Neutron diffraction studies of the 1:1 and 2:1 cocrystals of benzene-1,2,4,5-tetracarboxylic acid and 4,4′-bipyridine

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The 1:1 and 2:1 cocrystals of benzene-1,2,4,5-tetracarboxylic acid (BTA) and 4,4′-bipyridine (BPY) have been studied using neutron diffraction at 215 and 20 K, respectively. BTA and BPY crystallize in a 1:1 ratio with 1.8 molecules of water, *viz.* 4,4′-bipyridinium 2,5-dicarboxybenzene-1,4-dicarboxylate 1.8-hydrate, $C_{10}H_{12}N_2^{2+} \cdot C_{10}H_4O_8^{2-} \cdot 1.8H_2O$, (I), in the space group $P\bar{1}$, with both BTA and BPY lying on inversion centres. BTA and BPY crystallize in a 2:1 ratio, *viz.* 4,4′-bipyridinium bis(2,4,5-tricarboxybenzoate), $C_{10}H_{12}N_2^{2+} \cdot 2C_{10}H_5O_8^{-}$, (II), in the space group *Cc*. The crystal structure of the 1:1 cocrystal contains one short N—H⋯O hydrogen bond [N⋯O = 2.6047 (19) Å] and one intramolecular O—H⋯O hydrogen bond [O⋯O = 2.423 (3) Å]. The crystal structure of the 2:1 cocrystal contains two N—H⋯O hydrogen bonds [N⋯O = 2.639 (3) and 2.674 (2) Å], and two intramolecular [O⋯O = 2.404 (3) and 2.420 (3) Å] and four strong intermolecular O—H⋯O hydrogen bonds [O⋯O = 2.613 (3), 2.718 (3), 2.628 (3) and 2.739 (3) Å].

Comment

As part of an investigation into N—H⋯O and O—H⋯N hydrogen bonds (Cowan *et al.*, 2001a,b; Cowan, Howard, Leech *et al.*, 2001; Cowan, Howard, Leech & Williams, 2001), we have produced cocrystals of benzene-1,2,4,5-tetra-carboxylic acid (BTA) and 4,4′-bipyridine (BPY). In the short N⋯O hydrogen bond observed in the cocrystal of 4-methyl-pyridine and pentachlorophenol (Steiner *et al.*, 2001), the H atom lies closer to the N atom at 20 K, and migrates across the

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hydrogen bond to lie closer to the O atom at 296 K. We have recently (Cowan *et al.*, 2003) observed an identical phenomenon of H-atom migration in one of the two short N⋯O hydrogen bonds in the 1:2 cocrystal of BTA and BPY, whose structure was first described by Lough *et al.* (2000). It was speculated that similar novel behaviour may be observed in the N⋯O hydrogen bonds of the 2:1 and 1:1 cocrystals, the structures of which have recently been reported (Zhu *et al.*, 2003; Ruiz-Pérez *et al.*, 2004; Fabelo *et al.*, 2005).
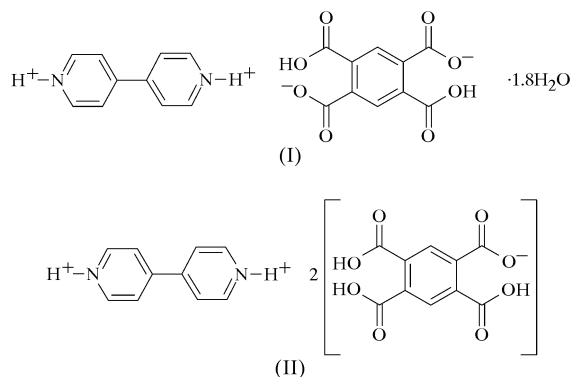
BTA and BPY crystallize in a 1:1 ratio as a molecular salt, (I), with two molecules of water, in space group $P\bar{1}$. The BTA and BPY molecules are linked by strong N—H⋯O hydrogen bonds to form infinite one-dimensional chains. The disordered water molecules lie in a channel along the *a* axis between parallel chains of BTA and BPY molecules (Fig. 1). The structure of (I) has been discussed previously by Fabelo *et al.* (2005).

