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Crystal structure of iron(III) perchlorate nonahydrate

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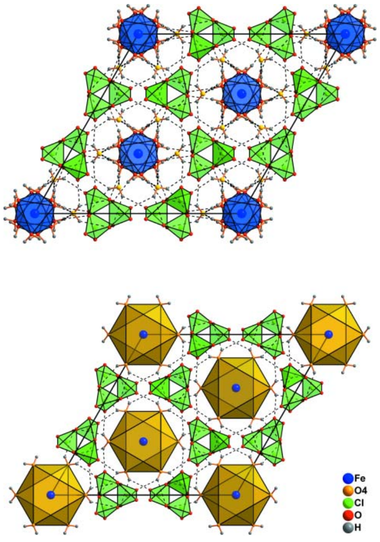
Since the discovery of perchlorate salts on Mars and the known occurrence of ferric salts in the regolith, there is a distinct possibility that the title compound could form on the surface of Mars. $[Fe(H_2O)_6](ClO_4)_3 \cdot 3H_2O$ was crystallized from aqueous solutions at low temperatures according to the solid–liquid phase diagram. It consists of $Fe(H_2O)_6$ octahedra (point group symmetry $\overline{3}$.) and perchlorate anions (point group symmetry .2) as well as non-coordinating water molecules, as part of a second hydrogen-bonded coordination sphere around the cation. The perchlorate appears to be slightly disordered, with major–minor component occupancies of 0.773 (9):0.227 (9).



1. Chemical context

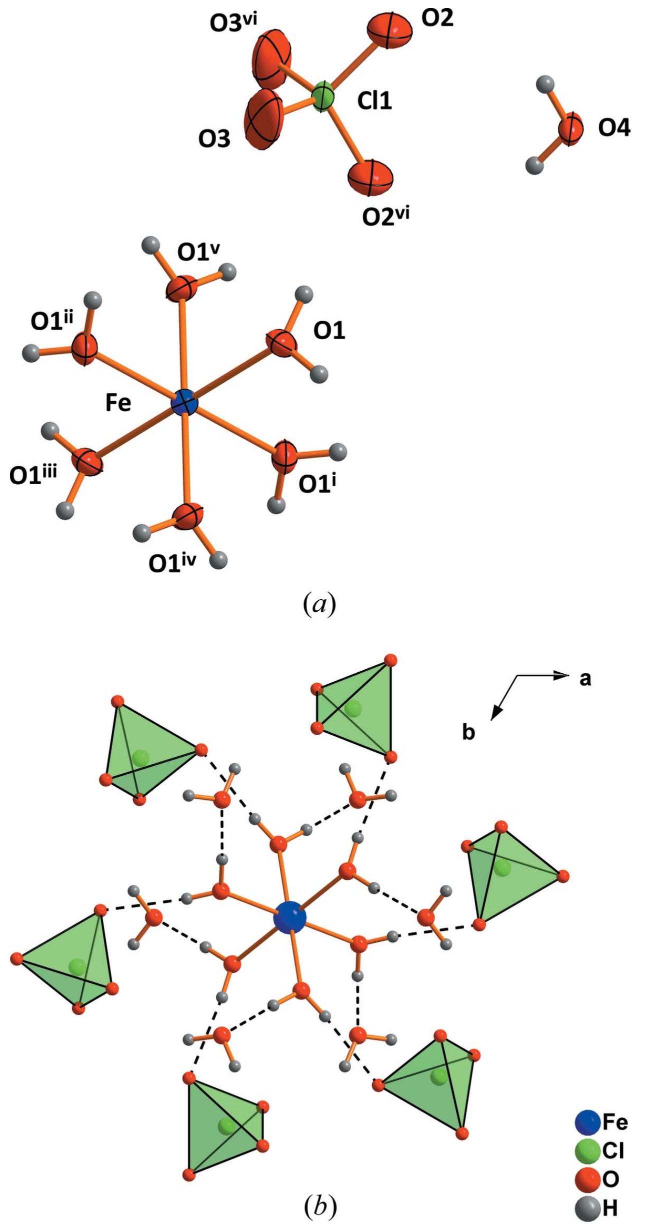
Since the discovery of perchlorate salts on the surface of Mars during the Phoenix expedition (Hecht *et al.*, 2009; Davila *et al.*, 2013; Kerr, 2013; Marion *et al.*, 2010; Navarro-González *et al.*, 2010), interest in the solubility and crystal structures of the perchlorate hydrate phases became more important (Chevrier, Hanley & Altheide, 2009; Catling *et al.*, 2010). Based on the red color of the planet, one can expect different iron phases, such as perchlorate and sulfate, to be important constituents of the regolith (Chevrier, Ulrich & Altheide, 2009; Chevrier & Altheide, 2008; Hennings *et al.*, 2013). While investigating the solubility of ferric perchlorate, we obtained the nonahydrate as a stable phase in the binary salt–water system.

