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Decaaquabis(μ_3-4-hydroxypyridine-2,6-dicarboxylato)bis(4-hydroxypyridine-2,6-dicarboxylato)tetramanganese(II) 3.34-hydrate: a new three-dimensional open metal–organic framework based on a tetranuclear Mn^{II} complex of chelidamic acid and undecameric stitching water clusters

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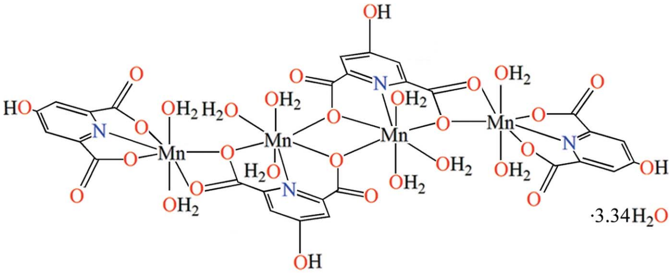
4-Hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid, $cdaH_3$) reacts with $MnCl_2 \cdot 2H_2O$ in the presence of 2-amino-4-methylpyrimidine in water to afford the tetranuclear title complex, $[Mn_4(C_8H_3NO_5)_4(H_2O)_{10}] \cdot 3.34H_2O$, built through carboxylate bridging. The tetranuclear complex sits on a centre of inversion at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). In the crystal, discrete undecameric $(H_2O)_{10.34}$ water clusters (involving both coordinated and uncoordinated water molecules, with one site of an uncoordinated water molecule not fully occupied) assemble these tetranuclear Mn^{II} complex units *via* an intricate array of hydrogen bonding into an overall three-dimensional network. The degree of structuring of the $(H_2O)_{10.34}$ supramolecular association of water molecules observed in the present compound, imposed by its environment and *vice versa*, will be discussed in comparison to that observed for the $(H_2O)_{14}$ supramolecular clusters in the case of the dinuclear complex $[Mn_2(cdaH)_2(H_2O)_4] \cdot 4H_2O$ [Ghosh *et al.* (2005). *Inorg. Chem.* **44**, 3856–3862].

Comment

It is widely recognized that fluctuations and the rearrangement dynamics of hydrogen-bonding interactions among water molecules determine the fascinating properties of bulk water. In order to better understand the co-operative nature of hydrogen-bonding interactions among a collection of water molecules, with the aim of creating models that could fully explain the properties of bulk water, water clustering within inorganic or organic crystal hosts has become an active research field within the realm of crystal engineering (Ludwig *et al.*, 2001). In particular, metal–organic frameworks (MOFs) composed of mainly transition metal ions and bridging organic ligands may provide voids suitable to accommodate small water clusters of different shape and dimensionality whose binding properties and degree of structuring depend on their surroundings and *vice versa* (for some examples, see Duan *et al.*, 2010; Ghosh *et al.*, 2004; Kang *et al.*, 2007; Ma *et al.*, 2005; Song *et al.*, 2007; Wei *et al.*, 2006; Aghabozorg *et al.*, 2010).



(I)

Recently, Ghosh *et al.* (2005) have reacted Mn^{II} acetate and 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid, $cdaH_3$) (1:1 reaction molar ratio) in an aqueous/pyridine solvent mixture (1:1 *v*/*v*) to afford the dinuclear complex $[Mn_2(cdaH)_2(H_2O)_4] \cdot 4H_2O$; in this complex, one-dimensional stair-like coordination polymers built through carboxylate- and aqua-bridging of metal centres are assembled by $(H_2O)_{14}$ supramolecular clusters of coordinated and uncoordinated water molecules into a three-dimensional MOF *via* hydrogen bonding. The stitching water cluster takes the shape of a central cyclic hexamer in a chair conformation, with two acyclic tetramers protruding from opposite corners of the hexamer. Following our interest in the coordination chemistry of proton-transfer systems obtained from N-, S- and O-donor ligands and polycarboxylic acids (Aghabozorg *et al.*, 2008; Mirzaei *et al.*, 2011), we have reacted manganese(II) chloride dihydrate with $cdaH_3$ and 2-amino-4-methylpyrimidine in a 1:2:4 molar ratio in aqueous solution. Colourless prismatic crystals were obtained upon slow evaporation of the reaction mixture corresponding to the microanalytical formulation $C_{14}H_{20}Mn_2N_2O_{17}$, which is very close to that reported by Ghosh *et al.* for the complex $[Mn_2(cdaH)_2(H_2O)_4] \cdot 4H_2O$ (Ghosh *et al.*, 2005); an X-ray diffraction analysis was undertaken to ascertain their nature.

