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Bis(L-glutamic acid) sulfate hemihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.033
wR factor = 0.087
Data-to-parameter ratio = 6.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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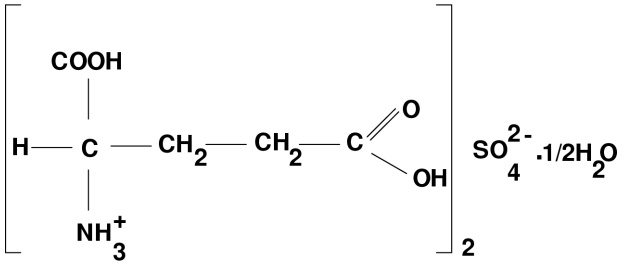
The unit cell of the crystal structure of the title compound, $2C_5H_{10}NO_4{\cdot}SO_4{\cdot}0.5H_2O$, contains eight crystallographically independent glutamic acid residues protonated at the N atom, four sulfate anions and two water molecules. The glutamic acid residues are in different conformations. Both the α- and γ-carboxyl groups are involved in strong O—H···O hydrogen bonding; at the same time each residue shows a different hydrogen-bonding scheme. Owing to the differences in conformational features and hydrogen-bonding patterns of each residue, there is no pseudosymmetry or higher symmetry in the structure.

Comment

Glutamic acid is a dicarboxylic amino acid which is a significant constituent in proteins. It also plays an important role in the metabolism of sugar and fats. The crystal structures of L-glutamic acid (Hirokawa, 1955), L-glutamic acid hydrochloride (Sequeira *et al.*, 1972), DL-glutamic acid monohydrate (Ciunik & Glowiak, 1983) and anhydrous DL-glutamic acid (Dunitz & Schweizer, 1995) have been reported. In order to determine the hydrogen-bonding pattern and the conformation of protonated glutamic acid cation in the crystal structure of its sulfate, the X-ray diffraction study of the title compound, (I), was undertaken.



(I)

The unit cell contains eight crystallographically independent protonated glutamic acid residues, four independent sulfate anions and two water molecules (Fig. 1). An attempt to look for higher symmetry using the *LEPAGE* program (Spek, 1999) resulted in a *C*-centred monoclinic cell with a transformation $(100/\bar{1}02/0\bar{1}0)$. However, the intensity data did not conform to a monoclinic system (R_{int} = 0.58).

The average bond lengths and angles of the sulfate anions confirm nearly ideal tetrahedral symmetry. The geometries of the glutamic acid residues agree well with L-glutamic acid hydrochloride (Sequeira *et al.*, 1972). In the present study, the doubly bonded O atoms of α- and γ-carboxyl groups are

