# organic compounds

# Supramolecular hydrogen-bonded networks in adeninediiium hemioxalate chloride and adeninium semioxalate hemi(oxalic acid) monohydrate

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In 9$H$-adenine-1,7-diium hemioxalate chloride, $C_5H_7N_5^{2+}\cdot0.5C_2O_4^{2-}\cdot Cl^-$, (I), adenine is doubly protonated, while in 7$H$-adenin-1-ium semioxalate hemi(oxalic acid) monohydrate, $C_5H_6N_5^+\cdot C_2HO_4^-\cdot0.5C_2H_2O_4\cdot H_2O$, (II), adenine and one oxalate anion are both monoprotonated. In (I), the adeninium cation forms $R_2^2(8)$ and $R_1^2(5)$ hydrogen-bonding motifs with the centrosymmetric oxalate anion, while in (II), the cation forms $R_2^1(6)$ and $R_1^2(5)$ motifs with the centrosymmetric oxalic acid molecule and $R_1^2(5)$ and $R_2^2(9)$ motifs with the monoprotonated oxalate anion. Linear hydrogen-bonded trimers are observed in (I) and (II). In both structures, the hydrogen bonds lead to the formation of two-dimensional supramolecular hydrogen-bonded sheets in the crystal packing. The significance of this study lies in the analysis of the interactions occurring *via* hydrogen bonds and the diversity seen in the supramolecular hydrogen-bonded networks as a result of such interactions.

## Comment

Adenine offers five available proton attachment sites (basicity order N9 > N1 > N7 > N3 > N10-exocyclic) which afford a wide range of neutral tautomers and protonated forms, and it has been the subject of numerous theoretical (Sponer *et al.*, 2002; Turecek & Chen, 2005) and experimental investigations (Crespo-Hernandez *et al.*, 2004; Chen & Shuhua, 2005). Carboxylic acids have been used widely as pattern-controlling functional groups for the rational design of organic solids (Desiraju, 1989; Melendez & Hamilton, 1998). Oxalic acid, in principle, exists in three ionization states, *viz.* singly charged (semioxalate), doubly charged (oxalate) and neutral (oxalic acid). The present study reports the structures of the title compounds, (I) and (II), as a continuation of our ongoing programme on the structure elucidation of adducts formed between nucleobases and carboxylic acids (Sridhar & Ravikumar, 2007*a*,*b*, 2008).



(I)



(II)
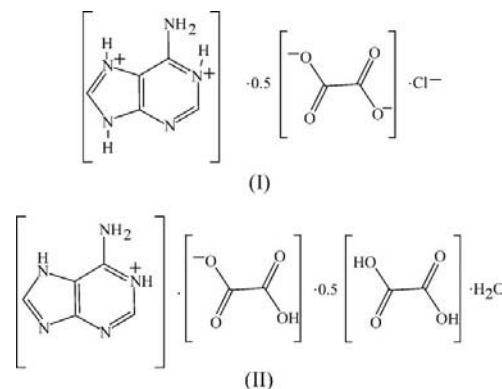
The asymmetric unit of (I) consists of one diprotonated adeninium cation, half an oxalate anion lying across an inversion centre and one chloride anion (Fig. 1), while the asymmetric unit of (II) contains one monoprotonated adeninium cation, one monoprotonated oxalate anion, half an oxalic acid molecule lying across an inversion centre and one water molecule (Fig. 2). The water molecule is disordered over two sites (O7 and O7′) with occupancies of 0.622 (19) and 0.378 (19), respectively.