The structure of the title compound, $[Mn_4(cdaH)_4(H_2O)_{10}] \cdot 3.34H_2O$, (I), consists of a discrete linear tetranuclear Mn^{II} cluster sitting on an inversion centre in which each metal centre adopts a heptacoordinated pentagonal–bipyramidal geometry (Fig. 1). Each terminal Mn^{II} centre in the cluster is axially coordinated to two water molecules and to a tridentate $cdaH^{2-}$ dicarboxylate unit in the equatorial plane. An NO_4 coordination in the pentagonal equatorial plane is completed by the O-atom donors of a bidentate carboxylate group from the 2-position of another $cdaH^{2-}$ unit (Fig. 1). Each of the two Mn^{II} ions in the middle of the

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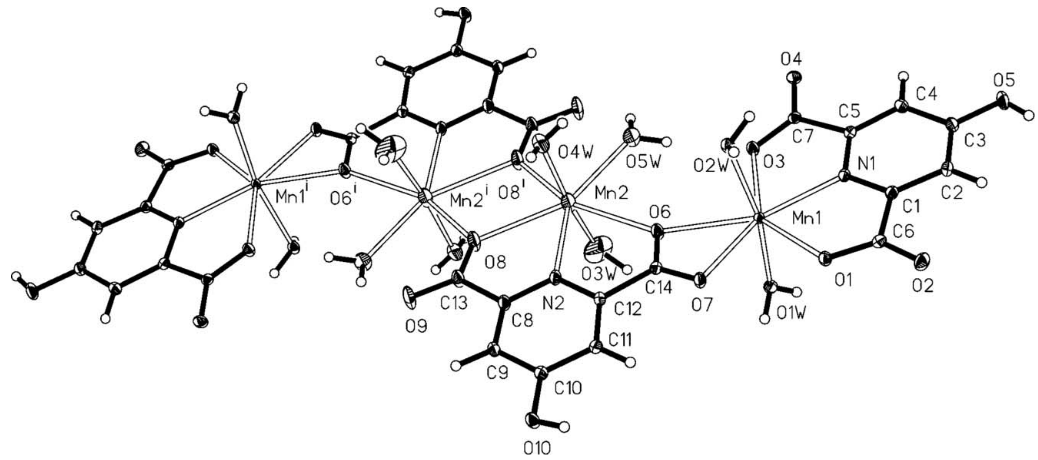

Figure 1
View of the discrete tetranuclear Mn^{II} unit in the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

