

Two solid phases of pyrimidin-1-ium
hydrogen chloranilate monohydrate
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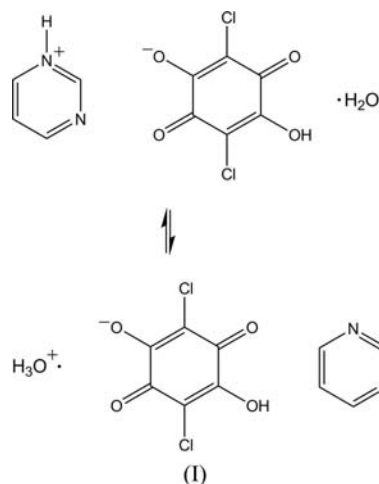
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The crystal structures of two solid phases of the title compound, $C_4H_5N_2^+ \cdot C_6HCl_2O_4^- \cdot H_2O$, have been determined at 225 and 120 K. In the high-temperature phase, stable above 198 K, the transition temperature of which has been determined by ^{35}Cl nuclear quadrupole resonance and differential thermal analysis measurements, the three components are held together by $O-H \cdots O$, $N \cdots H \cdots O$, $C-H \cdots O$ and $C-H \cdots Cl$ hydrogen bonds, forming a centrosymmetric 2+2+2 aggregate. In the $N \cdots H \cdots O$ hydrogen bond between the pyrimidin-1-ium cation and the water molecule, the H atom is disordered over two positions, resulting in two states, *viz.* pyrimidin-1-ium–water and pyrimidine–oxonium. In the low-temperature phase, the title compound crystallizes in the same monoclinic space group and has a similar molecular packing, but the 2+2+2 aggregate loses the centrosymmetry, resulting in a doubling of the unit cell and two crystallographically independent molecules for each component in the asymmetric unit. The H atom in one $N \cdots H \cdots O$ hydrogen bond between the pyrimidin-1-ium cation and the water molecule is disordered, while the H atom in the other hydrogen bond is found to be ordered at the N-atom site with a long N–H distance [1.10 (3) Å].

Comment

The crystal structures of diazine (pyridazine, pyrimidine or pyrazine)–chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) (2/1) systems have been determined at room temperature (Ishida & Kashino, 1999*a,b*) and recently re-determined at 110 K for the pyridazine and pyrazine compounds (Gotoh *et al.*, 2008). In each compound, the diazine and chloranilic acid molecules are connected by strong $N \cdots H \cdots O$ hydrogen bonds [$N \cdots O = 2.582$ (3), 2.615 (2) and 2.590 (4) Å for the pyridazine, pyrimidine and pyrazine compounds, respectively, at room temperature] to afford a

centrosymmetric 2:1 unit. H-atom motions attributable to dynamically disordered H atoms in these hydrogen bonds have been detected by 1H NMR and ^{35}Cl nuclear quadrupole resonance (NQR) measurements for the pyridazine compound (Nihei *et al.*, 2000*a*), the pyrimidine compound (Ikeda *et al.*, 2005) and the pyrazine compound (Nihei *et al.*, 2000*b*). Recently, measurements of ^{14}N NQR and multi-temperature X-ray diffraction were made for the pyridazine compound and the temperature dependence of the population ratio of two disordered sites of the H atom in the $N \cdots H \cdots O$ hydrogen bond, *i.e.* H-atom migration was determined (Seliger *et al.*, 2009). On the other hand, in the crystal structures of pyridazine–chloranilic acid (1/1) (Gotoh & Ishida, 2008) and pyrazine–chloranilic acid (1/1) (Ishida & Kashino, 1999*c*), such short hydrogen bonds have not been observed. The hydrogen bonds between the base and the acid are fairly long [$N \cdots O = 2.6138$ (13)–2.6621 (13) and 2.719 (3) Å for the pyridazine and pyrazine compounds, respectively] and the H atoms are ordered.