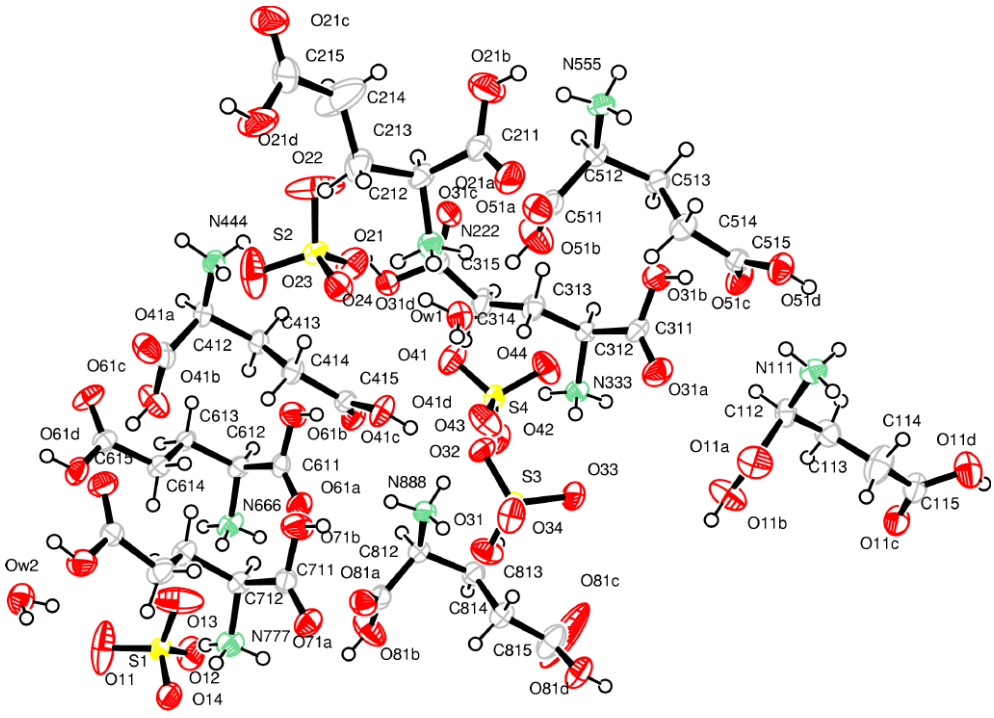


Figure 1
The asymmetric unit of the title compound with the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

labelled *A* and *C*, and the single-bonded O atoms are labelled *B* and *D*.

The backbone conformation angle ψ^1 indicates the *cis* form for all eight residues. For all residues except II and III, the branched side-chain conformation angle χ^1 is in the sterically least favoured closed *gauche*-I conformation, and χ^2 is in the *trans* form, as found in L-glutamic acid hydrochloride (Sequeira *et al.*, 1972). In the case of residues II and III, the conformation angle χ^1 is in the *trans* form for the former [−172.2 (6)°] and the sterically most favoured open *gauche*-II conformation for the latter [−64.6 (4)°].

The conformation angles χ^{31} and χ^{32} indicate the *cis* and *trans* form for all residues except for residue II, where the conformation is in the *trans* and *cis* form [−179.0 (7) and −2 (1)°].

All the O atoms of sulfate anions are involved in hydrogen bonding with the amino and γ-carboxyl groups or water molecules. This plays a vital role in stabilizing the structure (Fig. 2).

All the α-carboxyl O atoms (*B*) form strong O—H···O hydrogen bonds with γ-carboxyl O atoms (*C*), with the exception of residues II and V, which form a strong O—H···O hydrogen bond with water molecules. These amino acids are interconnected by the hydrogen bonding as corrugated sheets, as found in DL-lysine complexes (Saraswathi *et al.*, 2001).

The γ-carboxyl O atoms (*D*) form strong O—H···O hydrogen bonds with sulfate anions in a three-dimensional hydrogen-bonding network. Interestingly, residue VIII forms a chelated O—H···O hydrogen bond with the sulfate anion.

There are three types of N—H···O hydrogen bonding in the crystal of the title compound, *viz*. two-centred, three-centred and chelated three-centred hydrogen bonding. Two-centred N—H···O hydrogen bonding is observed in the case of amino N atom with (i) the α- and γ-carboxyl O atom (*A* and *C*) and (ii) the sulfate anions in all residues except residue III. It is very interesting to note that, among these, residues I and IV are involved only in two-centred N—H···O hydrogen bonds. Three-centred hydrogen bonds are observed in residues II, III, V and VIII, involving the amino N and the carboxyl O atoms (*A* and *C*). Chelated three-centred hydrogen bonding is present in residues III, V, VI and VII, involving the amino N atom of the glutamic acid residue and the O atoms of the sulfate anion (Jeffrey & Saenger, 1991). Interestingly, in the case of residue III, only the three-centred and chelated type of hydrogen bonding are observed, while in the case of residue VII, two such chelated three-centred hydrogen bonds are involved.

In the amino group of residues I and IV, a class I hydrogen-bonding pattern, involving three two-centred hydrogen bonds (Jeffrey & Saenger, 1991), is present. In the case of residues II, VI and VIII, a class II hydrogen bonding, with one three-centred hydrogen bond and two two-centred hydrogen bonds, is observed, while in the case of residues V and VII, a class III hydrogen bond, with two three-centred hydrogen bonds and one two-centred hydrogen bond, is observed. Interestingly, in the case of residue III, the sterically least favourable class IV hydrogen-bonding pattern, with only three-centred hydrogen bonding, is observed. In general, the class II hydrogen-