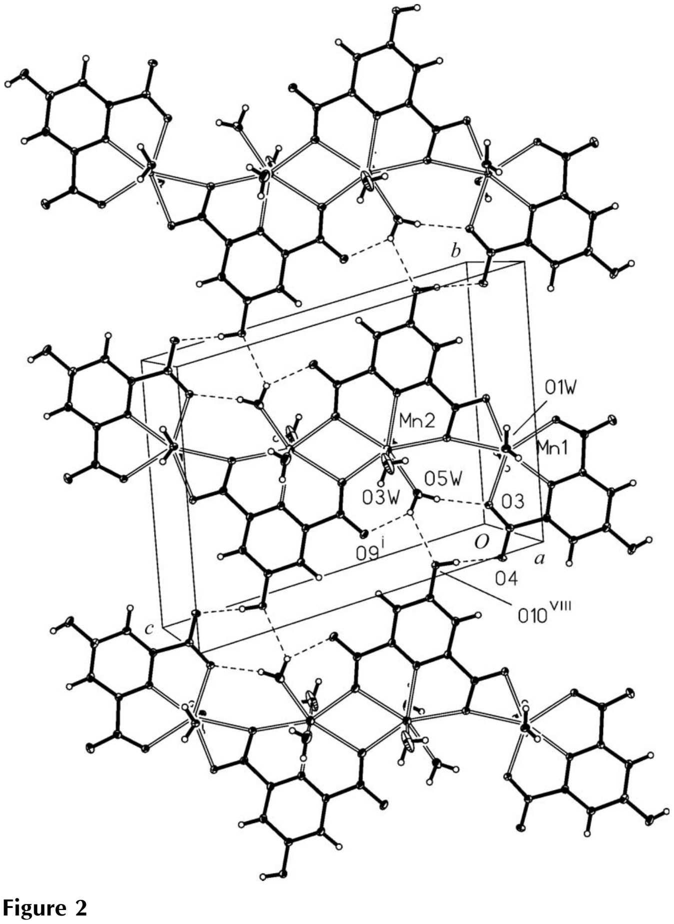

Figure 2
A partial view of one strip of hydrogen-bonded (see Table 2) tetranuclear Mn^{II} clusters in the title compound running along the *b* axis. Displacement ellipsoids are drawn at the 50% probability level. Two different bimolecular cyclic hydrogen-bonding motifs, *viz.* $R_3^3(8)$ and $R_2^4(14)$, are formed. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (viii) $x, y - 1, z$.]

tetranuclear cluster still features two axially coordinated water molecules. The equatorial plane is occupied by a third coordinated water molecule, by the pyridine N-atom donor and two carboxylate O-atom donors at the 2- and 6-positions of the previous cdaH^{2-} unit connected to a terminal Mn^{II} centre in the cluster, and by one carboxylate O-atom donor at the 6-position from the cdaH^{2-} unit that is a symmetry equivalent to the last one. In this way, the two Mn^{II} centres in the middle of the tetranuclear cluster feature an NO$_4$ coordination in the equatorial plane as do the terminal Mn^{II} centres, and are directly connected to each other by a carboxylate bridge (see Fig. 1, and Table 1 for selected geometric parameters). Interestingly, an identical tetranuclear Cd^{II} cluster has been described by Das *et al.* (2009) in the compound [Cd$_4$(cdaH)$_4$(H$_2$O)$_{10}$]·4H$_2$O, obtained from pyridine-2,4,6-tricarboxylic acid (ptcH$_3$) upon conversion of the carboxyl group in the 4-position to a hydroxy group.

In (I), the water molecules equatorially coordinated to the middle Mn^{II} centres of the tetranuclear cluster and the hydroxy groups from the cdaH^{2-} units bridging these metal ions generate *via* hydrogen bonds strips of interacting clusters which propagate along the *b* axis, and for each strip the clusters lie on the same plane (see Fig. 2 and Table 2 for the hydrogen-bond geometry). The above-described strips stack on top of each other along the *a* axis interacting *via* hydrogen bonds at the axially coordinated water molecules to give two-dimensional extended sheets whose thickness roughly corresponds to the length of the linear tetranuclear Mn^{II} cluster (see Fig. 3 and Table 2). Parallel offset two-dimensional extended sheets of hydrogen-bonded [Mn$_4$(cdaH)$_4$(H$_2$O)$_{10}$] linear clusters interact with each other *via* hydrogen bonds involving both axially metal-coordinated and cocrystallized water molecules (see Fig. 4 and Table 2) to give a three-dimensional network. Undecameric (H$_2$O)$_{10.34}$ stitching clusters can be envisaged (Fig. 4) between each pair of interacting two-dimensional sheets [the O7*W* water site was found to be partially occupied, with an occupancy factor of 0.669 (8)]. Analogously to what was observed for the stitching (H$_2$O)$_{14}$ supramolecular clusters in the compound [Mn$_2$(cdaH)$_2$(H$_2$O)$_4$]·4H$_2$O (Ghosh *et al.*, 2005), in the present case the (H$_2$O)$_{10.34}$ clusters can also be described as a central cyclic assembly of water molecules (a smaller square tetramer in this case) buttressed by acyclic water assemblies (two trimers and a