A very short intramolecular hydrogen bond is formed [O11—H1⋯O21, with O⋯O = 2.423 (3) Å] between the carboxylic acid group and the carboxylate group. Even though the O⋯O separation is very short for an O—H⋯O hydrogen bond, the H atom is asymmetrically positioned. There is no evidence of disorder in the difference Fourier map or in the anisotropic displacement parameters of the H atom (Fig. 2).

A strong charge-assisted N—H⋯O hydrogen bond [N4—H4⋯O22, with N⋯O = 2.6047 (19) Å] (Gilli *et al.*, 1994) is formed between the BTA and BPY molecules. Although this is chemically very similar to the short N—H⋯O hydrogen bond in the 2:1 cocrystal [N⋯O = 2.521 (2) Å; Lough *et al.*,
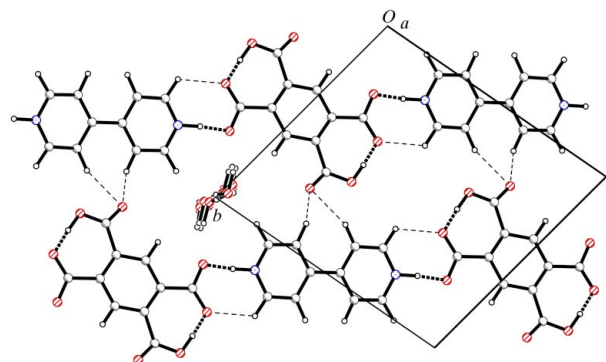

Figure 1
A packing diagram for (I), viewed perpendicular to the hydrogen-bonded chains. Hydrogen bonds are indicated by dashed lines. The disordered water molecules are visible in the large channel.

organic compounds

2000], it is much longer. Surprisingly, the longer hydrogen bond is accompanied by a parallel C—H⋯O hydrogen bond (C9—H9⋯O21) forming a commonly observed motif, while the shorter hydrogen bond has no parallel C—H⋯O bond.

The observed deterioration of the crystal below 200 K meant we could not verify the existence or absence of H-atom migration. In the observed cases, H-atom migration has been from the O atom at room temperature to the N atom at low temperature. The H-atom position at 215 K [1.102 (3) Å from the N atom] suggests that significant H-atom migration does not occur. To observe significant H-atom migration, we would expect the N—H distance to be 1.2–1.3 Å at 215 K.

The water molecules were modelled as disordered over four positions, and were refined with the O—H bond lengths and the H—O—H bond angle restrained. Most of the residual nuclear density lies around the water molecules and the model only approximates the true disorder. The occupancy factors of the water molecules were refined and then fixed so that the isotropic displacement parameters were physically reasonable. It was not sensible to refine anisotropic displacement parameters for any of the atoms in the water molecules. The overall occupancy summed to 1.8 water molecules per unit cell.

BTA and BPY crystallize in a 2:1 ratio as a molecular salt, (II), with the formula $C_{10}H_{10}N_2{}^{2+}\cdot 2C_{10}H_5O_8{}^-$. The BTA molecules are connected by O—H⋯O hydrogen bonds in a two-dimensional mesh. The BPY molecules thread through gaps in the mesh and connect the layers together *via* N—H⋯O hydrogen bonds (Fig. 3). The structure of (II) has been discussed previously by Zhu *et al.* (2003) and Ruiz-Pérez *et al.* (2004).

Our structure of (II) disagrees with both published structures. The structure of Zhu *et al.* (2003) [Cambridge Structural Database (CSD; Allen, 2002) refcode IRETII] was refined in the space group C2/c with one BTA molecule and one half of a BPY molecule in the asymmetric unit. Refinement of the low-temperature structure of (II) in C2/c results in unacceptable anisotropic displacement parameters and the refined R factor was only ~10%. It is possible that the C2/c phase occurs at room temperature, or that different crystallization conditions

produce a polymorph. The heavy-atom structure and space group of Ruiz-Pérez *et al.* (2004) (CSD refcode IRETII01) agree with our structure. However, their placement of the H atoms is incorrect, including three H atoms curiously attached to the carbonyl O atoms in the carboxylic acid groups.