We report here the structures of two solid phases of the title compound, (I), which shows a solid–solid phase transition at about 198 K determined by ^{35}Cl NQR. In the ^{35}Cl NQR measurements in the temperature range 77–328 K, two reso-

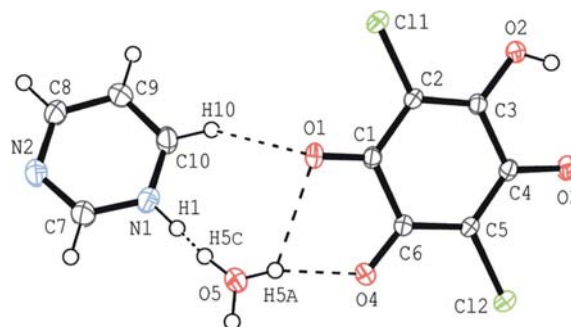


Figure 1

The molecular structure in the high-temperature phase (225 K) of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The $O-H \cdots O$, $N \cdots H \cdots O$ and $C-H \cdots O$ hydrogen bonds are indicated by dashed lines.

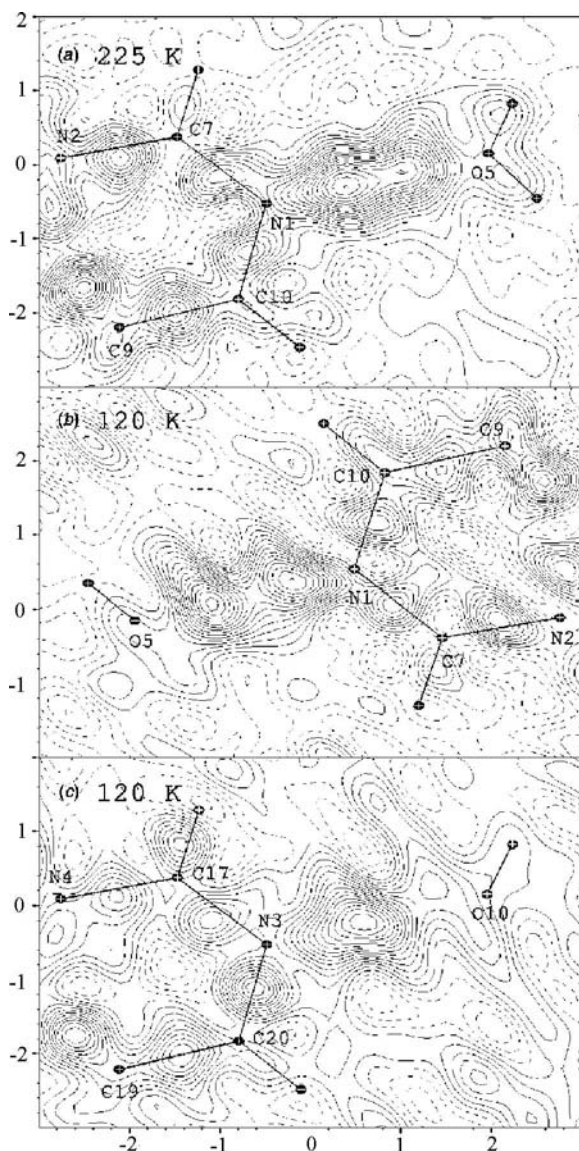


Figure 2
Difference Fourier maps (a) of the high-temperature phase, (b) of the low-temperature phase and (c) associated with the N···H···O hydrogen bond between the pyrimidine and water molecules. Maps were calculated on the mean plane of O5/N1/C7 or O10/N3/C17 from a model containing all atoms apart from the H atom in the hydrogen bond. The contours are at $0.03 \text{ e } \text{Å}^{-3}$ in (a) and $0.05 \text{ e } \text{Å}^{-3}$ in (b) and (c), and dashed lines indicate negative contours.

nance lines were observed in the high-temperature range above 198 K; the ^{35}Cl NQR frequencies observed at 321 K are 35.973 and 35.449 MHz. Below 198 K, the resonance lines split into four lines (36.565, 36.357, 35.974 and 36.011 MHz at 77 K). This indicates that a phase transition occurs around 198 K, accompanying a change in the number of crystallographically independent Cl atoms, *i.e.* a change from two independent Cl atoms in the high-temperature phase to four in the low-temperature phase (Armstrong & van Driel, 1975). The detailed NQR results are reported elsewhere (Asaji, 2010). The phase transition was also detected by differential thermal analysis (DTA) operated in the range 150–295 K, which showed a broad and weak heat anomaly with onset and