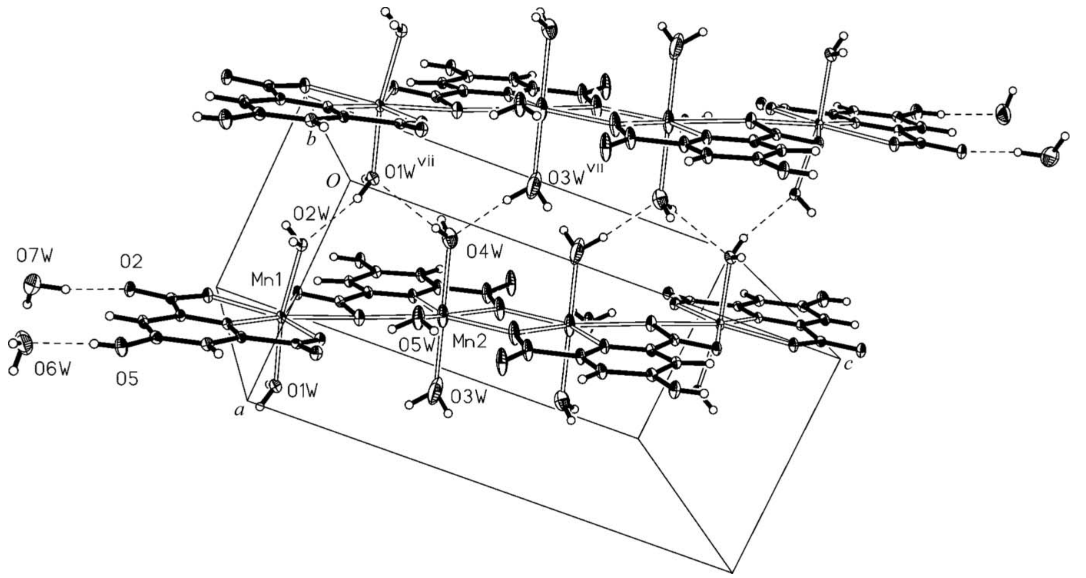

Figure 3
A partial view of the tetranuclear Mn^{II} clusters in the title compound stacking along the *a* axis and interacting *via* hydrogen bonds at the axially coordinated water molecules. Displacement ellipsoids are drawn at the 50% probability level. Two very close fused $R_2^2(8)$ hydrogen-bonding motifs can be envisaged in the hydrogen-bonding pattern responsible for the stacking. [Symmetry code: (vii) $x - 1, y, z$.]