A short intramolecular hydrogen bond is formed between a carboxylate group and the adjacent carboxylic acid group in both BTA molecules. Again, as in (I), despite the very short O⋯O separation for an O—H⋯O hydrogen bond, the H atom is positioned asymmetrically. There is no evidence of disorder in the difference Fourier map or in the isotropic displacement parameters of the H atom (Fig. 4). There are two relatively long N—H⋯O charge-assisted hydrogen bonds, both with ordered H-atom positions close to the N atoms. No H-atom migration is expected, for the same reasons as stated for (I). Four short but unremarkable O—H⋯O hydrogen bonds are also formed, linking the BTA molecules into two-dimensional meshes. Full hydrogen-bond parameters are listed in Table 2.

In both (I) and (II), three independent short O—H⋯O intramolecular hydrogen bonds are formed between a carboxylic acid group and an adjacent carboxylate group attached to a benzene ring. These are among the shortest hydrogen bonds studied by neutron diffraction. In similar short intramolecular hydrogen bonds studied by neutron diffraction, the H atom is rarely found to be equidistant from the O atoms (Wilson, 2000). In the crystal structure of pyridine-2,3-dicarboxylic acid, a short asymmetric intramolecular hydrogen bond is formed and the asymmetry is ascribed to the N atom in the pyridyl ring (Kvick *et al.*, 1974; Takusagawa & Koetzle, 1979). Similar short intramolecular hydrogen bonds between carboxylic acid and carboxylate groups have been studied in detail by neutron diffraction and *ab initio* calculations in maleate ions (Hsu & Schlemper, 1980; Olovsson & Olovsson, 1984; Vanhouteghem *et al.*, 1987; Wilson *et al.*, 2003), and the asymmetry in the H-atom position, when it occurs, is ascribed to intermolecular effects. In imidazolium hydrogen maleate (Sakhawat Hussain *et al.*, 1980), the H atom is found to be centred, but on deuteration the D atom is found to be asymmetrically placed. In the structure of lithium
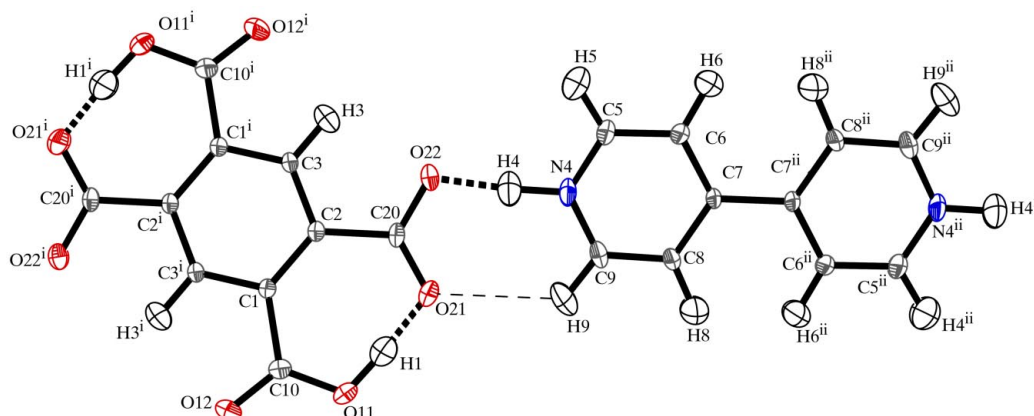

Figure 2
A plot of (I) from the 215 K neutron data. Displacement ellipsoids are drawn at the 50% probability level. The heavy dashed lines indicate strong hydrogen bonds and the thin dashed line indicates a weak C—H⋯O hydrogen bond. [Symmetry codes: (i) 1 − x, 1 − y, −z; (ii) −x − 1, −y, 1 − z.]

hydrogen phthalate (Küppers *et al.*, 1985), there are two phthalate ions forming intramolecular hydrogen bonds, one of which is symmetrical while the other is asymmetrical with respect to the H-atom position.