Adeninium cations can be either mono- or diprotonated and the bond lengths and angles are dependent on the degree of protonation (Hingerty *et al.*, 1981; Langer & Huml, 1978). This canonical tautomeric form contains three basic N atoms. The most basic site (p$K_a$ = 4.2) is N1, which accepts the first
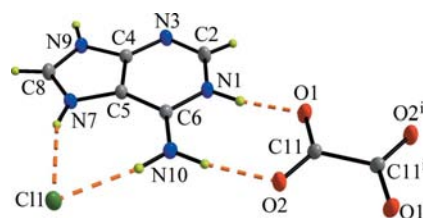


**Figure 1**
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x + 2$, $-y + 1$, $-z + 1$.]
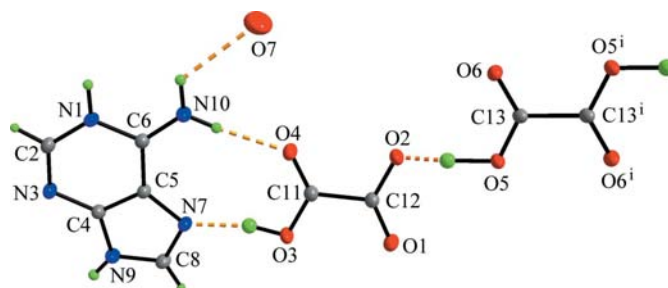


**Figure 2**
A view of the structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The minor component of the disordered O7′ water molecule has been omitted for clarity. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x + 4$, $-y + 1$, $-z + 2$.]
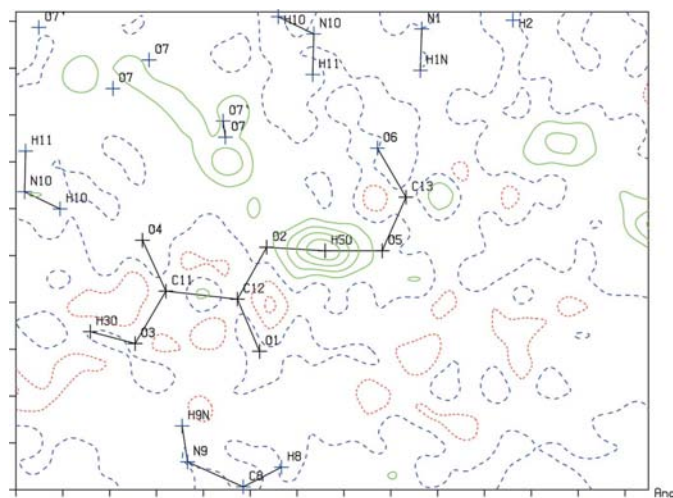
doi:10.1107/S0108270109011780

**Figure 3**
A contoured Fourier difference map slice in the plane of the carboxylic acid group of (II), with the site occupancy of atom H5O set at 0.001. The refined positions of the atoms are shown by '+' marks. The contour intervals are 0.1 e Å$^{-3}$.

proton, and the next protonation occurs at N7 and then at N3. In (I), atoms N1 and N7 are protonated, while in (II) only atom N1 is protonated. This is evident from the increase in the ring angle at the sites of protonation, namely N1 and N7. The internal angles at N1 and N7 (Tables 1 and 3) are increased from the reported values of 119.8 and 104.4°, respectively, in unprotonated adenine (Voet & Rich, 1970). The adenine base is nearly planar, with an r.m.s. deviation from the least-squares plane through the nine atoms of the base (N1/C2/N3/C4–C6/N7/C8/N9) of 0.002 Å in each structure. The maximum deviations from these planes are 0.005 (2) Å for atom C2 of (I) and 0.017 (2) Å for atom C5 of (II).