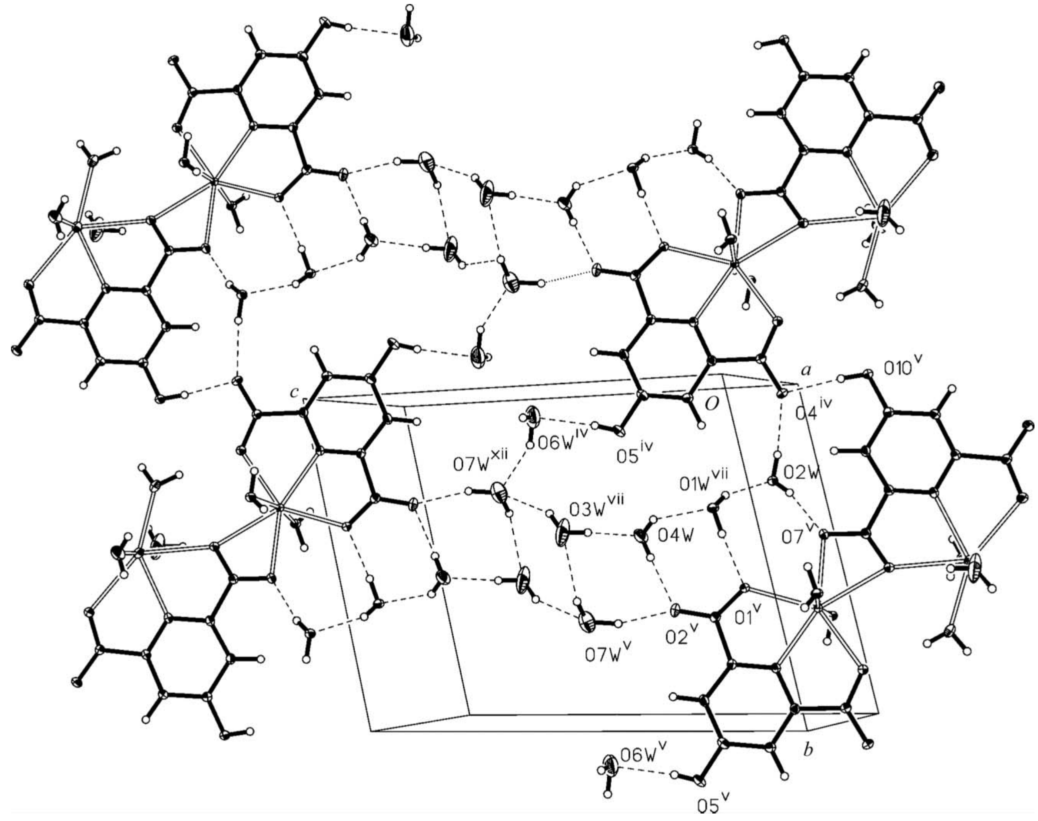

Figure 4
View of the $(H_2O)_{10.34}$ clusters stitching parallel offset two-dimensional extended sheets (Figs. 2 and 3) of hydrogen-bonded $[Mn_4(cdaH)_4(H_2O)_{10}]$ linear clusters in the title compound, showing displacement ellipsoids drawn at the 50% probability level. A linear $R_3^2(11)$–$R_3^3(8)$–$R_3^3(8)$–$R_4^3(8)$–$R_4^4(8)$–$R_4^3(8)$–$R_3^3(8)$–$R_3^3(8)$–$R_3^2(11)$ sequence of nine fused hydrogen-bonding motifs together with two $R_7^6(19)$ and one $R_6^6(22)$ loop can be envisaged in the hydrogen-bonding stitching motif. The water molecules with labels involving O1*W*–O4*W* are coordinated to Mn atoms (not shown). [Symmetry codes: (iv) $-x + 1, -y, -z$; (v) $-x + 1, -y + 1, -z$; (vii) $x - 1, y, z$; (xii) $x - 1, -y, -z + 1$.]

monomer in this case). The hydrogen-bonding stitching pattern determined by the $(H_2O)_{10.34}$ clusters features a linear sequence of seven fused *R*(8) cyclic motifs ending at each extremity with an *R*(11) loop (Fig. 4) [for graph-set notation, see Bernstein *et al.* (1995)]. Interestingly, in the compound $[Cd_4(cdaH)_4(H_2O)_{10}]\cdot 4H_2O$ (Das *et al.*, 2009), which features the same stoichiometry as the title compound and a very similar tetranuclear $\mathrm{Cd^{II}}$ cluster in its structure, only acyclic branched $(\mathrm{H_2O})_5$ clusters determine the packing in the crystal lattice. This may be due to the fact that the $[\mathrm{Cd_4(cdaH)_4(H_2O)_{10}}]$ tetranuclear $\mathrm{Cd^{II}}$ cluster is not perfectly flat unlike the tetranuclear $\mathrm{Mn^{II}}$ cluster in $[\mathrm{Mn_4(cdaH)_4(H_2O)_{10}}]$; a small twisting along the Cd–Cd–Cd–Cd axis causes the axially coordinated water molecules to assume a reciprocal disposition in which the $\mathrm{H_2O}$–Cd–$\mathrm{H_2O}$ vectors are not parallel.

Experimental

The reaction of $\mathrm{MnCl_2\cdot 2H_2O}$ (12 mg, 0.075 mmol), 2-amino-4-methylpyrimidine (30 mg, 0.30 mmol) and $\mathrm{cdaH_3}$ (33 mg, 0.15 mmol) in deionized water (10 ml) afforded colourless prismatic crystals of the title compound (35% yield) upon slow evaporation of solvent from the reaction mixture at room temperature. Analysis found (calculated for $\mathrm{C_{14}H_{20}Mn_2N_2O_{17}}$): C 28.10 (28.11), H 3.35 (3.37), N 4.63% (4.68%).