The asymmetry in the intramolecular hydrogen bonds in structures (I) and (II) is clearly caused by the intermolecular N—H···O hydrogen bonds. The asymmetry in the hydrogen bond is also evident in the C—O distances in the carboxylate/carboxylic acid groups, which are, in (I), characteristic of a carboxylic acid group and a carboxylate group. The carboxylate group acts as the acceptor for both intra- and intermolecular hydrogen bonds. In the cocrystal of BTA and guanidinium (Sun *et al.*, 2002), the H atom was found in the centre of the intramolecular hydrogen bond, although in that case the carboxylate/carboxylic acid groups are both acceptors for similar intermolecular hydrogen bonds and the C—O distances are hybrid between the carboxylate/carboxylic acid cases.
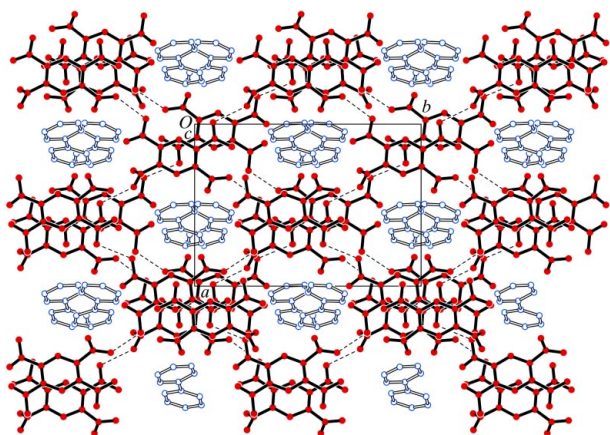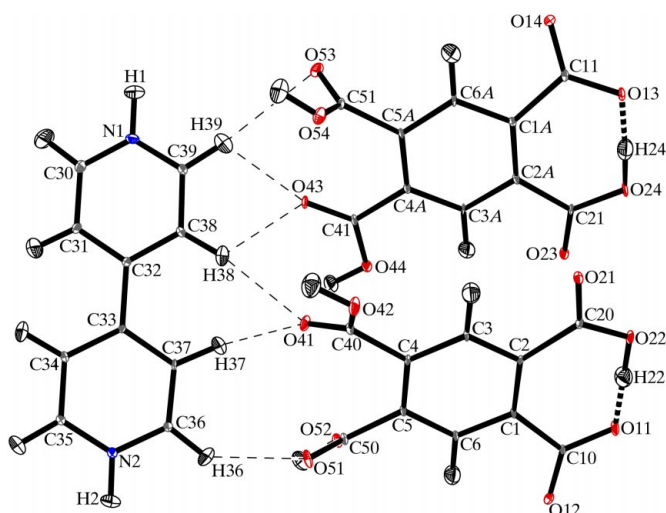

Figure 3
A packing diagram for (II), viewed along the *c* direction. The BPY molecules are shown with hollow bonds and the BTA molecules are shown with solid bonds. H atoms have been omitted for clarity. The two-dimensional BTA networks are parallel to the page and the BPY molecules thread through the gaps.

Figure 4
A plot of (II) from the 20 K neutron data. Displacement ellipsoids are drawn at the 50% probability level.

Aromatic interactions between delocalized π-electron systems in crystal structures have long been recognized (Robertson, 1951) and are characterized by perpendicular distances of $\sim$3.4 Å between aromatic rings. Hunter *et al.* (2002) explain π–π interactions by treating the π-electron system and the σ system, in which they include the nuclei and the σ electrons, as separate, and by considering the electrostatic interactions between them.

In structure (I), the BTA molecules form π-stacked columns. In (II), there are no conventional π–π interactions; the BTA molecules do not stack with the delocalized aromatic interactions 'face-to-face', but with the aromatic rings adjacent to the ring formed by the intramolecular hydrogen bonds. The most obvious example of a similar interaction is in the crystal structure of diphthalimidodiethylamine phthalic acid hydrate (Barrett *et al.*, 1998), in which the phthalic acid molecule is pincered between the benzene groups in the the U-shaped diphthalimidodiethylamine. The motif also occurs in cocrystals of BTA and 4-methylpyridine (Biradha & Zaworotko, 1998; centre–centre = 3.538 Å), phenylethylammonium hydrogen phthalate (Kozma *et al.*, 1994; centre–centre = 3.649 Å) and bis(*p*-dimethylaminophenyl)phenylcarbenium hydrogen phthalate phthalic acid (Mitchell *et al.*, 1996; centre–centre = 3.713 Å). This interaction could be interpreted in some cases as a π–π interaction with a large offset between the rings. The description of π–π interactions as electrostatic interactions would include those interactions in which the attraction is between the σ-electron system of the benzene ring and the charges in the polar C—O bonds in the hydrogen-bonded ring. Further examples, with evidence that this motif would form in preference to other possible motifs, are required to determine if these are true intermolecular interactions or simply geometrical coincidences caused by other interactions.