The oxalic acid and oxalate entities of (I) and (II) are planar. In (II), the centrosymmetric oxalic acid molecule and the monoprotonated oxalate anion are linked by a short hydrogen bond, apparently symmetric, with its H atom centrally located. The refined isotropic atomic displacement parameter of atom H5O is somewhat larger than those of the amide H atoms, the positions and atomic displacement parameters of which were also refined. A contoured Fourier difference map produced by *PLATON* (Spek, 2009), in which the site-occupation factor of atom H5O had been set to 0.001, clearly shows that the maximum of the electron density is at atom H5O, but it is quite smeared out along the O···O axis (Fig. 3). In the crystal structure of a macrocycle, Linden *et al.* (2006) described a similar situation, stating that the refined position of the H atom does not necessarily truly represent the majority of the electron-density distribution and may give a misleading impression of the symmetric nature of the hydrogen bond. In the structure of (II), the O5—H5O···O2 hydrogen bond appears to be symmetrical, or disordered across the two possible 'normal' sites closer to atoms O5 and O2. For O—H···O hydrogen bonds, as the O···O distance approaches 2.4 Å, the O—H and H···O distances both approach 1.2 Å. This then becomes a symmetric structure, with the H atom centred between the two heavy atoms.
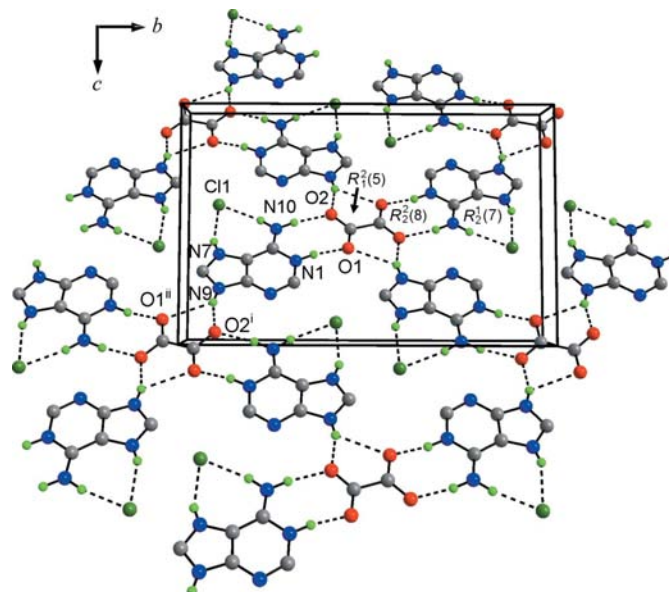


**Figure 4**
A packing diagram for (I), viewed down the *a* axis. Dashed lines indicate N—H···O and N—H···Cl hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity. Only atoms involved in the hydrogen bonding are labelled. [Symmetry codes: (i) $x - 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$; (ii) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$.]

According to Alcock (1990), symmetric hydrogen bonds typically display a shorter (about 2.47 Å) O···O distance, whereas asymmetric hydrogen bonds have a longer O···O distance (about 2.5–3.0 Å). Similar hydrogen bonds are found in acid salts of dicarboxylic acids in which hydrogen dicarboxylate ions are linked by short hydrogen bonds into extended chains (Speakman, 1972). Under this circumstance, it is not possible to distinguish between the neutral oxalic acid molecule and the monoprotonated oxalate anion in the present structure.

Hydrogen-bonded systems generated from organic cations and anions are of special interest because they would be expected to show stronger hydrogen bonds than neutral molecules (Reetz *et al.*, 1994; Bertolasi *et al.*, 2001; Mathew *et al.*, 2002; Bulut *et al.*, 2003). In (I), two types of hydrogen bond are observed, N—H···O and N—H···Cl (Table 2), while in (II), three types are observed, N—H···O, O—H···O and O—H···N (Table 4).