Crystal data

$[\mathrm{Mn_4(C_8H_3NO_5)_4(H_2O)_{10}]\cdot 3.34H_2O}$
$M_r = 1184.47$
Triclinic, $P\overline{1}$
$a = 6.6765$ (3) Å
$b = 10.9615$ (5) Å
$c = 14.1513$ (7) Å
$\alpha = 102.309$ (1)°
$\beta = 95.097$ (1)°
$\gamma = 91.581$ (1)°
$V = 1006.69$ (8) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 1.35$ mm^{-1}
$T = 100$ K
0.17 × 0.13 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.783$, $T_{\max} = 0.899$
11968 measured reflections
5282 independent reflections
4390 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 1.02$
5282 reflections
317 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.03$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1W	2.1825 (14)	Mn2—O3W	2.203 (3)
Mn1—N1	2.2138 (16)	Mn2—O5W	2.2183 (17)
Mn1—O2W	2.2403 (14)	Mn2—O8$^{\mathrm{i}}$	2.2426 (16)
Mn1—O3	2.2566 (14)	Mn2—O4W	2.2938 (18)
Mn1—O7	2.2594 (14)	Mn2—N2	2.2950 (17)
Mn1—O1	2.3070 (14)	Mn2—O6	2.4232 (15)
Mn1—O6	2.4538 (14)	Mn2—O8	2.4633 (16)
O1W—Mn1—N1	100.00 (6)	O5W—Mn2—N2	136.46 (6)
O1W—Mn1—O2W	168.64 (5)	O8$^{\mathrm{i}}$—Mn2—N2	135.39 (6)
N1—Mn1—O2W	90.19 (6)	O4W—Mn2—N2	87.02 (6)
O3—Mn1—O1	141.05 (5)	O8$^{\mathrm{i}}$—Mn2—O6	154.34 (6)
O3W—Mn2—O5W	92.02 (9)	O8$^{\mathrm{i}}$—Mn2—O8	68.60 (6)
O3W—Mn2—O4W	174.44 (8)	O6—Mn2—O8	134.95 (5)
O5W—Mn2—O4W	82.59 (7)	Mn2—O6—Mn1	154.03 (7)
O3W—Mn2—N2	97.87 (8)	Mn2$^{\mathrm{i}}$—O8—Mn2	111.40 (6)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WA\cdots$O2W^{ii}	0.77	2.06	2.799 (2)	159
O1W—H1$WB\cdots$O1$^{\mathrm{iii}}$	0.84	1.82	2.651 (2)	176
O2W—H2$WA\cdots$O4$^{\mathrm{iv}}$	0.83	1.97	2.804 (2)	173
O2W—H2$WB\cdots$O7$^{\mathrm{v}}$	0.79	1.92	2.687 (2)	166
O3W—H3$WA\cdots$O7W^{vi}	0.89	1.98	2.800 (4)	152
O5—H5$O\cdots$O6W	0.77	1.95	2.712 (3)	173
O3W—H3$WB\cdots$O4W^{ii}	0.87	2.02	2.890 (3)	173
O4W—H4$WA\cdots$O1W^{vii}	0.73	2.32	2.949 (2)	144
O4W—H4$WB\cdots$O2$^{\mathrm{v}}$	0.84	1.90	2.725 (3)	169
O5W—H5$WA\cdots$O10$^{\mathrm{viii}}$	0.81	2.36	2.966 (3)	133
O5W—H5$WA\cdots$O9$^{\mathrm{i}}$	0.81	2.09	2.734 (3)	137
O5W—H5$WB\cdots$O3	0.85	2.11	2.932 (2)	165
O10—H10$O\cdots$O4$^{\mathrm{ix}}$	0.83	1.86	2.683 (2)	174
O6W—H6$WA\cdots$O7W^{x}	0.88	1.80	2.608 (4)	153
O6W—H6$WB\cdots$O9$^{\mathrm{xi}}$	0.80	2.10	2.869 (3)	161
O7W—H7$WA\cdots$O2	0.96	1.79	2.725 (3)	163
O7W—H7$WB\cdots$O3W^{iii}	0.99	2.14	2.899 (5)	132
O7W—H7$WB\cdots$N2$^{\mathrm{iii}}$	0.99	2.37	3.070 (4)	127

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

The H atoms of the OH groups and water molecules were localized in difference Fourier syntheses and refined with a riding model with fixed isotropic displacement parameters $[U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O})]$. H atoms on C atoms were placed in calculated positions with C—H = 0.95 Å and included in the refinement with a riding model with fixed isotropic displacement parameters $[U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})]$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: QS3009). Services for accessing these data are described at the back of the journal.

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