2. Structural commentary

The central Fe atom is situated on a threefold inversion axis and is octahedrally coordinated by six water molecules in the first, and by six water molecules as well as six perchlorate tetrahedra in the second coordination spheres (Fig. 1). The water molecules of the second coordination sphere (O4 and symmetry equivalents) are connected to perchlorate tetrahedra (Fig. 2*a*) *via* hydrogen bonds (Table 1). Six O4-water molecules form a second, larger octahedron outside the octahedron of the first coordination shell (Fig. 2*b*). The perchlorate anion, situated on a twofold rotation axis, appears to be slightly disordered, with major:minor component occupancies of 0.773 (9):0.227 (9).

3. Supramolecular features

From the unit cell of ferric perchlorate nonahydrate (Fig. 3*a*), it is obvious that the O4 atoms form a secondary hydration shell around the $Fe(H_2O)_6$ units. This becomes clearer when drawing the second octahedra as water coordination poly-



(*a*)

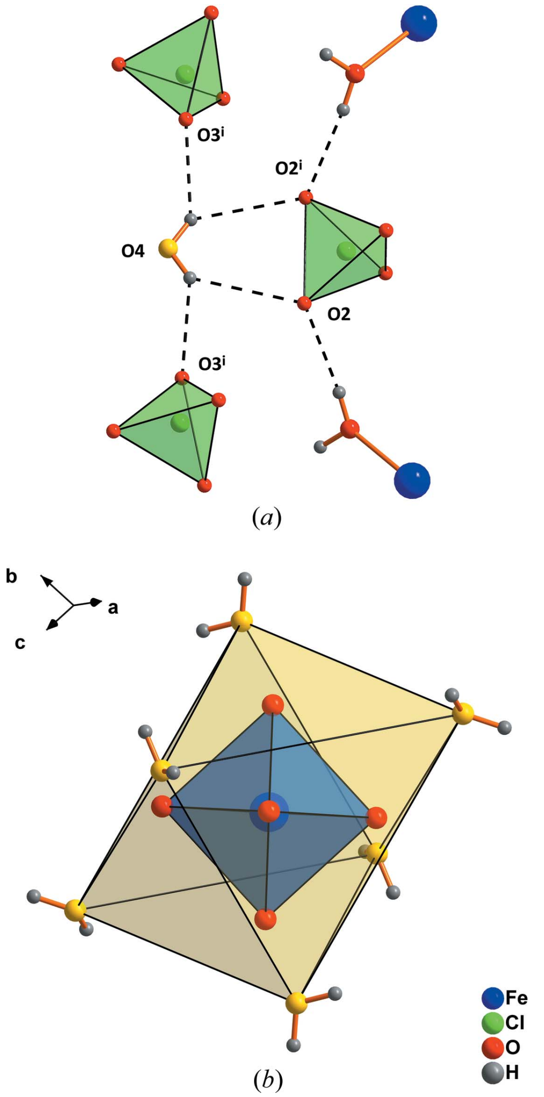
(*b*)

Figure 1
The molecular units (*a*) and second coordination sphere (*b*) of ferric perchlorate nonahydrate. Dashed lines indicate hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability limit. The minor disorder component of the ClO_4 tetrahedron has been omitted. [Symmetry codes: (i) $x - y, x, 1 - z$; (ii) $-x + y, -x, z$; (iii) $-x, -y, 1 - z$; (iv) $-y, x - y, z$; (v) $y, -x + y, 1 - z$; (vi) $\frac{2}{3} - x, \frac{1}{3} - x + y, \frac{5}{6} - z$.]

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$O2^{i}	0.83 (5)	1.92 (5)	2.745 (5)	174 (4)
O1—H1$A\cdots$O2$'^{i}$	0.83 (5)	2.33 (5)	3.153 (14)	170 (4)
O1—H1$A\cdots$O3$'$	0.83 (5)	2.27 (5)	2.864 (17)	129 (4)
O1—H1$B\cdots$O4^{ii}	0.82 (5)	1.83 (5)	2.642 (3)	173 (4)
O4—H4$\cdots$O2	0.84 (4)	2.39 (4)	3.073 (5)	139 (4)
O4—H4$\cdots$O3^{iii}	0.84 (4)	2.13 (4)	2.796 (4)	136 (4)
O4—H4$\cdots$O2$'$	0.84 (4)	2.13 (5)	2.812 (17)	138 (4)
O4—H4$\cdots$O3$'^{iii}$	0.84 (4)	2.12 (4)	2.708 (12)	127 (4)

Symmetry codes: (i) $-x + \frac{2}{3}, -x + y + \frac{1}{3}, -z + \frac{5}{6}$; (ii) $-x + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{2}{3}$; (iii) $y + \frac{1}{3}, -x + y + \frac{2}{3}, -z + \frac{2}{3}$.