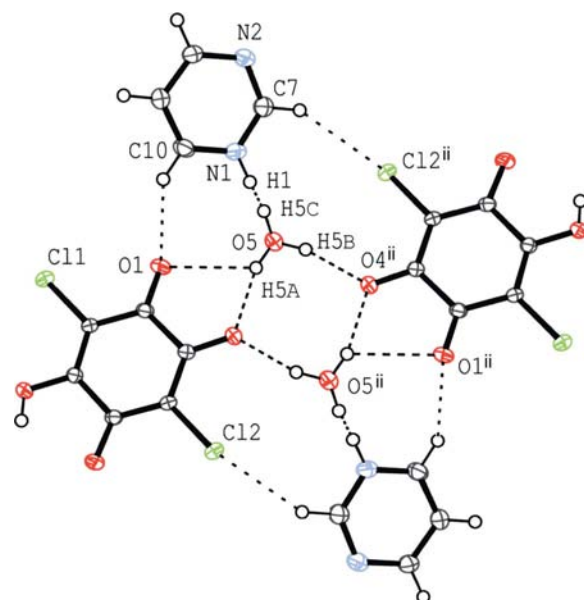


Figure 3
A view of the centrosymmetric 2+2+2 aggregate in the high-temperature phase. The O—H···O, N···H···O, C—H···O and C—H···Cl hydrogen bonds are indicated by dashed lines. [Symmetry code: (ii) $-x + 1, -y + 2, -z + 1$.] Atoms H1 and H5C have site-occupation factors of 0.5.

peak temperatures of 200 (1) and 206 (1) K, respectively, on heating, and 201 (1) and 197 (1) K on cooling.

Fig. 1 shows the asymmetric unit in the high-temperature phase determined at 225 K, where the three components are held together by O—H···O, N···H···O and C—H···O hydrogen bonds (Table 1). The dihedral angle between the pyrimidine ring (N1/C7/N2/C8—C10) and the anion ring (C1—C6) is $30.43(6)^\circ$. An acid–base interaction involving a proton transfer occurs through the water molecule. The transferred proton is shared by the pyrimidine and water molecules, resulting in two disordered states, *viz.* pyrimidin-1-ium–water and pyrimidine–oxonium. This disordered feature in the short N···H···O hydrogen bond [$\text{N1}\cdots\text{O5} = 2.5440(15) \text{ Å}$] is confirmed in a difference Fourier map (Fig. 2a), where two distinct peaks are observed between the pyrimidin-1-ium cation and the water molecule. The asymmetric units related by an inversion centre are connected by O—H···O and C—H···Cl hydrogen bonds (Table 1), forming a centrosymmetric 2+2+2 aggregate (Fig. 3). These aggregates are further connected through an O—H···O hydrogen bond between the hydrogen chloranilate anions related by a twofold screw rotation axis (Fig. 4).

The asymmetric unit of the low-temperature phase determined at 120 K is shown in Fig. 5. This unit is a 2+2+2 aggregate of the three components; there are two crystallographically independent molecules for each component and the four independent Cl atoms in the crystal, being consistent with the ^{35}Cl NQR result. Although this phase crystallizes in the same space group and has a similar molecular packing, the centrosymmetry of the 2+2+2 aggregate (Fig. 3) and the twofold screw rotation symmetry between the anions (Fig. 4) in the high-temperature phase are lost, resulting in a doubling of the *a* axis as shown in Fig. 6. For the low-temperature phase,

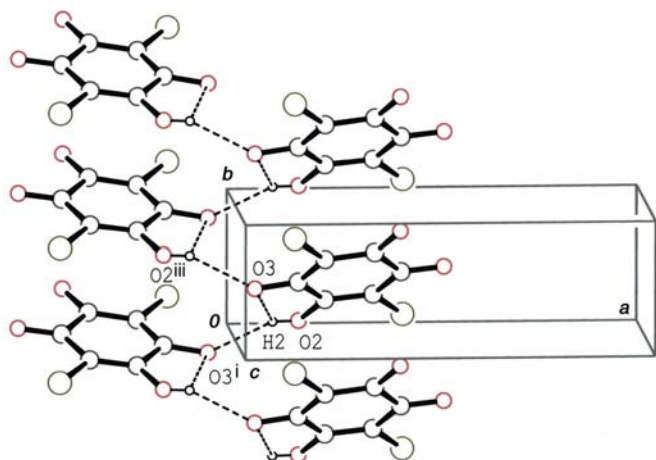


Figure 4
A partial packing view of the hydrogen chloranilate anions in the high-temperature phase. The O—H...O hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$]