One of the main aims of this study was to obtain neutron diffraction data on short N—H···O/O—H···N hydrogen bonds. The strength of the hydrogen bonds is apparently very sensitive to the intermolecular environment. There is a variation in the N···O distances between 2.5220 (17) and 2.674 (2) Å in the hydrogen bonds formed between BTA and BPY in the three cocrystals of these components.

No hydrogen bonds as short as those in the 2:1 cocrystal (Lough *et al.*, 2000) are observed in (I) and (II), and therefore we do not expect H-atom migration. However, in the cocrystal of BTA and 1,7-phenanthroline (Arora & Pedireddi, 2003), there is an N—H···O hydrogen bond with an N···O distance of 2.562 (2) Å and an N—H distance of 1.31 (3) Å at room temperature. Although this is longer than the values of 2.5220 (17) Å in the 2:1 cocrystal and 2.506 (3) Å in 4-methylpyridine and pentachlorophenol (Steiner *et al.*, 2001), it is likely that H-atom migration may be exhibited upon cooling to low temperature. Neutron diffraction is required to verify this prediction.

Experimental

Cocrystals of BTA and BPY in a 1:1 ratio [compound (I)] were formed in $\sim$80% yield by heating BTA and BPY in a 1:1 ratio (1:1 mmol) in H_2O (1 ml) for 2 d at 453 K in a 23 ml Teflon-lined Parr

vessel under autogenous pressure. Phase purity was established by powder X-ray diffraction and elemental analysis. Typical crystal size was 1–2 mm³. Larger specimens of up to 5 mm³ could be obtained by cyclic heating and cooling of the bombs between 373 and 453 K. An identical procedure, using different ratios of the constituents, was used to produce 2:1 cocrystals [compound (II)] of similar size.

Compound (I)

Crystal data

$C_{10}H_{10}N_2^{2+} \cdot C_{10}H_4O_8^{2-} \cdot 1.8H_2O$
$M_r = 442.40$
Triclinic, $P\bar{1}$
$a = 3.7747$ (2) Å
$b = 10.8587$ (5) Å
$c = 11.9519$ (6) Å
$\alpha = 99.626$ (3)°
$\beta = 97.726$ (3)°
$\gamma = 95.515$ (3)°
$V = 475.07$ (4) Å³
$Z = 1$

$D_x = 1.546$ Mg m⁻³
Neutron radiation
$\lambda = 1.302$ Å
Cell parameters from 1196 reflections
$\theta = 5$–55°
$\mu = 0.16$ mm⁻¹
$T = 215$ (2) K
Needle, brown
$2.0 \times 0.8 \times 0.5$ mm

Data collection

D19 diffractometer, ILL
ω scans
Absorption correction: integration (*D19ABS*; Matthewman *et al.*, 1982)
  $T_{min} = 0.861$, $T_{max} = 0.933$
1983 measured reflections
1654 independent reflections

1426 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 55.0°$
$h = -2 \rightarrow 4$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.081$
$S = 1.06$
1654 reflections
249 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 1.6121P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ fm Å⁻³
$\Delta\rho_{min} = -0.55$ fm Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11—H1···O21	1.056 (4)	1.370 (4)	2.423 (3)	174.6 (4)
N4—H4···O22	1.102 (4)	1.505 (3)	2.6047 (19)	175.1 (3)
C6—H6···O12^i	1.080 (3)	2.252 (4)	3.199 (2)	145.3 (4)
C8—H8···O12^{ii}	1.083 (4)	2.401 (4)	3.362 (2)	147.2 (4)
C9—H9···O21	1.080 (3)	2.592 (4)	3.302 (2)	122.6 (3)
O1—H1A···O22	0.977 (19)	2.10 (2)	2.919 (16)	140 (2)
O2—H2A···O22	0.971 (18)	1.922 (15)	2.851 (15)	159 (2)
O3—H3A···O22	0.982 (10)	1.849 (12)	2.809 (12)	164.9 (17)
O4—H4A···O22^{iii}	0.97 (2)	2.031 (18)	3.00 (2)	174 (3)

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

Compound (II)