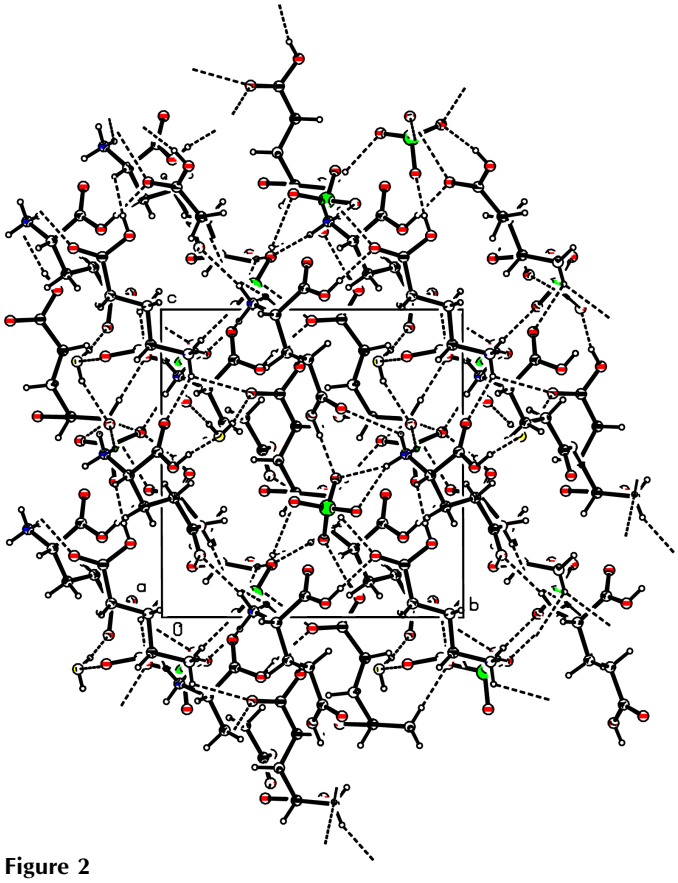


Figure 2
Packing diagram of the crystal, viewed down the *a* axis.

bonding pattern is the most favoured configuration and occurrence of class IV is rare.

Both water molecules form O—H···O hydrogen bonds with the sulfate anions and the γ-carboxyl group (*C*) of the glutamic acid residues.

In the present study, the residues are aggregated as characteristic layers along the diagonal plane parallel to (011). The glutamic acid residues II, IV, VI and VIII, sulfate anions 2 and 3, and the O*W*1 water molecule are interconnected by hydrogen-bonded ribbons as a linear chain along the diagonal (011) plane (Fig. 3). Similarly, residues I, III, V and VII, sulfate anions 1 and 4, and the O*W*2 water molecule are interconnected by hydrogen-bonded ribbons (Fig. 4) running as an infinite chain parallel to the same diagonal plane and lying in between two adjacent ribbons of the first type.

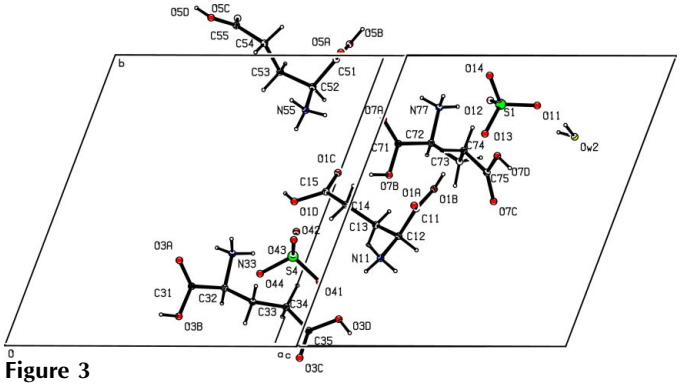


Figure 3
Packing diagram of the crystal, viewed down the *b* axis (for the sake of clarity only glutamic acid residues II, IV, VI and VIII, sulfate anions 2 and 3, and the first water molecule are shown).