(*a*)

(*b*)

Figure 2
The connection scheme of water molecules of the second coordination sphere by hydrogen bonds (*a*) and the formation of a secondary hydration shell (yellow) around the cations (*b*). The minor disorder component of the ClO_4 tetrahedron has been omitted for clarity. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $\frac{2}{3} - x, \frac{1}{3} - x + y, \frac{5}{6} - z$.]

hedra (yellow, Fig. 3*b*). The water molecules of the second coordination sphere are closer [4.143 (4) Å] to the Fe atom than the perchlorate tetrahedra [4.271 (4) Å].

4. Database survey

For crystal structure determination of other perchlorate nonahydrates, see: Davidian *et al.* (2012) for the Al, Ga and Sc salts and Hennings *et al.* (2014) for the strontium salt. For crystal structure determinations of other Fe^{III} salts with a high water content, see: Schmidt *et al.* (2013); Lindstrand (1936).

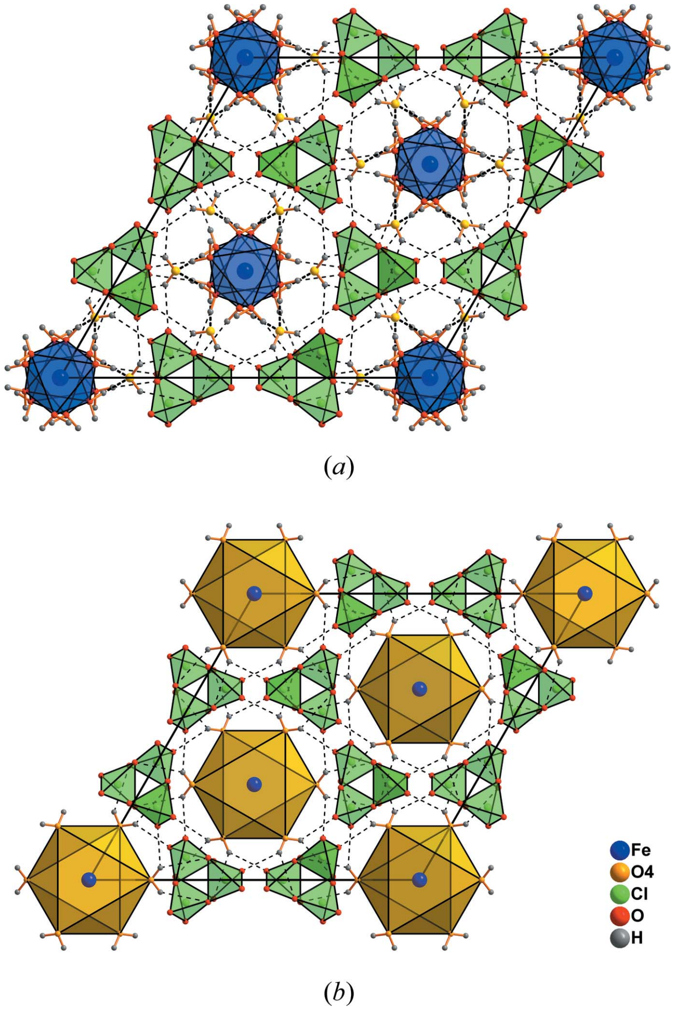
5. Synthesis and crystallization

Iron(III) perchlorate nonahydrate crystallized from an aqueous solution of 54.41 wt% $Fe(ClO_4)_3$ thermostated at

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Fe(H_2O)_6](ClO_4)_3 \cdot 3H_2O$
M_r	516.34
Crystal system, space group	Trigonal, $R\bar{3}c{:}H$
Temperature (K)	100
a, c (Å)	16.1930 (15), 11.2421 (11)
V (Å^3)	2552.9 (5)
Z	6
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.46
Crystal size (mm)	0.54 × 0.37 × 0.19
Data collection	
Diffractometer	STOE IPDS 2T
Absorption correction	Integration (Coppens, 1970)
$T_{\min}$, $T_{\max}$	0.531, 0.755
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8865, 659, 641
R_{int}	0.075
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.092, 1.11
No. of reflections	658
No. of parameters	60
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.64, −0.80

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2009), *SHELXS97* and *SHELXL2012* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).