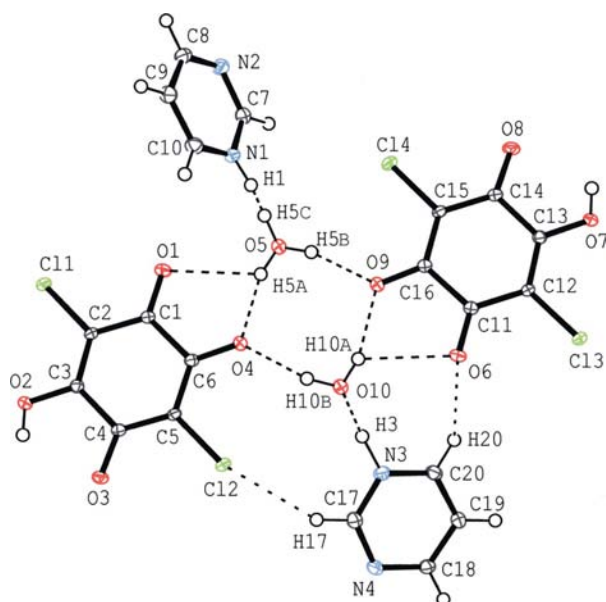


Figure 5
The molecular structure in the low-temperature phase (120 K) of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The O—H...O, N...H...O, C—H...O and C—H...Cl hydrogen bonds are indicated by dashed lines. Atoms H1 and H5C have site-occupation factors of 0.5.

a nonstandard setting of space group No. 14, *viz.* $P2_1/n$, was selected in order to facilitate comparison of the two phases. In the 2+2+2 aggregate, the pyrimidin-1-ium cation and the water molecule are connected by short hydrogen bonds [N1...O5 = 2.5207 (15) Å and N3...O10 = 2.5285 (15) Å; Table 2]. The difference Fourier map (Fig. 2b) shows two peaks between N1 and O5. On the other hand, between N3 and O10 only one diffuse peak is observed near the centre of the N...O vector (Fig. 2c). The maximum lies closer to N3 than O10, and a long N—H bond [N3—H3 = 1.10 (3) Å] is obtained. The dihedral angle between the pyrimidine ring (N3/C17/N4/C18—C20) and the anion ring (C11—C16) is 28.30 (5)°, comparable with the

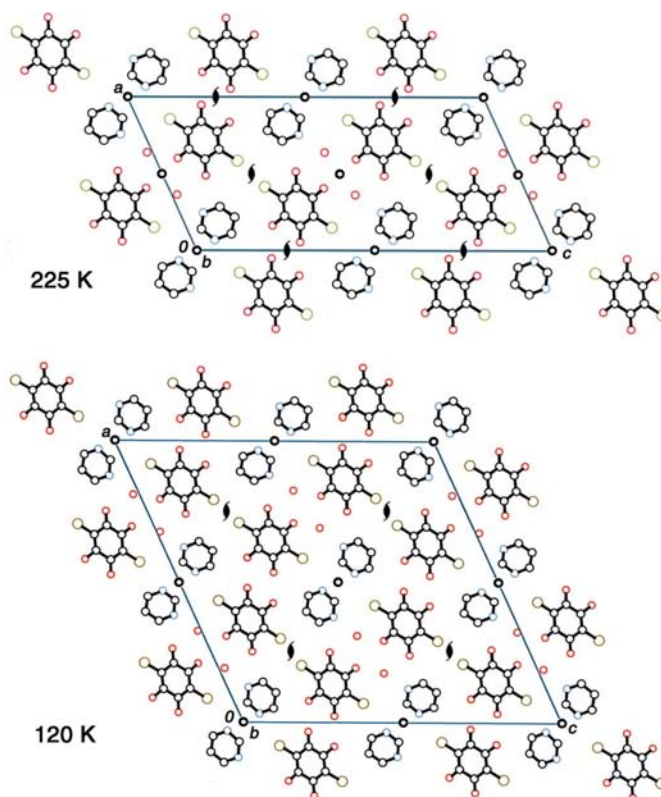


Figure 6
Packing diagrams of the high- and low-temperature phases, viewed down the *b* axis. The twofold screw axes and the inversion centres are shown by black symbols. The space group in the high-temperature phase is $P2_1/c$, while the space group in the low-temperature phase is taken to be $P2_1/n$ in order to show the structural relationship between the two phases. All H atoms have been omitted for clarity.