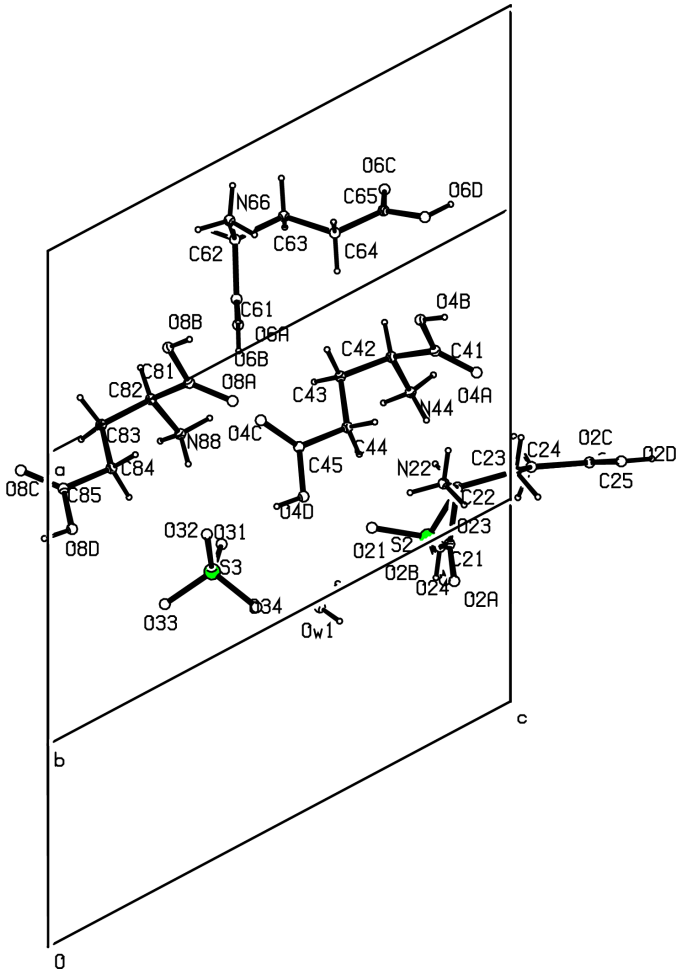


Figure 4
Packing diagram of the crystal, viewed down the *c* axis (for the sake of clarity only glutamic acid residues I, III, V and VII, sulfate anions 1 and 4, and the second water molecule are shown).

Experimental

The title compound was crystallized by slow evaporation from an aqueous solution of L-glutamic acid and sulfuric acid in a 2:1 stoichiometric ratio.

Crystal data

$2C_5H_{10}NO_4^+\cdot SO_4^{2-}\cdot 0.5H_2O$
M_r = 401.35
Triclinic, *P*1
a = 12.536 (2) Å
b = 12.596 (2) Å
c = 13.306 (2) Å
α = 79.09 (1)°
β = 62.05 (1)°
γ = 65.88 (1)°
V = 1693.9 (5) Å^3
Z = 4
D_x = 1.574 Mg m^{-3}
D_m = 1.568 Mg m^{-3}
D_m measured by flotation in carbon tetrachloride and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 11.3–13.6°
μ = 0.26 mm^{-1}
T = 293 (2) K
Block, colourless
0.6 × 0.6 × 0.5 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.730, T_{max} = 0.776
6238 measured reflections
6238 independent reflections
5814 reflections with $I > 2\sigma(I)$
θ_{max} = 25.0°
$h = 0 \rightarrow 14$
$k = -13 \rightarrow 14$
$l = -13 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.087
S = 1.03
6238 reflections
936 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.7347P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0219 (11)
Absolute structure: Flack (1983); 298 Friedel pairs
Flack parameter = 0.06 (6)

Table 1
Selected geometric parameters (Å, °).