(*a*)

(*b*)

Figure 3
The unit cell of iron(III) perchlorate nonahydrate with coordination polyhedra of the first (*a*) and second (*b*) coordination sphere. The minor disorder component of the ClO_4 tetrahedron has been omitted for clarity. Dashed lines indicate hydrogen bonds.

263 K after 2 d. To prepare this solution, ferric perchlorate nonahydrate (Fluka, pure) was used. The content of Fe^{III} ions was analysed using gravimetric analysis by precipitation with ammonia. All crystals are stable in their saturated solution over a period of at least four weeks.

The samples were stored in a freezer or a cryostat at low temperatures. The crystals were separated and embedded in perfluorinated ether for X-ray diffraction analysis

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were placed in the positions indicated by difference Fourier maps. No further constraints were applied.

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supporting information

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Crystal structure of iron(III) perchlorate nonahydrate

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-RED* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Iron(III) perchlorate nonahydrate

Crystal data

$[Fe(H_2O)_6](ClO_4)_3 \cdot 3H_2O$
$M_r = 516.34$
Trigonal, $R\bar{3}c{:}H$
$a = 16.1930$ (15) Å
$c = 11.2421$ (11) Å
$V = 2552.9$ (5) Å^3
$Z = 6$
$F(000) = 1578$
$D_x = 2.015$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 47287 reflections
$\theta = 7.0$–$29.7°$
$\mu = 1.46$ mm^{-1}
$T = 100$ K
Needle, colorless
0.54 × 0.37 × 0.19 mm

Data collection

STOE IPDS 2T
diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration
(Coppens, 1970)
$T_{\min} = 0.531$, $T_{\max} = 0.755$
8865 measured reflections
659 independent reflections
641 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.075$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 2.5°$
$h = -20 \rightarrow 20$
$k = -20 \rightarrow 20$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.092$
$S = 1.11$
658 reflections
60 parameters
0 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0269P)^2 + 23.9134P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Fe1	0.0000	0.0000	0.5000	0.0188 (3)	
O1	0.07420 (15)	0.11666 (15)	0.3991 (2)	0.0252 (5)	
O4	0.3333	0.47858 (17)	0.4167	0.0247 (6)	
Cl1	0.3333	0.2540 (19)	0.4167	0.0329 (3)	0.773 (9)
O2	0.4134 (3)	0.3438 (3)	0.3808 (4)	0.0342 (8)	0.773 (9)
O3	0.3070 (3)	0.1914 (3)	0.3110 (4)	0.0481 (12)	0.773 (9)
Cl1′	0.3333	0.254 (7)	0.4167	0.0329 (3)	0.227 (9)
O2′	0.3946 (11)	0.3499 (13)	0.3527 (16)	0.0342 (8)	0.227 (9)
O3′	0.2699 (12)	0.1716 (10)	0.3602 (15)	0.0481 (12)	0.227 (9)
H1A	0.129 (3)	0.158 (3)	0.417 (4)	0.047 (12)*	
H1B	0.048 (3)	0.138 (3)	0.357 (4)	0.051 (13)*	
H4	0.375 (3)	0.468 (3)	0.388 (4)	0.054 (13)*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0157 (3)	0.0157 (3)	0.0251 (5)	0.00784 (15)	0.000	0.000
O1	0.0165 (10)	0.0195 (10)	0.0341 (11)	0.0050 (8)	−0.0004 (8)	0.0045 (8)
O4	0.0269 (15)	0.0164 (9)	0.0344 (16)	0.0135 (8)	0.0102 (12)	0.0051 (6)
Cl1	0.0221 (5)	0.0137 (4)	0.0659 (8)	0.0110 (2)	−0.0180 (5)	−0.0090 (2)
O2	0.0180 (19)	0.0381 (15)	0.051 (2)	0.0174 (13)	−0.0027 (15)	0.0098 (16)
O3	0.045 (3)	0.0345 (19)	0.067 (3)	0.0210 (19)	−0.0055 (19)	−0.0276 (19)
Cl1′	0.0221 (5)	0.0137 (4)	0.0659 (8)	0.0110 (2)	−0.0180 (5)	−0.0090 (2)
O2′	0.0180 (19)	0.0381 (15)	0.051 (2)	0.0174 (13)	−0.0027 (15)	0.0098 (16)
O3′	0.045 (3)	0.0345 (19)	0.067 (3)	0.0210 (19)	−0.0055 (19)	−0.0276 (19)