angle of 30.43 (6)° in the high-temperature phase, while a larger dihedral angle of 54.12 (5)° is observed between the N1/C7/N2/C8—C10 and C1—C6 rings. The dihedral angles between the two base rings and between the two acid rings are 44.86 (6) and 1.49 (5)°, respectively. These angles indicate that the phase transition is accompanied by a considerable rotation of one pyrimidine molecule (N1/C7/N2/C8—C10) around the N...H...O hydrogen bond, breaking the C—H...O and C—H...Cl hydrogen bonds.

Experimental

Single crystals of the title compound were obtained by slow evaporation from a methanol solution (120 ml) of chloranilic acid (0.84 g) with pyrimidine (0.32 g) at room temperature. As crystallization was not performed under anhydrous conditions, the presence of a water solvent molecule in crystals of the title compound is not surprising. The same single crystal was used for the X-ray diffraction experiments at 225 and 120 K. This crystal was cooled from room temperature to 225 K within several minutes and the diffraction data were collected. After collection of the data, the crystal was further cooled to 120 K, and then the diffraction data were collected again.

For the ^{35}Cl NQR measurement, a pulsed spectrometer base on a gated amplifier (Matec 525) was used. The sample temperature was controlled within ± 0.5 K over the sample volume using an electronic

controller (LakeShore 331) and measured with an accuracy of ± 0.5 K by use of a gold+0.07% ion versus chromel thermocouple (Asaji *et al.*, 2007). DTA was performed by use of a homemade apparatus. The heating and cooling rates were *circa* 5 K min^{-1} . The samples used for NQR and DTA measurements were identified by comparing the observed X-ray powder pattern with that derived from the present single-crystal data.

Compound (I) at 225 K

Crystal data

$\text{C}_4\text{H}_5\text{N}_2^+\cdot\text{C}_6\text{HCl}_2\text{O}_4^-\cdot\text{H}_2\text{O}$	$V = 1161.12$ (11) \AA^3
$M_r = 307.09$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.6621$ (7) \AA	$\mu = 0.58$ mm^{-1}
$b = 3.75947$ (18) \AA	$T = 225$ K
$c = 26.7435$ (16) \AA	$0.36 \times 0.13 \times 0.08$ mm
$\beta = 114.208$ (2) $^\circ$	

Data collection

Rigaku R-AXIS RAPID II diffractometer	21678 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	3377 independent reflections
$T_{\min} = 0.890$, $T_{\max} = 0.955$	3061 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.075$	$\Delta\rho_{\text{max}} = 0.53$ e \AA^{-3}
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.17$ e \AA^{-3}
3377 reflections	
190 parameters	
4 restraints	

Compound (I) at 120 K

Crystal data

$\text{C}_4\text{H}_5\text{N}_2^+\cdot\text{C}_6\text{HCl}_2\text{O}_4^-\cdot\text{H}_2\text{O}$	$V = 2282.16$ (14) \AA^3
$M_r = 307.09$	$Z = 8$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 25.5952$ (9) \AA	$\mu = 0.59$ mm^{-1}
$b = 3.71581$ (13) \AA	$T = 120$ K
$c = 26.3761$ (9) \AA	$0.36 \times 0.13 \times 0.08$ mm
$\beta = 114.5289$ (13) $^\circ$	

Data collection

Rigaku R-AXIS RAPID II diffractometer	36273 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	6635 independent reflections
$T_{\min} = 0.867$, $T_{\max} = 0.954$	5959 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.078$	$\Delta\rho_{\text{max}} = 0.76$ e \AA^{-3}
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.25$ e \AA^{-3}
6635 reflections	
377 parameters	
6 restraints	

For both phases, all H atoms were found in difference Fourier maps, and then C-bound H atoms were positioned geometrically (C—H = 0.94 \AA at 225 K and 0.95 \AA at 120 K) and treated as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O-bound H atom in the hydrogen chloranilate anion was refined freely. In the high-temperature phase, the H atom in the N \cdots H \cdots O hydrogen bond was found to be disordered

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (I) at 225 K.