In (I), the Watson–Crick edge (atoms N1 and N10) of the adeninium cation links an oxalate anion through N—H···O hydrogen bonds, which results in a heterosynthon $R_2^2(8)$ hydrogen-bonding motif (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995). This heterosynthon $R_2^2(8)$ motif is one of the classic motifs observed in adeninium carboxylate structures (Sridhar & Ravikumar, 2008*a*,*b*; Byres *et al.*, 2009). The oxalate anion, lying across a centre of inversion, thus forms a linear trimer through hydrogen bonds with the two adjacent adeninium cations (Fig. 4). In (II), the Watson–Crick edge (atoms N1 and N10) forms hydrogen bonds with a centrosymmetric oxalic acid molecule and a water molecule. Interestingly, both atoms N1 and N10 are involved in a three-centred hydrogen-bonding pattern (Jeffrey & Saenger, 1991).
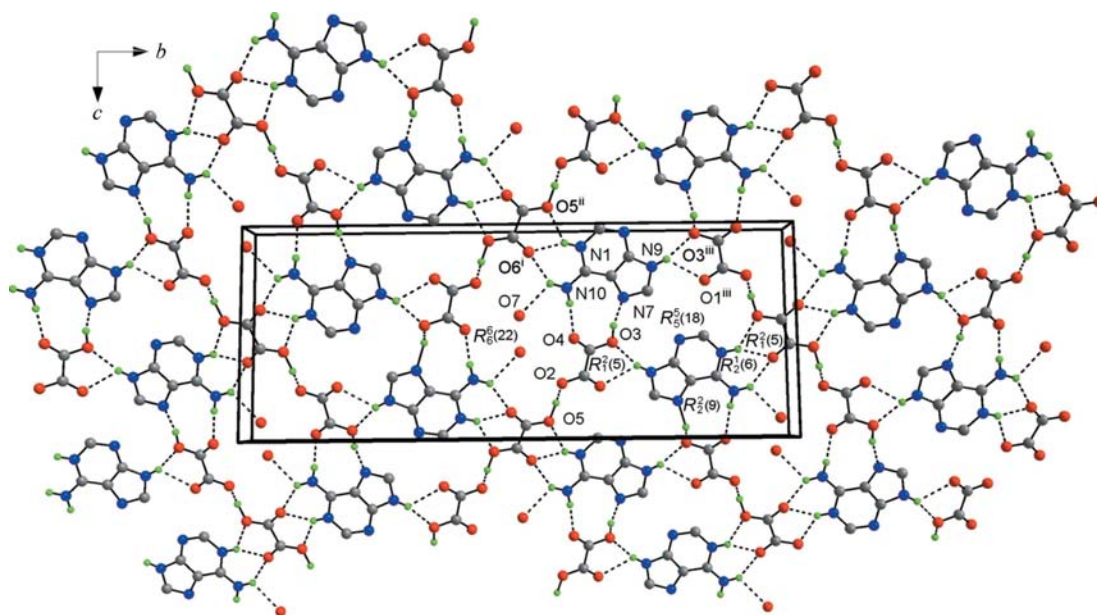
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**Figure 5**
A packing diagram for (II), viewed down the *a* axis. Dashed lines indicate N—H···O, O—H···O and O—H···N hydrogen bonds. H atoms not involved in hydrogen bonding and the minor component of the disordered water molecule O7′ have been omitted for clarity. Only atoms involved in the hydrogen bonding are labelled. [Symmetry codes: (i) $-x + 2$, $-y + 1$, $-z + 1$; (ii) $x - 2$, $y$, $z - 1$; (iii) $x - 1$, $-y + \frac{3}{2}$, $z - \frac{1}{2}$.]

The N—H···O hydrogen bonds with the oxalic acid molecule generate $R_2^1(6)$ and $R_1^2(5)$ hydrogen-bonding motifs and combine with the centrosymmetric anion to give a linear hydrogen-bonded trimer (Fig. 5).

The Hoogsteen face (atoms N10 and N7) of (I) forms N—H···Cl hydrogen bonds with the Cl$^-$ ion, thereby creating an $R_2^1(7)$ motif. Furthermore, cation–anion trimers are interlinked by three-centred hydrogen bonds involving atom N9 of the adeninium cation and carboxylate atoms O1($-x + 1$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$) and O2($x - 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$) of a symmetry-related oxalate anion, thereby generating an $R_1^2(5)$ motif. In (II), the Hoogsteen face (atoms N10 and N7) links the oxalic acid molecule through N—H···O and O—H···N hydrogen bonds and forms an $R_2^2(9)$ motif. This $R_2^2(9)$ motif is interlinked by three-centred hydrogen bonds involving atom N9 of the adeninium cation and atoms O1 and O3 of the monoprotonated oxalate anion at ($x - 1$, $-y + \frac{3}{2}$, $z - \frac{1}{2}$), thereby generating an $R_1^2(5)$ motif. Furthermore, the oxalic acid molecule and the monoprotonated oxalate ion form a short three-segment centrosymmetric hydrogen-bonded linear rod.