O11*A*—C111	1.213 (5)	O51*A*—C511	1.198 (4)
O11*B*—C111	1.301 (5)	O51*B*—C511	1.297 (5)
C115—O11*C*	1.202 (5)	C515—O51*C*	1.227 (5)
C115—O11*D*	1.306 (5)	C515—O51*D*	1.290 (5)
O21*A*—C211	1.207 (5)	O61*A*—C611	1.204 (4)
O21*B*—C211	1.296 (5)	O61*B*—C611	1.310 (5)
C215—O21*C*	1.158 (6)	C615—O61*C*	1.202 (5)
C215—O21*D*	1.323 (6)	C615—O61*D*	1.307 (5)
O31*A*—C311	1.195 (5)	O71*A*—C711	1.197 (5)
O31*B*—C311	1.311 (5)	O71*B*—C711	1.313 (5)
C315—O31*C*	1.216 (5)	C715—O71*C*	1.197 (5)
C315—O31*D*	1.284 (5)	C715—O71*D*	1.304 (5)
O41*A*—C411	1.197 (5)	O81*A*—C811	1.199 (5)
O41*B*—C411	1.317 (5)	O81*B*—C811	1.313 (5)
C415—O41*C*	1.216 (5)	C815—O81*C*	1.183 (6)
C415—O41*D*	1.301 (5)	C815—O81*D*	1.288 (6)
O11*A*—C111—C112—N111	−1.9 (5)	O51*A*—C511—C512—N555	−18.2 (5)
N111—C112—C113—C114	61.3 (5)	N555—C512—C513—C514	78.2 (4)
C112—C113—C114—C115	175.1 (4)	C512—C513—C514—C515	170.2 (3)
C113—C114—C115—O11*C*	−61.4 (7)	C513—C514—C515—O51*C*	−41.7 (5)
C113—C114—C115—O11*D*	120.7 (5)	C513—C514—C515—O51*D*	139.9 (3)
O21*A*—C211—C212—N222	−29.5 (5)	O61*A*—C611—C612—N666	−6.3 (5)
N222—C212—C213—C214	−172.2 (6)	N666—C612—C613—C614	62.9 (4)
C212—C213—C214—C215	−167.5 (7)	C612—C613—C614—C615	−179.7 (3)
C213—C214—C215—O21*C*	−179.0 (7)	C613—C614—C615—O61*C*	−13.5 (5)
C213—C214—C215—O21*D*	−1.8 (11)	C613—C614—C615—O61*D*	167.4 (3)
O31*A*—C311—C312—N333	−16.3 (5)	O71*A*—C711—C712—N777	−3.1 (5)
N333—C312—C313—C314	−64.6 (4)	N777—C712—C713—C714	72.2 (4)
C312—C313—C314—C315	−161.4 (3)	C712—C713—C714—C715	168.9 (3)
C313—C314—C315—O31*C*	49.6 (6)	C713—C714—C715—O71*C*	−22.9 (6)
C313—C314—C315—O31*D*	−129.7 (4)	C713—C714—C715—O71*D*	159.9 (4)
O41*A*—C411—C412—N444	−1.3 (5)	O81*A*—C811—C812—N888	−7.9 (5)
N444—C412—C413—C414	67.1 (4)	N888—C812—C813—C814	72.0 (4)
C412—C413—C414—C415	177.5 (3)	C812—C813—C814—C815	173.0 (4)
C413—C414—C415—O41*C*	−19.5 (5)	C813—C814—C815—O81*C*	−6.8 (9)
C413—C414—C415—O41*D*	161.5 (3)	C813—C814—C815—O81*D*	172.8 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11*B*—H1*B*···O21*C*^{i}	0.82	1.83	2.644 (4)	176
O21*B*—H2*B*···O*W*2^{ii}	0.82	1.72	2.525 (5)	165
O31*B*—H3*B*···O51*C*	0.82	1.93	2.733 (4)	165
O41*B*—H4*B*···O71*C*	0.82	1.92	2.720 (4)	164
O51*B*—H5*B*···O*W*1	0.82	1.70	2.495 (4)	163
O61*B*—H6*B*···O41*C*	0.82	1.86	2.657 (4)	164
O71*B*—H7*B*···O11*C*^{iii}	0.82	1.78	2.591 (4)	169
O81*B*—H8*B*···O31*C*^{iv}	0.82	1.81	2.625 (5)	177
O11*D*—H1*H*···O34^{v}	0.82	1.77	2.585 (4)	173
O21*D*—H2*F*···O12^{vi}	0.82	1.76	2.555 (4)	161
O31*D*—H3*F*···O14^{vii}	0.82	1.81	2.604 (4)	162
O41*D*—H4*F*···O32	0.82	1.78	2.577 (4)	163