Geometric parameters (Å, º)

Fe1—O1$^{\rm i}$	2.007 (2)	Cl1—O2	1.439 (18)
Fe1—O1$^{\rm ii}$	2.007 (2)	Cl1—O3$^{\rm vi}$	1.479 (17)
Fe1—O1$^{\rm iii}$	2.007 (2)	Cl1—O3	1.479 (17)
Fe1—O1$^{\rm iv}$	2.007 (2)	Cl1′—O3′$^{\rm vi}$	1.37 (6)
Fe1—O1$^{\rm v}$	2.007 (2)	Cl1′—O3′	1.37 (6)
Fe1—O1	2.007 (2)	Cl1′—O2′$^{\rm vi}$	1.54 (7)
Cl1—O2$^{\rm vi}$	1.439 (18)	Cl1′—O2′	1.54 (7)
O1$^{\rm i}$—Fe1—O1$^{\rm ii}$	180.00 (9)	O1$^{\rm v}$—Fe1—O1	180.00 (10)
O1$^{\rm i}$—Fe1—O1$^{\rm iii}$	91.19 (9)	O2$^{\rm vi}$—Cl1—O2	112 (2)
O1$^{\rm ii}$—Fe1—O1$^{\rm iii}$	88.81 (9)	O2$^{\rm vi}$—Cl1—O3$^{\rm vi}$	105.8 (3)

O1^{i}—Fe1—O1^{iv}	88.81 (9)	O2—Cl1—O3^{vi}	109.42 (19)
O1^{ii}—Fe1—O1^{iv}	91.19 (9)	O2^{vi}—Cl1—O3	109.42 (19)
O1^{iii}—Fe1—O1^{iv}	180.00 (10)	O2—Cl1—O3	105.8 (3)
O1^{i}—Fe1—O1^{v}	91.19 (9)	O3^{vi}—Cl1—O3	114 (2)
O1^{ii}—Fe1—O1^{v}	88.81 (9)	O3′^{vi}—Cl1′—O3′	106 (7)
O1^{iii}—Fe1—O1^{v}	91.19 (9)	O3′^{vi}—Cl1′—O2′^{vi}	124.0 (13)
O1^{iv}—Fe1—O1^{v}	88.81 (9)	O3′—Cl1′—O2′^{vi}	105.4 (10)
O1^{i}—Fe1—O1	88.81 (9)	O3′^{vi}—Cl1′—O2′	105.4 (10)
O1^{ii}—Fe1—O1	91.19 (9)	O3′—Cl1′—O2′	124.0 (13)
O1^{iii}—Fe1—O1	88.81 (9)	O2′^{vi}—Cl1′—O2′	94 (6)
O1^{iv}—Fe1—O1	91.19 (9)		

Symmetry codes: (i) *y*, −*x*+*y*, −*z*+1; (ii) −*y*, *x*−*y*, *z*; (iii) *x*−*y*, *x*, −*z*+1; (iv) −*x*+*y*, −*x*, *z*; (v) −*x*, −*y*, −*z*+1; (vi) −*x*+2/3, −*x*+*y*+1/3, −*z*+5/6.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···Cl1	0.83 (5)	2.86 (5)	3.642 (2)	157 (4)
O1—H1*A*···O2^{vi}	0.83 (5)	1.92 (5)	2.745 (5)	174 (4)
O1—H1*A*···O2′^{vi}	0.83 (5)	2.33 (5)	3.153 (14)	170 (4)
O1—H1*A*···O3′	0.83 (5)	2.27 (5)	2.864 (17)	129 (4)
O1—H1*B*···O4^{vii}	0.82 (5)	1.83 (5)	2.642 (3)	173 (4)
O4—H4···O2	0.84 (4)	2.39 (4)	3.073 (5)	139 (4)
O4—H4···O3^{viii}	0.84 (4)	2.13 (4)	2.796 (4)	136 (4)
O4—H4···O2′	0.84 (4)	2.13 (5)	2.812 (17)	138 (4)
O4—H4···O3′^{viii}	0.84 (4)	2.12 (4)	2.708 (12)	127 (4)

Symmetry codes: (vi) −*x*+2/3, −*x*+*y*+1/3, −*z*+5/6; (vii) −*x*+1/3, −*y*+2/3, −*z*+2/3; (viii) *y*+1/3, −*x*+*y*+2/3, −*z*+2/3.