I/\sigma(I) = 20.0$. The quoted R_{int} value (0.07) comes from scaling all single and composite reflections involving domain 1. For the generation of an HKLF5 file, all observations containing domain 1 were chosen. Single reflections that also occur in composites were omitted for merging.

Given the low data-to-parameter ratio, atomic displacement parameters of the non-H atoms of Cf in (I) were subjected to rigid-bond and similarity restraints, while the bond lengths and 1,3 distances in the two Cf molecules were restrained to be the same with an s.u. value of 0.02 Å. In the structure of (II), seven water O atoms (OW1–OW7) were modelled with split sites, with their occupancies set to either 0.5:0.5 or 0.6:0.4, one O atom (OW14) was modelled as half-occupied and the remaining six as fully occupied. The strategy for assigning site occupancies for OW1–OW7 and OW14 consisted of refining different models in which a variable number of occupancies were fixed and/or allowed to refine, so as to obtain an optimal R factor. Occupancies were fixed in the final refinement.

For both structures, H atoms belonging to Cf were positioned geometrically and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}$(parent). In both structures, N-bound H atoms in the Cf molecules were clearly visible in a difference Fourier map but were positioned geometrically and constrained to ride during refinement. For (I), hydroxy H atoms were first located in a difference Fourier map and subsequently geometrically optimized and constrained to ride on their parent atom using a variable C—C—O—H torsion angle (AFIX 147 instruction in *SHELXL97*) and $U_{iso}(H) = 1.5U_{eq}$(O). For (II), H atoms for the eight ordered water molecules were clearly visible in a difference Fourier map. Their positions were refined subject to O···H and H···H distance restraints of 0.85 (1) and 1.50 (3) Å, respectively [0.83 (1) Å for OW15—H152], with $U_{iso}(H) = 1.5U_{eq}$(O). The H atoms of the disordered water molecules could not be located, and they cannot easily be placed to form a consistent hydrogen-bonding pattern. These H atoms were therefore omitted from the structure model.

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008*b*); molecular graphics: *ORTEP-3 for Windows* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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