Crystal data

$C_{10}H_{10}N_2^{2+} \cdot 2C_{10}H_5O_8^-$
$M_r = 664.49$
Monoclinic, Cc
$a = 12.009$ (1) Å
$b = 15.484$ (1) Å
$c = 15.221$ (1) Å
$\beta = 112.273$ (3)°
$V = 2619.2$ (3) Å³
$Z = 4$
$D_x = 1.685$ Mg m⁻³

Neutron radiation
$\lambda = 1.3108$ (1) Å
Cell parameters from 3055 reflections
$\theta = 5$–50°
$\mu = 0.14$ mm⁻¹
$T = 20$ (2) K
Bar, yellow
$2.2 \times 1.0 \times 0.7$ mm

Data collection

D19 diffractometer, ILL
ω scans
Absorption correction: Gaussian (*D19ABS*; Matthewman *et al.*, 1982)
  $T_{min} = 0.841$, $T_{max} = 0.891$
3741 measured reflections
2647 independent reflections

2628 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 55.2°$
$h = -4 \rightarrow 14$
$k = -19 \rightarrow 13$
$l = -19 \rightarrow 17$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.048$
$S = 1.12$
2647 reflections
615 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 12.8939P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ fm Å⁻³
$\Delta\rho_{min} = -0.46$ fm Å⁻³
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.000155 (17)
Absolute structure: Flack (1983), with 92 Friedel pairs
Flack parameter: 0 (10)

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O22—H22···O11	1.079 (5)	1.333 (5)	2.404 (3)	172.6 (4)
O24—H24···O13	1.076 (5)	1.348 (5)	2.420 (3)	173.2 (4)
N1—H1···O12^i	1.049 (4)	1.635 (4)	2.674 (2)	169.5 (4)
N2—H2···O14^{ii}	1.050 (4)	1.665 (4)	2.639 (2)	151.9 (3)
O42—H42···O11^{iii}	1.011 (5)	1.612 (5)	2.613 (3)	169.8 (4)
O52—H52···O21^{iv}	1.004 (4)	1.717 (4)	2.718 (3)	174.7 (4)
O44—H44···O13^{iv}	1.007 (4)	1.637 (4)	2.629 (3)	167.2 (4)
O54—H54···O23^{iii}	1.004 (5)	1.740 (5)	2.739 (3)	173.2 (4)
C31—H31···O24^v	1.085 (4)	2.228 (5)	3.191 (3)	146.7 (4)
C34—H34···O52^{iii}	1.080 (4)	2.482 (5)	3.414 (3)	143.9 (4)
C34—H34···O22^v	1.080 (4)	2.467 (4)	3.155 (3)	120.5 (3)
C35—H35···O22^v	1.071 (4)	2.549 (5)	3.154 (3)	115.0 (3)
C35—H35···O43^{vi}	1.071 (4)	2.494 (4)	3.042 (3)	110.7 (3)
C36—H36···O51	1.082 (4)	2.364 (5)	3.219 (3)	134.8 (4)
C36—H36···O21^{iv}	1.082 (4)	2.414 (5)	3.134 (3)	122.8 (3)
C37—H37···O41	1.083 (4)	2.193 (5)	3.140 (3)	144.9 (4)
C38—H38···O41	1.081 (4)	2.351 (4)	3.420 (3)	169.7 (4)
C38—H38···O43	1.081 (4)	2.564 (4)	3.044 (3)	106.0 (3)
C39—H39···O23^{iii}	1.082 (4)	2.592 (5)	3.108 (3)	108.4 (3)
C39—H39···O43	1.082 (4)	2.493 (5)	2.994 (3)	107.0 (3)
C39—H39···O53	1.082 (4)	2.692 (5)	3.739 (3)	162.9 (4)

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

X-ray diffraction experiments were performed prior to the neutron experiments to verify the identity of the crystals. The initial structural models for the neutron refinements were taken from our X-ray diffraction results. Neutron scattering factors were taken from Sears (1992). All H atoms were refined with anisotropic displacement parameters except for those in the disordered water molecules in (I).

For both compounds, data collection: *MAD* (Barthelemy *et al.*, 1984); cell refinement: *RAFD19* (Filhol, 1998); data reduction: *RETREAT* (Wilkinson *et al.*, 1988); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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