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1—H1 \cdots O5	0.86 (4)	1.69 (4)	2.5440 (15)	175 (4)
O2—H2 \cdots O3	0.78 (2)	2.19 (2)	2.6279 (12)	116.2 (18)
O2—H2 \cdots O3 ⁱ	0.78 (2)	2.02 (2)	2.6995 (12)	146 (2)
O5—H5A \cdots O1	0.83 (2)	2.43 (2)	2.9467 (13)	122 (2)
O5—H5A \cdots O4	0.83 (2)	1.91 (2)	2.7169 (14)	163 (2)
O5—H5B \cdots O4 ⁱⁱ	0.84 (2)	1.87 (2)	2.6888 (14)	165 (2)
O5—H5C \cdots N1	0.86 (4)	1.69 (4)	2.5440 (15)	171 (4)
C7—H7 \cdots Cl2 ⁱⁱ	0.94	2.76	3.6031 (13)	150
C10—H10 \cdots O1	0.94	2.46	3.2179 (16)	138

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I) at 120 K.

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1—H1 \cdots O5	0.86 (3)	1.67 (4)	2.5207 (15)	172 (4)
O2—H2A \cdots O3	0.79 (2)	2.18 (2)	2.6246 (11)	116.1 (18)
O2—H2A \cdots O3 ⁱ	0.79 (2)	2.09 (2)	2.7694 (11)	146 (2)
N3—H3 \cdots O10	1.10 (3)	1.44 (3)	2.5285 (15)	173 (3)
O5—H5A \cdots O1	0.84 (2)	2.40 (2)	2.9075 (14)	120 (2)
O5—H5A \cdots O4	0.84 (2)	1.86 (2)	2.6706 (14)	163 (2)
O5—H5B \cdots O9	0.84 (2)	1.83 (2)	2.6446 (13)	163 (2)
O5—H5C \cdots N1	0.85 (4)	1.67 (4)	2.5207 (15)	175 (4)
O7—H7A \cdots O8	0.80 (3)	2.21 (2)	2.6423 (12)	114.4 (19)
O7—H7A \cdots O3 ⁱⁱ	0.80 (3)	1.95 (2)	2.6606 (12)	148 (2)
O10—H10A \cdots O6	0.82 (2)	2.43 (2)	2.9519 (12)	122 (1)
O10—H10A \cdots O9	0.82 (2)	1.93 (2)	2.7201 (14)	163 (2)
O10—H10B \cdots O4	0.84 (2)	1.87 (2)	2.6916 (13)	166 (2)
C9—H9 \cdots O2 ⁱⁱⁱ	0.95	2.56	3.3331 (15)	139
C10—H10 \cdots O1 ^{iv}	0.95	2.39	3.1896 (16)	142
C17—H17 \cdots Cl2	0.95	2.76	3.6189 (13)	151
C20—H20 \cdots O6	0.95	2.44	3.2072 (15)	138

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{5}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y + \frac{3}{2}, -z + \frac{1}{2}$; (iv) $x, y + 1, z$.

over two positions in a difference Fourier map. The positional parameters of the disordered H atom were refined, with bond restraints [O—H = 0.83 (2) \AA and N—H = 0.87 (2) \AA], and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N}, \text{O})$. The site occupancies were initially refined and then fixed at 0.5:0.5 in the final refinement. Other water H atoms were refined, with bond-length restraints O—H = 0.83 (2) \AA . In the low-temperature phase, one of the H atoms in the N \cdots H \cdots O hydrogen bonds was found to be disordered. A similar treatment was applied, with bond-length restraints O—H = 0.84 (2) \AA and N—H = 0.88 (2) \AA , and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N}, \text{O})$. Other water H atoms were refined, with bond-length restraints O—H = 0.84 (2) \AA , while the ordered N-bound H atom was refined freely. Except where otherwise indicated, the U_{iso} values of positionally refined H atoms were also refined freely.

For both compounds, data collection: *PROCESS-AUTO* (Rigaku/MSK, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *WinGX* (Farrugia, 1999); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3036). Services for accessing these data are described at the back of the journal.

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