O51*D*—H5*F*···O41^{viii}	0.82	1.78	2.595 (4)	172
O61*D*—H6*F*···O42^{iii}	0.82	1.86	2.659 (4)	166
O71*D*—H7*F*···O33^{iii}	0.82	1.86	2.625 (4)	155
O81*D*—H8*E*···O22^{i}	0.82	2.20	2.958 (6)	153
O81*D*—H8*E*···O23^{i}	0.82	2.39	3.081 (6)	142
N111—H11*A*···O24^{v}	0.89	1.82	2.708 (4)	171
N111—H11*B*···O42^{viii}	0.89	2.18	2.943 (5)	144
N111—H11*C*···O51*C*	0.89	2.13	2.998 (4)	164
N222—H22*A*···O24	0.89	1.89	2.767 (4)	168
N222—H22*B*···O44^{ix}	0.89	1.95	2.801 (4)	159
N222—H22*C*···O51*A*	0.89	2.15	2.913 (4)	144
N222—H22*C*···O61*C*^{viii}	0.89	2.40	2.835 (4)	110
N333—H33*A*···O43	0.89	1.93	2.795 (4)	164
N333—H33*A*···O44	0.89	2.46	2.992 (4)	119
N333—H33*B*···O33	0.89	2.08	2.886 (4)	151
N333—H33*B*···O32	0.89	2.49	3.061 (4)	122
N333—H33*C*···O71*C*^{v}	0.89	2.34	3.070 (4)	139
N333—H33*C*···O41*A*^{v}	0.89	2.36	3.036 (4)	133
N444—H44*A*···O14^{vii}	0.89	1.92	2.804 (4)	172
N444—H44*B*···O23	0.89	1.94	2.797 (5)	161
N444—H44*C*···O21*A*^{x}	0.89	2.23	2.922 (4)	134
N555—H55*A*···O31^{vii}	0.89	2.15	2.928 (4)	146
N555—H55*A*···O34^{vii}	0.89	2.39	3.193 (4)	151
N555—H55*B*···O11^{ii}	0.89	1.95	2.727 (5)	145
N555—H55*C*···O71*A*^{vii}	0.89	2.41	3.095 (4)	134
N555—H55*C*···O11*C*^{xi}	0.89	2.48	3.056 (4)	123
N666—H66*A*···O34^{x}	0.89	1.92	2.798 (4)	166
N666—H66*A*···O33^{x}	0.89	2.59	3.254 (4)	132
N666—H66*B*···O13	0.89	2.02	2.844 (5)	154
N666—H66*C*···O21*C*^{xii}	0.89	2.03	2.807 (4)	145
N777—H77*A*···O13	0.89	2.20	2.962 (5)	143
N777—H77*A*···O14	0.89	2.21	2.992 (5)	147
N777—H77*B*···O22^{iv}	0.89	1.97	2.830 (5)	162
N777—H77*B*···O21^{iv}	0.89	2.62	3.084 (5)	114
N777—H77*C*···O31*C*^{iv}	0.89	2.43	3.160 (5)	140
N888—H88*A*···O43	0.89	1.84	2.717 (4)	169
N888—H88*B*···O31	0.89	1.95	2.827 (4)	170
N888—H88*C*···O41*C*	0.89	2.40	3.084 (4)	134
N888—H88*C*···O61*A*	0.89	2.48	3.151 (4)	133
O*W*1—H1*WA*···O21	0.85 (6)	1.88 (6)	2.732 (4)	175 (5)
O*W*1—H1*WB*···O61*C*^{viii}	0.79 (6)	2.07 (6)	2.803 (5)	155 (5)
O*W*2—H2*WA*···O11	0.81 (7)	1.96 (7)	2.706 (5)	151 (6)
O*W*2—H2*WB*···O81*C*^{iii}	0.94 (8)	1.78 (8)	2.725 (6)	174 (6)

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

The H atoms attached to water molecules were located and refined in the isotropic approximation (O—H = 0.79–0.94 Å). All other H atoms were placed in geometrically calculated positions and included in the refinement in a riding-model approximation with U_{iso} equal to $1.2U_{eq}$ of the carrier atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997);

program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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