In (I), the combination of N—H···O and N—H···Cl hydrogen bonds involving adeninium cations, oxalate anions and Cl$^-$ ions leads to short hydrogen-bonded rods. Each rod is further interlinked to its adjacent glide-related rods by intermolecular three-centred N—H···O hydrogen bonds, thereby generating extended two-dimensional hydrogen-bonded sheets parallel to the (102) plane (Fig. 4).

In (II), $R_2^1(6)$ and $R_1^2(5)$ motifs between the adeninium cation and centrosymmetric oxalic acid molecules form hydrogen-bonded trimers. These trimers are flanked by intermolecular N—H···O interactions through the three-centred hydrogen bonds involving the monoprotonated

oxalate anions [$R_1^2(5)$ motif] and extend parallel to the *b* axis, thereby generating short hydrogen-bonded rods. Each such rod is further interlinked to its adjacent rods by intramolecular N—H···O, O—H···O and O—H···N hydrogen bonds (Fig. 5), thereby generating $R_5^5(18)$ and $R_6^6(22)$ motifs. Thus, the combination of N—H···O, O—H···O and O—H···N hydrogen bonds leads to the formation of infinite two-dimensional supramolecular hydrogen-bonded sheets which lie parallel to the ($10\bar{2}$) plane.

It is very interesting to note that, in the present study, an adeninium–adeninium self-association base pair is not observed, although this is one of the characteristic features observed in two previously reported structures (Sridhar & Ravikumar, 2007*a,b*).

## Experimental

To obtain suitable crystals of (I), adenine (0.135 g, 1 mmol) and oxalic acid (0.09 g, 1 mmol) were dissolved in a mixture of hydrochloric acid (2–3 drops) and water (10 ml) and the solution was allowed to evaporate slowly. Crystals of (II) were obtained by slow evaporation of an equimolar solution of adenine (0.135 g, 1 mmol) and oxalic acid (0.18 g, 2 mmol) in water (20 ml).

### Compound (I)

*Crystal data*

| | |
|---|---|
| C$_5$H$_7$N$_5^{2+}$·0.5C$_2$O$_4^{2-}$·Cl$^-$ | $V = 828.24$ (13) Å$^3$ |
| $M_r = 216.62$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 4.3758$ (4) Å | $\mu = 0.44$ mm$^{-1}$ |
| $b = 17.1354$ (15) Å | $T = 294$ K |
| $c = 11.1188$ (10) Å | $0.21 \times 0.18 \times 0.13$ mm |
| $\beta = 96.558$ (2)° | |

**Table 1**
Selected geometric parameters (Å, °) for (I).

| C11—O1 | 1.2471 (18) | C11—O2 | 1.2511 (19) |
|---|---|---|---|
| C6—N1—C2 | 123.58 (13) | O1—C11—O2 | 125.65 (14) |
| C8—N7—C5 | 107.94 (13) | | |

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N1—H1N$\cdots$O1 | 0.95 (2) | 1.74 (2) | 2.685 (2) | 171 (2) |
| N7—H7N$\cdots$Cl1 | 0.81 (2) | 2.28 (2) | 3.041 (1) | 156 (2) |
| N9—H9N$\cdots$O2$^{i}$ | 0.85 (2) | 1.83 (2) | 2.645 (2) | 159 (2) |
| N9—H9N$\cdots$O1$^{ii}$ | 0.85 (2) | 2.47 (2) | 3.037 (2) | 125 (2) |
| N10—H10$B\cdots$O2 | 0.95 (2) | 1.88 (2) | 2.822 (2) | 171 (2) |
| N10—H10$A\cdots$Cl1 | 0.93 (2) | 2.21 (2) | 3.130 (2) | 166 (2) |

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

*Data collection*

| | |
|---|---|
| Bruker SMART APEX CCD area-detector diffractometer | 1455 independent reflections |
| | 1411 reflections with $I > 2\sigma(I)$ |
| 7683 measured reflections | $R_{int} = 0.027$ |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.090$ | |
| $S = 1.09$ | |
| 1455 reflections | $\Delta\rho_{max} = 0.30$ e Å$^{-3}$ |
| 148 parameters | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |

## Compound (II)

*Crystal data*

| | |
|---|---|
| $C_5H_6N_5^+\cdot C_2HO_4^-\cdot 0.5C_2H_2O_4\cdot H_2O$ | $V = 1119.05 (17)$ Å$^3$ |
| $M_r = 288.21$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 3.6222 (3)$ Å | $\mu = 0.15$ mm$^{-1}$ |
| $b = 28.131 (3)$ Å | $T = 294$ K |
| $c = 11.1101 (10)$ Å | $0.19 \times 0.16 \times 0.09$ mm |
| $\beta = 98.696 (2)°$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX CCD area-detector diffractometer | 1982 independent reflections |
| | 1891 reflections with $I > 2\sigma(I)$ |
| 10683 measured reflections | $R_{int} = 0.020$ |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.037$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.103$ | |
| $S = 1.14$ | |
| 1982 reflections | $\Delta\rho_{max} = 0.34$ e Å$^{-3}$ |
| 215 parameters | $\Delta\rho_{min} = -0.23$ e Å$^{-3}$ |
| 6 restraints | |

All N-bound H atoms of the adeninium cations of (I) and (II), and O-bound H atoms of the oxalic acid molecule and the mono-protonated oxalate ion of (II), were located in a difference Fourier map and their positions and isotropic displacement parameters refined. All other H atoms were located in a difference density map, positioned geometrically and included as riding atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. In (II), the water molecule is

**Table 3**
Selected geometric parameters (Å, °) for (II).

| C11—O4 | 1.204 (2) | C12—O2 | 1.271 (2) |
|---|---|---|---|
| C11—O3 | 1.299 (2) | C13—O6 | 1.225 (2) |
| C12—O1 | 1.214 (2) | C13—O5 | 1.273 (2) |
| C2—N1—C6 | 123.72 (15) | O1—C12—O2 | 127.72 (16) |
| C8—N7—C5 | 104.32 (14) | O6—C13—O5 | 126.64 (15) |
| O4—C11—O3 | 124.86 (16) | | |

**Table 4**
Hydrogen-bond geometry (Å, °) for (II).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N1—H1N$\cdots$O6$^{i}$ | 0.91 (2) | 1.91 (2) | 2.755 (2) | 153 (2) |
| N1—H1N$\cdots$O5$^{ii}$ | 0.91 (2) | 2.34 (2) | 3.002 (2) | 130 (2) |
| N9—H9N$\cdots$O3$^{iii}$ | 0.85 (2) | 2.07 (2) | 2.873 (2) | 157 (2) |
| N9—H9N$\cdots$O1$^{iii}$ | 0.85 (3) | 2.31 (3) | 2.877 (2) | 124 (2) |
| N10—H10$\cdots$O4 | 0.87 (3) | 1.96 (3) | 2.830 (2) | 175 (2) |
| N10—H11$\cdots$O6$^{i}$ | 0.91 (3) | 2.14 (3) | 2.893 (2) | 139 (2) |
| N10—H11$\cdots$O7′ | 0.91 (3) | 2.23 (3) | 2.807 (6) | 121 (2) |
| N10—H11$\cdots$O7 | 0.91 (3) | 2.34 (3) | 2.906 (6) | 120 (2) |
| O3—H3O$\cdots$N7 | 1.00 (4) | 1.69 (4) | 2.668 (2) | 166 (3) |
| O5—H5O$\cdots$O2 | 1.22 (4) | 1.25 (4) | 2.469 (2) | 176 (3) |

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

disordered over two sites (O7 and O7′) and the site-occupation factors refined to 0.622 (19) and 0.378 (19). The anisotropic displacement parameters of atoms O7/O7′ were restrained to be similar [SIMU instruction in *SHELXL97* (Sheldrick, 2008)], and the direction of motion along the axis between these atoms was also restrained (DELU instruction in *SHELXL97*). The H atoms of the disordered molecule could not be located reliably. Contoured difference Fourier maps only indicate significant electron density at the location of one potential H-atom site and the electron density of the disordered water molecule is smeared along the O7$\cdots$O7′ axis. Therefore, the water H atoms were not included in the model.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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